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Out-of-plane rheological behaviour of paper: the effect of furnish composition, basis weight and drying shrinkage

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ABSTRACT

The effect of amplitude and duration of compression pulse on strain response of paper was studied over a wide range: time duration varied from 4 to 512 ms and stress amplitude from 2 to 35 MPa. Hand sheets made of mechanical and chemical pulp and their blends were used. The behaviour of surface and bulk structures on compressive stress was studied by varying the basis weight of the sheets. Additionally, the effect of drying shrinkage on compressive strain behaviour was examined. The results indicated that large differences occur between pulps in both time and stress-dependent response of compressive strain. Additionally, drying shrinkage and basis weight had also significant impact on strain behaviour.

INTRODUCTION

Basic building elements of paper sheet are typically wood fibres, which are composed of same basic polymers –cellulose, hemicelluloses and lignin - despite of large variety of wood species used in papermaking. In fine structure of wood fibre several concentric layers can be detected, see Fig. 1. In pulping process the adjacent fibers in wood are separated and the outermost layers (ML, P, S1) of fibre are usually removed at the same time. Secondary wall is composed of three sublayers (S1, S2, S3). The cell wall layers the both amorphous and branched hemicelluloses together with amorphous lignin form a matrix (glue), which is reinforced by highly crystalline fibrils that are composed of bundles of cellulose molecule chains. Fibrils, especially in the thickest layer S2 form helically wound spirals around the fiber axis. The fibril angle, in which fibril spirals around the fibre is important factor determining the strength of fibre.[2,3,4]

Significant differences in fiber morphology (length, diameter, wall thickness) and physical properties (coarseness, basis weight) exist between wood species (hardwood, softwood) but also within same tree (early wood, late wood).

Fibres are separated from each other either mechanically or chemically in the pulping process. Although there are a set of different choices in both pulping techniques, the most significant differences are the results of the chemical composition and mechanical structure of pulps. The chemical composition is conserved in mechanical pulping whereas in chemical pulping the lignin is mostly dissolved from the fibre walls. The consequence is that mechanically pulped fibres are stiff and rigid while chemically pulped fibre are soft and flexible. These basic fibre properties have strong effect on the mechanical behaviour of paper prepared from them.

In papermaking process, a suspension composed of water and 0.5-1.0 % pulp fibers

is evenly distributed to a moving porous fabric through which excess water is drained. In some phase of dewatering, surface tension forces between fibers start to interact and weak inter-fiber bonds are created. During drying process, the bonds gain more strength and finally a porous fiber network is formed. The porous volume of dry paper (before calendering) is usually more than 50 % of the total volume.[5,6,7,9]

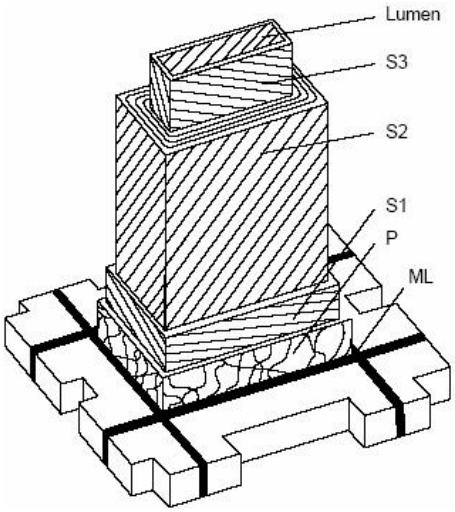

Figure 1. The simplified fine structure of cell wall in wood fibre is shown. Cell wall is built up by middle lamella (ML), primary wall (P) and secondary walls (S1, S2, and S3). The middlemost hollow is called lumen (the figure is from Paper Physics, K. Niskanen (1998), Fapet Oy).

How paper structure behaves under out-of-plane compressive stress and what provides the resistance is also considered in previous studies. According to these works, a following summary can be drawn: first, at small loads, the collapse of the large interfibre pore structure begins. This phase probably involves bending of more flexible fibres, fibre slippage and shear deformation and also collapse of individual thin walled fibres. Second, at intermediate loads, the structure is more packed and the collapse of intra fiber pore structure takes place. Local stress peaks may cause fracture of some rigid and brittle mechanical fibers. In addition, some interfiber bond breakage may occur. Finally, at large loads, the paper sheet is fully densificated and fiber fracture begins. In examination of paper behaviour under compressive stress SEM and CLSM has been utilized[5,7,8,9,10].

The above-described compression behaviour of paper is common for cellular materials. The presence and importance of paper compressive strain behaviour in papermaking and converting processes are discussed by authors recently.[1]

In the current work the primary interest was in clarifying some of the fundamental factors behind paper compression behaviour under dynamic stress. To fill that purpose, furnish composition, basis weight, stretching/drying history and forming method (layered/conventional) were varied in preparing the hand sheets for the tests. In the compression tests conducted under laboratory environment, amplitude and dwell time of single and cyclic stress pulses were changed.

EXPERMENTAL

Materials

A set of laboratory hand sheets with different furnish compositions were manufactured for the tests. Hand sheets were chosen due to their isotropic structure. This selection enables comparative study of compression behaviour of sheets made of different pulps without the effect of machine and cross-machine directions or other factors not known with commercial papers. Sheets were prepared from mechanical and chemical pulp according to SCAN-C 26:76 apart from the following exception: the drying plates were replaced by blotters in order to avoid two sidedness. This choice allows the hand sheets to shrink modestly during drying. In one separate experiment, drying shrinkage was varied in order to study its effect on paper compressive behaviour.

The pulps used were obtained from Finnish pulp mills. Chemical pulp (CHEM)

was Aki Botnia pine (bleached sulphate softwood pulp) from Äänekoski mill beaten to 500 ml CSF with a Valley laboratory hollander. Mechanical pulp was unbleached softwood SC TMP pulp with 60 ml CSF from Jämsänkoski mill. Sheets were made both from pure pulps and blends. Also three-layer sheets were made with 40 g/m^2 TMP in the middle layer and 20 g/m^2 CHEM at the surfaces. The pulp percentual portion in the sheet is shown in short notation of the sheet, which is used hereafter. Notations are TMP100, CHEM100, TMP80CHEM20, conventional and layered TMP50CHEM50.

Tests were conducted under controlled conditions: temperature 23^{o}C and humidity 50%RH. The samples were conditioned at least 24 h before testing. Some hand sheet properties which have influence on compression behaviour are summarized in Table 1. Round sample of 10 mm in diameter was used in testing the compressive behaviour.

In addition, samples were manufactured to study the effect of surface roughness on compressive strain. For that purpose, a basis weight series was prepared where the basis weight was changed from 40 to 120 gsm in steps of 20 gsm. Table 2 demonstrates the variation of some hand sheet properties with grammage for TMP50CHEM50 sample. Basis weight series were manufactured earlier also from TMP100 and CHEM100, but other properties besides grammage and thickness were not measured from those sheets.

Table 1. Basic properties of tested hand sheets.

Property	TMP100	TMP80CHEM20	TMP50CHEM50	TMP50CHEM50, layered	CHEM100
Caliper/sheet	150 µm	138 µm	124 µm	155 µm	106 µm
Density	412 kg/m^3	443 kg/m^3	497 kg/m^3	506 kg/m^3	580 kg/m^3
Basis weight	60 gsm	60 gsm	60 gsm	80 gsm [c)]	60 gsm
Moisture [a)]	9,7 %	10 %	8,9 %	9,7 %	8,4 %
Bendtsen [b)]	68 ml/min	74 ml/min	83 ml/min	100 ml/min	185 ml/min
Roughness [d)]	1204 ml/min	1222 ml/min	1180 ml/min	1735 ml/min	1538 ml/min
Scott bond	220 J/m^2	239 J/m^2	257 J/m^2	---	431 J/m^2

a) Hand sheet moisture at 23 ^{o}C , 50 % RH, b) Air permeability measurement (SCAN-P 26:78), 10cm^2, c) Three-layer hand sheet with 20gsm chemical pulp at surfaces and 40gsm mechanical pulp in the middle, d) Average Bendtsen roughness of both surfaces, samples were too rough for PPS measurement.

Table 2. Basic properties of TMP50CHEM50 hand sheets with different grammages.

Property	Unit	40 gsm	60 gsm	80 gsm	100 gsm	120 gsm
Caliper/sheet	µm	90	123	154	187	218
Density	kg/m^3	442	500	525	542	561
Bendtsen [b)]	ml/min	124	79	62	56	44
Roughness [d)]	ml/min	1033	1161	1476	2005	2080
Scott bond	J/m^2	270	260	283	285	313

Testing equipment

Compression experiments were performed using a novel platen-press tester presented in previous work.[1] Briefly, the sample is placed between two platens under predetermined load. Electromechanically actuated cylinder generates the compression pulse applied to the sample. Both compressive force and thickness change are recorded simultaneously. For that purpose, test-rig is instrumented with three eddy-current distance sensors and a quartz crystal force gauge. Thickness change is defined as the average change in distance between the platens. All sensors are located in the fixed upper platen. Available performance range depends on the relation between force, displacement and speed, but compressive forces up to 5 kN with duration even down to 1 millisecond can be produced. Due to the actuator, stroke length is limited to 160 µm, which is yet enough for dry paper testing. Test cell area including platens and sensors can be surrounded with special climate

chamber where testing conditions can be varied: temperature is adjustable from 20 to 80 °C and relative humidity from 5 to 50-90 %RH, the upper limit depending on temperature. Measurements are run under computer control, using special data acquisition software operating in conjunction with data acquisition board.

Experiments

Series of compression tests were made on one sample sheet using either single or cyclic stress pulses with rectangular shape and constant rise rate. Both holding time and stress amplitude were changed independently. With single pulse, holding time was varied from 4 to 512 ms under given 10 MPa stress. In cyclic tests, stress peak amplitude was increased from around 2MPa to 35 MPa, while the 64 ms holding time and 32 ms relaxation time between pulses was fixed, see Fig. 2. Before testing, sample was positioned to 100 kPa static offset-load to make sure that there is an adequate initial contact between the sample and the press plates right from the beginning. Offset load was kept on for a while after stress release of single stress pulse and between stress pulses in case of cyclic loading. Tests were repeated five or more times for every trial point and the shown results are averages of those measurements. In addition, the effect of machine compliance under load was eliminated from the results.

In the analysis, logarithmic strain is used due to high strain levels. The total strain (ε_t) is divided into subcomponents including instant elastic strain (ε_i) and creep strain (ε_c) which are obtained from loading phase of the strain curve and to elastic (ε_e) and plastic strain (ε_p) found from the post peak or unloading phase of the strain curve. The delayed elastic (viscoelastic) component is not separated from the total strain but it is included in elastic strain. Different strain components are located by utilising the peaks of first derivate of strain. The strain components are linked to each other by following equations: $\varepsilon_t = \varepsilon_i + \varepsilon_c$, $\varepsilon_t = \varepsilon_e + \varepsilon_p$.

In sequential loading tests, sample permanent density is different between single pulses. At the beginning of certain pulse, density is a combination of initial density and permanent strain gained in previous pulse. This relation is utilized in defining the ratio of incremental strain components as function of density (Fig. 5).

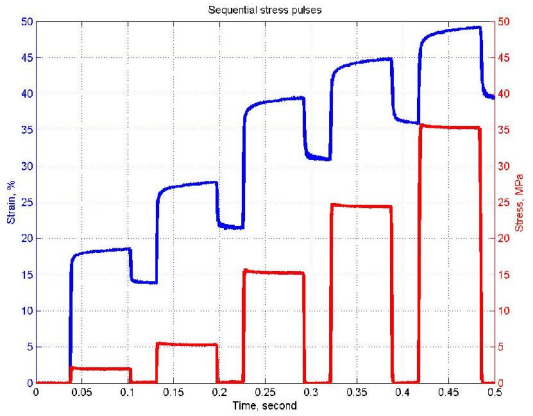

Figure 2. An example of sequential loading (lower curve) and the corresponding strain response of uncalandered handsheet sample. Pulse duration was 64 ms and relaxation time between pulses was 32 ms.

RESULTS AND DISCUSSION

First some comments on the measured basic properties. For handsheets made of mechanical dominated pulp the initial density and the average roughness is clearly smaller when compared to sheets made of chemical pulp. Differences of physical properties originate from used fibres and how they form the network. Fines properties are also important. Typically rigid mechanical fibres form sparse network with rough surface, which can be smoothened by fines whereas flexible chemical fibres form compact network with smoother surface. Equilibrium moisture content is larger for mechanical pulp sheets. Basis weight has significant effect on most physical properties as well.

Single pulse loading

It was investigated how the paper compressive strain changes under constant load. Samples were loaded over a different periods of time ranging from 4 to 512 ms using single rectangular shaped stress pulses with 10 MPa amplitude and constant rise rate. The behaviour of different strain parameters was extracted from the test data. Fig. 3 shows results of this parameter-time behaviour from which following observations can be made:

- Increasing holding time from 4 ms to 512 ms has a rather moderate effect on total strain.
- Instant compressive strains have good correlation with initial sheet densities: mechanical pulp dominated sheets have much higher compressive strains than sheets containing more chemical pulp.
- Although a larger part of the total strain is elastic in mechanical pulp dominated sheets, elastic strain decreases and turns into plastic faster with time.
- Surprisingly, there is no difference in compression behaviour between conventional and layered three-ply samples.
- Compressive behaviour of pulp blends seems to be clearly additive with chemical pulp content.

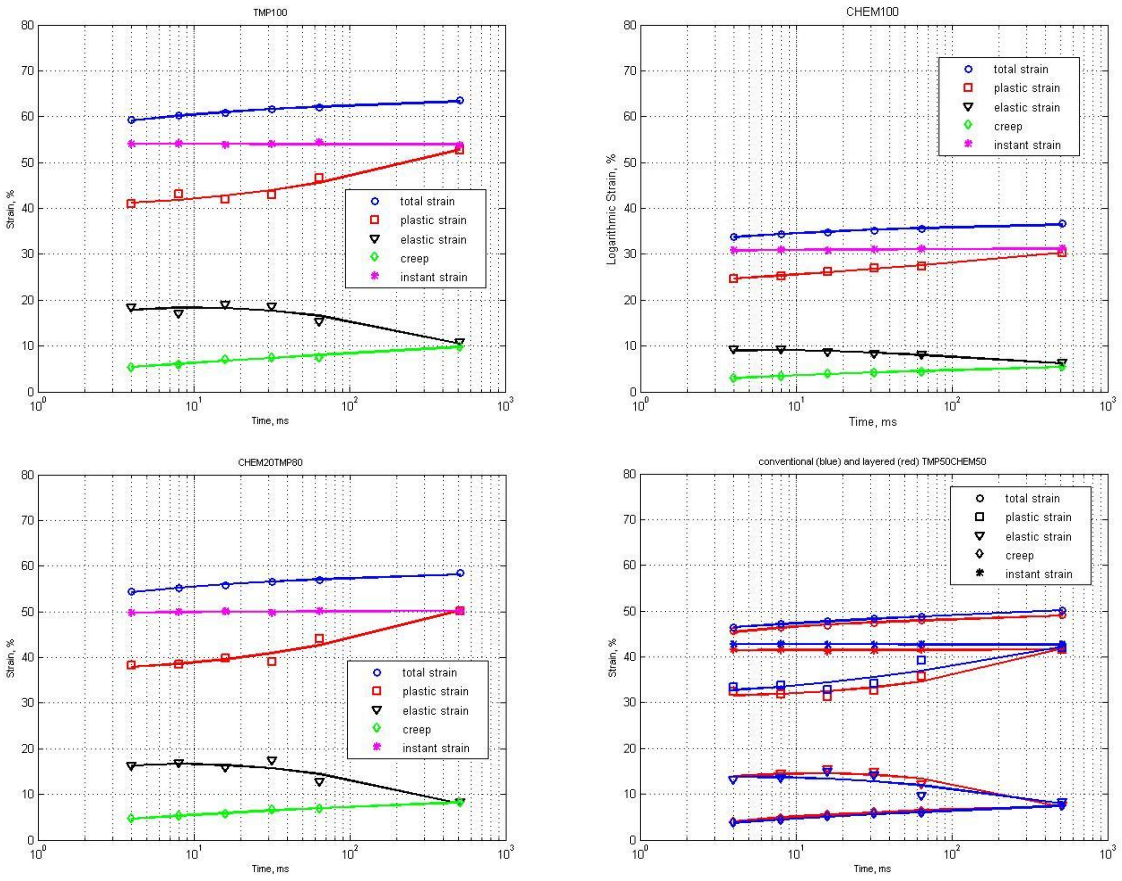

Figure 3. Strain vs. time for different samples: hand sheets made of both pure mechanical pulp (TMP100) (top left) and pure chemical pulp (CHEM100) (top right) and hand sheets made of pulp blends CHEM20TMP80 (bottom left), conventional pulp blend and layered three-ply sheet TMP50CHEM50 (bottom right).

Cyclic loading

The effect of stress level on compressive strain of paper was studied using sequential stress pulses with constant dwell time and increasing amplitude. Characteristic stress and strain data for the tests are shown in Fig. 2. In this type of cyclic loading, paper behaves differently in every single stress pulse. Behaviour is primarily dominated by paper density. For uncalandered handsheet, the initial density is low and the sheet does not return to its original shape after single stress pulse but a permanent strain remains. How permanent strain and other strain components behave with increasing stress is plotted in Fig. 4. The increment of permanent strain in relation to increment of total strain changes as densification proceeds: larger part of total strain increment recovers and paper turns from elasto-plastic into nearly elastic material. How the plastic-elastic transfer takes place in two extreme cases, the strain ratio of increments – increment of plastic strain to increment of total strain- is plotted against density for sheets made of pure pulps in Fig. 5. Similarly, the growth of total strain with stress slows down with increasing density.

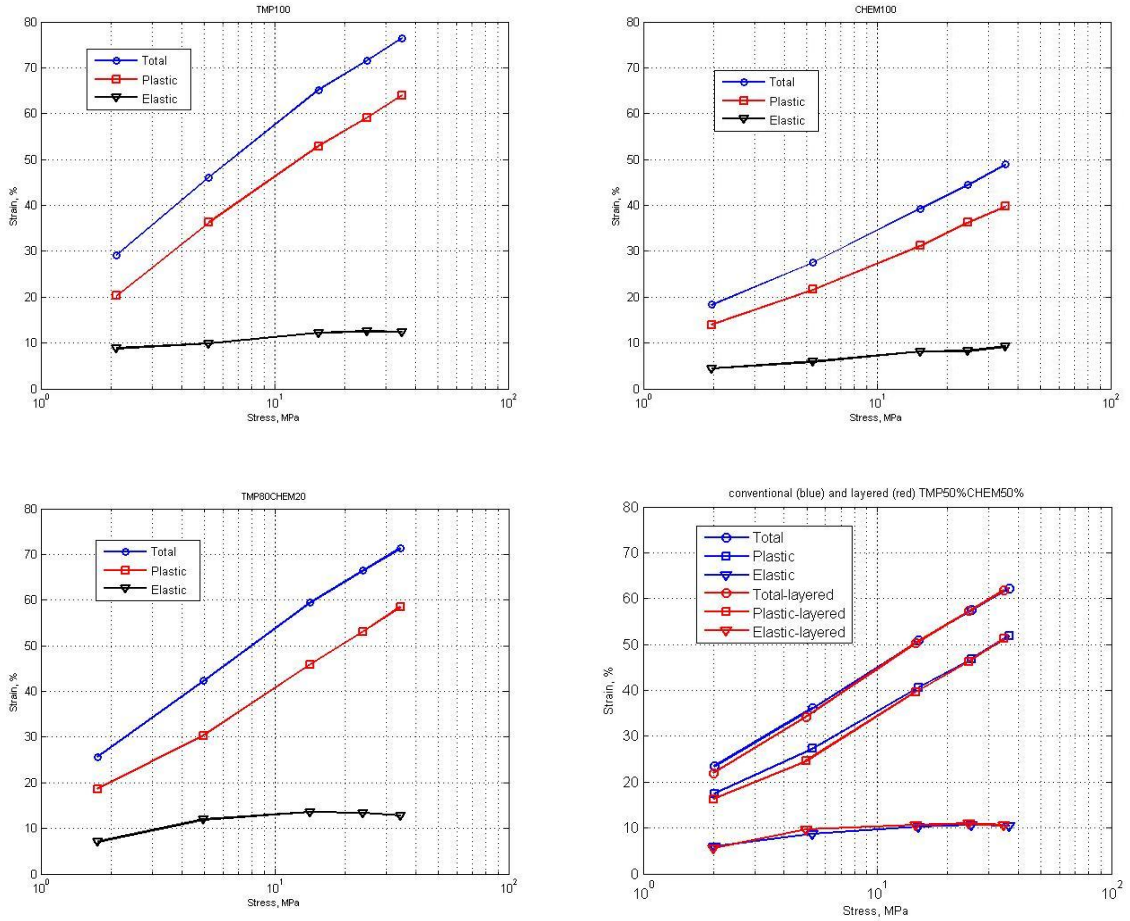

Figure 4. The behaviour of total strain and its components as a function of stress for same hand sheets as in Fig. 3.

Findings from experiments with different loading amplitudes:

- Stress level has a significant impact on paper strain and resulting density.
- The part of permanent strain from total strain increases with increasing stress for all samples, when the strains are related to initial density, see Fig. 4.
- Chemical pulp containing sheet is clearly more plastic when the ratio between increments of plastic and total strains of pulps are compared in same density, see Fig. 5.
- Stress amplitude was raised using cyclic loading, but the results are in practice identical with the ones made earlier using single pulse loading[1].

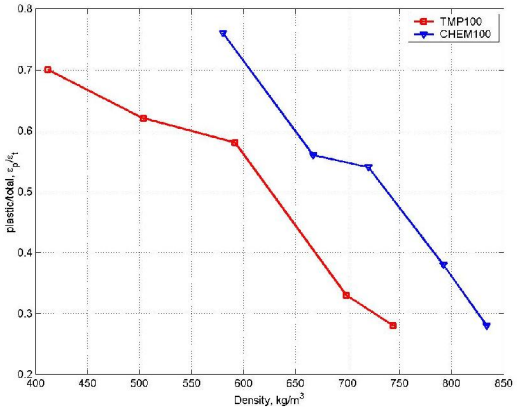

Figure 5. The ratio between increments of plastic and total strain with density in cyclic loading with increasing amplitude is shown.

Drying shrinkage

Measurements were made to demonstrate the effect of drying induced shrinkage on paper compressive strain. Three separate shrinkage levels were allowed. First, the wet samples were uniaxially strained 2 % in-plane direction with shrinkage restricted during subsequent drying. Second, the shrinkage was fully restricted, but no strain was applied. Third, the samples were dried without restriction. These tests were made using custom-made experimental set-up build in Lloyd universal test machine (type LR 10K). The increase in solid content was monitored continuously during drying and three different samples were tested: CHEM100, TMP100 and TMP80CHEM20. Samples for compression tests were taken from the middle region of the hand sheet. Compression tests were carried out using single rectangular shaped stress pulses with 10 MPa amplitude and 64 ms duration.

Fig. 6 shows the compression behaviour with drying shrinkage. For both chemical pulp sheet and pulp mixture sheet total and plastic compression increases when it is switched from restricted to free shrinkage drying. Mechanical pulp sheet has different behavior: largest total and plastic strains are gained when paper is stretched during drying. Free shrinkage produces still a bit higher total strain than pure restricted drying.

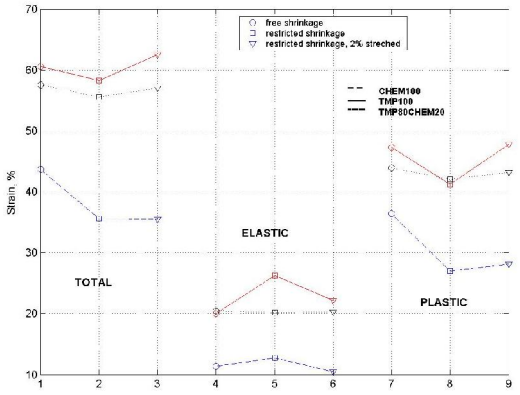

Figure 6. Variations in paper strain components resulting from drying induced shrinkage.

Elastic strain has different behaviour than those of plastic and total strains. Biggest changes are in pure pulp sheets whereas pulp mixture sheet has not notable changes. Restricted shrinkage produces largest elastic strains.

Basis weight

Strain behaviour of paper surface and internal structure was investigated by varying the basis weight of samples. Sometimes paper is understood as a structure formed by internal layer and two surfaces. How to distinguish the surface and internal strain behaviour from each other is the key question.

It was measured that paper thickness increases linearly with basis weight, see upper plot in Fig. 7. Based on this known connection, it has been previously proposed[2] that internal layer increases with basis weight according to the product of basis weight and some constant slope but no changes happen in surfaces, which are responsible of the non-zero constant in linear relationship.

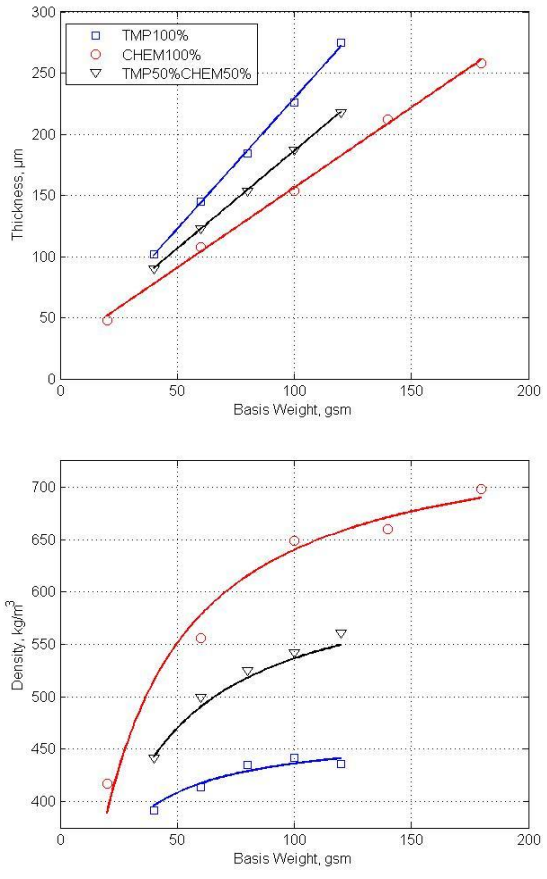

Figure 7. Basis weight dependence of measured thickness (upper figure) and density for different pulps is presented.

Due to this thickness - basis weight behaviour, paper density has nonlinear (hyperbolic) relation with basis weight, see lower plot in Fig. 7. Density approaches to its limiting value at high basis weight levels, in which point internal structure dominates the surfaces and the density is same as internal layer density.

Despite the good fitting results, there are some shortcomings in the linear proposition. For instance, at the limit of zero basis weight, when internal structure has disappeared and the upper and lower surfaces locate on top of each other, thickness reaches a nonzero value, which is arising from the surfaces. To avoid this non-physical behaviour at zero basis weight, also the surface thickness portion in thickness model should depend on basis weight somehow. Another indication of connection between basis weight and surface thickness is the increase of roughness values with basis weight (see Table 2).

To fulfil the shortcomings of linear relationship, the constant value of surface thickness was rejected and an assumption of power law behaviour between surface thickness and basis weight was made. This nonlinear thickness model was consistent with the linear model at measured dataset, showing apparently linear behaviour. Although excellent correlation was gained in comparison of data with the nonlinear thickness model, the reliability of the fitted parameters suffered from too few data points. The model still followed the first impression of the expected behaviour better than linear model.

How the above-described density variation with basis weight affect compressive strain is shown in Fig. 8. The examination is shown for TMP50CHEM50, from which the basic properties were known (see table 2).

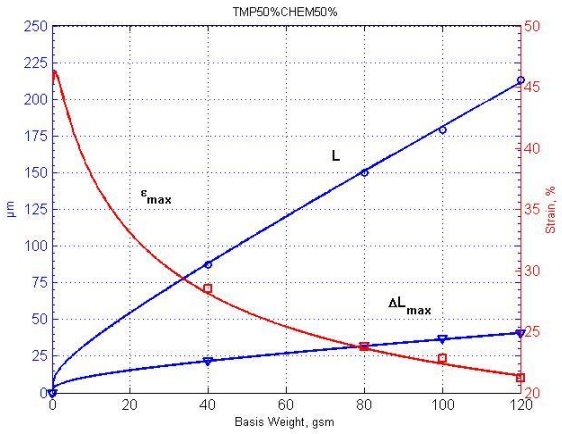

Figure 8. Thickness L, maximum compression ΔL_{max} and strain ε_{max} are plotted against basis weight. The few data points have markers but the lines are predicted through the models for thickness, maximum compression and strain.

According to Fig. 8 the difference between maximum compression and thickness increases strongly with basis weight and this is seen also in maximum strain. The maximum (instant) compressive strain of examined papers can be explained purely by basis weight and applied stress.

CONCLUSIONS

This study considered compressive strain behaviour of hand sheets made of both pure pulps and mixed blends.

Significant differences were seen in compressive strain between samples. Duration of compression pulse had small effect on total strain in the tested time range, but the remaining plastic strain increased and the elastic strain decreased notably with time for mechanical pulp dominated sheets. Similar but lot smaller effect was seen for chemical pulp sheet, which is an interesting result.

Stress on the other hand had large effect on all strain components. The portions of elastic and plastic parts of total strain at same density depended on pulp type: chemical pulp sheet is evidently more plastic than mechanical pulp sheet. At high stress levels, total densities approach each other regardless of pulp and the elastic nature takes over. Although density is a major factor in paper strain behaviour, it does not explain by itself the whole behaviour, which can be concluded from these results.

In drying induced shrinkage tests, chemical pulp sheet showed large differences in plastic and total strains when shrinkage was allowed during drying compared to situations where shrinkage was restricted. This behaviour was most likely resulting from differences in sample densities due to drying method. Pulp mixture sheet had similar behaviour with pure chemical pulp sheet, but mechanical pulp sheet behaved differently: restricted shrinkage together with stretching under drying produced largest compressive strains for mechanical pulp sheet. This outcome is not explained with density differences.

In tests with different basis weights, where only paper surface/bulk relation was assumed to vary, big differences were found in paper compression behaviour. The apparent thickness, density and compression behaviour of chemical pulp sheet was more sensitive to basis weight than that of mechanical pulp sheet. This is due to the fact that surface roughness or thickness was not independent of basis weight but changed considerably with it. At high basis weights surface thickness looses its effect. Therefore, heavier basis weights had smaller strain, which is controlled by bulk structure, whereas for lighter basis weights surfaces dominate the compression behaviour. According to the analysis made, total strain in single compression pulse can be explained by applied stress and basis weight for studied samples.

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REFERENCES

1. Ponkkala, T., Kunnari V., and Retulainen, E., (2005), "Characteristics of out-of-plane rheological behaviour of paper", Annual Transactions of Nordic Rheology Society, Vol. 13, pp. 263-268.
2. Niskanen, K., (1998), "Paper Physics", Papermaking Science and Technology, Fapet Oy, Helsinki, pp. 55-87.
3. Scott, W.E., (1996), “Principles of Wet End Chemistry”, Tappi Press, Atlanta, pp.10-14.
4. Sjöström, E., (1993), “Wood Chemistry: fundamentals and appkications”, Academic Press, Inc., London, pp.1-20.
5. Feygin, V.B, (1999), "Modelling paper strain in a calender nip", Tappi Journal, Vol. 82: No. 8, pp. 183-188.
6. Pawlak, J.J., and Keller, D.S., (2005), "The compressive response of a stratified fibrous structure", Mechanics of Materials 37, pp. 1132-1142.
7. Pawlak, J.J., and Keller, D.S., (2004), "Relationships between the local sheet structure and z-direction compressive characteristics of paper", Journal of pulp and paper science, Vol. 30 No. 9, pp. 256-262.
8. Browne, T.C., Crotogino, R.H., and Douglas, W.J.M., (1995), "The effect of paper structure on behaviour in a calender nip", Journal of pulp and paper science, Vol. 21 No. 10, pp. 343-347.
9. Haslach, H.W., (1996), "A model for drying-induced microcompressions in paper: buckling in the interfiber bonds", Composites Part B, Vol. 27B: No. 1, pp. 25-33.
10. Retulainen, E., Moss, P., Nieminen, K., (1997) “Effect of calendering and wetting on paper properties”, Journal of Pulp and Paper Science, Vol. 23: No 1, pp. 34-39.