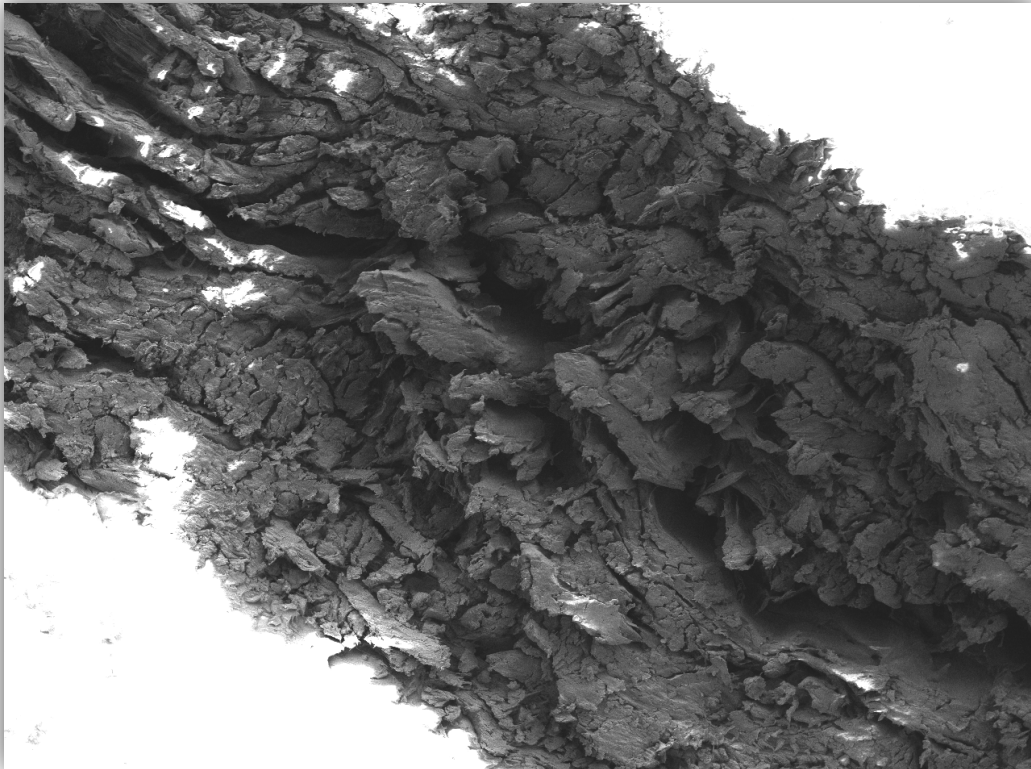




CHALMERS
UNIVERSITY OF TECHNOLOGY

**Fibre-Fibre Interactions and Phase Transitions of Lignocellulosic
Substrates**

Nazlican Caglar

Supervisors and stakeholders: Tiina Nypelö, Anette Larsson, Gunnar Westman, Anders Brolin,
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MASTER THESIS

FIBRE-FIBRE INTERACTIONS AND PHASE TRANSITIONS OF
LIGNOCELLULOSIC SUBSTRATES

NAZLICAN CAGLAR



DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
CHALMERS UNIVERSITY OF TECHNOLOGY
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ABSTRACT

The purpose of this study was to reveal critical factors to improve fibre-fibre adhesion and interactions to target entanglement and sealing of lignocellulosic substrates without using external additives. The molecular composition and moisture content were selected as parameters to be examined for consistent sealing of the selected lignocellulosic substrates. The moisture was expected to enhance sealing by interrupting highly ordered hydrogen bonded cellulosic materials by swelling of the fibres and to enable plasticization. The fibres of lignocellulosic substrates were brought into close contact at elevated temperature in compression. Glass transition temperature as a phase transition detected by DSC (differential scanning calorimetry) and the sealing was noted to be stimulated by lignin plasticization. The sealing has been achieved for selected materials: unbleached Kraft, bleached Kraft, HT-CTMP (High Temperature Chemothermal mechanical pulp), dissolving pulp and cellulose filter paper. The mechanical tests for the sealed paper and paper itself revealed that strength of the seal of unbleached Kraft was higher than any other paper grade; bleached Kraft, dissolving pulp, cellulose filter paper, respectively. The lowest seal strength has been recorded for HT-CTMP. The sealed HT-CTMP paper strength is higher than that of the HT-CTMP hand sheet. Further reversibility tests revealed that seal of unbleached Kraft and HT-CTMP were permanent and the seal of bleached Kraft, dissolving pulp and cellulose filter paper were transient.

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1. INTRODUCTION

The pulp and paper industry operate tremendous amounts of lignocellulosic substrates every year to produce paper products (Ek, Gellerstedt et al. 2009). The adhesives that are mainly applied to paper products is to induce sealing and they are usually either water-based where the water acts as a carrier or wax applied hot in the molten state to paper. The added wax incorporated in or on the surface of the material acts as the adhesive in heat sealing. However, utilization of the adhesives is not environmentally friendly due to challenges in recycling, and industry is facing an increasing pressure in terms of environmental regulations to decrease excessive usage of chemicals. Thus, new technologies must be applied to carry the paper sealing industry. The lignocellulosic substrates containing cellulose as a main component, do not melt hence may not be sealed only with elevated temperatures without adhesives. However, in this demanding industry innovative approaches can shape the paper sealing technologies without using additives. Altered thermal phase transitions and utilization of the other residual pulp components, lignin and hemicellulose provide a path for this.

1.1. OBJECTIVE

The objective of the thesis is to perform the additive free sealing of the selected lignocellulosic substrates by inducing phase transitions in elevated temperature and pressure and stimulate the fibre-fibre interactions. Thermal phase transitions refer to melting and glass transition in the pulp grades. We also suggest plasticization as a way to induce molecular mobility in the substrates and allow adhesion due to component infusion. Water can induce plasticization by allowing swelling of the structure and reduced molecular interaction in the substrate prior to compression. This can be primary step towards established new connections. Lignin in elevated temperatures can experience increase in mobility, flexibility and establish adhesion during compression.

2. BACKGROUND

Wood produced by the seed-bearing plants from trees (Ek, Gellerstedt et al. 2009). Diagnostically each tree can be divided into several parts named as top, stem, branches, leaf and root. Generally, the stem is the vital part of the tree employed for the transport, mechanical support, growth and protection and used mainly for the pulping industry since the stem has the

highest amount of cellulose (higher than 50%) comparing to other parts of the tree. Each wood tissue is comprised of a variety of different cell types having different roles in tree that can act differently in paper products (Henriksson, Lennholm et al. 2009). Differences come from variability of the structure of the different cell types. Also, different cell wall organization and chemical composition are responsible for arising the differences within the cell. Wood cells are composed of a number of cell wall layers forming primary, secondary cell. It is comprised of three major chemical components named: cellulose, hemicellulose, lignin. In simple definition, within the cell wall, cellulose is composed of glucose units which are organized into chains and further fibril bundles. Cellulose microfibrils are aggregated into macro-fibrils and arrange around the cell wall. Due to strong intermolecular interactions within the microfibrils and chains via hydrogen bonds, high molecular weight, stiffness, hydrophobicity and the special morphological organizations of cellulose, the structure is resistant to dissolution.

The hemicelluloses as the amorphous component are associated with cellulose and it has a non-hierarchical structure. Lignin is defined as it encrusts both hemicellulose and cellulose and it provides stiffness to cell wall and mechanical support. Individual cells are connected by intercellular middle lamella region which is rich in lignin and the total 29-25% of the total lignin is present in this layer. It is suggested to be that lignin is covalently linked to hemicellulose.

2.1. PULPING TECHNOLOGY

Wood consist of fibres acquired from wood and the purpose of the pulping process is to release the fibres from the wood matrix. Mainly, it can be achieved either by chemical pulping or mechanical pulping (Hubbe, Venditti et al. 2007).

2.1.1. MECHANICAL PULPING

Mechanical method of pulping demands a lot of electric power; however, the whole wood material is used (Ek, Gellerstedt et al. 2009). Therefore, the yield is higher compared to chemical pulping. In the process, the wood and wood chips are grinded and the fibres in the wood is released to obtain mechanical pulp. Generally, by the process, some easily dissolved carbohydrates and extractives are perished and the pulp yield is affected, resulting in pulp yield of 90%. The fibres of mechanical pulp are stiff, and the lumens are not collapsed. Mechanical pulp contains fines which consists of fragments from the fibre wall and broken fibres giving good optical properties to mechanical pulp. Mechanical pulp strength can be

improved, if the pulp compromises a higher portion of long fibres. By increasing the temperature, lignin in the middle lamella can be softened in mechanical pulping. The rupture occurs in secondary wall or primary wall of the fibre resulting in less fines formation. The wood chips can be pretreated with steam at 120 °C in another type of mechanical pulping called refiner pulping which is a method that chips are fed into the center of two refining disc. This method is called thermomechanical pulp (TMP). As another mechanical pulping method, the wood chips can be treated with sodium sulphite solution and the softening point of lignin is decreased. This type of mechanical pulping process is called Chemo-Thermo Mechanical Pulp (CTMP).

2.1.2. CHEMICAL PULPING

In chemical pulping, half of the wood becomes pulp, the other half is dissolved (Ek, Gellerstedt et al. 2009). The yield is lower compared to mechanical pulp. The main objective in chemical pulping is to remove lignin and release the fibres. Not all of the lignin can be removed at the pulping stage, thus pulp is produced with some lignin remaining in the pulp. The lignin which is left in pulp can be determined by Kappa number.

Kraft pulping is the most dominant chemical pulping method. It has four main stages including steaming as a pretreatment, impregnation of wood chips with chemicals such as sodium hydroxide and sodium sulphide named white liquor. Further steps are delignification as degradation and solubilization of lignin with hydrogen sulphide as the main delignifying agent and blowing as another step to lower temperature and pressure to terminate chemical reactions to reach the fibre /liquor mixture. The several bleaching stages are involved as a chemical process aimed to remove the color in the pulp derived from extractives, residual lignin or carbohydrate side products. As a macromolecule application of lignin after Kraft pulping, the dissolved lignin can be used as adhesives like phenol formaldehyde resins or binders in many technical applications (Lora and Glasser 2002, Bouajila, Limare et al. 2005).

2.2. PAPER MAKING

Dilute slurry of fibres and fillers are transferred to moving wire along with retention aids and wet strength agents and form paper (Brännvall 2009). Clumps of intertwined fibres in paper cling to each other via hydrogen bonding at their contact points (Brännvall 2009). Thus, the

surface is defined by the degree of fibre compression and collapse. After the water is extracted by pressing the paper web by steel rolls, paper is dried to a final moisture content.

2.3. WETTABILITY OF PAPER AND HORNIFICATION

When the fibres or paper are wetted, free water may enter the pores and capillaries. Hydrogen bonding between water and cellulose may occur especially in the amorphous part of the lignocellulose material (Minor 1994). According to Minor (1994), after the removal of water, part of the existent carboxylic acid groups in the lignocellulosic structure can interact with hydroxyl groups in neighboring polymeric chains and establish covalent lactone bridges. These lactone bridges can further change the physical properties of the polymeric material such as wet stiffness or wet modulus of elasticity. This covalent crosslinking cannot be broken by water molecules and only fades under the specific chemical conditions which can reverse the lactone formation.

Hornification refers to the stiffening of the polymer structure of lignocellulosic materials by drying or water removal (Minor 1994). When conditioned wood pulp fibres are dried, the internal fibre volume may shrink due to structural changes in wood pulp fibres. With increasing temperature at drying, the capillary pressure in porous system is increased, since rapid evaporation results in faster water removal from the pores. Only water bound in the cell remains and free water is removed from the cell voids. Hornification can affect paper and pulp tensile properties, since drying of fibres causes a loss of large pores and reduction of surface area (Stone and Scallan 1965). Wet pressing has also been found to contribute to hornification (Maloney, Li et al. 1997). In Figure 1, fully swollen, never dried cell wall has been dried and microfibrillar coalescence has been observed as a hornification behavior.

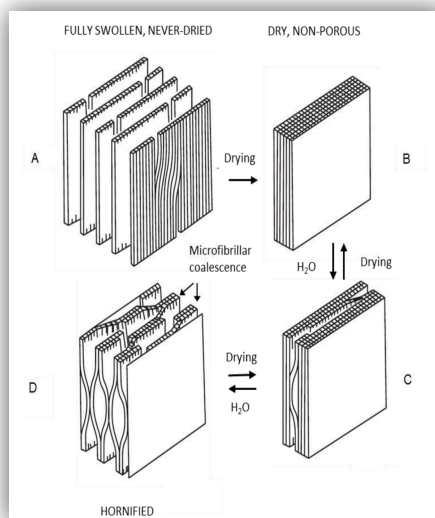


Figure 1. Cell wall behavior during drying(MALONEY, LI ET AL. 1997).

The drying process closes the capillary voids that are not completely reopened by newly entering water. As a result, the irreversible hornified cell wall is less prone for swelling and less flexible compared to the state before drying. Hornification is a feature for especially of low-yield wood pulps like chemical pulps (Jayme and Hunger 1957). Mechanical pulps do not hornify to the extent chemical pulps do. The hornification can be described as an enhancement in the degree of crosslinking within the fibre microstructure, since cross-linking is viewed as an irreversible or partially irreversible connection of interfibrillar hydrogen bonding.

2.4. ADHESION IN PAPER AND HIGH-PRESSURE COMPRESSION

The adhesion theories that have been examined in bonding of cellulose fibres in paper include mechanical interlocking, adsorption or wetting theory, diffusion theory, and the theory of weak boundary layers (Gardner, Oporto et al. 2008). The bonding of cellulose fibres in paper is primarily dependent on hydrogen bonding between the fibres that occurs as the wetted fibres dry in contact with each other and the bonding strength of the fibres can change greatly depending on the methods that has been used to prepare the fibres with the pulping, bleaching and refining process.

To stimulate hydrogen bonding between swollen fibres close contact between adjacent hydroxyl groups is required. Since refined fibres have a fibrillar structure that contributes to adhesion, cellulose fibres interact in water (Gardner, Oporto et al. 2008). Introduction of water can interrupt the fibre structure for swelling. However, due to its strong intermolecular

interaction within the microfibrils, cellulose is resistant to dissolution and liberation. There are also indications of dry adhesion that facilitated by pressure and temperature. Solid compressed cellulose powder under high pressure without additives at elevated temperature (up to 160 °C) shows improved the mechanical properties (Vaca-Medina, Jallabert et al. 2013). This improved mechanical property is even higher for lower crystalline cellulose samples. The surface areas of compressed cellulose samples decrease at high compression temperature, fibers are merged into a smooth structure. Besides, the loss of specific volume is observed combined with a decrease in the material surface area which indicates partial interdiffusion of the fibers' external parts. Interdiffusion can be observable on the SEM images where individual fibers are more difficult to identify due to loss of the interparticle porosity. This significantly improves the mechanical properties of compressed cellulosic materials.

Lignin plasticization could be achieved by several means as a potential route to increase adhesion between fibres induce bonding (Bouajila, Limare et al. 2005). The bonding strength of plasticized specimens can be associated interactions of lignin-lignin and polysaccharide-lignin crosslinking reaction at high temperatures above the glass transition (T_g) with compression under certain pressure. The *in situ* plasticization of lignin also increases the mechanical properties of compressed cellulosic materials.

2.5. PHASE TRANSITIONS AND THERMAL DECOMPOSITION PROPERTIES OF WOOD COMPONENTS

The molecular composition as the amount of holo-cellulose, lignin and extractives defines the thermal degradation of lignocellulosic substrates (Henriksson, Lennholm et al. 2009). Decomposition temperature can be detected by thermal gravimetric analysis (TGA) by the measurement of changes in specimen mass with temperature by thermogravimetric analyzer (Brown 2001). It is a combination of an electronic microbalance device with a furnace and a temperature programmer which allows the sample to be simultaneously weighed and heated. The mass loss is record with increasing temperature.

Hemicellulose is more prone for degradation by elevated temperature than cellulose and lignin. Thus, majority of hemicelluloses that are natively present in pulp, depolymerize or are extracted in pulping process. However, some of the hemicelluloses are retained in pulps and their depolymerization occurs between 180-350 °C. Thermal degradation of lignin is defined to

take place between the temperatures of 250-500 °C (Poletto, Zattera et al. 2012). Softwood Kraft lignin is considered sensitive to thermal induced reactions and the molecular characteristic can be altered severely with irreversible crosslinking induced by temperature (Cui, Sadeghifar et al. 2013).

The thermal decomposition of cellulose is generally initiated via a thermally activated decomposition of the cellulose fibrils (Hillis 1984). With elevated temperatures, cleavage of the glycosidic linkages of cellulose starts and it reduces the polymerization degree of cellulose. The decomposition occurs in the range 240-370 °C and the temperature range is specific to the given cellulose specimen, in this case the Kraft pulp. According to the Criado method, the Kraft pulp degradation occurs by diffusion and the heat transfer which is affected by the arrangement and packing of cellulose crystals (Poletto, Pistor et al. 2011). Decomposition temperatures 180-210 °C for hardwood and, 210-250 °C for the softwood pulps have been proposed (Thoorens, Krier et al. 2014).

DSC (Differential Scanning Calorimetry) can be used to determine glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m). Glass transition in DSC is seen as an endothermic step and it is a phenomenon where polymers undergo a second order phase transition (Wunderlich 2005). The glass transition is a phenomenon observed typically in linear amorphous polymers. Many physical properties change at the glass transition temperature including coefficient of thermal expansion, heat capacity, refractive index and mechanical damping. All these parameters are dependent on the relative degree of freedom for molecular motion within a given polymeric material and it can be used to detect the glass transition temperature. There are some factors that can influence the glass transition of the material:

- The presence of side groups of the polymer backbone that they increase the energy required to rotate the molecule in the main polymer chain.
- The presence of rigid structures in the polymer backbone like phenylene groups.
- Crosslinking.
- Hydrogen bonds between polymer chains.

- Relative molar mass, that higher molar mass polymers have less capability of movement

For lignin, glass transition reflects the degree of intermolecular association. Decrease in T_g is an indication of plasticization potential (Lisperguer, Perez et al. 2009). It can be generalized that the glass transition temperature of lignin is mainly in the temperature range of 110-150 °C. In temperatures below 200 °C, the DSC thermogram curve generally shows an endothermic reaction for lignin that can be attributed to the removal of moisture around 100 °C. When the temperature keeps increasing further, lignin shows an exothermic peak around 365 °C which indicates melting.

It is hard to get a correct value for the glass transition temperature of cellulose, since the glass transition temperature is severely dependent on the moisture content of the cellulose material. (Poletto, Zattera et al. 2012). Moisture dependency of glass transition can be found on Figure 2. According to previous experiments of Salmén & Back, Batzer & Kreibich and Szczesniak, with increasing water content of the cellulose, the glass transition temperature decreases (Salmén and Back 1977, Batzer and Kreibich 1981). However, the second heating runs generally are more reliable to reflect the true glass transition temperature since there is no endothermic peak observed in second heat run.

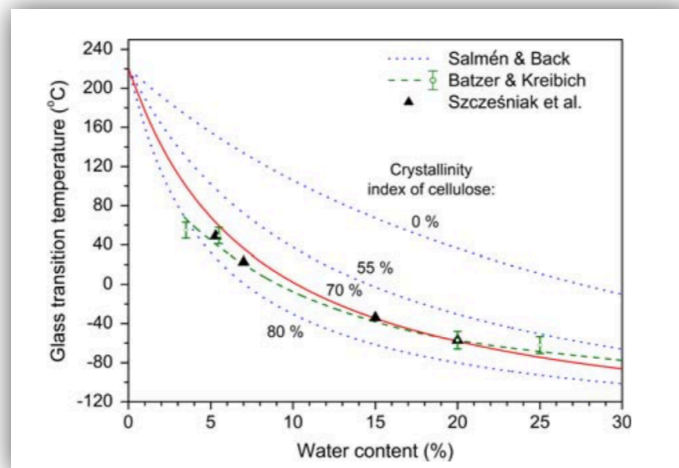


Figure 2. The glass phase transition temperature of cellulose versus water content (Salmén And Back 1977).

2.6. PAPER STRENGTH IN RELATION TO HUMIDITY

The bonding and hydrophobicity of cellulose makes it possible to hold paper together (Hubbe, Venditti et al. 2007). On the other hand, increasing moisture deteriorates paper strength. Due to hygroscopic nature of paper, it contains 4-7% moisture in ambient conditions. Rise in relative humidity (RH) increases also paper moisture content (Figure 3). Paper moisture content experiences hysteresis behavior and the moisture content in a specific RH is dependent on the conditioning cycle (Hubbe, Venditti et al. 2007). Consequently, paper strength is dependent on the moisture content and moisture history.

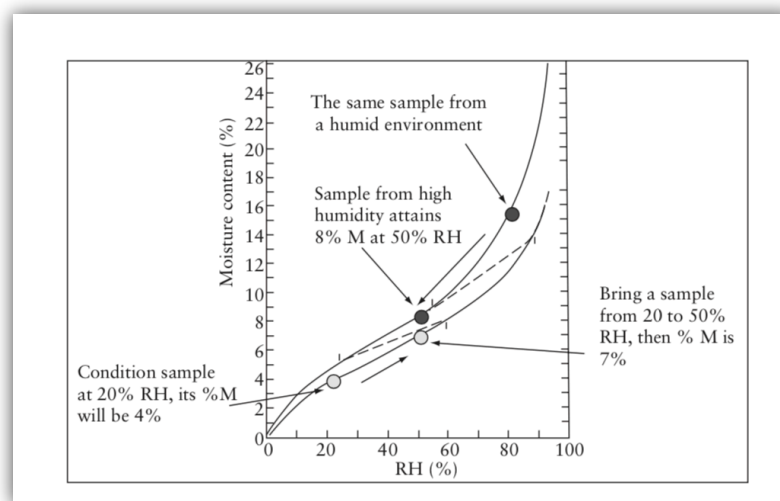


Figure 3. Hypothetical paper moisture content curve with increasing and decreasing ambient humidity (HUBBE, VENDITTI ET AL. 2007).

2.7. TENSILE TESTING OF PAPER

Paper mechanical properties are described by tensile strength, strain and Young's modulus. Normalization to grammage or density is required when several paper grades are compared (Mark, Habeger et al. 2001). A typical stress-strain behavior is shown in Figure 4.

As the motion of the cross-head increases, the tension load denoted as F in Figure 4 increases along with increasing the displacement of the paper strip denoted as Δl . $F_{\max}$ is the maximum strength of the paper test specimen and S_t is a point where fracture occurs at the paper strip. S_b can be calculated from the slope of the linear part of the curve and it denotes the tensile stiffness, Young's Modulus.

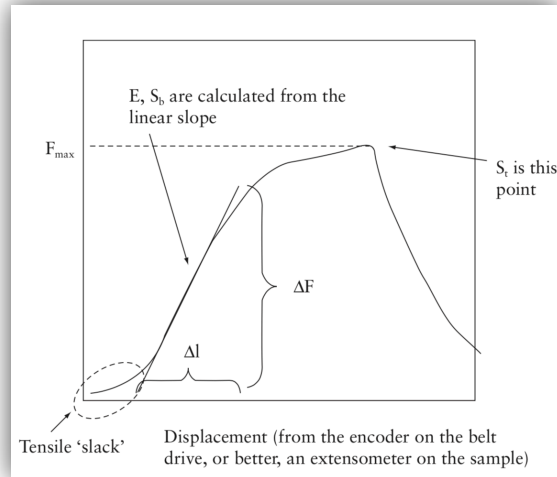


Figure 4. A load-displacement relationship for a paper tensile test (Mark, Habeger Et Al. 2001).

Strain is the relative displacement and it can be denoted as $\frac{\Delta l}{l}$ or ϵ . The stress is force unit per area, and it is denoted as σ . The tear index can be defined as tearing strength divided by basis weight and tearing resistance is primarily a property of the inner structure of the sheet. Moisture content of the paper has a large effect on its tearing resistance. Higher moisture content and higher relative humidity of the test environment increase the tearing resistance. Tensile index can be defined as the tensile strength in N/m divided by grammage of the paper specimens.

3. METHODS AND MATERIALS

3.1. MATERIALS

Bleached Kraft, unbleached Kraft, dissolving pulp and HT-CTMP (High Temperature Chemo thermo mechanical pulp) were supplied by Stora Enso in the form of hand sheets with target grammage of 100 g/m². Whatman filter paper was used as a reference manufactured from cotton linters. The hand sheets of each grade are shown in Figure 5. Unbleached Kraft, bleached Kraft and HT-CTMP are softwood, however dissolving pulp is hardwood. For cellulose filter, it is unknown whether it is softwood or hardwood.

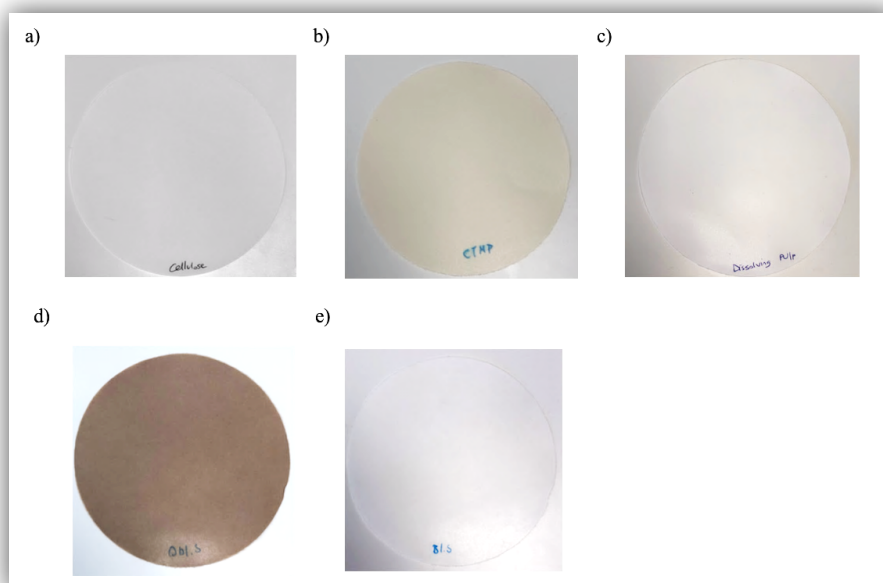


Figure 5. Paper hand sheets of a) cellulose filter paper, b) HT-CTMP, c) dissolving pulp, d) unbleached Kraft and e) bleached Kraft.

Bleached Kraft pulp generally consists of cellulose and hemicellulose and small amount of lignin and extractives (Popescu, Tibirna et al. 2008). Unbleached Kraft fibres consist of 65–75 % cellulose, 17–32 % hemicellulose, and 3–8 % lignin in comparison to bleached Kraft with 70–80 % cellulose and 20–30 % hemicellulose and 1 % lignin (Stenius, Yhdistys et al. 2000). The residual lignin and hemicellulose content decreases with bleaching and the unbleached Kraft is more heterogeneous than the bleached Kraft with intact individual fibres (Beg and Pickering 2008). The unbleached Kraft is reported to have fractions of middle lamellae on fibre surfaces that are characteristic of lignin deposits (Yan, Li et al. 2004).

Surface of HT-CTMP fibres comprises cellulose, amorphous hemicellulose and lignin (Börås and Gatenholm 1999) (Figure 6). The distribution of the surface component can be allocated as 40 % of carbohydrates as hemicellulose and cellulose, 28 % of lignin and 32 % of extractives. The lignin phase can be denoted as irregular patches at the surface (Leask and Kocurek 1987). The surface composition and morphology of HT-CTMP is distinct from other pulp grades of this study in that lignin is expected to reside dominantly on the fibre surfaces (Mjoberg 1981).

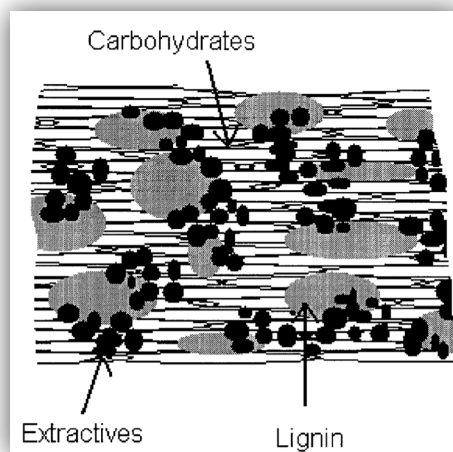


Figure 6. Fibre surface structure of HT-CTMP.

Dissolving pulp is a pulp with high cellulose content, and it is not used for paper production but production of cellulose derivatives and regenerated cellulose (Yasnovsky and MacDonald 1983). It is lignin free and it has low amount of hemicellulose compared to paper grade pulp. It can be produced from both Kraft and Sulfite processes by introducing a pre-hydrolysis step prior to Kraft cooking. Degradation of hemicellulose prior to cooking causes high cellulose content. Hydrolysis results in partial dissolution of hemicellulose.

3.2. PAPER SPECIMEN PREPARATION

The dimension of the paper test specimen is an important parameter particularly for the test specimens for mechanical testing. To prepare a test specimen in accordance with TAPPI, the paper specimens were cut 20 mm wide and 60 mm long to allow 60 mm distance between the clamping (Figure 7). The strips were cut with a paper cutter. The sealing zone is 20 mm × 20 mm.

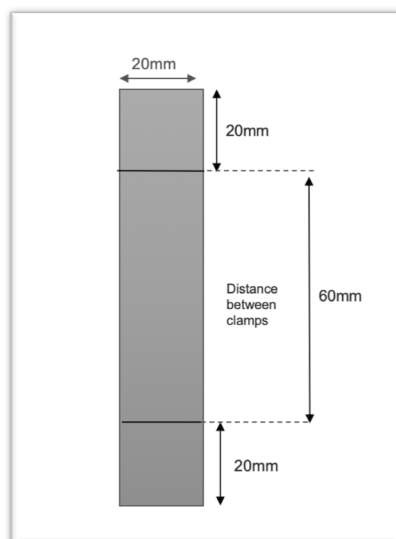


Figure 7. Paper test specimen for tensile Testing

3.3. CONDITIONING THE PAPER GRADES

The paper grades were either conditioned or wetted prior to the experiments. Conditioning was performed in 11 %, 55 %, 75 %, 95 % RH. That were created using saturated salt solutions: 11 % with NaCl, 55 % using MgNO_3 , 75 % using and 95% using K_2SO_4 . Each saturated salt solution was placed in a chamber along with humidity measurement device to ensure that desired humid condition was achieved. The moisture content and percentage of the paper grades was recorded for 7 days and 24 hours.

The moisture content of the paper specimens was determined with gravimetric method using drying in the oven for 2 hours at 104°C .

Another method to make the paper specimens wet was using pipette to add water without preconditioning each specimen. Each paper specimen was wetted just before the compression test. The moisture content of the specimens was also examined gravimetrically.

3.4. COMPRESSION

Compression of paper was performed with a hot press (Fontjine Holland). The metal plates were used to transfer the heat from the hot press to the paper specimens. Teflon pieces were used between the metal plates and the paper specimens were placed in between the Teflon pieces. Stainless-steel gauge foil with respect to the selected the thickness of the paper specimens was also placed in between top and bottom Teflon pieces and the paper specimens.

The paper specimens were placed properly on the metal plates accordingly the confluent part of the paper that must be 20 mm x 20 mm. The scheme for the hot press technique is shown in Figure 8.

Both plates were provided with a cooling system that could be used after pressing the specimens at elevated temperatures. As an example, if the paper specimens were pressed at 180 °C, it took 5 minutes to cool down to 80 °C with cooling system. The ambient conditions were 21 °C and 30 % RH.

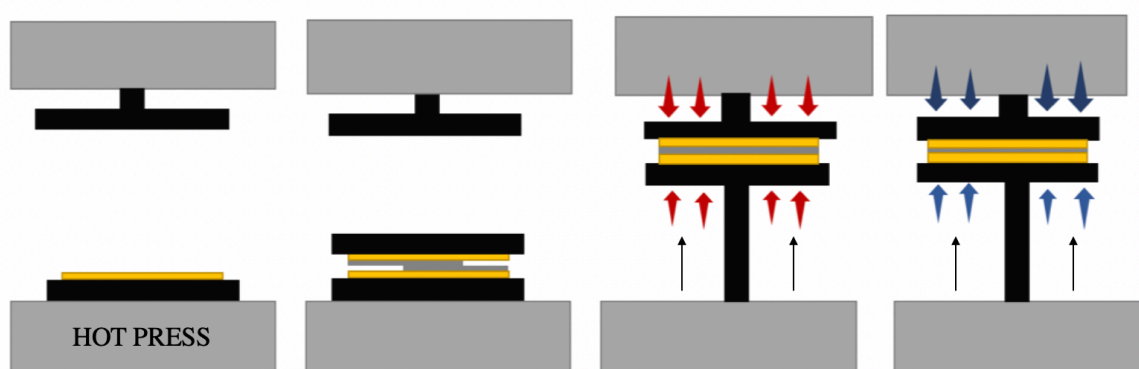


Figure 8. Scheme of the set up for compression of paper specimen

Moisture content of the paper specimen for swelling of fibres, temperature and pressure were chosen as the variables to initiate and enhance the fibre-fibre interactions. First set of experiments was done with the specimens which were conditioned in a humidity chamber for 7 days at RH 95 %. Since, it was asserted that moisture content conditioned specimens were insufficient for convenient sealing, the remaining of experiments were performed using wetted specimens. At this case only the junction part which was 20 mm x 20 mm wetted by additional water. Temperature was selected to be below the decomposition but above the glass transition temperature of the specimen. The pressure force was also selected as constant as 45kN.

3.5. THERMAL CHARACTERIZATION

All of the paper grades were heated using heating rate of 10 K/min from 25 °C to 600 °C to detect the decomposition temperature. DSC was performed in nitrogen atmosphere with a heating rate of 10 °C /min. The first heating temperature range scanned was from 25 °C to 220 °C. After first heating run, the cooling run was performed within the temperature range 200 °C

to -10 °C and then the second heating run was performed from -50 °C to 250 °C. The grades which were investigated by TGA/DSC were wetted with additional water method, since the highest moisture level was been reached by that method.

3.6. TENSILE TESTING OF THE PAPER AND THE SEAL

Paper testing was performed in accordance with TAPPI standard with adaptation to the seal using Instron tensile tester. Minimum of 10 specimen for each paper grade was tested. Paper specimens were clamped in the jaws and the paper strips must be aligned with the clamps. The extension rate was 25mm/min.

3.7. REVERSIBILITY TEST

Sealed paper specimens were placed in a cup filled with distilled water at room temperature and the sealed paper specimens was shaken for at least 2 days to determine whether the seal is disintegrated.

3.8. LIGHT MICROSCOPE AND SCANNING ELECTRON MICROSCOPY (SEM)

The paper specimens and sealed paper specimens were embedded in an epoxy and cut by microtome for light microscope and Scanning Electron Microscopy (SEM). Paper specimens were mounted on a metallic holder and then platinum sputtered with EMITECH K550X-J25. Images were taken from the sealed zone of paper specimens with Leo Ultra 55 or JEOL JSM-7800F Prime.

4. RESULTS AND DISCUSSION

4.1. MOISTURE CONTENT

Cellulose filter paper that was conditioned 24 hours in the 11, 55, 75 and 95 % relative humidity reached a moisture content increase (from ambient) of 1.54, 1.86, 2.09 and 2.50 wt.%, respectively. Clearly a moisture gradient can be generated but the final humidity contents are low. Increasing the conditioning time to 7 days resulted in moisture content of 12.82 wt.% with the highest RH level used. After conditioning for 7 days, it is shown that the highest moisture percentage was achieved by HT-CTMP by 18 % and the lowest moisture percentage was recorded for cellulose filter paper (Table 1). Highest moisture contents were

reached by the wetting method. The highest moisture percentage was recorded for HT-CTMP and the lowest moisture percentage was recorded for dissolving pulp. This can be related to differences of water permeability properties of the paper grades.

Table 1. Moisture content of conditioned and wetted paper grades

<i>Paper Grades</i>	<i>Moisture content (wt.%) of paper grades in a humidity chamber for 7 days</i>	<i>Moisture content (wt.%) of paper grades in a humidity chamber for 7 days</i>
<i>HT-CTMP</i>	18.75	49.22
<i>Unbleached Kraft</i>	17.99	36.59
<i>Bleached Kraft</i>	15.20	32.61
<i>Cellulose Filter Paper</i>	12.82	39.98
<i>Dissolving pulp</i>	15.53	27.63

4.2. THERMAL CHARACTERISTIC OF THE LIGNOCELLULOSIC SUBSTRATES

4.2.1. DEGRADATION TEMPERATURE

For each different paper grades, decomposition temperature data was collected and shown in Table 2. The highest decomposition temperature was recorded for the cellulose filter at 300 °C. The cellulose filter paper was followed by bleached Kraft to decompose at 290 °C. For unbleached Kraft and dissolving pulp, decomposition started at 285 °C. For HT-CTMP, it was recorded at 250 °C.

The reason that decomposition temperature was different for each pulp grade is due to the different molecular composition. The volatilization of different components occurs at different temperature ranges. Hemicelluloses generally decompose at 225-325 °C and for cellulose decomposition temperature is generally 325-375°C, whereas lignin decomposes gradually over

the 250-500 °C temperature range (Brown 2001). Therefore, it is expected to observe higher decomposition temperature for cellulose filter paper, since it contains higher amount of cellulose compared to other pulp grades.

Table 2. Density, decomposition temperature and the end set point of TGA data of the specimens

<i>Paper grades</i>	<i>Density (kg/m³)</i>	<i>Decomposition Temperature (°C)</i>	<i>End set point(°C)</i>
<i>Cellulose</i>	652	300	397
<i>Bleached Kraft</i>	750	290	390
<i>Unbleached Kraft</i>	815	285	390
<i>Dissolving Pulp</i>	822	285	385
<i>HT-CTMP</i>	796	250	395

The similar decomposition temperature of bleached Kraft and dissolving pulp can be attributed to molecular compositions of these grades. The expectation was that the lignin content affects the decomposition temperature of the unbleached Kraft pulp. Popescu et al. has reported that bleached Kraft pulp has higher decomposition temperature due to more compact and more oriented structure of the bleached Kraft pulp fibre compared to unbleached Kraft (Popescu, Tibirna et al. 2008). However, in the current study there was no significant difference of its decomposition compared to the dissolving and bleached Kraft pulp.

4.2.2. GLASS TRANSITION TEMPERATURE (T_G)

The glass transition temperature for each paper grade can be found at the Table 3.

Table 3. The glass transition temperature for the various paper grades

<i>Paper grades</i>	<i>The midpoint glass transition temperature (°C)</i>
<i>Bleached Kraft</i>	155
<i>Unbleached Kraft</i>	140
<i>Dissolving pulp</i>	150
<i>HT-CTMP</i>	180
<i>Cellulose Filter Paper</i>	145

According to DSC thermograms at Appendix Figure 1, each paper grade experienced water evaporation stage seen as an endothermic peak. Generally, this endothermic transition was observed in between 25 °C to 125 °C at the first heating run. At the second heating run, endothermic peak was not observed, since all free water was evaporated at the first heating stage. In Appendix Figure 1, It was found out that glass transition temperature was higher for unbleached Kraft and HT-CTMP compared to other paper grades. Bleached Kraft's glass transition temperature was detected to be 155 °C. Onset point is 125 °C which was the beginning temperature for the glass transition and end set point could be advocated as 180 °C. Thus, T_g was defined in the middle of this characteristic temperature region and it was 155 °C.

For unbleached Kraft, glass transition temperature was detected as 140 °C. Onset point can be asserted as 120 °C and end set point can be also advocated as 160 °C. Thus, T_g was defined to be 140 °C. According to DSC result, onset point was determined as 110 °C for cellulose filter paper and end set point can be also advocated as 180 °C. Thus, T_g was defined as a temperature region as 145 °C. For HT-CTMP, onset point was determined as 150 °C and end set point can be also advocated as 210 °C. Thus, T_g was defined as a temperature region as 180 °C. For dissolving pulp, onset point was determined as 130 °C and end set point can be also advocated as 180 °C. Thus, T_g was defined as a temperature region as 155 °C.

The one of reasons that the glass transition can vary for each pulp grade is the presence of side groups of the polymer backbone that increase the energy required to rotate the molecule in the main polymer chain and the amount of crosslinked polymer within the lignocellulosic

substrate (Brown 2001). One of the major constituents of HT-CTMP is lignin associated as complex phenolic polymer. Hence, the presence of lignin was assumed to be the reason that glass transition temperature HT-CTMP was detected higher than other pulp grades such as bleached Kraft which contains trace amount of the lignin. However, for bleached Kraft, the glass transition temperature is higher compared to unbleached Kraft, although unbleached Kraft contains a complex cross-linked phenolic polymer. Since bleaching process was applied to Kraft, the pulp grade structure became more compact and oriented denoting the excessive stability of the bleached Kraft. Hence, the glass transition temperature of bleached Kraft was detected higher than unbleached Kraft.

For cellulose filter paper and dissolving pulp, glass transition was detected to be lower than unbleached and bleached Kraft, since the presence of rigid structures in the polymer.

4.3. HOW DOES COMPRESSION AFFECT SUBSTRATE INTERACTIONS?

All the substrate grades were sealed using 200 °C, 45kN and 30 second pressing time using a cooling system was applied (Table 4). Exclusion of cooling system and reducing the pressing time from 30 seconds to 5 seconds led to that the Kraft grades and the dissolving pulp did not form a seal. Only reduction of sealing time resulted in no sealing with bleached Kraft pulp. The importance of the cooling system was taken as an indication that a certain moisture content must be provided to paper grade to acquire a sealing. Without using the cooling system, the conditioned specimens lost some of the moisture already prior to compression and did not promote to obtain sealed paper specimens. Therefore, the compression experiments were continued using wetting paper specimens with additional water. Addition to amount of water in the structure, the durability of composites after compression was dependent on the temperature which were released from the elevated pressure. This could be another reason to use a cooling system to cool the specimen below the T_g and then release them to room temperature. Cooling each specimen to 80 °C made them reach the glassy state in a controlled manner.

Table 4. Sealing efficiency of the conditioned paper specimens (RH 95%)-The symbol of cross denoting that the paper specimens were not sealed in that condition

<i>Paper grades</i>	<i>Cooling system</i> <i>5sec compression</i>	<i>Cooled to room</i> <i>temperature</i> <i>5 sec</i> <i>compression</i>	<i>Cooling system</i> <i>30sec</i> <i>compression</i>	<i>Cooled to room</i> <i>temperature</i> <i>30 sec</i> <i>compression</i>
<i>Cellulose filter paper</i>	✓	✓	✓	✓
<i>HT-CTMP</i>	✓	✓	✓	✓
<i>Bleached Kraft</i>	✗	✗	✓	✗
<i>Unbleached Kraft</i>	✓	✗	✓	✗
<i>Dissolving Pulp</i>	✓	✗	✓	✗

An operating window for sealing was created for the wetted paper specimens and it was itemized in Appendix Figure 2. The sealed paper specimens were identified within a sealing zone (Appendix Figure 2) which has been marked with black as an operating window for sealing. The sealed paper specimens which were cooled with cooling system were marked as blue star and the sealed specimens which were cooled to room temperature were marked with red cross. Non sealed paper specimens were marked as round purple symbol located outside the operating window of sealing.

A common operating window for the sealed paper specimens was identified (Figure 9) by compiling the individual sealing zones (Appendix Figure 2). The red lined region in Figure 9 indicates the exact operating window evidently that all different paper grades have been sealed in that zone.

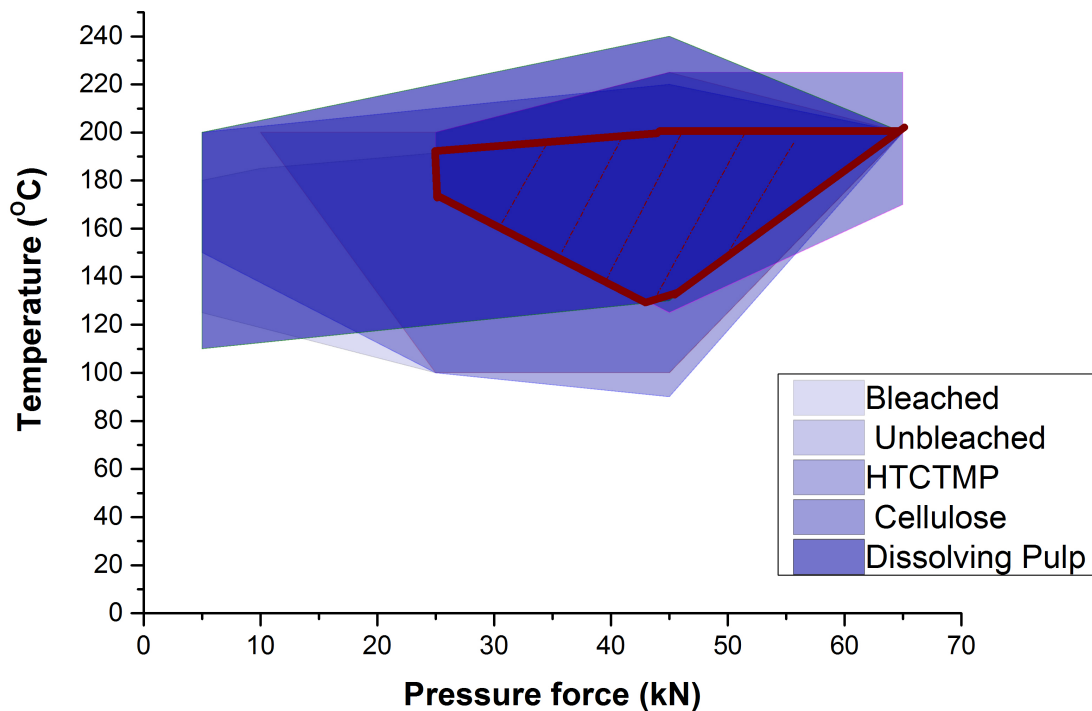


Figure 9. Common compression operating window for all paper grades

The sealing achieved in 100 °C to 225 °C range can be a consequence of induced adhesive bonding between contiguous paper grades promoted by compression and phase transition to create an available physical state called rubbery state. It can be done by increasing the contact area by deforming the paper specimens by pressure to induce plasticization of especially lignin and hemicellulose (Zhang, Wu et al. 2012). When the paper specimens are brought into close contact under pressure with elevated temperatures, capillary pressure in porous structure of the cell wall of the lignocellulosic substrate increases with increasing temperature. Rapid evaporation occurs first for water removal from the pores of the cell wall along with compression, since the paper specimen were wetted before. After water removal, specimens in a state of proximate contact are available for the rubbery state while stimulating the adhesive bonding to compose a sealing. Particularly for the paper grades which contain significant amount of lignin at the fibre surface, lignin plasticization promotes the sealing. For the paper grades which contains less amount of lignin, lignin plasticization impact can be ignored. Only hemicellulose plasticization can be considered.

Table 5. Pre and post compression thickness of paper grades

<i>Paper grades</i>	<i>Average Thickness of the paper grade before compression(mm)</i>	<i>Average Thickness of the sealed zone after compression(mm)</i>	<i>Densification percentage (%)</i>
<i>Cellulose filter paper</i>	0.136	0.18	66
<i>Dissolving Pulp</i>	0.189	0.245	65
<i>Bleached Kraft</i>	0.126	0.184	73
<i>Unbleached Kraft</i>	0.126	0.193	76
<i>HT-CTMP</i>	0.137	0.182	66

When the paper specimens were compressed, several physical changes could be observed. One of the physical changes recorded significantly is the densification. The sealed zone of the paper strips was densified by the combination effect of the phase transition, elevated temperature and high-pressure force (Table 5). The thickness of the seal was the highest for dissolving pulp and the lowest thickness value for cellulose filter paper. According to densification percentage results, the most compressible paper kind was unbleached Kraft and the least one dissolving pulp.

A color change was observed at elevated temperatures particularly on the sealed zone for some paper grades. The coloration can be attributed the molecular composition of the selected lignocellulosic substrates and that high hemicellulose content within the paper grades promotes the color change due to likely hemicellulose degradation above 180 °C. No significant color change was observed at any temperature and pressure range for cellulose filter paper since the cellulose filter paper constituted major amount of cellulose noticeably than hemicellulose. For bleached Kraft, the color change was observed at the sealed zone above 200 °C compression (Figure 9a). For unbleached Kraft, the color change was not detectable due to paper's intrinsic brown color.

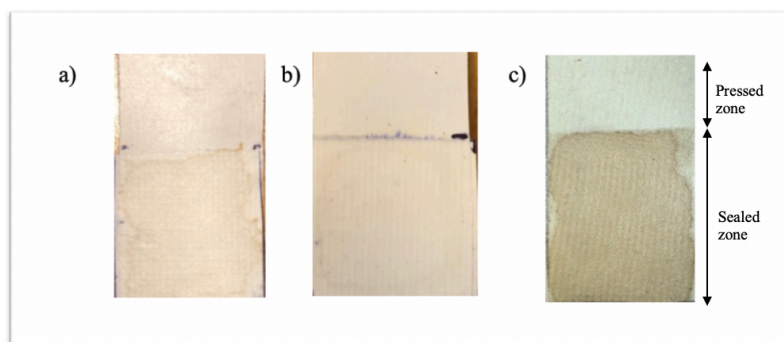


Figure 9. Sealed zone of the compressed specimens above 200 °C of a) Bleached Kraft b) Dissolving pulp c) HT-CTMP.

Color change was not significant for dissolving pulp and it can be explained by the low hemicellulose content similar to cellulose filter paper. The most significant color change was observed for HT-CTMP as shown in Figure 9c. At elevated temperatures, HT-CTMP specimens were compressed and the sealed zone changed its color from light yellow to brown above 180 °C, that is already below its decomposition temperature. Hence, the temperature of 180 °C, pressure 45 kN and sealing time of 30 sec was chosen as the common sealing condition for all the paper grades.

4.4. TENSILE STRENGTH OF THE PAPERS AND SEALS

The tensile strength-strain determination was normalized with the paper density (Appendix Figure 3). The normalized average of the maximum strength of bleached Kraft is $5.29 \times 10^5 \text{ Pa}/(\text{kg}/\text{m}^3)$, for unbleached Kraft, the highest strength among the grades, $6.34 \times 10^5 \text{ Pa}/(\text{kg}/\text{m}^3)$, is recorded and for dissolving pulp $3.35 \times 10^5 \text{ Pa}/(\text{kg}/\text{m}^3)$. For HT-CTMP, the average of the maximum strength is the lowest among the pulp paper grades $1 \times 10^5 \text{ Pa}/(\text{kg}/\text{m}^3)$ and for cellulose filter paper even lower, $6.98 \times 10^4 \text{ Pa}/(\text{kg}/\text{m}^3)$. Tear and tensile index have been found to be directly proportional to the cellulose/hemicellulose ratio (Molin and Teder 2002). Tear index decreases while tensile stiffness and tensile index increased with decreasing cellulose/hemicellulose ratio. The interpretation of the results is that an increase in the amount of hemicelluloses presented by less stiff and brittle fibres.

A consequence of high yield process product, HT-CTMP is expected to have lower maximum strength. An increased pulp yield by the mechanical pulping at constant lignin content implies an increased amount of hemicellulose, since the cellulose yield only can be

varied to a minor extent. Paper grades can be compared with varying hemicellulose contents and it has been found that with mechanical pulping tear index decreases with an increased hemicellulose content. Low tensile index causes lower maximum strength along with reduced tensile stiffness.

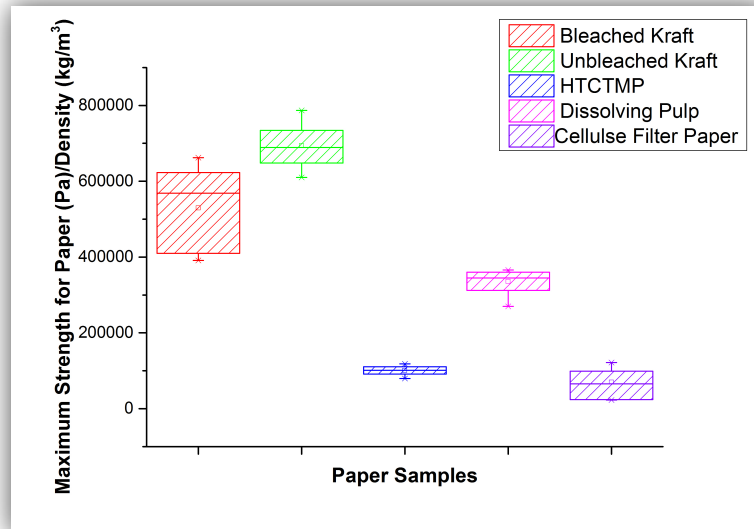


Figure 10. Maximum tensile strength of the various paper grades

Maximum strength of dissolving pulp was the lowest among the chemical pulps. It has been suggested that low tear index depends on hemicellulose content. More hemicellulose and more lignin gives a more brittle paper has been reported (Kettunen, Laine et al. 1982). However, decrease in tear index can be due to the decrease in the number of fibres per unit weight of paper in chemical pulps (Vinje and Worster 1969). Unbleached Kraft specimens have the highest maximum strength among the inspected grades and is hence the stiffest material. The explanation can be also related to tear index that cause by the decrease in hemicellulose and increase in lignin content gives a stiffer material compared to bleached Kraft.

The crack position of the paper grades varied from the middle until the 0-18 mm from the middle and beyond (Figure 11). The specimens cracked beyond the 0-18 mm position were excluded from the result data for further evaluation.

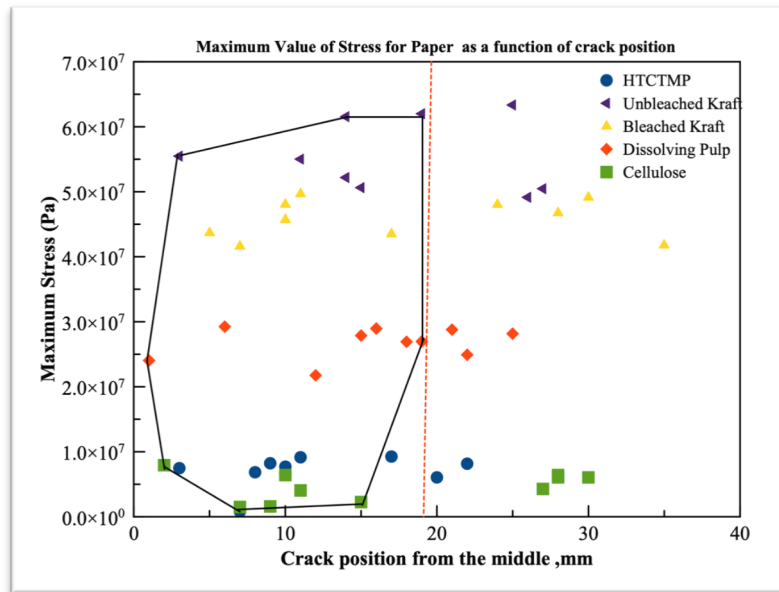


Figure 11. Crack position of paper grades from the middle of tensile testing with respect to maximum stress.

Young's modulus and normalized tensile strength of the sealed paper grades are presented in Figure 12 and 13 (raw data in Figure 4 in the Appendix). The maximum strength of bleached Kraft is $2.38 \times 10^5 \text{ Pa}/(\text{kg}/\text{m}^3)$. The unbleached Kraft is the strongest with $3.51 \times 10^5 \text{ Pa}/(\text{kg}/\text{m}^3)$. The average of the maximum strength of bleached Kraft is $2.49 \times 10^5 \text{ Pa}/(\text{kg}/\text{m}^3)$. For HTCTMP, the average of the maximum strength is $1.66 \times 10^5 \text{ Pa}/(\text{kg}/\text{m}^3)$ and for cellulose filter paper, $5.52 \times 10^4 \text{ Pa}/(\text{kg}/\text{m}^3)$.

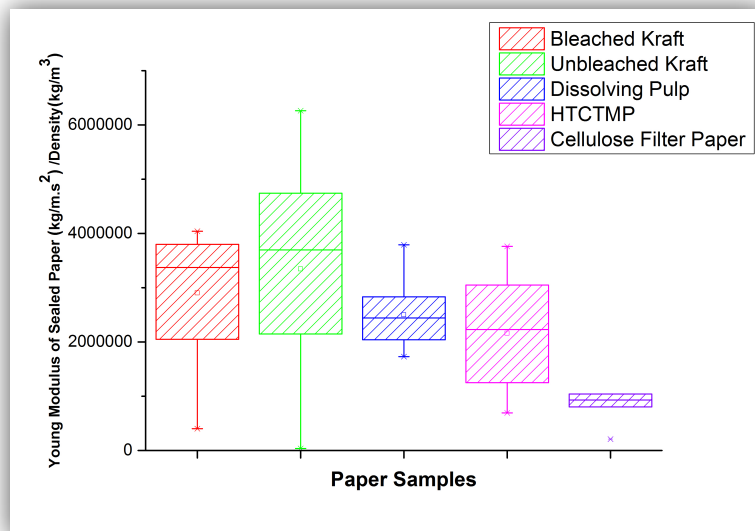


Figure 12. Young's modulus of sealed paper grades normalized to seal density.

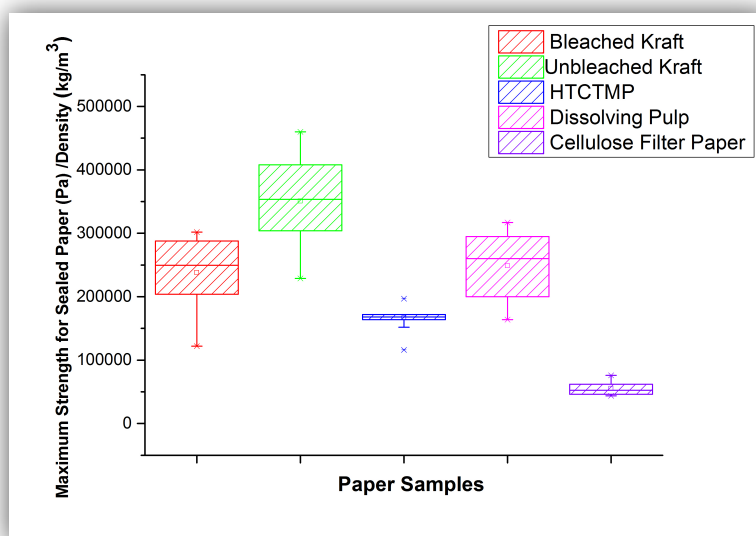


Figure 13. Maximum strength of sealed paper grades normalized to seal density.

The average seal strength of the unbleached Kraft is higher than any of the other paper grades (Figure 13). Respectively, dissolving pulp and bleached Kraft seal strengths are higher than HT-CTMP and cellulose filter paper. Several explanations can describe the phenomena that the seal strength of unbleached Kraft has higher since the paper itself has the highest ultimate strength among the others. The tensile stiffness of the paper inherently affects the seal properties at this case. As another explanation of the stronger seal properties of unbleached Kraft is the lignin plasticization. Plasticized lignin between lignocellulosic substrates that are brought to close contact, stimulates robust seals. Since, only HT-CTMP and unbleached Kraft have considerable amount of lignin, lignin plasticization can be ignored for other paper grades. Although lignin is also a major constituent of HT-CTMP like unbleached Kraft, the seal strength shown as maximum strength is detected as the lowest among the other. Even though the seal properties of HT-CTMP was expected to be the same with unbleached Kraft, the lower tensile stiffness and tear index of HT-CTMP itself hinders the seal strength. However, it is noticed that the seal strength of the HT-CTMP is higher than the inherit HT-CTMP paper strength which can be associated as a unique property of sealed HT-CTMP paper grades due to excessive plasticization.

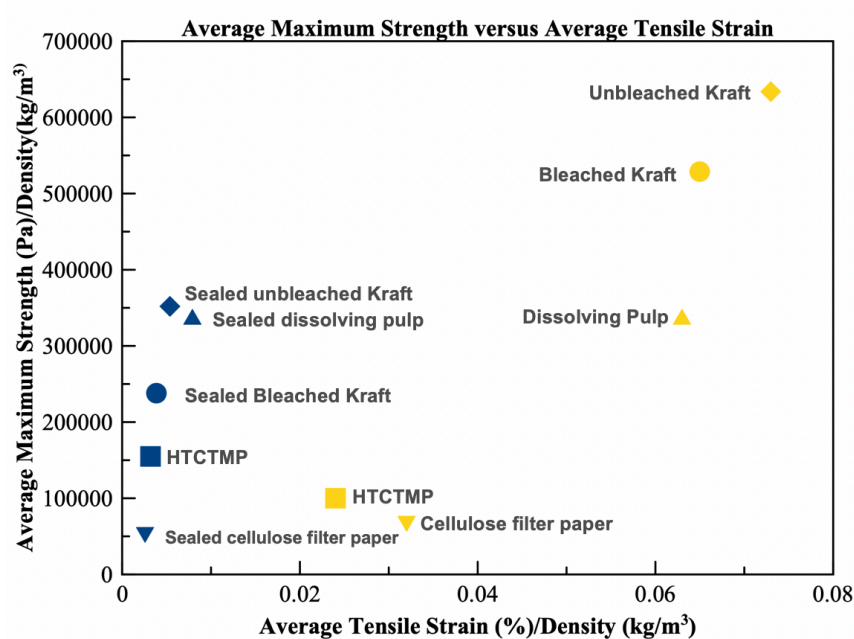


Figure 14. Average tensile strain versus average maximum strength of paper (yellow) and seal (blue) normalized to density.

Bleached Kraft, unbleached Kraft and dissolving pulp test specimens break from the seal which is denoted as 0 mm as a crack position in Figure 15. HT-CTMP and cellulose filter paper specimens dominantly crack from the paper indicating that the seal is stronger than the paper.

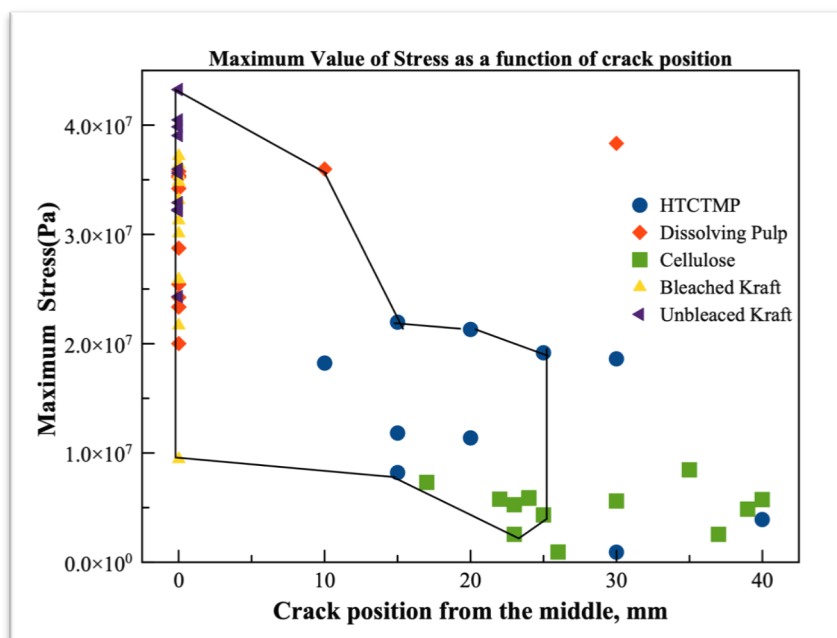


Figure 15. Crack position of sealed paper specimens from the middle of tensile testing with respect to maximum stress.

4.5. VISUALIZATION OF THE SEAL

Seal of cellulose filter paper appeared separated when an inspection has been performed by light microscope (Figure 16a and b). Dissolving pulp (Figure 16c and d), bleached Kraft (Figure 16e and f), and HT-CTMP (Figure 17c and d) seal appeared connected. Seal of unbleached Kraft separated (Figure 17a and b), however was deemed to be due to interaction with epoxy rather than a poor seal.

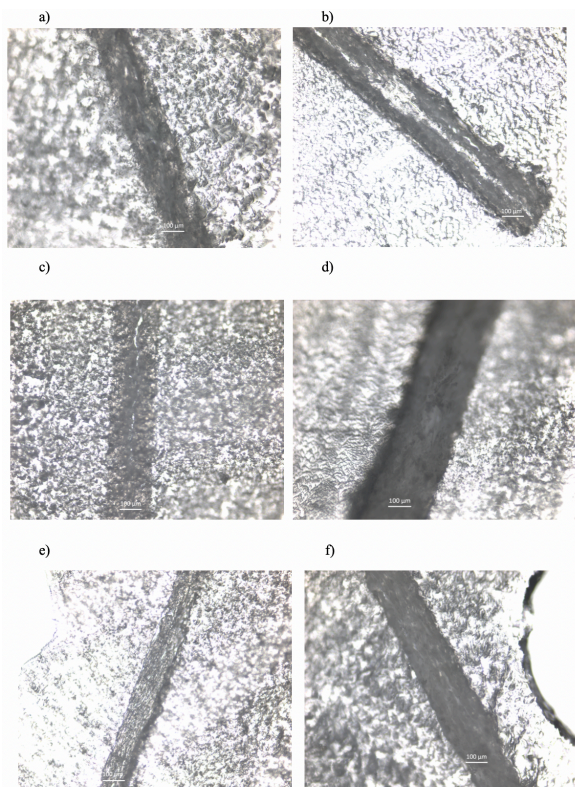


Figure 16. Light microscope images a) cellulose b) sealed cellulose filter paper c) dissolving pulp d) sealed dissolving pulp e) bleached Kraft f) sealed unbleached Kraft specimen.

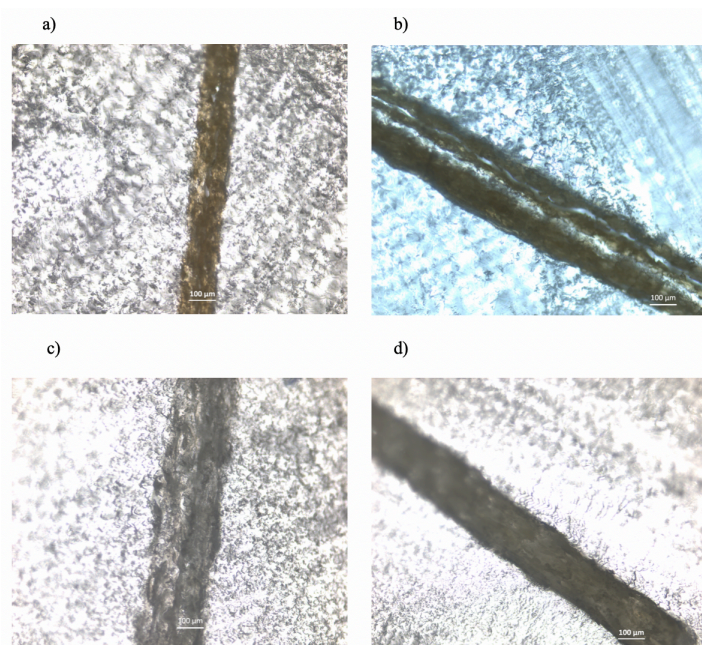


Figure 17. Light microscope images a) Unbleached Kraft b) Sealed unbleached Kraft c) HT-CTMP d) Sealed HT-CTMP specimen.

SEM inspection of HT-CTMP seal revealed that the two substrates are not completely intertwined together, and a separation is observable (Figure 18).

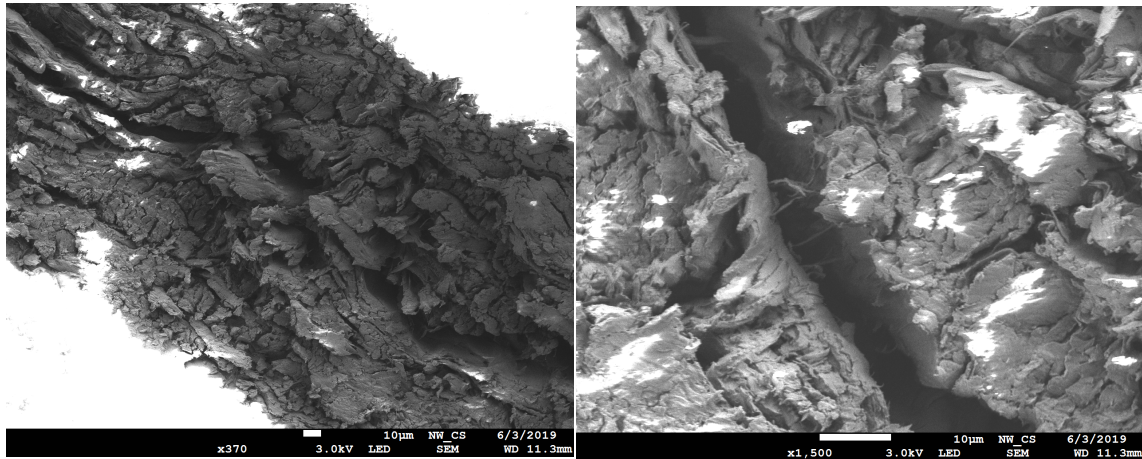


Figure 18. Sealed HT-CTMP specimen SEM micrographs with different magnifications.

4.6. REVERSIBILITY TEST

Specimens which were pressed at 180 °C and 45 kN were placed in distilled water vials and shaken for 48 hours. The seal of bleached Kraft, cellulose filter paper and dissolving pulp disintegrated instantly. The seal of unbleached Kraft and HT-CTMP paper specimens were intact after 48 hours in water (Figure 19). Once, these paper grades were taken out to dry at room temperature, it was observed that the seal can be torn apart by force. However, it was observed that after drying HT-CTMP and unbleached Kraft at room temperature paper specimens were stayed connected. Thus, permeant additive free sealing has been reached only for unbleached Kraft and HT-CTMP.

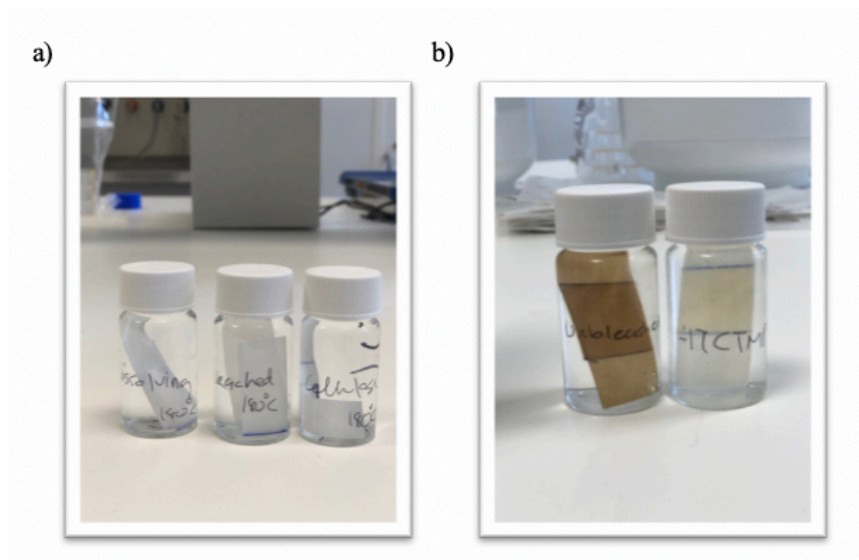


Figure 19. Reversibility test for a) Dissolving pulp, bleached Kraft, cellulose filter paper b) unbleached Kraft, HT-CTMP sealed paper specimens placed in distilled water.

5. WHAT IS THE MECHANISM BEHIND THE SEALING?

When the paper specimens are either conditioned or wetted by water, the fibres of the paper specimens start to swell. Although the individual fibres are bonded to each other with hydrogen bonds, more hydrogen bonding occurs between water molecules and fibres by swelling (Figure 20, left). Once the paper specimens are brought into close proximity by compression, the structure densifies. At elevated temperatures, plasticization of the polymers occurs to act as adhesive to seal the paper grades. The plasticization of lignin can either occur *in situ* at the surface of the fibres particularly for HT-CTMP, since the fibre surface contains lignin (Figure 20a). It is also known that in high temperature and pressure lignin can be liberated and can migrate in pulp. Given that the conditions of this thesis work are changed to higher temperature or pressure, there is a possibility that lignin migrates to the sealing zone to act as adhesive at the junction point (Figure 20b). However, at the current condition the situation presented in Figure 20a is more likely to occur.

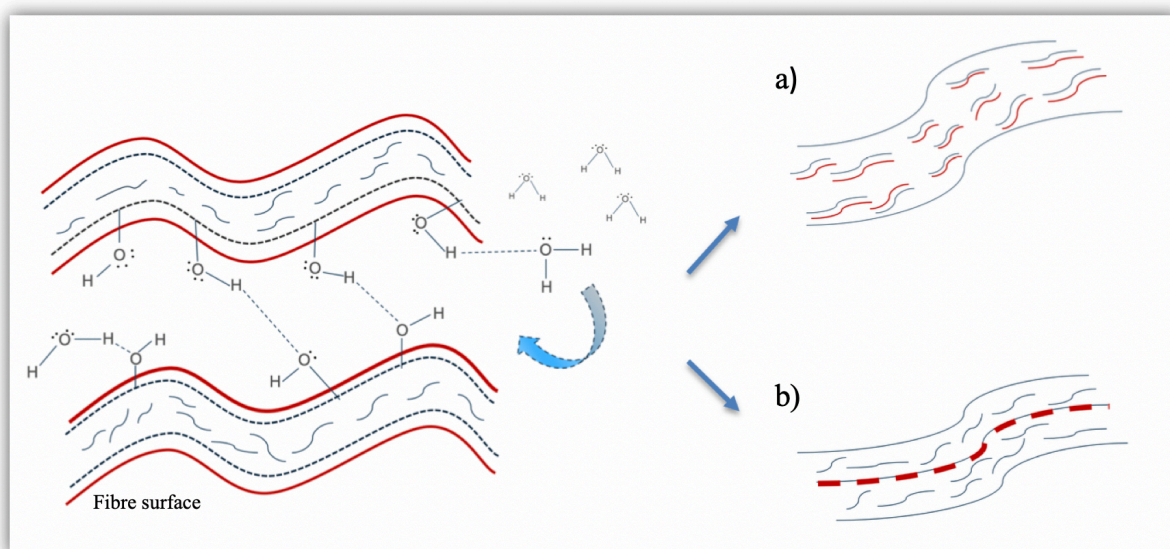


Figure 20. Scheme of fiber structure and hydrogen bonding between fibers (left). The red lines represent lignin. Sealing mechanism via a) lignin plasticization at the surface of the fibres and the case when b) plasticized lignin migrates to the sealed zone.

6. CONCLUSIONS

With this thesis work, an alternative solution method was investigated to promote innovations and sustainability with additive free sealing as a packaging solution particularly for paper industry. The critical factors have been revealed for additive free sealing as humidity, elevated temperature and pressure and lignin plasticization. Paper specimen must be conditioned to certain humidity level and compressed at elevated temperatures to initiate affinity between them. Elevated temperature is vital to be combined with the sealing and it must be above potential glass transition temperature but below the degradation temperature. The main mechanism for the sealing of the inspected substrates was found to be lignin plasticization. Grades with trace amount of lignin sealed in ambient conditions however the seals were not resistant to wetting. Sealed paper grades with significant amount of lignin were resistant to water wetting and the seal remained permanent. The mechanism of the dry seal and how to improve sealing of grades without lignin remains unrevealed.

7. FUTURE WORK

The work performed indicates the importance of chemical composition of the paper grades to the sealing performances. A follow-up work to this master thesis should focus on determination of molecular composition of the intrinsic paper grades and potential changes in it in humidity, high temperature and pressure. A method such as HPLC (High-performance liquid chromatography) can be employed for molecular composition determination.

There are several variables especially for the compression test which were not tested for each different paper grade. Such as sealing zone dimensions and compression time as an important variable must be tested for further studies. Challenging the compression parameters of this study towards shorter pressing time, higher pressure and additional means to promote the sealing such as irradiation are a natural next step.

Development of nonreversible sealing for grades without lignin or low amount of lignin such as bleached Kraft should be taken as a follow-up challenge, since especially for bleached Kraft, which is widely used in paper industry, nonreversible additive free sealing must be achieved by testing other variables or chemically modifying the surface of the fibres.

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9. APPENDIX

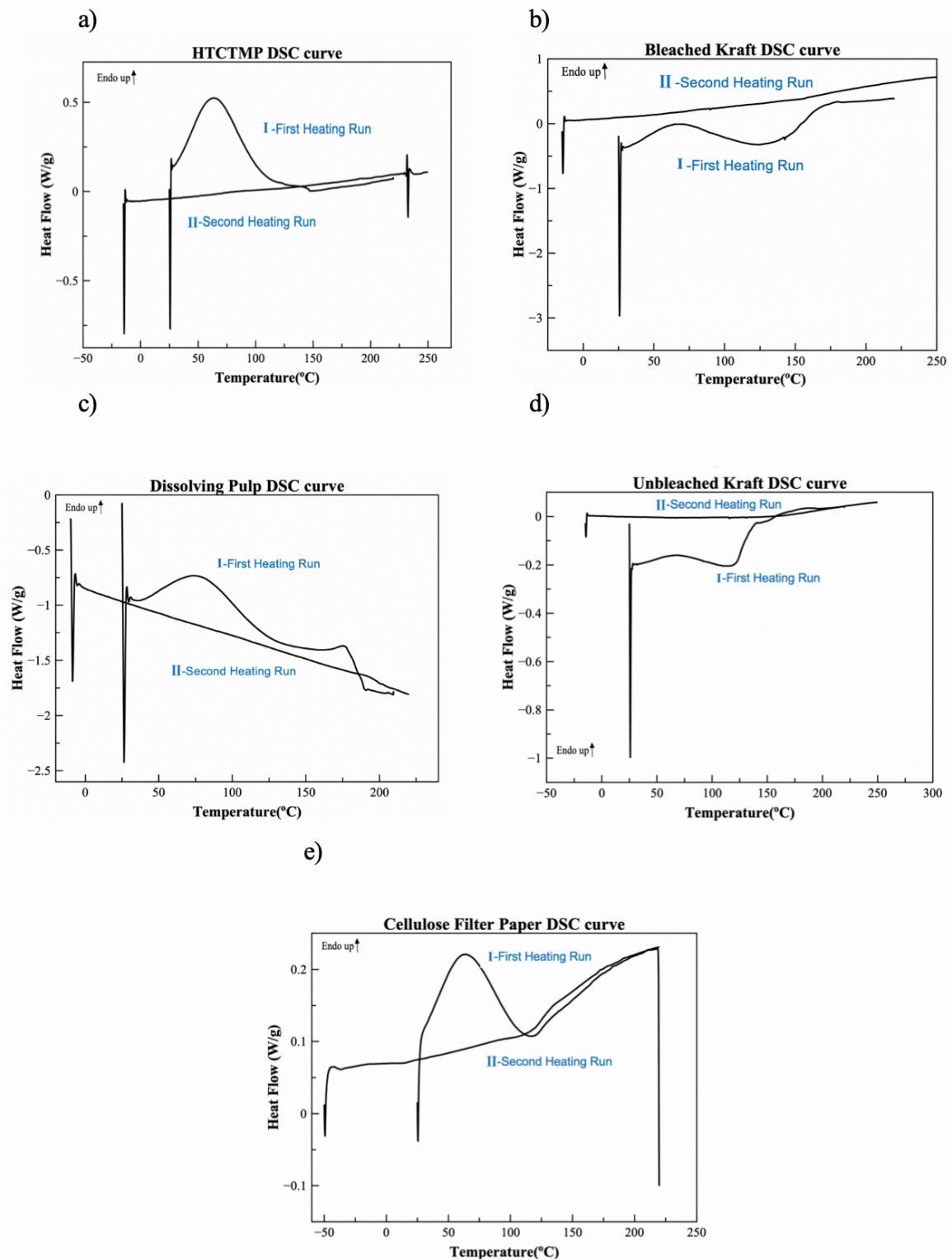


Figure 1. DSC thermograms for a) HT-CTMP b) Bleached Kraft c) Dissolving Pulp d) Unbleached Kraft e) Cellulose filter paper.

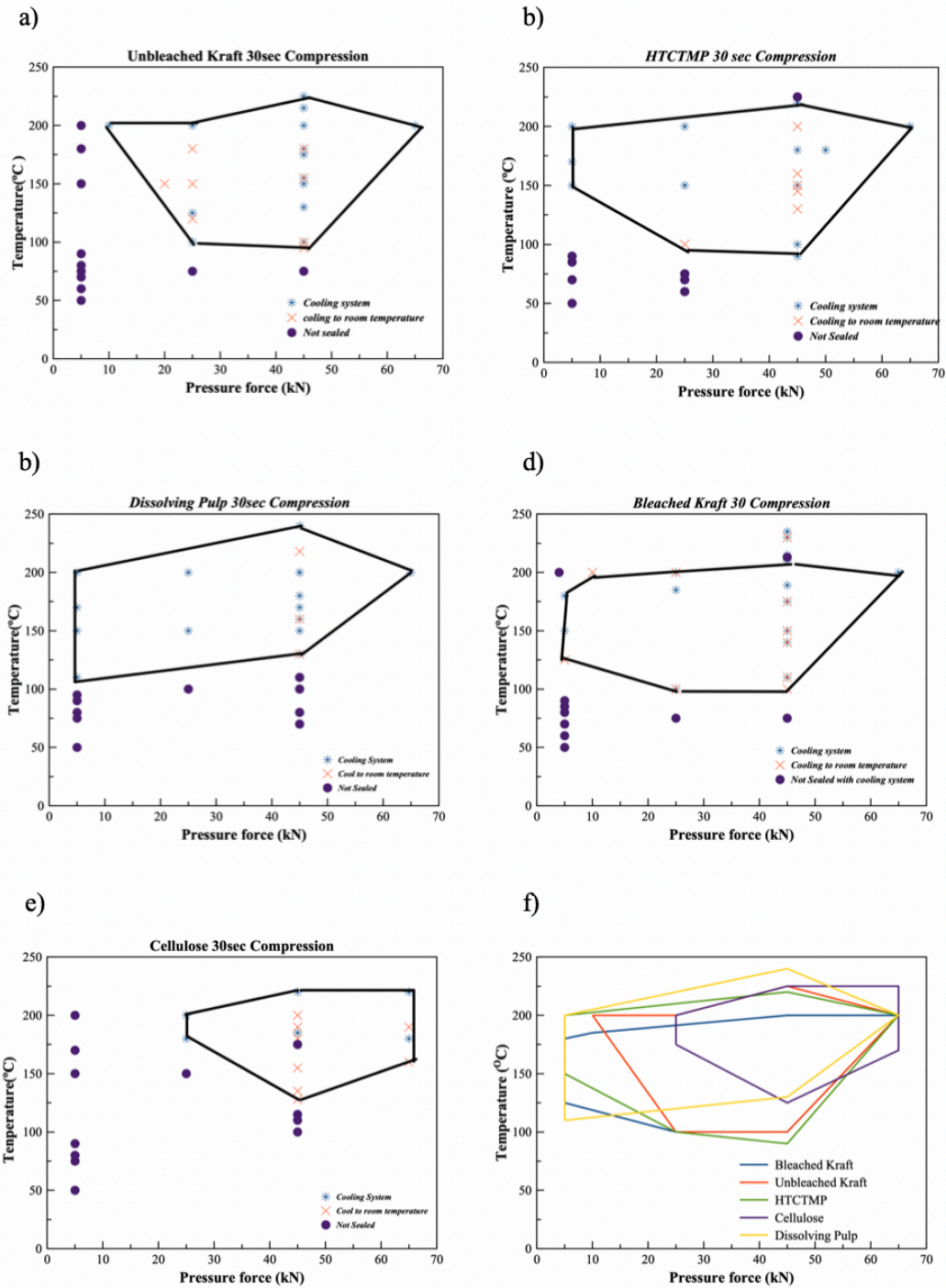


Figure 2. Operating window of temperature with respect to compression of a) Unbleached Kraft b) HT-CTMP c) Dissolving Pulp d) Bleached Kraft e) Cellulose filter paper. The sealed paper specimens which were cooled with cooling system are marked with a blue star and the sealed specimens which were cooled to room temperature are marked with red cross. Non sealed paper specimens are marked as round purple symbol located outside the operating window of sealing. The common operating window is presented in f).

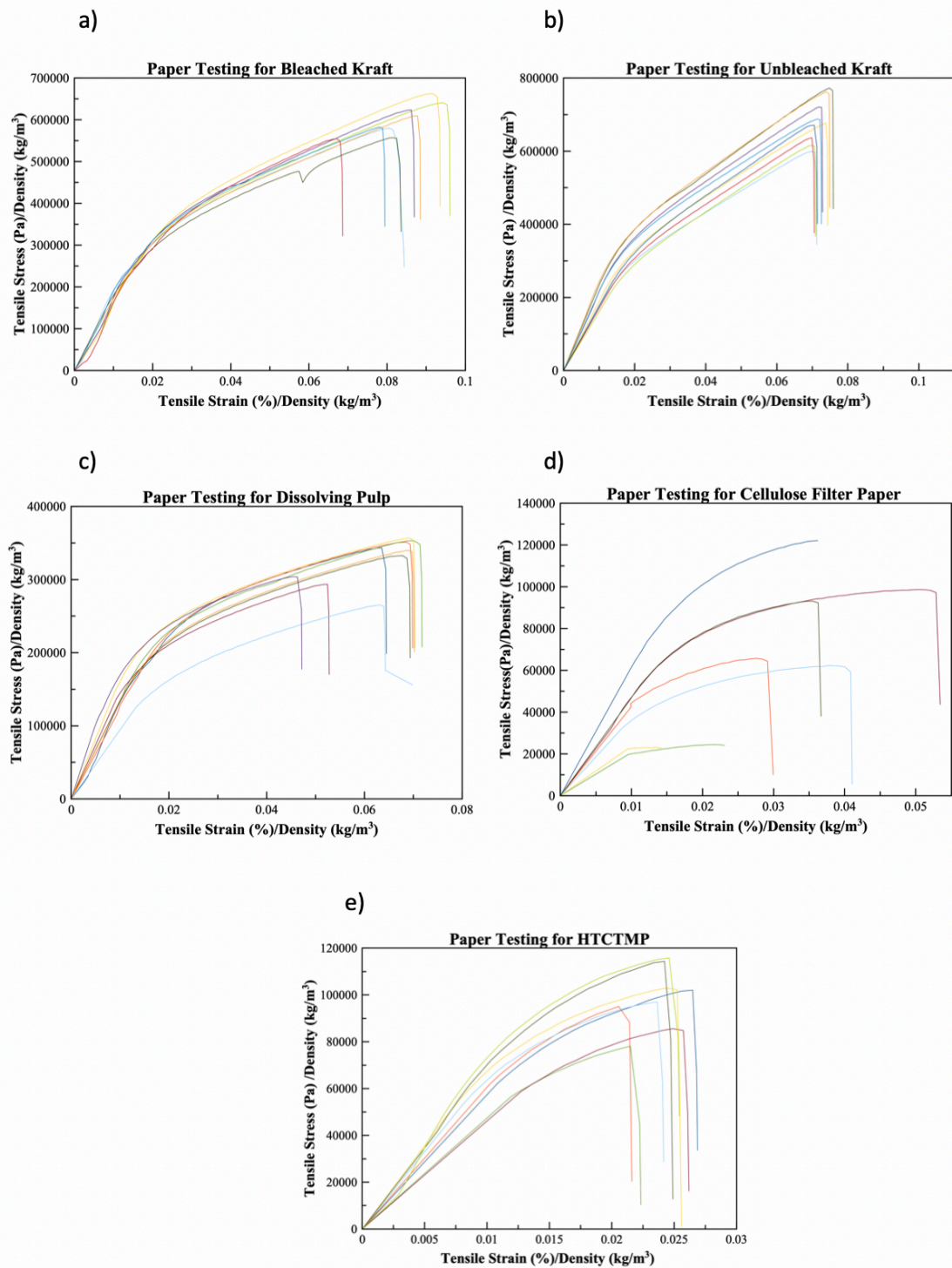


Figure 3. Tensile stress versus strain of a) Bleached Kraft b) Unbleached Kraft c) HT-CTMP d) dissolving pulp e) Cellulose filter paper.

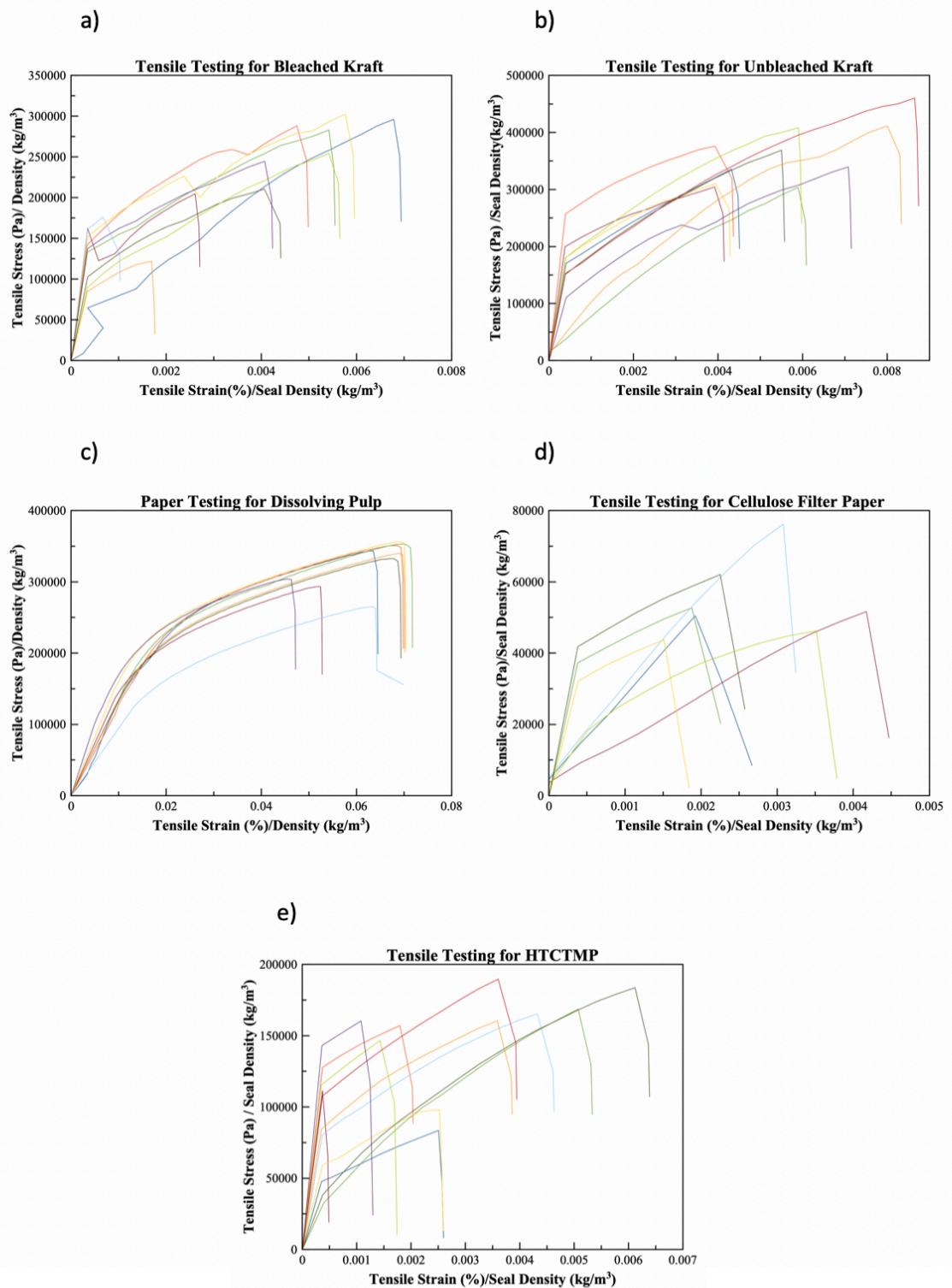


Figure 4. Tensile stress versus strain of a) Unbleached Kraft b) Bleached Kraft c) Dissolving Pulp d) HT-CTMP e) Cellulose filter paper