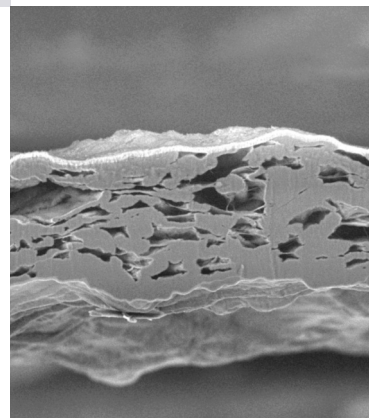


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Formability of paper and its improvement

Alexey Vishtal



Formability of paper and its improvement

Alexey Vishtal

VTT Technical Research Centre of Finland Ltd

Thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in Auditorium 1702, at Tampere University of Technology, on the 4th of June, 2015, at 12:00.



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Cover image: Trays prepared from moldable paper developed by VTT. Courtesy of Marja Juvonen.

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Abstract

Paper and paperboard are the most utilized packaging materials in the world, accounting for one third of the total packaging market by volume. This position has been achieved due to several advantageous features of paper such as: renewability, biodegradability, recyclability, and unmatched printability. Paper can be produced anywhere in the world, using local resources and at relatively low cost, which also makes it the most sustainable packaging material. Despite these beneficial features, paper packaging is in tough competition with plastic materials. The competitiveness of paper is mitigated by barrier properties, sensitivity to moisture, and limited ability to be converted into advanced 3D shapes with added functionality. The ability of paper and paperboard to be formed into 3D shapes is described as formability, or sometimes, mouldability. The investigation of formability is the core of the present thesis work.

Formability can be conditionally defined as the ability of paper to be formed into 3D shapes without defects in appearance and functionality. Formability as a mechanical property represents a group of parameters which vary according to the type of forming process used. The primary objective of this thesis is to improve the formability of paper by increasing its extensibility. Such paper can be used to replace certain plastics in thermoforming packaging lines. An additional objective is the characterization of formability as a mechanical property of paper and the development of a testing platform for the evaluation of formability.

It was found that the formability of paper in fixed blank forming processes is governed by the extensibility and tensile strength of paper. On the other hand, in sliding blank forming processes, it is dependent on the compressive properties of paper, elastic recovery, and the paper-to-metal coefficient of friction. The criteria of good formability are also different in these two cases, as fixed blank process formability is evaluated via the maximum depth of the shape, i.e. the deeper the shape, the better the formability. In the sliding blank process, formability is evaluated via the visual appearance of the shapes, i.e. the shapes with less profound compressive wrinkles and defects reflect good formability of paper. These results were established by comprehensive investigation of different forming processes and comparison of the outcome with the mechanical properties of paper.

Taking into account the hypothesis that the formability of paper is governed by the extensibility of paper, a set of methods for its improvement was suggested. These

methods included combined high- and low-consistency treatment of fibres, spraying of agar and gelatine, in-plane compaction of paper and unrestrained drying. High-consistency treatment of fibres under elevated temperature induces permanent deformations to fibres such as microcompressions and dislocations, which in turn may decrease the axial stiffness of fibres, promoting shrinkage of paper and fibres. The low-consistency treatment straightens the fibres and induces the fibrillation of fibres to promote bonding, while microcompressions in fibres still exist. The spraying of agar and gelatine is likely to modify the character of the fibre joints by making them more deformable, and the drying shrinkage is also increased due to polymer addition. Finally, the fibre network was subjected to in-plane compaction and drying shrinkage which lead to buckling and fibre and network compression.

As a result of the mechanical modification of fibres and improvement of bonding by the addition of agar and a combination of agar and gelatine, the extensibility of unrestrained dried paper was increased from 4% points (untreated fibres) to 15–18% points (mechanical treatment and addition of polymers). The extensibility can be increased further by up to 30% points in one direction by compaction. This corresponds to tray-like shapes with a depth of 2–3 cm, depending on the curvature. Such values of formability are the highest reported so far in the scientific literature.

The approach for the production of formable paper developed in this thesis work allows the production of a paper-based material with unmatched formability, which can replace certain types of plastic packaging. Replacement of plastics with paper improves the sustainability of packaging in general, and reduces the harmful environmental impact of non-degradable and non-renewable packaging.

Keywords: formability, extensibility, packaging, 3D forming, paper, fibres, bonding, compaction

Preface

The work in this thesis was carried out at the VTT Technical Research Centre of Finland Ltd. during the period of 2011–2015. As VTT has broad expertise in the field of fibre-based material, it has been a great honour and privilege to work in such an environment. This work was funded by the Finnish Bioeconomy Cluster's (FiBiC) Future Biorefinery (FuBio and FuBio JR2) and the Advanced Cellulose materials (Acell) programmes and by the VTT Graduate School. In addition, the International Doctoral Programme in Bioproducts Technology (PaPSaT) has provided funding for participation in scientific conferences and in many interesting courses. COST Action FP1003 (Impact of renewable materials in packaging for sustainability – development of renewable fibre and bio-based materials for new packaging applications) has provided many interesting training opportunities and EFPRO (European Fibre and Paper Research Organisation) provided funding for a short-term scientific mission to Technical University of Dresden in 2012. I am grateful to all my funders for providing me with the possibility to conduct high quality research and networking.

My deepest gratitude goes to Dr. Elias Retulainen, my supervisor at VTT, for providing inspiration and guidance through the whole Ph.D. process and for always being open to discussion. My thanks to Prof. Jurkka Kuusipalo from Tampere University of Technology for guiding me through the whole Ph.D. process and for being very flexible and helpful regarding all legal issues. I also wish to thank all of my collaborating colleagues at VTT, my fellow Ph.D. students in the field, and especially the technical personnel at VTT Jyväskylä for valuable discussions and relevant advices. Dr. Kristiina Poppius-Levlin and Dr. Jukka Ketoja, former and current coordinators of the VTT Graduate School, are thanked for their support in reaching the doctoral degree.

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Jyväskylä, April 2015

Alexey Vishtal

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List of publications

This thesis is based on the following original publications which are referred to in the text as I–VII. The publications are reproduced with kind permission from the publishers.

- I Vishtal A. and Retulainen E. 2012. Deep-drawing of paper and paperboard: the role of material properties. *Bioresources*, 7(3), 4424–4450.
- II Vishtal A. and Retulainen E. 2014. Boosting the Extensibility Potential of Fibre Networks: A Review. *Bioresources*, 9(4), 7951–8001.
- III Vishtal A., Hauptmann M., Zelm R., Majschak J.P. and Retulainen E. 2013. 3D Forming of Paperboard: The Influence of Paperboard Properties on Formability. *Packaging Technology and Science*, 27(9), 677–691.
- IV Zeng X., Vishtal A., Retulainen E., Sivonen E. and Fu S. 2013. The Elongation Potential of Paper – How should fibres be deformed to make paper extensible? *Bioresources*, 8(1), 472–486.
- V Vishtal A. and Retulainen E. 2014. Improving the extensibility, wet web and dry strength of paper by addition of agar. *Nordic Pulp and Paper Research Journal*, 29(3), 434–443.
- VI Vishtal A., Khakalo A., Rojas O.J. and Retulainen E. 2015. Improving the extensibility of paper: sequential spray addition of gelatine and agar. *Nordic Pulp and Paper Research Journal*, 30(3), pages to be assigned.
- VII Vishtal A. and Retulainen E. 2014. An approach for improved 3D formability of paper. *IPW*, 12, 46–50. (Peer-reviewed, published under normal peer-review process as a full paper presented at the Zellcheming conference 2014.)

Author's contributions

I The author suggested the concept of the article. The author performed a comprehensive literature and patent analysis and wrote the article together with Elias Retulainen.

II The author performed a comprehensive literature analysis and wrote the article together with Elias Retulainen.

III The author had the main role in planning and performing the experiments which also included the development of a new method for wrinkle quantification. The author interpreted the results and wrote the article together with the co-authors.

IV The author had the principal role in the development of a combined high- and low-consistency method of pulp refining and performed related experiments. The author interpreted the results from these experiments and wrote the corresponding parts of the article together with the co-authors. The results of this article have also been used in the PhD thesis of Dr. Zeng Xiling at the South China University of Technology.

V The author led and performed all the experiments in this paper. The author interpreted the results of the whole paper and wrote the article together with Elias Retulainen.

VI The author suggested the concept of the joint interaction of agar and gelatine towards improving the extensibility of paper. The author performed the majority of the experimental work and wrote the paper with the co-authors.

VII The author developed the idea of a multitask approach for the improvement of the formability of paper-based materials together with Elias Retulainen and performed the related experiments. The author wrote the article together with Elias Retulainen.

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Publications I–VII

Abstract

List of abbreviations

| | |
|-------|--|
| 2D | Two-dimensional |
| 3D | Three-dimensional |
| A | Agar in certain figures descriptions |
| AFM | Atomic Force Microscopy |
| BHF | Blank Holding Force |
| C | Compaction in certain figures descriptions |
| CD | Cross Direction |
| DS | Dry Solids |
| FDA | US Food and Drug Administration |
| G | Gelatine in certain figures descriptions |
| HC | High Consistency |
| HCLC | High- and Low-consistency mechanical treatment |
| LC | Low Consistency |
| MD | Machine Direction |
| MDL | Maximum Drawing Limit |
| MFA | Microfibrillar Angle |
| MFC | Microfibrillated Cellulose |
| QCM-D | Quartz Crystal Microbalance Dissipation |
| PLA | Poly lactide |
| PHB | Polyhydroxybutyrate |
| RBA | Relative Bonded Area |
| RCT | Ring Crush Test |

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| REACH | Registration, Evaluation, Authorisation and Restriction of Chemicals |
| SBR | Styrene-butadiene resin |
| SEM | Scanning Electron Microscopy |
| SR | Schopper Riegler |
| TEA | Tensile Energy Adsorption |
| WRV | Water Retention Value |
| X | Crosslinker (AmZrCarb) in certain figures descriptions |

Glossary of terms

| | |
|---------------------|--|
| 3D forming | any forming process that yields 3D shapes. In this thesis, these processes are limited to use with paper materials. |
| Air forming | a 3D forming process where the shape is formed by air blowing against the female mould, or can be used with vacuum assist as well. Fixed blank forming process. |
| Blank Holding Force | the force (or pressure) with which a blank holder compresses the paper at the edge areas, restraining the sliding of the blank into the cavity. |
| Blank Holder | a typically plate-shaped metal part of the forming device which holds the sample area that is not in direct contact with the forming dies in the initial phase of forming. |
| Crack | An initiation of the mechanical failure of the material when rupture in paper has initiated but not completely separated, or separation takes place only in the surface layer. |
| Deep-drawing | a 3D forming process, where paper is formed between the forming die and forming cavity. Unincreased blanks are typically used. A sliding blank forming process. |
| Discoloration | a change in the colour of the paper after forming occurring as a result of excessive heating due to high friction and/or improperly adjusted temperature. |
| Extensibility | the general ability of a material to increase its length under the applied load. Extensibility is defined at the point of failure of material. This |

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| | term was used in this thesis to characterize general tensile deformation of paper. |
| Hot Pressing | a fixed blank forming process which employs metal tools to form paper. |
| Failure of material | a complete separation of the rupture line which cancel any further use of the material. |
| Fixed blank process | a forming process in which the blank holding force is high enough to avoid any sliding of the paperboard blank. The shape is formed by straining the paper. |
| Formability | a complex term describing behaviour of paper-like material in 3D forming and the final results of the forming. The understanding of formability differs from process to process. |
| Formability strain | a numerical parameter obtained from the 2D formability tester. Indicates the extension of the material under the downward movement of the metal die, typically under the action of the elevated temperature. |
| Forming gap | the ratio between the thickness of the paperboard and the distance between the forming die and forming cavity (referred to as mould clearance in tray pressing). |
| Maximum Drawing Limit | the biaxial strain which the paper could tolerate without failure in 3D forming with 3D spherical forming device |
| Mould clearance | see Forming gap. |
| Mouldability | see Formability. |
| Multivac® | a type of industrial forming device, used in form-fill-seal packaging lines. |
| Press Forming | see tray pressing. |
| Shape stability | the ability of the shape to keep the designed dimensions after forming. |
| Sliding blank process | a forming process in which the blank holding force is low, to allow sliding of the paperboard into the mould or forming cavity; formation of wrinkles is inevitable with this kind of forming process. |

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| Stamping | see Tray pressing. |
| Thermoforming | In this thesis, thermoforming means any fixed blank forming process using heated metal tools to form a 3D shape. |
| Tray pressing | a sliding blank forming process which is used for making trays and plates using a precreased blank and heated metal tools. Limited blank holding force is used. Industrial scale process. |
| Wrinkles | compressive folds formed in paper upon forming due to lateral contraction, especially in the sliding blank forming process. |
| Vacuum forming | a 3D forming process where material is formed by creating a vacuum in the female mould. Pressurized air assist might also be used. Fixed blank-forming process. |

1. Introduction

1.1 Background of the study

Paper and paperboard packaging is the recyclable and sustainable alternative to glass, metal and especially plastic packaging. Deservedly, paper-based packaging accounts for 34% of the global packaging market, being the most commonly used consumer and industrial packaging material in the world (Rhim 2010, FSC 2013). Paper packaging has a great potential to increase its market share in future, although this potential is mitigated by certain functional drawbacks of paper. These drawbacks include poor barrier properties, susceptibility to moisture and limited convertibility into complex 3D objects. The barrier properties and moisture resistance can be improved by the introduction of functional coating and films (Andersson 2008); however, there are no straightforward methods to enhance the convertibility of paper into 3D objects. This significantly limits the array of available designs for paper and thus its potential uses.

The limited design possibilities originate from the poor formability of paper, which determines the ability of paper to be formed into 3D objects (Svensson *et al.* 2013). Overcoming the inadequate formability of paper-based material is the key issue in the development of advanced 3D packaging from paper, to replace plastic packaging (Svensson *et al.* 2013, Kunnari *et al.* 2007; Östlund *et al.* 2011; Post *et al.* 2011, Larsson *et al.* 2014).

The formability of paper does not refer to any specific mechanical property of paper per se, but is a generic term explaining how well paper performs in a particular forming process *i.e.* the runnability and visual appearance of shapes. Formability is a complex set of mechanical properties explaining the response of paper to particular deforming forces, specific to the forming process in question. The forming process determines the actual meaning of formability as well as the criteria of good formability. In general, forming processes for paper can be divided into two groups, with respective different requirements for formability: processes in which the paper blank is fixed and processes in which the paper blank is allowed to slide. The deformation mechanisms of paper in these processes are different, which also means that the criteria and requirements of good formability are different as well.

Research in the field of the formability of paper-based materials has recently attracted a lot of attention from research organizations and industry (Svensson *et al.* 2013, Kunnari *et al.* 2007; Östlund *et al.* 2011; Post *et al.* 2011, Leminen *et al.* 2013, Huang and Nygård 2012, Linvill and Östlund 2014, Ford *et al.* 2014 Hauptmann and Majschak 2011, Tanninen *et al.* 2014a and 2014b). The results of these studies indicate that by modifying the mechanical properties of paper and adjusting the forming process, it is possible to produce complex 3D objects from paper without creasing, gluing or folding, via the thermoforming pathway. Further improvement of paper formability is essential to increase the share of sustainable and recyclable packaging on the market.

1.2 Research problem

Paper and paperboard are great packaging materials in terms of sustainability and recyclability; however, they are not as versatile as plastics with respect to being converted into various shapes. This is due to the poor formability of paper. Improvement of formability would enable the production of advanced 3D shapes for packaging by using paper-based materials in thermoforming lines, in a way similar to plastics. However, what is the formability of paper, how to measure it and how to improve it? This thesis work aims to provide answers to these questions.

1.3 Objectives of the thesis work

The primary objective of this thesis was to develop a paper-based material with improved formability for the production of advanced 3D shapes in thermoforming lines.

The secondary objective of this thesis was to study the phenomenon of the formability of paper and to characterize it as a mechanical property of paper.

1.4 Hypotheses

The experimental approaches and theoretical considerations used in this thesis have been based on certain hypotheses, which can be formulated as follows:

- The results of the 3D forming process, *i.e.* the formability of paper, correlate with the structure and mechanical properties of paper. Extensibility of paper is one central property in this respect.
- The higher the extensibility, the better the formability of paper.
- Extensibility can be improved by modifying the material on different levels: fibres, interfibre bonding and network structure.

- Extensible fibres are essential for the formation of an extensible fibre network. The extensibility of fibres can be improved by the introduction of microcompressions and dislocations in mechanical treatment.
- Interfibre bonds in the fibre network can be modified by polymers that introduce suitable deformation characteristics to the fibre contacts.
- The extensibility potential of the network can be improved by the contraction and compressive deformation of the fibre network, using processes such as drying shrinkage and in-plane compaction.
- Treatments on different levels, *i.e.* fibres, bonds, and network, can be combined to yield additional improvements in extensibility and respective 3D formability.

1.5 Scope of the research

The fibre raw materials and additives were selected in such a way that production of paper-based material with improved formability would remain compatible with modern paper and paperboard machines. Also, the implementation of the treatments should not require major capital investments.

The study was carried out on laboratory scale using one kind of fibre material, bleached softwood kraft pulp, which is abundantly available in the Nordic countries.

The additives and chemicals used for the production of paper-based material must not be of concern in respect to the FDA and REACH list of hazardous chemicals, since the primary use of the developed material is in food packaging.

The cost of the developed paper-based formable material should not be significantly higher than the cost of typical paperboard used for packaging purposes.

This work focuses on the improvement of formability via increasing the extensibility of paper. Nevertheless, formability can be improved by modifying other mechanical properties of paper and process parameters in the forming process, as revealed later in this thesis.

Chemical modification of the fibre material may significantly improve the extensibility of the fibres and paper; however, it was beyond the scope of this thesis, since it would significantly increase the cost of the material and might not necessarily be compatible with paper machine conditions.

There are several 3D forming processes which can be used with paper. The primary aim was to improve the performance of paper in thermoforming processes (fixed blank processes).

1.6 Structure of the study

The structure of this thesis work with the clarification of how, and in which publications, the objectives of this thesis were resolved is presented in the block diagram shown in Fig. 1.

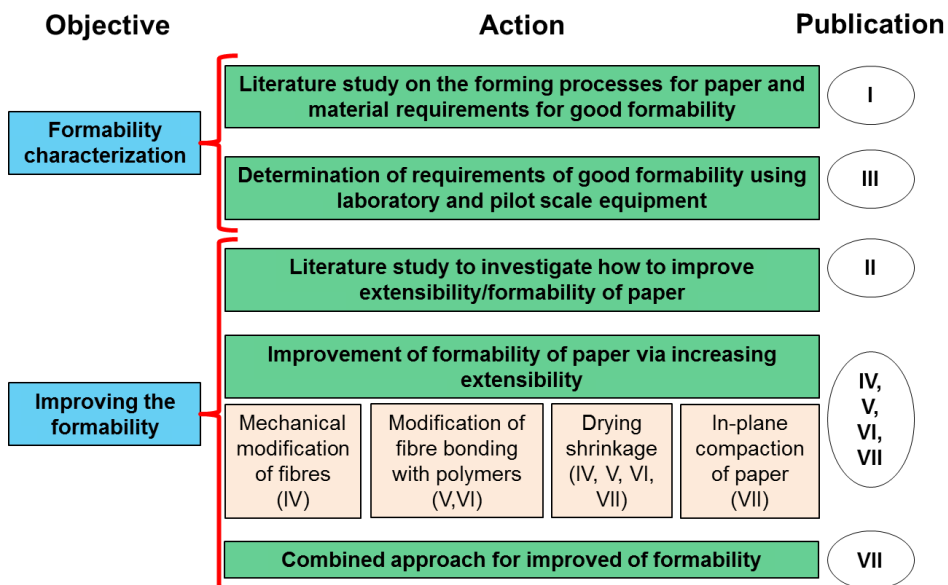


Figure 1. Block diagram depicting the structure of this dissertation.

2. Literature review

2.1 Formability of paper-based materials

Paper formability is a generic term, the meaning and respective requirements of which are dependent on the type of forming process. Thus, 3D forming processes used with paper will be discussed in more detail. Despite the relative novelty of 3D forming of paper in respect to industrial manufacturing processes, the forming of complex 3D objects from paper was known from the middle of the 17th century when the old art of origami originated in Japan. However, in respect to the production of packaging, 3D forming of paper has a much shorter history of only around eight decades. In his pioneering work, Scherer (1932) described a deep-drawing process for paper materials, followed by Heinz (1966, 1967). After this, development of 3D forming processes shifted to industry, when the current machinery and forming processes for paper and paperboard were developed (Quick and Mitchell 1990, Miller 1964, Miller 1979, Kawano and Kondo 2000, Helmrich 2011). In the early 2010s, an urgent need for a more sustainable alternative to plastics initiated a revival of the scientific and industrial interest in developing new forming processes for paperboard and improving the deformation characteristics of paper. These processes are aimed at producing novel kinds of packaging in order to replace plastics in rigid packaging (Svensson *et al.* 2013, Kunnari *et al.* 2007; Östlund *et al.* 2011; Post *et al.* 2011, Leminen *et al.* 2013, Huang and Nygård 2012, Linvill and Östlund 2014, Hauptmann and Majschak 2011, Tanninen *et al.* 2014).

At the present moment, there are only two types of forming processes for paperboard in commercial use: stamping (tray pressing, press forming) for the production of trays and plates, and the Multivac® type (vacuum-assisted air forming a.k.a. thermoforming) of process for the production of sealable trays for sliced cold cuts and cheeses. The emerging technologies in paper forming include deep-drawing, hydroforming and hot pressing (stamping with a fixed blank). The current industrial and emerging forming processes can be classified as shown in Fig. 2.

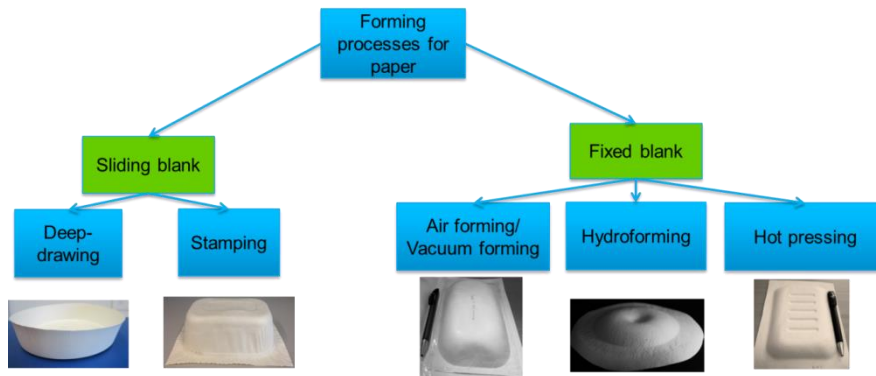


Figure 2. Conditional classification of forming processes according to the type of blank holding, with examples of the shapes produced using appropriate laboratory testing equipment.

According to Fig. 2, forming processes can be divided into two main groups: sliding and fixed blank processes. In the sliding blank process, forming is due to the sliding of paper into the mould and lateral contraction of paper that causes the microfolding of paper. Microfolding occurs either by the creasing lines (press forming) or stochastically (deep-drawing). In the fixed blank process, paper is formed via straining of paper. However, it should be noted that this classification is conditional, because the blank holding force can be adjusted during the process for a particular paperboard to yield the shape with the best possible appearance. Thus, paper can be strained in the sliding blank process, and lateral microfolding may occur to some extent in the fixed blank process. As a rule of thumb, the shapes produced in the sliding blank process are non-sealable due to wrinkles but have a relatively high depth, while shapes produced in the fixed blank are sealable but have significant limitations in depth. These two types of forming processes are described in detail below.

2.1.1 Sliding blank forming processes

The sliding blank forming processes are represented by deep-drawing and stamping. The stamping is also referred to as paperboard pressing, press forming, tray pressing and plate pressing. Typically, industrial stamping machinery has several units, starting with an unwinder (in the case of a roll-fed machine) or sheet feeder (in the case of a sheet-operated machine); the next unit is the die cutting and creasing unit where the paperboard is cut into the blanks and respective creasing lines are made; and finally the forming unit itself where the blank is formed by means of metal tools, which are either electromechanically or hydrodynamically driven (Leminen *et al.* 2013). Optionally, the paperboard forming line can be equipped with a quality control unit and stacking unit for ready shapes. Typical products of industrial stamping process are shown in Fig. 3.



Figure 3. 3D shapes obtained from current industrial forming processes (press forming).

The shapes in Fig. 3 have wrinkles formed at the location of the creasing lines; these wrinkles create voids which restrict the possibility of the gas-tight sealing of such shapes (Leminen *et al.* 2013, Leminen *et al.* 2015a). Wrinkles can also form in random places, which cause shape instability and impaired visual appearance (Wallmeier *et al.* 2015). The major challenges in production with the industrial stamping process are irregular wrinkle formation, cracks in the shapes, and the problems related to the convertibility of the barrier coatings (e.g. pinholes in the creases) (Tanninen *et al.* 2014, Leminen *et al.* 2013). The runnability of the forming process and the visual appearance of the shapes are maintained through the adjustment of several parameters such as the force of the forming die, blank holding force, creasing pattern, which are adjusted based on empirical methods; for the particular type of paperboard used and for the particular 3D shape (Hauptmann *et al.* 2014).

One other important parameter is the mould clearance, which is the gap between the female and male mould at the final position of the forming die. Typically, it is more or less equal to the thickness of the paperboard or slightly lower ($\text{thickness} \times 0.65\text{--}0.85$), providing compression and smoothening of the paperboard edges to improve the visual appearance of the shape. Too small a mould clearance would cause high stress concentration and possibly lead to high paper-to-metal friction, which would eventually lead to mechanical failure of the material or formation of cracks in the 3D shapes (Leminen *et al.* 2013).

The deep-drawing process is somewhat different from stamping. Forming in deep-drawing is performed in between the male die and the forming cavity, while the female mould can be absent, present as a counter holder or used to emboss the bottom of the shape. Conventionally, paper blanks in the deep-drawing process are not creased, and also shapes do not necessarily have edges or trims, although it depends on the particular process configuration (Hauptmann and Majschak 2011). A schematic representation of the deep-drawing process can be found in Fig. 4.

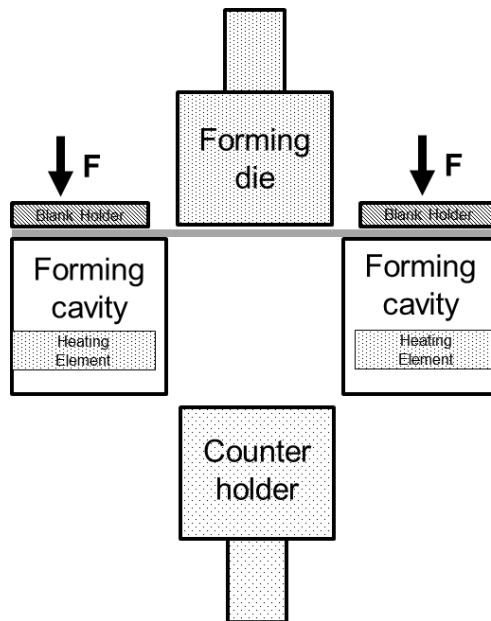


Figure 4. Schematic representation of the deep-drawing process.

The deep-drawing process operates as follows: the paper blank is transferred to the forming machine where it is clamped by a blank holder with a predetermined force (1–3 kN, typically); subsequently, the male die starts a downward movement towards the counter holder along the forming cavity, which is where the actual forming occurs. Finally, the shape is released from the forming device. The whole forming sequence can be as short as a couple of seconds (Hauptmann and Majschak 2011).

The process concept described above is relatively new and has not yet been applied on industrial scale. It should be noted that in practical applications the difference between deep-drawing and stamping can be negligible, *i.e.* certain elements of both processes can be combined to yield the best achievable quality products, as for instance in the production of paper plates. The selection of process parameters such as the die force and blank holding force is performed empirically, in the same way as in industrial stamping. The forming gap is another parameter similar to mould clearance in industrial stamping which directly affects the forming result (Hauptmann and Majschak 2011). The forming gap is the distance between the edge of the forming cavity and the edge of the die. This distance is varied according to the thickness of the materials. Too small a forming gap increases the out-of-plane and in-plane shear and forces. This can lead to the formation of cracks and eventual failure of material in the formed shape. Typically, the gap is around $0.7 \cdot \text{thickness of the paperboard}$. Too large a forming gap, on the other hand, leads to the poor appearance of the shape due to wrinkles, whose formation is less restricted (Hauptmann and Majschak 2011).

2.1.2 Fixed blank processes

The main difference between fixed blank forming processes and sliding blank forming processes is in the predominant mode of the paper deformation. In fixed blank processes, tensile deformation prevails over compressive deformation. The fixed blank forming process yields shapes, which are restricted in depth (2–3 cm maximum approximately, depending on curvature), but with smooth and even edges that can be sealed with barrier films. Also, shapes produced using this type of forming process are typically free of post-forming defects related to shape instability. Fixed blank forming processes have some industrial applications but have not yet been widely applied (Ford *et al.* 2014). For instance, paperboard has been used in form-fill-seal forming machines as a direct replacement for plastics (Fibreformpack 2015).

Fixed blank forming processes can be distinguished on the basis of the type of forming tools that are used. They can be divided into hydroforming, hot pressing and air forming (vacuum forming) shown in Fig. 5, A, B and C, respectively.

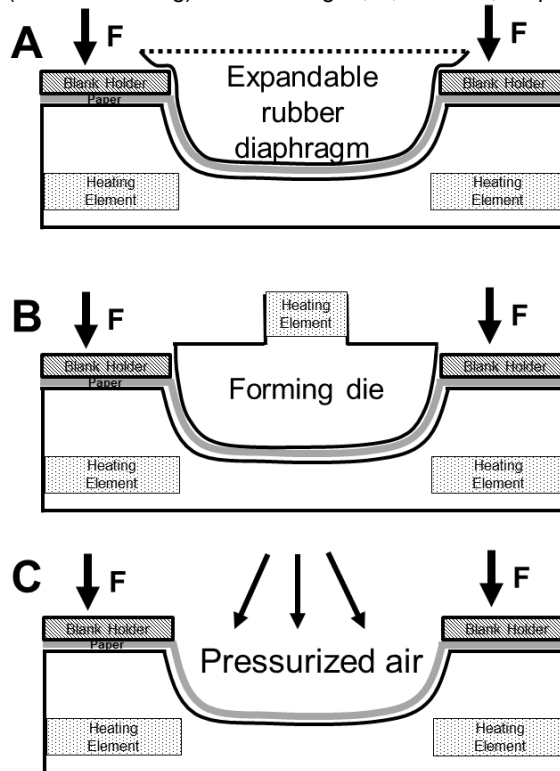


Figure 5. Schematic representation of the different fixed blank forming processes – A: hydroforming, B: hot pressing, C: air forming.

The hydroforming process (Fig. 5 “A”) employs an expandable rubber balloon to form the paper; it is expanded using a certain liquid towards the forming cavity

until a certain hydraulic pressure is reached. The forming process setup is somewhat similar to that of bursting strength measurement in paper testing (Östlund *et al.* 2011). The primary advantage of this process is in the even distribution of the load which allows the full utilization of the extensibility potential of paper, avoiding wrinkle formation even in the most complex of shapes (Kawano and Kondo, 2000). At the present moment, this process has only been applied on laboratory scale. A detailed description of forming devices and process features can be found in (Östlund *et al.* 2011, Groche *et al.* 2012, Post *et al.* 2014).

Hot pressing (Fig 5 “B”) is, in principle, similar to the industrial stamping of paperboard with the exception that there is no sliding of the paper blank into the forming cavity, and the paper is formed almost entirely due to straining. In comparison with the stamping process, the depth of the shape in this process is restricted, and it is determined by the extensibility of the paper. The edge trim of the shape is readily sealable. The process is easy to scale up and can be operated at high production speed, using for instance, an electromechanical drive. The main limiting factor for the utilization of this process on industrial scale is the absence of suitable paper grades with the high extensibility and post-forming stiffness to create paperboard shapes with a suitable depth for use as packaging.

Air forming (a.k.a. vacuum forming, thermoforming) (Fig. 5 “C”) is an industrial-scale process for the forming of plastic materials. It is also used with special formable grades of paperboard, in the Multivac® types of forming devices (Packworld.com 2014). In air forming, paper is heated and formed by means of the pressurized air and/or vacuum in a sealed forming chamber, and after this trays are die cut from the web. In this case, as well as in hydroforming, the load is quite evenly distributed within the paper, which allows the full utilization of the extensibility potential of paper. In addition to high strength and elongation, as in all fixed blank forming processes, in air forming paper should have very low air permeability to enable forming. Unfortunately, this method, despite the high industrial relevance, has not been extensively studied in respect to the forming of paper, and to the recent knowledge of the author no publications about it exist.

2.1.3 Summary

The 3D forming processes for paper differ in many respects. First of all, in the types of deforming forces and relevant stresses arising in paper: primarily tensile deformation in fixed blank processes and lateral contraction, out-of-plane and in-plane compression, frictional and shear stresses in the sliding process. In addition, process features such as the forming tool, speed of operation, production speed, and blank holding force can be used to distinguish 3D forming processes from each other. It is evident that the requirements of good formability should be determined in accordance with the target 3D forming process. The only common feature in forming processes is the use of the heat, which aims at such effects as the softening of paper, drying and “freezing” of the shape after forming and the reduction of friction. The influence of the elevated moisture level and temperature on formability is considered in the relevant chapter (2.4).

2.2 Insufficient formability: Defects in the formed shapes

As mentioned earlier, the formability of paper is a relatively abstract term, which is used to describe the result of 3D forming. If the shape is intact and there are no observable imperfections, paper is considered to have good formability. But how to characterize mediocre or bad formability, and how to identify what is wrong in the forming process or which properties of the material should be improved to avoid imperfections? In order to diagnose the problem and find a solution based on the process parameters or material properties, the typical defects in the shapes need to be addressed. Typical defects in 3D forming are summarized below.

2.2.1 Cracks and failure of the material

The most obvious and most detrimental defects for the functionality of shapes are cracks and subsequent mechanical failure of material. These defects originate in the zones where the stress has exceeded the strength of the material. The most common type of stress in fixed blank forming is tensile deformation, which leads to the tensile failure of paper. In the sliding blank process, cracks and failure of material occur due to more complex deformation phenomena which include shear, compressive, and tensile stresses coupled with high paper-to-metal friction. Typically, stress concentrates in the zones of high curvature and sharp edges (Fig. 6).

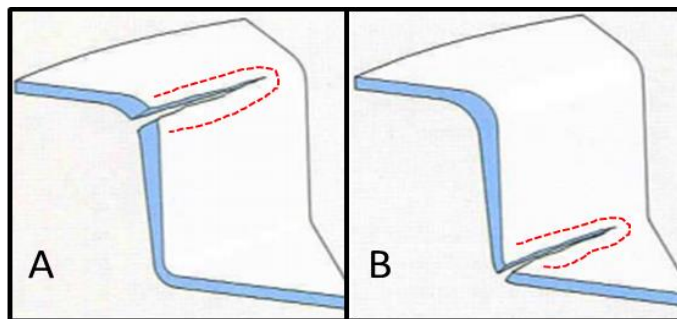


Figure 6. Typical locations of cracks in formed shapes.

In the fixed blank process, measures to cope with cracks are associated with decreasing the depth of the shapes, and adjusting the force or pressure of the forming instrument, primarily. In sliding blank processes, the blank holding force and friction can be decreased to avoid the formation of cracks. However, the selection of paper material with suitable mechanical properties for formation of the given shape is important.

2.2.2 Post-forming instability of shapes

Paper is a viscoelastic plastic material (Alava and Niskanen 2003) and after forming, it experiences post-forming deformations caused by elastic recovery. This may lead to the inaccurate reproduction of the desired shape due to the spring back and deflection of the side walls. This is especially common in the shapes produced in the sliding blank forming process, where the side walls of the shapes can deflect to a certain angle from the original design of the shape. The deflection and spring back of the shapes occurs due to the elastic recovery of paper and excessive drying in forming. Once paper is released from the forming machine, it adsorbs moisture, which in turn releases mechanical stresses and causes hygroexpansive deformation.

In the fixed blank forming process, shape instability issues are mainly associated with improper drying and the subsequent release of the drying stresses caused by moisture adsorption. Spring back and deflection are quite limited, because the paper used in such processes has a relatively high plastic deformation. This problem can be mitigated by careful adjustment of the dryness of paper before forming and conditioning of the shapes after forming (Hauptmann and Majschak 2011). The spring back effect is demonstrated in Fig. 7.

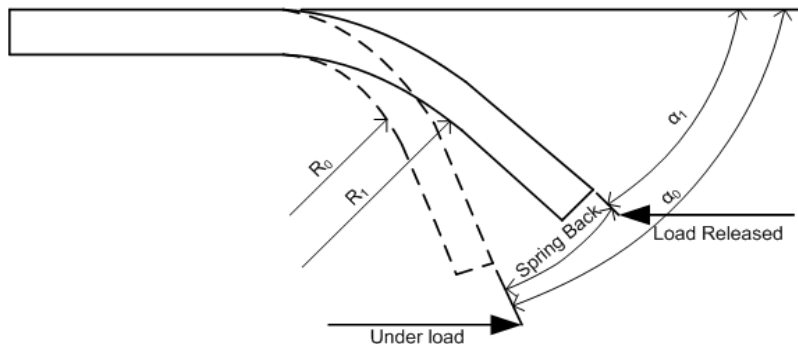


Figure 7. Graphic representation of the spring back effect, Radius R_0 and angle α_0 represent the designed dimensions of the shape after forming; radius R_1 and angle α_1 indicate dimensions after elastic recovery has taken place.

2.2.3 Wrinkles

Wrinkling occurs mainly due to the action of compressive forces oriented in the transverse direction (Johnson and Urbanik 1987; Urbanik 1992; Bhattacharyya *et al.* 2003; Hosford and Caddell 2007). Wrinkling is the most common defect in sliding blank forming processes. Wrinkling leads to an uneven height on the upper surface of the package or in the side wall of the shape. This prevents gas-tight sealing, and has a detrimental effect on visual appearance. The formation of wrinkles and buckles can be controlled to a certain extent by adjusting the blank

holder force: the higher the force, the lower the probability of formation of wrinkles and buckles (Bogaerts *et al.* 2001; Hauptmann and Majschak 2011). However, a high blank holder force leads to increased tension and compression loads, which increases the possibility of crack formation and eventual failure of material.

One other way to partially control formation of wrinkles is by pre-creasing; this approach creates zones with locally reduced stiffness and elastic modulus (Tanninen *et al.* 2014). Thus, wrinkles are formed in the forming process in a controlled way, at predetermined places. The location of the creasing lines for each type of blank has been defined experimentally (Giamperi *et al.* 2011). By combining the tailored design of the pre-creasing lines and adjustment of the blank holding force in the process, a sealable shape can be produced (Leminen *et al.* 2015b). One other way to deal with wrinkles is to use material with low compressive strain and strength, which would lead to the formation of a large amount of shallow and small wrinkles; thus the surface of the material would look rather smooth.

In the fixed blank forming process, wrinkling mainly originates from the improperly distributed blank holding forces in the places of maximum lateral compressive stress. Side wall wrinkling of a cylindrical deep-drawn shape and in a shape produced by hot pressing is shown in Fig. 8.



Figure 8. The wrinkling in the side wall of a deep-drawn shape (sliding blank) (left) and flange wrinkling in a shape produced by hot pressing (fixed blank).

2.2.4 Blistering and discoloration

Blistering and discoloration are common defects that occur due to the overheating of paper in forming. Blistering is caused by high steam pressure inside the paperboard due to too rapid heating or the overheating of paper when water vapour and air cannot escape via the uncoated side, which causes internal delamination and blistering of the coated surface. This defect is especially common in coated, densely printed and/or multilayer grades where the density of the outer layers is high, and air permeability is low. Blistering appears as an uneven, bubbly surface. However, this defect can be easily avoided by adjusting the process conditions and selecting an appropriate barrier coating material with high adhesion to the paper material in order to withstand gas pressure.

Discoloration may occur due to high frictional forces; in certain cases, the surface of the paper may be overheated which in turn leads to discoloration, *i.e.*

yellowing or browning of the surface. Another possible cause of discoloration is the loss in light scattering coefficient due to extensive densification. This defect can be avoided by the appropriate selection of the temperature of the forming tools and by adjusting the forming gap or mould clearance. The discoloration of side wall of the shapes in the deep drawing process and blistering of PE coating in thermoforming process is shown in Fig. 9.



Figure 9. Upper image: discoloration in deep-drawn shapes (left), discoloration coupled with earing (right), courtesy of M. Hauptmann, Lower image: blistering of the fragment of the tray trim in thermoforming process.

2.3 The relation between formability and the forming process

The meaning and evaluators of good formability are dependent on the forming process. Once the forming processes for paper have been examined, it is possible to establish the relations between the forming process, good formability and the mechanical properties of paper material. Only a few papers have dealt with this problem, and mostly in respect to fixed blank forming processes (Post *et al.* 2014, Linvill and Östlund (2014), Östlund *et al.* 2011, Huang and Nygård 2012). The requirements for good formability in the sliding blank process, from a material point of view, were described in Publication III of this thesis. Based on the available information in the literature and hands-on knowledge of industrial converters, it is possible to establish a simple scheme (Fig. 10) which describes the relationship between the forming processes, criteria of formability and the mechanical properties of paper.

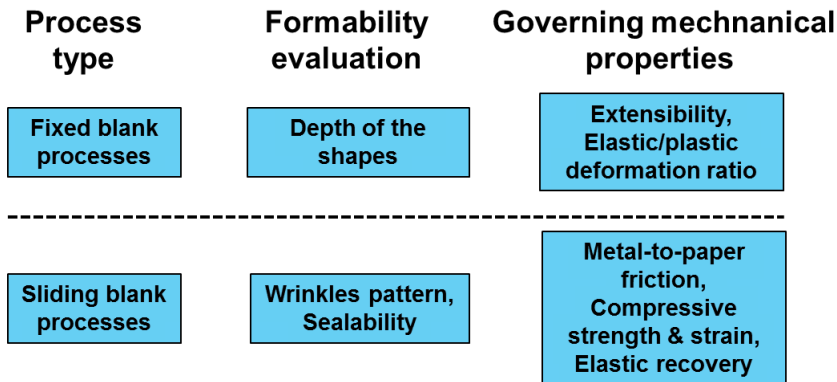


Figure 10. The relationship between forming process, criteria of good formability and required paper material properties.

From Fig. 10, the criteria of good formability and the mechanical properties on which they are dependent are completely different for these two types of forming processes. Recently, a two-stage forming process which combines elements of both the fixed and sliding blank processes was described (Hauptmann *et al.* 2013). This process combines the high depth of the shape obtained by the sliding blank process with the subsequent pressing or deep embossing of the pre-formed shape to create sealable edges, or a unique design. Essentially, the material requirements in this process concern both the fixed and sliding blank processes.

2.4 Influence of moisture and temperature on the deformation behaviour of paper

It can be expected that the softening of the polymers in paper under the action of elevated moisture and temperature is a key phenomenon, which enables all kinds of 3D forming processes of paper. The softening of paper allows higher plastic deformations in fibre joints and fibres to take place and the subsequent “freezing” of the shape upon cooling provides stiffness and shape stability. This chapter deals with the general influence of moisture and temperature on the deformation behaviour of paper as well as with the role of temperature and moisture in 3D forming processes.

2.4.1 The general effect of moisture and temperature on mechanical properties of paper

In order to understand the changes in the mechanical behaviour of paper caused by softening, the polymers that it is composed of should be examined. Chemical pulp fibres are mainly composed of hydrophilic polymers: cellulose and hemicelluloses. Lignin, the third constituent of fibres in paper, is not significantly

affected by the action of moisture, but it softens under elevated temperature (Salmén 1990).

The effect of increased temperature on the fibre level is mainly related to the reduction in the axial stiffness of the fibres due to the softening of the cell wall. On the paper level, weakening of the fibre-fibre bonds should also be taken into account. Water acts as a plasticizer by interacting with the intramolecular and intermolecular hydrogen bonds in cellulose and the intermolecular bonds between fibres and fibrils, and thus allows the deformation and rearrangement of the cellulosic microfibrils (Tsuge and Wada 1962; Goring 1963; Crook and Bennet 1962; Salmén and Back 1977b; Back and Salmén 1982; Waterhouse 1984; Caulfield 1990; Shiraishi 1991; Haslach 2000; Alava and Niskanen 2006). The data on the softening of wood polymers from the references (Andersson and Berkyto 1951; Goring 1963; Salmén and Back 1977a and 1980 Salmén *et al.* 1984; Back and Salmén 1989; Waterhouse 1984; Salmén 1990; Shiraishi 1991), support the prediction that all wood polymers in paper at a moisture content of around 6 to 8% soften at a temperature of 150 to 180°C.

The softening temperatures of wood polymers in paper depend largely on the moisture content of the polymers. In the absolutely dry state, amorphous cellulose, lignin and hemicelluloses have softening temperatures of 230°C, 205°C and 180°C, respectively. These values are significantly decreased already at 6% moisture content, which is typical for air-dry paper (Salmén 1990). High moisture content in paper weakens fibre bonds, allowing a certain degree of sliding between the fibres. This changes the stress-strain behaviour of paper towards higher extensibility and less stiffness. (Uesaka *et al.* 2001; Uesaka 2005; Brecht and Erfurt 1959; Back and Salmén 1989; Johnson *et al.* 1983; Retulainen *et al.* 1998; Sørensen and Hoffman 2003; Alava and Niskanen 2006).

The effect of moisture on the extensibility of paper is much stronger than that of temperature (Salmén and Back 1980; Kunnari *et al.* 2007). The joint effect of temperature and moisture can be demonstrated by failure envelopes for paper at different temperatures and moisture levels (Fig. 11).

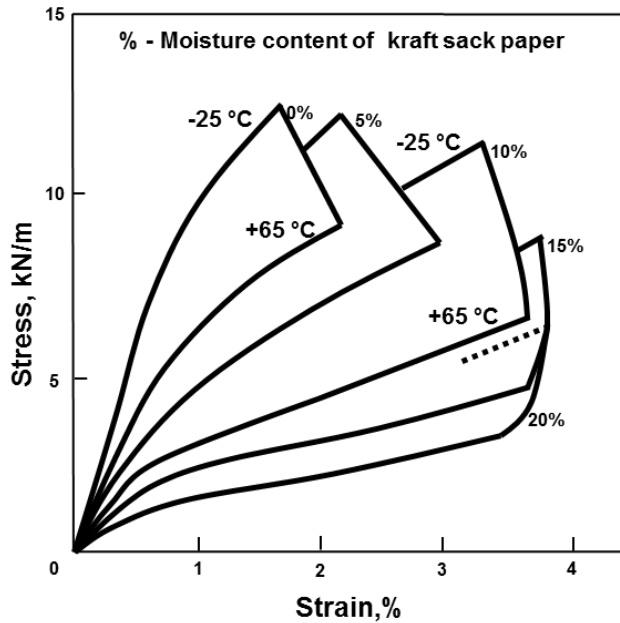


Figure 11. Failure envelopes for a kraft sack paper in the machine direction at temperatures from minus 25 to plus 65°C and moisture contents of 0, 5, 10, 15 and 20% (redrawn from the data of Salmén and Back 1980).

The response of paper to elevated moisture content is different in remoistening. The maximum extensibility can already be observed at 85 to 90% dryness (Andersson and Berkyto 1951). There is a clear difference in response to the high moisture content between unrestrained dried and restrained dried paper. The extensibility of unrestrained dried paper is not much affected by an increase in moisture content, while restrained dried paper, once moistened to a 17% moisture content, can be strained twice more than dry paper (Kunnari *et al.* 2007). Part of this may also be associated with the partial relaxation of the drying stresses in paper (Kimura 1978).

2.4.2 The role of moisture and temperature in the forming process

The influence of moisture and temperature on the results of forming is not as evident as in the case of the straining of paper. In forming, temperature and moisture affect the metal-to-paper friction, stiffness, strength and possible defects in the visual appearance of the 3D shapes. In the fixed blank process, the principal role of temperature and moisture is in increasing the deformability of paper; accounting for an increase of up to 2.5% points in the formability strain (Kunnari *et al.* 2007). The softening occurs during the 3D forming of paper; it is typically heated to temperatures of 60–120 °C at a moisture content of 6–12% (Kunnari *et*

al. 2007). However, there is a clear lack of information on what the typical temperature of paper in 3D forming is; usually only the temperature of the forming tools is indicated.

The paper temperature varies in accordance with the type of forming process and machinery used. In press-forming, the temperature of paper is controlled by heating the female and male metal tools, the forming time, and by the type of forming tools (Tanninen *et al.* 2014). Alternatively, paper can be heated in a separate module, prior to the actual forming. The moisture content in paper is equally important in respect to the convertibility of paper and results of 3D forming. It can be adjusted by conditioning the paper rolls in the climate chamber. The desirable moisture content of paper in press-forming is approx. 7–13% (Tanninen *et al.* 2014). A higher moisture content (>13%) would lead to a sharp decrease in the tensile strength; which would have a negative effect on the load-bearing ability and stress distribution within the network and eventually lead to the fracturing of the paper. The temperature and moisture effects are not independent, since at elevated temperature, the equilibrium moisture content of paper changes. Also, paper simply dries at elevated temperature.

In press-forming, the moisture content of paperboard decreases by 2.5%-points, within 0.5–1 seconds of the forming sequence, with the female mould at a temperature of 160–180 °C (Nevalainen 1997). The optimal temperature for good formability in the fixed blank forming process is highly dependent on the heating situation. In an open system, in which water can evaporate from the paper upon heating, the maximum extensibility/formability is reached at a temperature of 60 to 70 °C and 80 to 100 °C for chemical and mechanical pulps, respectively (Kunnari *et al.* 2007).

Another important effect of temperature and consequent drying in 3D forming is on the dimensional stability of the 3D shape after forming, *i.e.* the “freezing” of the shape after forming. 3D shapes formed without heating, or with inadequate heating, have worse spring back and deflection defects (Hauptmann and Majschak 2011).

2.4.3 Summary

Softening under elevated temperature/moisture is a key phenomenon enabling the 3D forming of paper. However, the numerical increase in formability/extensibility (in the case of the fixed blank process) is rather small. A pivot table summarizing the effects of moisture and temperature on formability in different forming processes is shown in Table 1.

Table 1. Optimal temperature and moisture content of paper in different 3D forming processes.

| Process | Optimal conditions | Practical considerations | Ref.* |
|--|--|--|-------|
| Sliding blank processes | | | |
| Stamping (tray pressing, press forming) | Tool temperature: 150–190 °C (for the female mould, no plastic coating on that side), 40–60 °C (for the male mould in contact with plastic coating), moisture content of paper 7–11%, very short forming time (0–1 seconds). | The temperature of tools may change in a long production run; high heat capacity of tools is needed. Softening and subsequent “freezing” provides shape stability. | 1,2 |
| Deep-drawing | Forming cavity: 140–180 °C, forming die: 60–100 °C, moisture content of paper 7–11%, short forming time (1–3 seconds). | Softening of the material is the key to avoid cracks and optimize wrinkle formation. Temperatures above 180 °C for forming the cavity lead to the discoloration of paper. Softening and subsequent “freezing” provides shape stability. Friction can be adjusted by varying temperature. | 3,4 |
| Fixed blank processes | | | |
| Hydro-forming | Temperature of the female mould 100–140 °C. Moisture content 10–15%, relatively long forming time (1–10 seconds). | The primary role of temperature and moisture here is in increasing the share of plastic deformation. | 5,6,7 |
| Hot pressing (Forming with heated metal tools) | Temperature of paper: 70–90 °C, moisture content of paper: 8–13%. | Optimal temperature tends to be higher for samples containing mechanical pulp. Temperature increases plastic deformation and decreases metal-to-paper friction coefficient. | 8 |

* 1-Tanninen *et al.* 2014a, 2-Tanninen *et al.* 2014b, 3-Hauptmann and Majschak 2011, 4-Wallmeier *et al.* 2015, 5-Linivill and Östlund 2014, 6-Groche *et al.* 2012, 7-Östlund *et al.* 2011, 8-Kunnari *et al.* 2007.

2.5 Improvement of the extensibility of paper: role of fibre raw material properties

The primary requirement for good formability in the fixed blank forming process is the high extensibility of paper (Östlund *et al.* 2011, Post *et al.* 2014); the fibre raw material should be selected with physical, structural and chemical attributes favourable to extensibility. This chapter considers the features related to the selection of the fibre raw material for the production of highly extensible paper.

2.5.1 Chemical composition of the fibre raw material

Papermaking fibres are primarily composed of cellulose and hemicelluloses but lignin, the third constituent, is present only in unbleached chemical pulps, semi-

chemical, thermo-mechanical, and mechanical pulps (Alén 2000). The relative share and internal structure of different natural polymers in fibres is of great importance for the mechanical properties of paper (Spiegelberg 1966).

2.5.1.1 Structural features of cellulose influencing the extensibility of fibres and paper

Cellulose is the main component of the fibres and therefore it is not surprising that to a major extent it determines the extensibility of fibres and paper themselves. Cellulose is a linear homopolymer which consists of a β -1,4-anhydroglucopyranose unit linked by glucosidic bonds. The anhydroglucopyranose units in the cellulose chain also contain hydroxyl groups at 2, 3, and 6 carbon atoms. The cellulose in papermaking fibres is present in two main states, crystalline and amorphous, with a respective ratio of around 3:1 for bleached wood pulp (Ward 1950; Fiskari *et al.* 2001). In addition to fully amorphous and crystalline cellulose, regions with not fully amorphous cellulose can be found, and they are typically regarded as the paracrystalline regions (Kulasinski *et al.* 2014). Other features of the cellulose structure include intra- and intermolecular hydrogen bonding, crystalline structure, alignment of crystallites, dimension of crystals, and the degree of crystallinity.

Cellulose is the stiffest chemical component (140 GPa) of fibres (Cintron *et al.* 2011, Wohlert *et al.* 2012). Basically, the elongation of cellulose takes place through two mechanisms: by elastic axial elongation of the cellulose molecules and by irreversible, time-dependent slippage between cellulose molecules (Altaner *et al.* 2014).

The breakage of hydrogen bonds upon straining primarily takes place in the amorphous part of the cellulose (Kong and Eichhorn 2005). The relative ratio between the interchain and intrachain hydrogen bonding might explain the higher deformability of the amorphous cellulose in comparison with the crystalline cellulose. The higher share of interchain hydrogen bonds allows higher mobility of the cellulose chains due to the partial breakage or rearrangement of these bonds until the moment of failure. The amorphous and paracrystalline parts of cellulose have about three times fewer intrachain hydrogen bonds while the amount of interchain hydrogen bonds is higher; this is one explanation for the higher deformability of amorphous cellulose (Kulasinski *et al.* 2014). In addition, only the amorphous part of cellulose can soften under the action of water and elevated temperature.

2.5.1.2 The influence of cellulose crystallinity on extensibility

Cellulose is capable of forming crystalline structures that have a detrimental effect on its deformation ability. One should remember that the degree of crystallinity is not a common term for Cellulose I, II, III, and IV and actually means a share of a particular crystalline structure (I, II, III, or IV) in a particular cellulose sample. Thus, Cel I and Cel II samples with the same degree of crystallinity would have different

mechanical properties. Among the different cellulose crystalline allomorphs, only two can be found in nature, Cellulose I α and I β (Atalla and Van den Hart 1984, Sugiyama *et al.* 2001).

The structure of amorphous cellulose has been studied much less than the respective crystalline forms (Kondo *et al.*, 2001; Kontturi *et al.*, 2011; O'Sullivan, 1997). Amorphous cellulose is the cellulose which lacks a long-range order and has greater disorder in the orientation of the cellulose chains, which can be observed using the X-ray technique (Paakkari *et al.* 1989).

The maximum theoretical strength of amorphous cellulose is about 800 \pm 100 MPa, and its yielding point occurs at around 7-8% extension (Chen *et al.* 2004). The stiffness of the crystalline and amorphous parts of the cellulose differs significantly (220 GPa for crystalline vs. 10.4 GPa for amorphous) (Sun *et al.* 2014). This drastic difference means that the softer amorphous part mainly determines the extensibility of the cellulose.

An increase in the crystallinity of the cellulose increases the strength and stiffness of the fibres; at the same time, it has a negative effect on their extensibility and flexibility (Ward 1950; Lee 1960; Parker 1962; Thygesen 2006). An increase in the proportion of amorphous cellulose in pulp is accompanied by an equivalent increase in extensibility and a decrease in elastic modulus (Page 1983). However, controlling the crystallinity of cellulose requires harsh chemical treatments with negative side effects, and is relatively costly to implement.

2.5.1.3 Influence of the hemicellulose content in pulp on the extensibility of paper

Xylans and mannans are the most common hemicelluloses in hardwood and softwood pulp fibres, respectively (Alén 2000). Hemicelluloses are amorphous polymers with a relatively low degree of polymerization (50 to 300), lower elastic modulus (7 GPa) and a significantly lower softening temperature than cellulose. Hemicelluloses improve the bonding potential of fibres and thus the extensibility of paper. According to Spiegelberg (1966) and Leopold and McIntosh (1961), high hemicellulose content in chemical pulp fibres is favourable for extensibility and strength, while Helmerius *et al.* (2010) did not observe any decrease in the elongation of paper even after removal of 60% of the xylan from birch pulp. Obermanns (1934) in his pioneering work claimed that there is a certain optimum for hemicellulose content in respect to strength; this optimal content depends on the origin of the pulp. Henriksson *et al.* (2008) showed that MFC films with high hemicellulose content had the highest tensile strength and strain, which was attributed to the decreased porosity of such films, *i.e.* better bonding. Hemicellulose removal has also been found to relate to the hornification (loss of swelling ability due to drying) of fibres (Oksanen *et al.* 1997). The extensibility of paper is related to their swelling ability (WRV) and the corresponding shrinkage potential of fibres.

2.5.1.4 Influence of lignin on extensibility

The selective removal of lignin from wood fibres improved their elongation by around 20%; notably, this effect was obtained when as little as 25% of the total lignin was removed from the fibres (Zhang *et al.* 2013). Further delignification did not improve the extensibility or tensile strength of the fibre. The effect of lignin removal might be associated with the rearrangement of the microfibrillar structure due to the slippage of fibrils in the fibres, besides the fact that lignin is actually a stiff and non-extensible polymer in dry state (Zhang *et al.* 2013). However, unlike crystalline cellulose, lignin may soften under the action of elevated temperature (Salmén 1990).

High lignin content has a detrimental effect on the extensibility of paper; mechanical pulps have a much lower elongation than chemical pulps (Hatton 1997). Lignin is present in the cell wall of the fibres, which negatively affects the bonding potential and flexibility of the fibres. Unbleached chemical pulp fibres (both kraft and sulphite) are capable of forming fibre-fibre bonds that are as strong as those in bleached pulp (Fischer *et al.* 2012; McIntosh 1963; Mayhood *et al.* 1962). Hartler and Mohlin (1975) claimed that the maximum bond shear strength between fibres occurred at a lignin content of 7% for unbleached kraft, and 10 to 12% for unbleached sulphite. The strength of bonds is known to strongly affect the strength and elongation of the fibre network.

It can be concluded that the chemical composition and structure of the wood polymers in the fibre raw material determines to a great extent the potential limits of extensibility, and as a consequence, the formability of paper. While selecting the fibre raw material, one should pay attention to the cellulose structure, content of hemicelluloses, and perhaps, to a lesser extent, lignin content. From the economic and technical points of view, the selection of bleached kraft pulp as the main fibre constituent of paper seems to be the most viable option for the production of extensible paper for use in 3D packaging.

2.6 Improvement of the extensibility of paper: structural aspects of the fibres that affect extensibility

Fibres are the primary constituents and load-bearing elements in paper. They have a strong influence on all the mechanical properties of paper, and extensibility is not an exception from this rule. Wood fibres are generally axially stiff and non-extensible. The typical elongation of wood pulp fibres is about 3 to 6%; however, juvenile softwood fibres may have extensibility of up to 20% points (Hardacker and Brezinski 1973; Bledzki and Gassan, 1999). Also, certain non-wood and synthetic fibres have extensibility that varies over a broad range, *i.e.* 50 to 800%. However, extensible fibres do not necessarily form extensible paper. In order to fulfil this requirement, fibres should be able to form sufficiently strong bonds and a network structure with even stress distribution (Seth 2005).

The morphological features of fibres are the key factors determining their mechanical properties. The main chemical component of fibres, cellulose, is stiff in an axial direction, with a theoretical modulus of the chain of around 250 GPa (Vincent 1999). When individual cellulose chains form a cellulose I β crystallite structure, the stiffness decreases to 140 GPa (Cintron *et al.* 2011). The stiffness is further decreased to approx. 60 GPa, for microfibrils (Sun *et al.* 2014), and finally to 20 to 40 GPa for fibres (softwood latewood) (Page and El-Hosseiny 1983). The decrease in stiffness and the corresponding increase in the extensibility of fibres in comparison with the cellulose molecule can be partially attributed to the spring-like arrangement of the microfibrils in the fibres. This alignment is described by the microfibrillar angle (MFA), which is determined as the angle between the axis of the fibre and the direction of the cellulose fibrils in the S2 cell wall layer (Barnett and Bonham 2004). The increase in elongation of the fibres due to a high MFA is explained by the untwisting of the spring-like structure, the sliding of fibrils under shear forces, and the higher flexibility of such fibres (Horn 1974; Page and El-Hosseiny 1983; Gurnagul *et al.* 1990; Martinschitz *et al.* 2008).

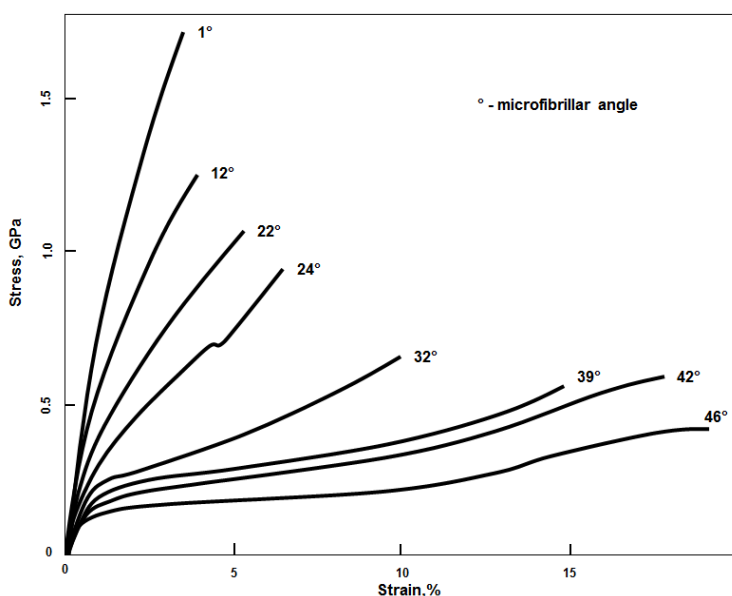


Figure 12. The relation between MFA and extensibility of chemical pulp fibres of black spruce (redrawn from the data of Page and El-Hosseiny 1983).

Fibres with a high MFA tend to have higher extensibility and lower stiffness than fibres with a low MFA (Fig. 12). Juvenile softwood fibres have higher extensibility than latewood fibres, which is explained by the higher MFA of juvenile fibres (Reiterer *et al.* 1999; Ljungqvist *et al.* 2005; Donaldson 2008; Hänninen *et al.* 2011).

The length and strength of fibres affect the extensibility of fibres and of the paper prepared from such fibres. The effect of the fibre strength on extensibility is much greater than the effect of fibre length (Kärenlampi and Suur-Hamari 1997, Kärenlampi and Yu 1997). The higher the fibre strength, the higher the paper extensibility. This assumption is valid only in the case of strong bonds between weak fibres. In the case of strong fibres, the strength and extensibility of paper would be determined by the strength of the fibre bonds. The influence of fibre length on the extensibility of paper in a zero-span test is almost negligible (Kärenlampi and Suur-Hamari 1997). On the other hand, there is a considerable increase in the work needed to complete the crack after the stress maximum. The influence of the fibre length on the extensibility of paper is likely to be more evident in the case of wet paper or weakly bonded fibres (Kärenlampi and Yu 1997). The simulation study of Kulachenko and Uesaka (2012) showed that an increase in fibre length from 1.5 to approx. 3 mm doubled the strain at break of the paper.

2.6.1 Summary

Based on the previous discussion, it is clear that the chemical and structural properties of fibres have a definite effect on the rupture elongation of fibres and paper. In natural fibres, the content of cellulose, hemicelluloses, and lignin varies, but what is even more important is that they have a different cell wall structure and dimensions, which may have a detrimental influence on the extensibility of fibres and paper. The mechanical, structural, and chemical properties of selected natural and synthetic fibres are shown in Table 2.

Table 2. Mechanical, structural, and chemical properties of selected natural and artificial fibres.

| Morphology | | | Mechanical properties | | Chemical composition | | | Ref. |
|-----------------------------|--------|------------|-----------------------|----------------------|---|-----------|-----------|----------|
| Origin | MFA, ° | Length, mm | Elongation, % | Elastic Modulus, GPa | Cellulose, % | Hemic., % | Lignin, % | |
| <i>Pinus silvestris</i> | 5–20 | 3–3.5 | 1.5–3.5 | 40 | Varies significantly according to the delignification method and its conditions | | | 1,2 |
| <i>Betula pendula</i> | 10–19 | 1–1.2 | 2–5.5 | – | | | | 1,2,3,16 |
| <i>Juniperus communis</i> | 30–40 | 0.83 | 5.4 | – | | | | 4,5,6 |
| <i>Eucalyptus Grandis</i> | 3–10 | 0.8–1.1 | 2–6 | 4–11 | | | | 17,18 |
| Coir | 40–49 | 20–150 | 20–50 | 4–6 | 46 | 0.3 | 45 | 1,2,7,8 |
| Cotton | 25–35 | 20–40 | 7.0–8.0 | 5–13 | 83 | 6 | ~1 | 1,9 |
| Flax | 8–11 | 20–50 | 2.7–3.2 | 20–30 | 64 | 12 | 12 | 1,11,10 |
| Viscose | – | Varies | 8–13 | 11 | 98–100 | 0.1–4 | Traces | 2,12 |
| Micro-fibrillated cellulose | – | Varies | 6.7–10 | 90–150 | 90–99 | Traces | Traces | 13 |
| Spandex | – | Varies | up to 800 | 0.025 | Polyurethane-based | | | 14,15 |
| Wool | – | 25–400 | 25–50 | 3.4 | Protein-based | | | 9 |

1-Peel 1999; 2-Bledzki and Gassan 1999; 3-Peura et al. 2008; 4-Hänninen et al. 2011; 5-Satyanarayna et al. 2009; 6-Satyanarayna 2010; 7-Martinschitz et al. 2008; 8-Mahato et al. 2009; 9-Haudek and Viti 1978; 10-Bos 2004; 11-Bourmaud 2013; 12-Lenz et al. 1994; 13-Eichorn et al. 2010; 14-Singha 2012; 15-Sun et al. 2012, 16-Spiegelberg 1966, 17-Hein and Lima 2012, 18-Downes et al. 2003

Some synthetic (spandex) and natural (coir) fibres have a notably high extensibility potential. These fibres, however, are not capable of creating a strong bonded network due to their limited ability to form interfibre hydrogen or covalent bonds.

2.7 Improvement of the extensibility of paper: Mechanical treatment of fibres

Fibres experience mechanical stress and deformations in many operations on their way from the wood yard to the paper machine (Rauvanto 2010). Basically, deformations in fibres occur due to shear and compressive stresses in refining, mixing, pumping, bleaching, and pulping (Forgacs and Mason 1958 and 1959; Seth 2005; Salmén and Hornatowska 2014). These stresses may cause positive and negative changes in fibre morphology with respect to extensibility (Ljungqvist *et al.* 2003). High-consistency (more than 20% dry solids content) mechanical treatment creates deformations in fibres that reduce the straightness and increase the extensibility of single fibres. These deformations are local structural changes in the fibre wall and MFA. Visually, they appear in the form of dislocations, microcompressions, curls, twists, folds, kinks, cuts, and external and internal fibrillation. Microcompressions (telescoping axial buckling along the fibre axis), curls, and dislocations (irregularities in fibres originating from the jamming or bending of the fibre) contribute to improving the extensibility of fibres. They may also increase the elongation of dry paper (but reduce tensile stiffness and elastic modulus). These deformations occur due to the action of compressive forces in the axial direction of the fibre (Dumbleton 1972, Joutsimo *et al.* 2005). Kinks in fibres have not been observed to have any effect on the extensibility of paper (Kibblewhite and Kerr 1980).

High-consistency refining of fibres increases the extensibility of fibres and paper via the creation of dislocations and microcompressions; however, at the same time, the strength of such paper is not increased (Jackson 1967, Seth 2005). Low-consistency refining also improves extensibility but drainage is impaired on account of fibrillation and respectively increased WRV (Ljungqvist *et al.* 2005). Combined high- and low-consistency mechanical treatment is a well-known method for improving the extensibility of paper. It unites the creation of fibre deformations in high- consistency treatment with the straightening of curled fibres in low-consistency refining, which improves the stress transfer ability of the fibre network and promotes bonding between fibres. However, low-consistency treatment should be relatively gentle in order to preserve the deformations in fibres. This combination imparts high extensibility to paper, while at the same time maintaining the dewatering resistance of the furnish at a low level (Ankerfors and Lindström 2011).

2.8 Improvement of the extensibility of paper: Chemical modification and additives

Chemical modifications and various additives are potential tools for increasing the extensibility of paper, and modifying mechanical behaviour in general. The chemical treatments and polymeric additives which are of possible use in the improvement of extensibility are described in this chapter.

2.8.1 Chemical modification of fibres

In general, there is no clear understanding of which chemical treatments are especially effective in improving extensibility and formability in the fixed blank forming process. The effects of chemical treatments may come via several indirect changes such as decreased crystallinity, modified fibre wall structure and secondary effects of increased swelling, drying shrinkage, and improved mechanical properties of bonds (strength, compliance). Also, the array of methods capable of enhancing the extensibility of paper is quite wide: grafting with various polymers, etherification, esterification, physicochemical adsorption of polyelectrolytes, blending with polymers, and introduction of functional groups.

The grafting (chemical or physical coupling of polymers on the surface of cellulose) of softwood fibres with methyl acrylate has been found to improve the elongation of paper from 1.1% to 5.9% points, which is explained by the increased swelling of fibres and subsequent drying shrinkage of paper (Rezai and Warner 1997a, b). The hydroxyethylation and hydroxypropylation of cellulose are beneficial for the strength and elongation of paper. Improvements in extensibility have been attributed to the stronger and more frequent fibre bonding, and increased drying shrinkage (Didwania 1968; Vuoti *et al.* 2013). The hexanoation of cellulose to a relatively high DS of 1.7 produces a thermoformable and water-resilient cellulose material with strain at break values of around 30% points (Matsumura *et al.* 2000). Selective oxidation of the C2–C3 hydroxyls of cellulose by periodate oxidation with sodium periodate to dialdehyde cellulose and the further reduction of aldehyde groups with sodium borohydride to form dialcohol cellulose has been found to be effective in improving the extensibility of fibres and paper. The elongation of single fibres increased from 60 μm to 180 μm . The increase in the extensibility of paper made from such fibres was more pronounced; the elongation of paper was increased from 4% (non-modified) to 23% points (oxidised and crosslinked). This indicates that the changes occur not only in the fibre structure but also in the character of interfibre bonding (Larsson *et al.* 2014).

2.8.2 Polymeric additives for improving the extensibility and formability of paper

Inclusion of various additives in the furnish or in the already formed fibre network is commonly used to enhance the dry and wet strength of paper. This approach dates back to the 19th century, when paper was sized with a mixture of caustic, wax, turpentine and fat so as to enhance extensibility (Nonnenmacher 1898). Most of the additives affect fibre-fibre bonding via the formation of new or modified interfaces. The strength of bonds relies on the topochemistry of the fibres and the type of binder present in the paper, if any (Akagane *et al.* 1979). A high degree of interfibre bonding allows distribution of tensile stresses in a more uniform way, utilizing the strength and straining potential of the fibres in the paper more

efficiently. Interfibre interactions during the distribution of the shrinkage stresses in drying also affect the fibre structure in the web.

Fines are readily available and known to improve paper strength; the addition of fines increases the RBA (relative bonded area) and drying shrinkage. The simultaneous addition of starch and kraft fines is especially beneficial for tensile strength improvement, and thus for extensibility, but also for drying shrinkage (Retulainen *et al.* 1993; Taipale *et al.* 2010). MFC can be added to the paper furnish for the improvement of strength and extensibility in the same way as fines (Klemm *et al.* 2011). An addition of 10% MFC to bleached hardwood pulp increases the strain at break of the paper by 5% points for sheets dried under restraint (Madani *et al.* 2011; Manninen *et al.* 2011).

Starch is a well-known dry strength additive for papermakers and its addition either to the wet end or by surface sizing positively affect not only the strength but also the extensibility of paper. Lindström *et al.* (1985) claimed that wet-end addition of cationic starch (4.2% to fibres) improves the extensibility of both filled (from 1.2% to 2.1% points) and unfilled (from 2.1% to 3.2%) paper by improving sheet consolidation (bonded area), increasing the specific bond strength and evening out the stress concentration in paper (Lindström *et al.* 2005). The surface addition of starch also improves extensibility by approx. 1% for restrained dried paper and by approx. 4% for unrestrained dried paper; in the latter case, the effect comes from the increased shrinkage of paper (Lipponen *et al.* 2005). In general, the surface addition of extensible material on the surface of paper even in relatively small amounts improves overall extensibility, because tensile failure is likely to originate from the less bonded surface layers of paper (Stockmann 1974). Thus, by strengthening and increasing the extensibility of the surface layer of paper, it is possible to postpone crack initiation and thus improve overall extensibility.

The formation of polyelectrolyte multilayers from polyacrylic acid polyallylamine hydrochloride on the surface of fibres can significantly improve the tensile strength and extensibility of paper (from 4 to 8% points) (Gustafsson 2012). By the introduction of several consequent layers of deformable polymers on the cellulose, it is possible to modify the viscoelastic nature of the fibre joints. This concept was previously verified with materials other than cellulose (Ankerfors *et al.* 2013).

2.8.3 Fibre-polymer and paper-polymer composite materials with improved extensibility

There are two principal ways to introduce polymers to paper: wet-end addition and impregnation of the pre-formed fibre network. In the first case, the effectiveness of the treatment is limited by insufficient retention in the fibre network, interference with the formation of hydrogen bonds, and poor adhesion of the polymer (usually hydrophobic) to fibres. When the polymer is added to an already formed fibre network, the increase in the extensibility of paper can be expected to be roughly

proportional to the amount of added polymer (Waterhouse 1976). However, this is dependent on the type of polymer used and percentage of the addition.

The addition of natural and synthetic latexes and resins can be used for the improvement of the elongation and strength of paper. The addition of styrene-butadiene latex in the amount of 30 mg/g to kraft pulp has improved the elongation of paper from 1.8 to 4% (Alince 1977). Addition to paper of a PLA latex dispersion in the amount of 20% is capable of improving the elongation by 5 to 10% points, and such paper has also demonstrated convertibility in the 3D forming process (Svensson *et al.* 2013).

Elastomeric polymers added in the amount of 20 to 40% to a fibre network can improve the extensibility of such material by up to 30 to 40% points (Waterhouse 1976). Materials made of 80% of pulp and 20% of PHB have a strain at break of around 36% (Cyras *et al.* 2009). It was found that the addition of polymers changes the character of the fibre bonding in such a way that the failure of the fibre network is caused by fibre failure, *i.e.* acrylate and the addition of SBR provide strong polymer-fibre and polymer-polymer bonds (Heyse *et al.* 1960).

Despite the evident advantages and relative simplicity, the addition of thermoplastic polymers can introduce some unwanted features into the production process of paper and its mechanical properties. Conventionally, thermoplastic polymers have poor compatibility with the cellulosic fibres, and thus require an additional thermal treatment (curing) in order to amalgamate the polymer within the fibre matrix (Herman *et al.* 1965, Yanulis 1965). Polymer melts and fills the free spaces between the fibres and forms fibre-polymer and polymer-polymer bonds, allowing a larger area for molecular contact between fibres, and thus positively contributing to the stress distribution between and within fibres and the fibre network (Alince 1977, 1979, 1991, 1999). The filling of the free space between the fibres with polymers reduces drying shrinkage. An addition of 5% polymer dispersion reduces shrinkage by 50% (de Ruvo 1979).

2.8.4 Summary

The utilization of additives is quite a straightforward method for improving the extensibility of paper, but they may compromise the paper manufacturing process and some paper properties. The effect of polymer addition relies on two principal factors: the adhesion between the polymer and fibres and the mechanical properties of the polymer itself. To achieve the best result, the polymer should have a strong adhesion to fibres, and be strong and deformable by itself. It can be assumed that the deposition of polymer at the fibre crossings may be the most beneficial for improving the deformation behaviour of a fibre network. The percentage of the addition of polymer should be selected in such a way that the paper production process and environment are not severely affected by the change in furnish (drainage, sticky deposits problems, steam consumption).

2.9 Improvement of the extensibility of paper: mechanical treatment of the fibre network

Paper can be compressed in-plane in order to improve extensibility. Compaction and creping are the most well-known methods of in-plane compressive treatment of the paper web, where compressive forces are applied to create deformations in the web. Improvements in elongation obtained by in-plane compression have a linear correlation with a decrease in the geometrical length and increase in the basis weight of the paper after treatment. An increase in extensibility is always accompanied by a decrease in tensile strength, and especially the elastic modulus of paper.

2.9.1 Creping

In creping, paper is adhered to the drying cylinder (most often a Yankee cylinder), and dried to a certain dryness (this varies based on the creping process, typically 70 to 85%), then it is released from the cylinder by means of a creping blade, which causes folding of the paper web, fibre rearrangements and sheet buckling (Welsh 1965). Creping yields highly extensible papers with an elongation in the range of 10 to 200%, and it is mainly utilized in tissue products requiring high softness. However, creped paper has limited utilization in packaging applications due to its wrinkly surface, low stiffness, and significantly decreased tensile strength. It is mainly used for cushioning and decorative purposes (Hernandez and Selke 2001; Welsh 1965). The creping processes can be distinguished into two main types: moist (wet) creping and dry creping. Moist creping (performed at 60 to 85% dry solids) provides a smaller decrease in tensile strength and stiffness; however, the increase in extensibility is lower in comparison with dry creping. This is explained by the ability of fibres to form hydrogen bonds after creping during the drying process. Among creping methods, dry creping (performed at 93 to 97%) produces the greatest increase in elongation and greatest decrease in strength and stiffness (Ramasubramanian 2001).

2.9.2 In-plane compaction of paper

Paper can be compacted either between a moving rubber blanket, steel roll and non-rotating nip bar (Clupak®), or between a steel roll covered with a rubber blanket and a heated steel roll (Expanda®). At the beginning of the compaction process, the rubber blanket is stretched in front of the nip before adhering to the paper fed into the nip. Once the paper with the rubber blanket passes the nip, the rubber blanket recoils because the straining force is released. Due to adhesion and a certain z-pressure, the paper shrinks together with the rubber blanket. The typical dryness of paper entering the nip is 60 to 65%, and the dryness is increased once the paper leaves the Clupak® unit. Compaction improves extensibility, but reduces the tensile strength, elastic modulus, and bending

stiffness of paper, although to a lesser extent than in creping. Compaction is mainly used in the production of sack and bag paper grades in order to increase the tensile energy absorption of such papers (Ihrman and Öhrn 1965; Welsh 1965; Hernandez and Selke 2001; Poppel *et al.* 2000; Ankerfors and Lindström 2011). The influence of compaction on the mechanical properties of paper can be demonstrated with the stress-strain curves (MD and CD) of paper before and after compaction, shown in Fig. 13.

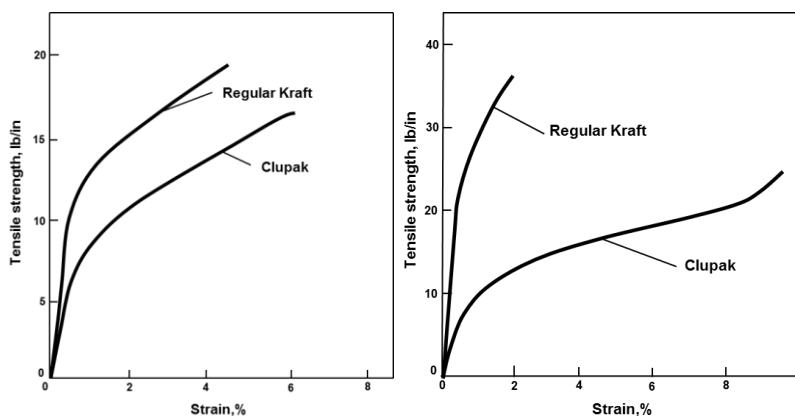


Figure 13. A comparison of the stress-strain curves of Clupak and Kraft sack paper in CD (left) and MD (right) (redrawn from the data of Shoudy 1959).

As can be seen from Fig. 13, compaction is an effective tool for the improvement of extensibility in the MD without a significant decrease in the ultimate tensile strength; moreover TEA is increased. In addition to the improvement in MD elongation, the extensibility also slightly increases in the CD. A 10% point gain in MD strain provides a 1 to 2% point increase in CD strain (Shoudy 1959; Welsh 1965). Paper can be compacted in both directions, to produce paper with more isotropic properties. This can be achieved by controlling the recoiling of the rubber blanket in the CD and by utilizing circumferentially grooved or inclined rolls (Welsh 1960; Cariolaro and Trani 2000; Kawasaki and Nagai 2003; Saitaka *et al.* 2006). The gain in elongation and decrease in tensile strength caused by compaction can be adjusted by varying the stretch of the rubber blanket, z-pressure, and moisture content of the paper entering the nip. A high stretch of the blanket leads to a higher gain in elongation, but to a significantly reduced stiffness of paper. High z-pressure reduces the gain in elongation, but maintains stiffness at a higher level. The higher the moisture content of paper, the higher the elongation can be; however, it is accompanied by decreased stiffness (Lahti *et al.* 2014; Welsh 1965; Ihrman and Öhrn 1965).

The elongation of paper is increased primarily due to the buckling of fibres and probably the incorporation of microcompressions in the fibres. A fine wrinkle pattern can be observed on the surface of paper. Steenberg (1949) has proposed that the extensibility of compacted paper comes through the extension of the

creases in fibres between the fibre joints. The decrease in ultimate tensile strength of paper is explained by damage to the fibres and by partially disrupted fibre-fibre bonds. Fibres after compaction appear to be curled, bent and buckled, and they have a higher plastic deformation, higher drying shrinkage potential and high-impact resistance due to the high energy absorption of curled fibres (Dumbleton 1972; Page and Seth 1980). Compaction of paper seems to be a feasible option for the production of paper for 3D forming, and it has been applied on an industrial scale (Hado *et al.* 2001; Billerud 2012).

2.9.3 Summary

The in-plane compressive treatments of the fibre network seem to be effective tools for the improvement of extensibility in MD, and even also in the CD direction of paper. Among these methods, compaction seems to fit the concept of formable paper best since it yields paper with significantly increased extensibility, while the stiffness is not decreased as much as in creping. Creping, despite the tremendous increases in extensibility, is not suitable for the production for formable paper due to severely decreased stiffness of paper and the grammage limitations of the Yankee cylinder.

2.10 Improvement of extensibility of paper – Influence of the paper drying method

The extensibility of paper is to a significant extent dependent on the drying method. Conventionally, the paper web is dried under MD tension, and due to this, wet paper experiences straining deformations that are further “frozen” in the paper structure during drying. This decreases the extensibility of paper. It is also possible for dry paper without restraint or with only minor restraint, allowing drying shrinkage. Impingement, IR (infrared), and air float (*e.g.* Fläkt) drying can be used in combination with cylinder drying for such a purpose. Float drying is most efficient for the development of drying shrinkage when applied to paper with a solids content of between 60 and 85% (Steenberg 2006). The higher the drying shrinkage, the higher the elongation of the paper (Fujiwara 1956; Page 1971; Htun and de Ruvo 1981; Htun *et al.* 1989; Waller and Singhal 1999; Wahlström *et al.* 1999). High extensibility of unrestrained dried paper is attributed to the removal of deformations in fibres caused by drying shrinkage during the straining of the paper. The mechanism of drying shrinkage of paper is believed to be as follows (Page and Tydeman 1966): fibres shrink laterally, which in turn causes axial shrinkage of the single fibres bonded to them, and eventually shrinkage of the whole web by means of interfibre crossings. Fibres shrink anisotropically; fibres can shrink up to 30% in the transverse direction, though the axial shrinkage is limited to 1 to 3%. Such a low value of longitudinal shrinkage can be attributed to the low microfibrillar angle and stiffness of crystalline microfibrils, which prevents lengthwise shrinkage (Page 1969, 1971). The extent of the drying shrinkage of

paper in unrestrained drying varies greatly, between 3 and 10%. This value is governed by lateral shrinkage of single fibres, which depends on the initial swelling of fibres, the number of bonds that transmit the shrinkage forces from one fibre to another, and the axial stiffness of the fibres, which resists axial shrinkage (Retulainen *et al.* 1998). Swelling and shrinkage of fibres can easily be controlled by the extent of refining. The lower the freeness value, the higher the swelling of fibres, which primarily depends on the extent and type of refining (Zeng *et al.* 2012). The addition of fines and micro- and nanofibrillated cellulose can also be used for shrinkage promotion (Lobben 1977, 1978; Sampson and Yamamoto 2011)

Paper shrinks more in the CD due to a lower restraint and a higher shrinkage potential as a result of fibre orientation. Moreover, MD tension creates a Poisson contraction in the CD. Fibres in the MD are also subjected to wet straining during manufacturing, which reduces the elongation of paper in this direction (Nanko and Wu 1995; Seth 2005). On modern paper machines, paper is stretched by 2 to 3% on its way from forming to the drying section. However, historically these values have been as high as 6 to 8% (Halme 1967).

2.11 Improvement of the extensibility of paper: Summary

The various factors that affect the extensibility of paper, and thus its formability, have been discussed in this chapter. There are several methods for the improvement of extensibility. Generally, these methods also have a negative impact on tensile strength and stiffness. A combination of certain methods may provide a broader operational window for mitigating the negative effects of treatment and unleashing the extensibility potential of paper. This combination of actions may include the selection of raw material, mechanical treatment of fibres and network, chemical modification of fibres or use of certain additives, coupled with a suitable drying method. The use of extensible fibres alone does not make paper with good formability. Therefore, in the production of formable paper, fibre structure, fibre bonding, and the structure of the fibre network need to be addressed at the same time.

3. Materials and methods

3.1 Materials

3.1.1 Pulp

The pulp used in the experiments was first-thinning bleached, once-dried pine kraft pulp kindly supplied by UPM Pietarsaari mill. The properties of first-thinning pulps are quite close to those of conventional pulp, although fibre length might be somewhat lower and the MFA somewhat higher than in conventional pulp. This pulp was used for the preparation of the handsheets in Publications IV, V, VI and VII.

3.1.2 Commercial paperboard

Commercial paperboard samples were supplied by Stora Enso Research Centre, Imatra. Selected properties of the paperboard samples are listed in Table 3. The commercial paperboard samples were used in Publication III.

Table 3. Mechanical and basic properties of the commercial paperboard samples used in this study.

| Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|----------------------------|------|------|------|------|------|------|------|
| Grammage, g/m ² | 190 | 198 | 210 | 250 | 257 | 263 | 314 |
| Thickness, µm | 242 | 268 | 280 | 395 | 346 | 363 | 406 |
| Density, kg/m ³ | 784 | 738 | 752 | 644 | 743 | 725 | 774 |
| Tensile index MD, Nm/g | 87.8 | 83.3 | 73.3 | 91.9 | 70 | 77.9 | 98 |
| Tensile index CD, Nm/g | 35.1 | 35.8 | 37.5 | 41.4 | 37.3 | 32.2 | 48.9 |
| Strain at break MD, % | 2.2 | 2.3 | 2.6 | 2.1 | 2.5 | 2.1 | 2.3 |
| Strain at break CD, % | 6.3 | 6 | 5.6 | 5 | 5 | 6 | 6.2 |

3.1.3 Polymers and additives

3.1.3.1 Agar

The agar used in this study was a typical food grade agar (also referred to as E406) obtained from Gourmetologia Oy, Finland. Agar was applied in Publications V, VI and VII of this thesis.

3.1.3.2 Ammonium zirconium carbonate

Ammonium zirconium (IV) carbonate (AmZrCarb) was purchased from Sigma-Aldrich, as a water solution with 1–2% of tartaric acid as a stabilizer (CAS Reg. No. 32535–84–5). It was applied in Publications V, VI and VII of this thesis.

3.1.3.3 Gelatine

Gelatine from porcine skin (Type A, ~300 g Bloom gel strength, #232-554-6), was obtained from Sigma-Aldrich (US). It was applied in Publication VI.

3.2 Methods

3.2.1 Mechanical treatment of fibres

The fibres were mechanically modified using different equipment, including a wing defibrator, E-compactor, Valley beater and PFI mill. The aim of the mechanical treatment was either to create deformations in fibres in high-consistency treatment or to modify bonding and the network structure using low-consistency refining. A number of parameters were varied in this treatment: the dry solids content of the pulp, refining intensity, refining temperature, etc. The combination of the high-consistency treatment of fibres and low-consistency refining was found to be the most effective in respect to the improvement of extensibility of paper. This treatment was applied to pulp in Publications IV, V, VI and VII of this thesis.

3.2.2 2D formability measurement

Formability measurements were performed with a 2D-formability tester developed by VTT (Fig. 14). It is equipped with a double-curved heated press (temperature up to 250 °C), blank holders, and an IR sensor (Omega® OS36) for measuring the paper temperature. The forming procedure is as follows: a paperboard sample (span length 60 mm, width 20 mm) is clamped by the blank holders and then the press is moved into contact with the sample and kept in this position for 0.5 seconds in order to heat the sample. Then, the press continues the downward movement until the mechanical failure of sample material. The velocity of the forming press is 10 mm/s (Kunnari *et al.* 2007).

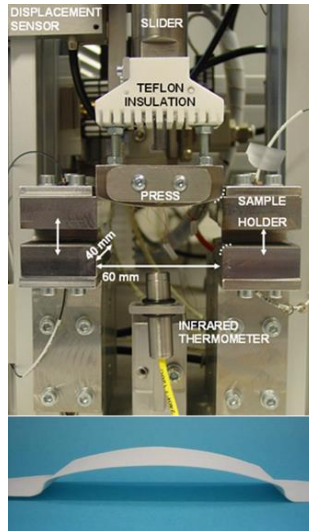


Figure 14. Outline of the 2D-formability tester and formed strip of paper.

Formability in the 2D-formability tester is characterized by the “formability strain” value. The formability strain is essentially the strain at break of paper strained by a heated double-curved metal press. The exact value of the formability strain is calculated from the vertical position of the forming die and the geometry of the sample strip at the moment of failure of paper. Paper with a relatively low grammage ($<100 \text{ g/m}^2$) is heated to the temperature of the press during this period, *i.e.* the temperature of the press equals the temperature of the paper. This device was utilized in Publications III, V, VI and VII of this thesis.

3.2.3 Measurement of 3D formability

The 3D formability of paper was determined in both the fixed and sliding forming processes. In the case of the fixed blank forming process (hot pressing), formability was defined as the maximum depth of the shapes (*i.e.* maximum drawing limit). In the sliding blank forming process (deep-drawing), formability was defined as the distance between the compressive wrinkles, which was measured according to a custom-developed algorithm.

3.2.3.1 Determination of the maximum drawing limit (3D formability in the fixed blank process)

The 3D forming device is similar in operation to the 2D-formability tester, apart from the shape of the die and the method of heat transfer. In this device, only the forming cavity is heated while the forming die is not. The temperature of the forming die was adjusted by conditioning it at the maximum possible proximity to

the forming cavity until it reached a stable temperature. The variable measured in these experiments was the value of the biaxial strain which the paper could tolerate without failure. The true value was determined if, in at least 9 out of 10 samples, the paper sustained the forming to a given depth without failure. This variable is referred to hereafter as the Maximum Drawing Limit (MDL). The MDL value was obtained using the geometrical dimensions of the forming die and mould (i.e. curvature of hemisphere, diameter, and mould clearance), thickness of paper and the depth position of the die at the end of forming; following simplifications were taken in account: no bending at the edges of blank and straining of paper in the z-direction was ignored. 3D forming device was used with the kind permission of the Stora Enso Research Centre of Imatra. This forming device was used in Publications III and V of this thesis.

3.2.3.2 Determination of formability in the deep-drawing process

In the deep-drawing process, wrinkles are the most important quality indicator in the shapes produced. The frequency of wrinkles is a reflection of the uniformity of the mechanical load distribution on the side wall of the 3D shape; they also reflect how uniform the material is, and thus were used as the formability indicator. Paperboard blanks were drawn into cylindrical shapes with a 25 mm high wall. The distance between the wrinkles was measured in the machine direction (MD) of the paper along a straight line parallel to, and 5 mm from the edge of, the 3D shape. The distance between the wrinkles was measured using a light microscope. The mean value of one hundred distances between wrinkles was taken as the result. An image of the cylinder wall and wrinkles is shown in Fig. 15. This testing method was used in Publication III of this thesis.



Figure 15. Photographical images of the formed shape with wrinkles and a closer magnification image of the compression wrinkles.

3.2.4 Compaction of paper

In-plane compressive treatment was performed using a compaction device constructed by VTT, Jyväskylä (Fig. 16). It has been built in a way to replicate the compaction process on laboratory scale. In this device, a paper sheet is fed in between two strained rubber belts, which are then pressed by a plate to a pre-determined pressure. Once the paper is pressed between the belts, tension is

released and the belts start to contract to regain the original length. The paper is contracted along with the contraction of rubber belts. After compaction, the paper was dried without restraint. The strain and the consequent strain recovery of the rubber belts was 13%. The compaction device was used in Publication VII of this thesis.

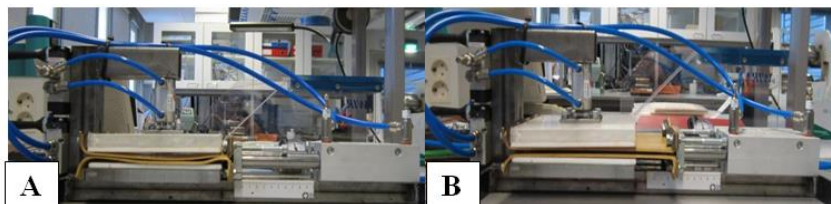


Figure 16. The compaction device in the non-strained (A) and strained position (B).

3.2.5 Determination of paper-to-metal friction coefficient

Friction tests were carried out using a custom-built friction measurement device at VTT. The device is composed of a heated steel plate (grade TOOLOX33®), and an electric drive with a voltage sensor (Kyowa® LVS – 100 GA) connected to a moving sledge via an inextensible cord. The paper sample is placed under the sledge and the voltage sensor is set to 1000 scans per second. Voltage in this case refers to the sliding resistance. The weight of the moving sledge was 892 grams.

Static friction was recorded as the voltage value at the moment when the sledge started to move. Dynamic friction was measured as the average value of force needed to move the sledge with the paper sample (65 mm wide x 65 mm long) for a path of 80 mm at a velocity of 19 mm/s. The Coulomb friction model was assumed to be valid in this case. Friction was measured only in Publication III.

3.2.6 Determination of the compression strength and strain

The compressive strain and strength were measured using the Ring Crush Test (RCT) by Zwick/Roell. The size of the sample was 8 mm wide x 152 mm long. In RCT testing paperboard sample may buckle and bend which may affect the measured compressive strength and strain values, thus width of the sample was reduced to 8 mm. A detailed description of the method can be found in Publication III.

3.2.7 Stress-strain properties

The stress-strain properties of the paperboard were measured in accordance with SCAN-P 38:12.

3.2.8 Out-of-plane spherical indentation test

A spherical indentation test to measure the z-directional stiffness (hardness) was made using a 1 mm diameter steel ball in a modified tensile tester. A pile of four sheets was used in the test. The test comprised a loading-unloading cycle in which the highest load was 25 N. The speed of loading and unloading was 25 mm/min and 1 mm/min, respectively. The recoverable elastic compressive strain was measured from the unloading curve. The loading and unloading stiffness values were estimated at the level of 10 N. A detailed description of the method can be found in Publication III.

3.2.9 Handsheet preparation

Two types of handsheets were prepared in this study. The first type, A4-size sheets with a grammage of 200 g/m², was prepared using the sheet former “Juupeli” developed by VTT (Oksanen *et al.* 2011). These handsheets were used for the preparation of the 3D shapes. The other type of handsheet was prepared according to the SCAN-C26 standard; with a target grammage of 60 g/m², with the exception that the unrestrained dried handsheets were dried between two synthetic wires with a gap of approx. 3 mm to avoid extensive cockling of the paper during drying. Due to drying shrinkage and polymer addition, the final grammage of the handsheets was higher, in the range of 68–73 g/m². A4-sized handsheets were prepared in Publication V and VI. SCAN-C26 handsheets were prepared in Publications IV, V, VI and VII.

3.2.10 Spraying of polymers

Agar and gelatine solutions were prepared by adding agar and gelatine powders into deionised hot water (approx. 90–95°C) under rigorous mechanical stirring. The stirring and heating of the resulting mixture was prolonged until the dissolution of the agar or gelatine was complete. The concentration of agar solution was 2% (by mass). A crosslinker (AmZrCarb) was added to the solutions for about 30 seconds before spraying. A relatively short mixing time before spraying was needed in order to avoid the extensive evaporation of ammonia from AmZrCarb and prevent the solutions from self-crosslinking. Solutions were sprayed onto wet sheets using a commercially available electrospray gun. The amount of added agar was controlled gravimetrically. Agar solutions can also be added to paper by different methods, *e.g.* rod and brush coating; however, these are not covered in this study. After spraying, the handsheets were wet pressed according to the

standard procedure (SCAN-C26). The spraying of polymers was used in Publications V, VI, and VII of this thesis.

3.2.11 Drying shrinkage measurement

The procedure applied for shrinkage potential measurement is described as follows: the handsheets were marked after wet pressing by making holes using a square plate with awls at each corner. The four punched holes defined a square with a known perimeter. After this, the handsheets were allowed to dry freely. The extent of shrinkage was calculated from the change in the perimeter using a high-resolution scanner and special software. Equation (1) was used for the calculation of the shrinkage,

$$\text{Shrinkage} = \frac{L_w - L_d}{L_w} \times 100\% \quad (1)$$

where L_w is the perimeter of the rectangular handsheet before drying and L_d is the perimeter of the dried handsheet.

3.2.12 Quartz Crystal Microbalance with Dissipation (QCM-D)

Gelatine and agar adsorption onto cellulose and the properties of the adsorbed layers were investigated by using a QCM-D instrument (model E4, QSense AB, Sweden). This instrument simultaneously measures changes in the resonance frequency and energy dissipation of an oscillating piezoelectric crystal upon increase/decrease in mass on the crystal surface.

A detailed description of the procedure, the method for the preparation of the model cellulose surface, and preparation of polymer solutions can be found in Publication VI.

3.2.13 Atomic Force Microscopy (AFM)

The surface morphologies of the cellulose, gelatine- and agar-coated cellulose films after QCM-D investigation were characterized by atomic force microscopy (AFM) in tapping mode with a Nanoscope IIIa multimode scanning probe microscope. The $3 \times 3 \mu\text{m}^2$ images were acquired at room temperature by using silicon cantilevers in an air atmosphere. Prior to the measurements, the samples were allowed to dry in a desiccator at room temperature overnight. No image processing except flattening was done. The rms surface roughness was measured from $3 \times 3 \mu\text{m}^2$ scan sizes.

3.2.14 SEM imaging

A scanning electron microscope (SEM, LEO DSM 982 Gemini FEG-SEM, NORAN Instruments, Inc.) was used to inspect the paper surfaces. A thin layer (approx.10 nm) of platinum was sputter-coated onto the sample surface prior to analysis. The SEM imaging of the samples was conducted using an acceleration voltage of 1.0 keV in secondary electron scattering mode. The SEM was operated in back-scattered electron mode at an emission current of approximately 100 μ A, using an accelerating voltage of 12.5 kV or 15 kV. The samples were previously coated with evaporated carbon using a BALZERS SCD 050 sputter coater equipped with a non-rotating base. The cross sections were prepared using a Hitachi IM4000 cross-section cutter prior to the SEM investigation.

4. Results and discussion

The results and discussion section of the present thesis is comprised of two parts. In the first part, the requirements for good formability are examined. The second part is devoted to the improvement of the formability of paper in the fixed blank process (essentially via improving the extensibility of paper). The section includes the results of the mechanical modification of fibres, improvement of fibre contact properties by addition of agar and gelatine to paper, and the modification of the fibre network by in-plane compressive treatment for the extensibility of paper and formability of paper.

4.1 Determination of the requirements for good formability

Scarce knowledge and somewhat controversial statements in the literature regarding the definition of formability for paper-based materials provided the motivation to carry out the present study. This study aimed to elucidate the measures of good formability for a particular forming process and to find out which mechanical properties of paper govern it. The definition of the formability of paper in the fixed blank process is clear; the deeper the shape, the better the formability. Secondary quality indicators such as shape stability, good convertibility in forming, and absence of visual defects should be taken into account as well.

However, the requirements for good formability in the sliding blank process are not that clear, since the depth of the shape is practically unlimited. In the industrial forming process (tray-pressing, press-forming), good formability is defined by whether the wrinkle pattern is according to crease lines (yes/no), cracks and pinholes in coating (yes/no) and shape stability after forming (amount of spring back and shape distortion). As for deep-drawing, where the blanks are not creased, the pattern of the wrinkle formation is the main quality parameter, if no other defects are observed. In the ideal case, wrinkles may form an almost even surface if they are distributed uniformly and at a small distance from each other. Therefore, the distance between the wrinkles would reflect the formability of the material after forming.

Once the measures of good formability are established, it is important to verify which mechanical and basic properties of paper contribute to it. In order to find the relation between the mechanical properties and measured formability of paper, a series of experiments with different forming devices were performed, which are reported in Publication III.

4.1.1 Formability requirements for the fixed blank forming process

The mechanical properties of different paperboard samples were compared with the formability of respective boards in a 2D-formability tester and in a 3D spherical forming device. The formability of the paperboard in the fixed blank forming process was found to correlate with the tensile strain and coefficient of metal-to-paper friction.

The relationship between the formability strain and maximum drawing limit and strain at break of the paperboard samples are shown in Figs. 17 and 18.

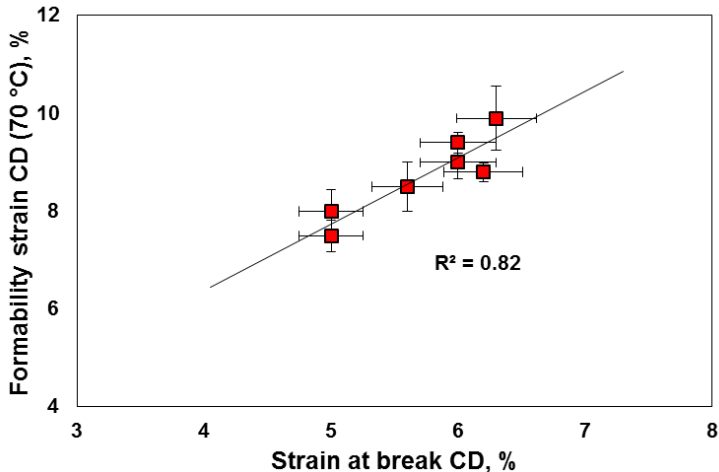


Figure 17. The correlation ($p < 0.01$) between the formability strain in the CD measured at 70 °C and the strain at break value (CD) of commercial samples. Error bars represent 95% confidence limits.

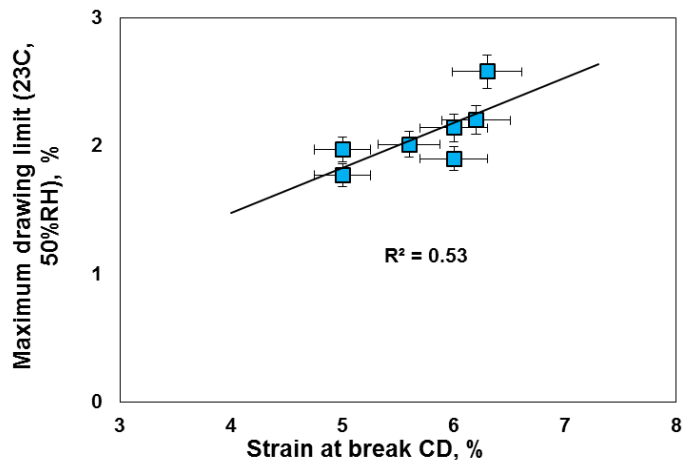


Figure 18. The correlation ($p = 0.07$) between the maximum drawing limit at 23 °C 50% RH and the strain at break value (CD) of commercial samples. Error bars represent 95% confidence limits.

The formability strain correlates well with the strain at break in the CD (Fig. 17) and MD (not shown) at a temperature of 70 °C and other tested temperatures. This correlation is quite obvious because the stresses experienced by the paper in the 2D formability tester are similar to the stresses in conventional stress–strain measurement.

Formability in the 3D spherical forming device was also found to correlate with the elongation of paper in the cross direction (CD) (Fig. 18), but the value of R^2 is not as high as for the 2D formability tester. No statistically significant correlation between MDL and elongation in the MD exists. This fact can be explained by the kind of straining deformation in the 3D spherical forming device (the straining in this case is close to the biaxial straining). Due to this, the MDL is also determined by the elongation in the CD of the paper. The straining deformation is clearly higher in the CD than it is in the MD, where the paper is strained in a hemispherical shape; however, the crack is still likely to be initiated by insufficient extensibility in the MD.

The metal-to-paper friction also correlates with formability in fixed blank processes, since the formation of frictional forces between the two surfaces (metal–paper) is inevitable. High friction in forming increases tension and the probability of crack formation and has a negative influence on the depth of the shapes.

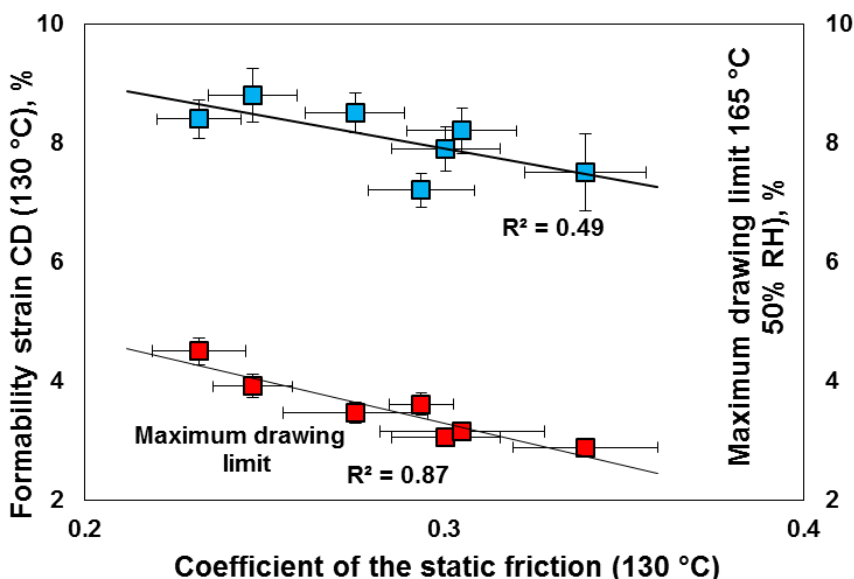


Figure 19. The correlations between the formability strain (130 °C), MDL (165 °C) and the coefficient of friction (130 °C). ($R^2=0.49$: $p=0.08$, $R^2=0.87$: $p<0.01$). Error bars represent 95% confidence limits.

As can be seen from Fig. 19, there is a correlation between the MDL measured at 165°C (50%RH, 23°C) and the coefficient of static friction at 130°C. The

correlation between the formability strain measured at 130°C and the coefficient of static friction at 130°C is not statistically significant, probably because of a relatively high deviation in the formability strain. High friction has a detrimental effect on the formability of the paperboard in the forming processes using a fixed blank. This can be explained by the fact that high static friction may lead to the ‘stick and slip’ of the die–paperboard interface and to uneven strain and stress distributions in the sample during the initial phase of forming. The same trend was also observed for the correlations measured at lower temperatures, although the correlations were weaker. It should be noted that friction is sensitive to the changing moisture content and temperature of paper. A high temperature decreases the paper-to-metal friction, whereas it is increased by high moisture content (Back 1991, Kawashima *et al.* 2008). This is valid in the case of both static and dynamic friction.

4.1.2 Formability requirements for the sliding blank forming process

The paper properties providing good formability are different in the sliding blank process from those in the fixed blank process. A formability criterion is the mean of distances between compressive wrinkles on the flange or side walls of the shapes, and it was found to correlate negatively with the dynamic friction coefficient (Fig. 20) and certain compressive properties (Fig. 21 and 22).

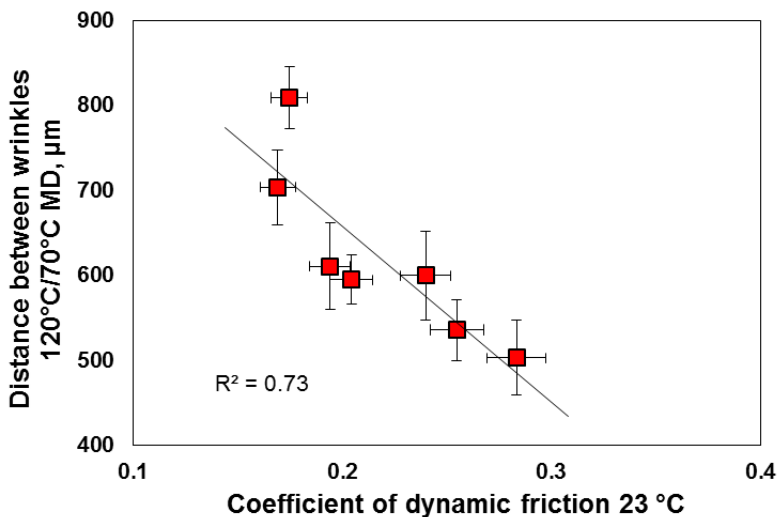


Figure 20. The statistically significant correlation ($p < 0.05$) between the coefficient of dynamic friction measured at 23 °C and the distance between wrinkles at 120/170 °C. Error bars represent 95% confidence limits.

As shown in Fig. 20, the high coefficient of dynamic friction has a positive influence on the appearance of the shape; *i.e.* there are more wrinkles, but they are smaller and smoother. The formation of a wrinkle requires that the local compressive stress exceed local frictional forces. Thus, high friction may reduce the area where wrinkles would start to propagate and eventually be formed. This decreases the distance between wrinkles and improves the appearance of the shape. It is quite probable that friction forces act in synergy with the blank holding force (BHF); BHF increases tension in the paper blank and correspondingly the lateral compressive contraction forces leading to the formation of wrinkles. Despite the fact that a high coefficient of dynamic friction may improve the visual appearance of the shape, it can also increase the probability of crack formation and may contribute to the discoloration (darkening) of the paper.

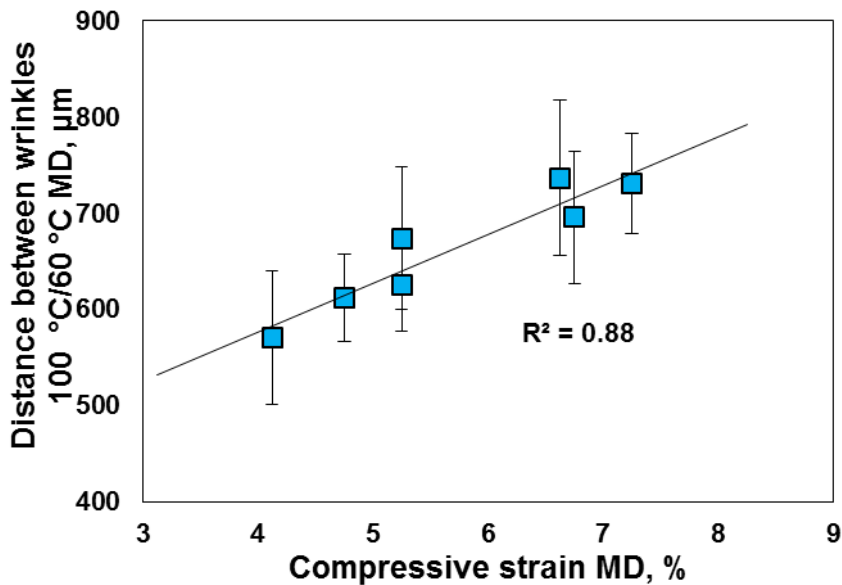


Figure 21. Correlation ($p < 0.01$) between compressive strain in the MD and the distance between wrinkles. Error bars represent 95% confidence limits.

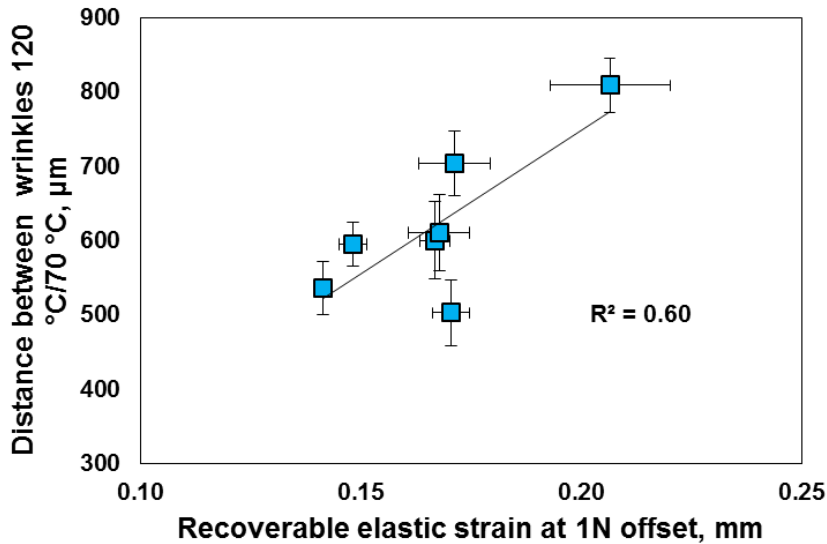


Figure 22. Correlation ($p < 0.05$) between the recoverable elastic strain in the z-direction (A) and the distance between wrinkles. Error bars represent 95% confidence limits.

Compressive properties of paperboard are another factor influencing wrinkle distribution. Wrinkles are formed because of compressive stresses, and the lower the compressive strain of paper, the shorter the distances between wrinkles and the better is the visual appearance. No correlation for compressive strength and distances between wrinkles was found; this might be due to the fact that, under forming conditions, transverse compressive forces exceed frictional forces.

The recoverable elastic strain in the z-direction measured with an indentation test also correlate with wrinkle distribution (Fig. 22). The more elastic the paperboard, the worse appearance it has; the stiffer the material is in the z-direction, the better appearance it has. Based on this, it can be hypothesized that stiff paperboard with a low elastic recoverable strain component would have good formability in sliding blank forming processes.

4.1.3 Influence of temperature and moisture on formability

The importance of elevated temperature and moisture of paper in 3D forming was emphasized in the literature part of this thesis. Additional experiments were performed to verify the influence of these factors on the formability in the particular forming devices utilized in this study. More detailed information about the effect of temperature and moisture on formability can be found in Publications III and V, VI, VII of this thesis. The influence of elevated temperature on the formability (2D) of

unrestrained dried paper prepared from softwood pulp with different initial moisture content is shown in Fig. 23.

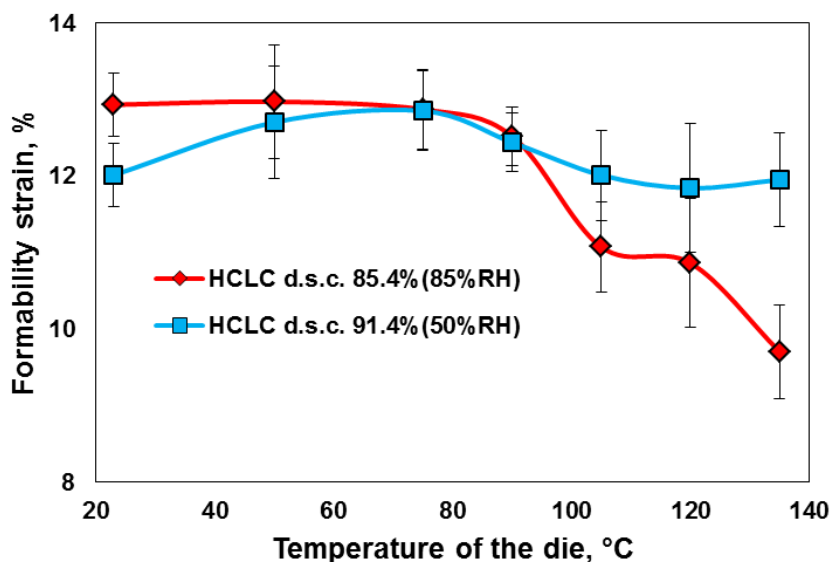


Figure 23. Influence of elevated temperature on the formability strain of paper samples conditioned at 23 °C 50% and 85% RH. Error bars represent 95% confidence limits.

As Fig. 23 illustrates, the character of the curve for the paper samples with elevated moisture content (85% RH) is different from that for paper conditioned at 50% RH. The former samples show higher initial formability strain values than the samples at lower moisture content. Moreover, consequent heating does not significantly improve the formability strain. However, in both cases, the highest formability strain values are achieved at a die temperature range of 60–80°C. In this case (grammage of paper is around 70 g/m²), the temperature of the die is equal to the temperature of the paper (Kunnari *et al.* 2007). These observations are in line with the fact that, at moderate moisture content, the polymers of bleached pulp soften at temperatures below 100 °C (Back and Salmén 1982). The decrease in the formability strain at temperatures higher than 100°C may be related to the excessive drying of the paper, high gradients of moisture content within the sample, and possibly too intense softening and weakening of the fibre bonds.

Generally, the same trends in the effect of moisture and temperature on formability were observed with the 3D spherical forming device (Publication III).

In 3D deep-drawing equipment, the role of temperature cannot be compared with that in other forming devices. However, the formation of wrinkles is highly dependent on the stiffness of paper and thus softening plays an important role here. Furthermore, forming was not possible at cavity temperatures of below 100

°C, probably due to the high paper-to-metal friction and lack of softening of the paper. Since the paper-to-metal friction coefficient to a major extent determines the forming results, it is important to consider the influence of temperature on the coefficient (Fig. 24).

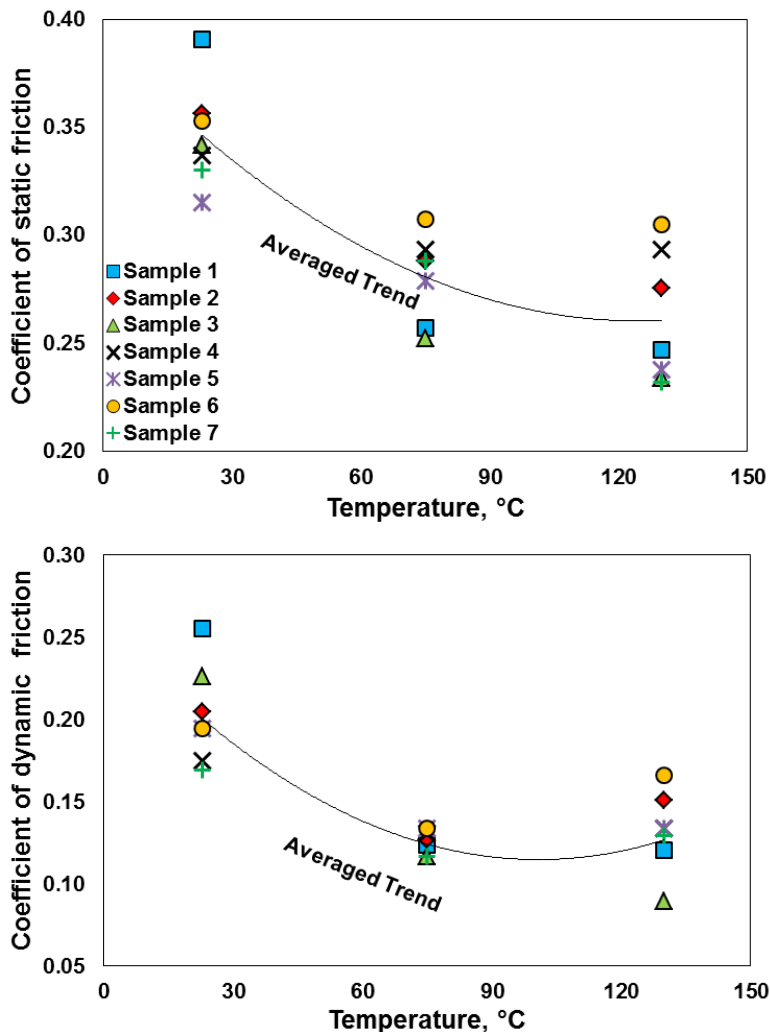


Figure 24. The influence of temperature on the static (A) and dynamic (B) paper-to-metal friction coefficient. Samples 1–7 are commercial paperboard samples used in Publication III.

As can be seen from Fig. 24, the paper-to-metal friction decreases with elevated temperature. This is the case for both static and dynamic friction. This may be explained by the lubricating action of evaporating moisture (Back and Salmen 1989, Kawashima *et al.* 2008). A slight increase in friction at a temperature of 130

°C can be explained by excessive drying of the paperboard by the end of the measurement.

In general, the optimal forming temperature in the 3D deep-drawing device was in the range of 140 °C to 180 °C (cavity temperature) and 60 °C to 100 °C (die temperature), depending on the thickness of the paperboard.

It is possible to conclude that the temperature in forming should be adjusted in such a way as to provide adequate softening of paper (*i.e.* decrease in recoverable elastic strain, decrease in compressive strength, increase in plastic deformation) and decrease in the paper-to-metal friction, while at the same time avoiding excessive drying. Thus, such factors as the heat transfer rate within the paperboard, the moisture evaporation rate, the softening properties of the fibre web and the effect of elevated temperature on friction should all be taken into account in the forming process with a sliding paper blank.

4.1.4 Summary

The information regarding the factors that influence the formability of paper materials in the fixed and sliding blank processes is summarized in Table 4. The fixed blank processes were represented by the 2D formability tester and 3D stamping, while the sliding blank processes were studied using a 3D deep-drawing device.

Table 4. Factors that influence formability in fixed and sliding blank forming processes.

| Category | Fixed blank | Sliding blank |
|---|---|--|
| | Stamping | Deep-drawing |
| Measured parameter | Depth of the shape | Wrinkle frequency in the MD |
| Formability criterion | Depth of the shape | Visual appearance |
| Formability limited by: | Insufficient elongation | Formation of wrinkles due to compressive contraction of the blank |
| Additional factors influencing formability | Paper-to-metal friction, drying of paper during forming | Paper-to-metal friction, thickness, density and grammage of the paper (see Publication III) |
| Mechanical properties determining the formability | Tensile strain and strength | Compressive strain and strength, thickness & density of material, z-directional elastic recovery |

The data shown in Table 4 was obtained experimentally on laboratory scale. However, it can still be applied to industrial forming processes with the same mode of deformation.

4.2 FIBRES: Effect of fibre deformations on extensibility

Mechanical treatments of fibres at high consistency are known to induce fibre deformations that contribute to the elongation potential of the paper (Seth 2005). Gentle laboratory beating at low consistency tends to straighten and lengthen fibres, and reduce fibre deformations (Mohlin *et al.* 1996, Seth 2005). The combination of the high- and low-consistency refining is also known as a method to improve the elongation and tensile energy absorption of paper with high air permeability (Sjöberg and Höglund 2007). This approach is used in the industry for the production of sack and bag grades of paper. The present chapter deals with the effects of high-consistency and combined high- and low- consistency refining on the extensibility of paper. The primary aim was to find a relevant and effective method for the creation of deformation favourable to the extensibility of paper.

In earlier studies, Zeng *et al.* (2012) have shown that certain HC treatments of fibres may significantly improve the extensibility of paper. The HC treatment method was further optimized in this work and compared with LC refining in a Valley beater. Finally, a combined HC and LC mechanical treatment method was suggested and applied. A detailed description of this treatment and its influence on the fibre structure and mechanical properties of paper can be found in Publication IV.

High-consistency treatment was aimed to create microcompressions and dislocations in the fibre wall, while low-consistency refining straightens the fibres and improves bonding. The influence of the HC, and the combined HC and LC treatment can be seen in Table 5.

Table 5. The effect of HC wing defibrator (WD) treatment and subsequent LC Valley beating (VB) on fibre parameters and drainage resistance.

| Sample | Fibre length, mm | Fibre width, μm | Shape factor, % | Kink/mm | Fines,% | SR number |
|-----------|------------------|----------------------------|-----------------|---------|---------|-----------|
| Untreated | 2.05 | 29.6 | 82.1 | 0.69 | 6 | 14 |
| WD | 1.9 | 30 | 79.6 | 0.87 | 8.5 | 14 |
| WD+ VB | 1.97 | 29.2 | 85.8 | 0.31 | 9.8 | 23 |

Apparently, HC treatment creates severe deformations in fibres, which are reflected in the decreased shape factor of fibres and the increased amount of kinks, while the drainage of pulp is unaffected. Subsequent LC treatment straightens the fibres, and increases the amount of fines and promotes fibrillation, which is reflected in the increased SR. The changes in the structure of fibres were also observed using polarized light microscopy (Fig. 25).

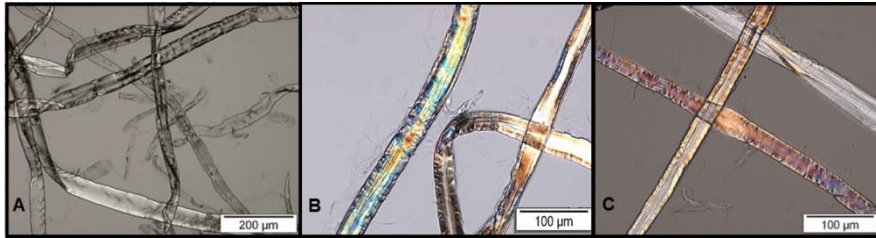


Figure 25. Polarized light microscopy images of the untreated pulp fibres (A), HC treated (B), and HC+LC treated (C), courtesy of S. Heinemann.

Untreated fibres have only some microcompressions, even though dislocation zones, kinks and curl are present. HC wing defibrator treated fibres have more curl, severe dislocations and also microcompressions. The microcompressions and dislocations can be observed as high-contrast lines perpendicular to the axis of the fibre (Thygesen and Ander 2005). The combined HC wing defibrator and LC Valley beater treated fibres are straighter, and tend to have fewer dislocation zones but also a considerable number of microcompressions can be seen. This suggests that microcompressions can be preserved well during LC beating, even though LC beating is able to straighten the fibres and release fibre curl and kinks as previously mentioned.

The data in Table 6 show the effect of combined HC wing defibrator treatment and LC Valley beating on the mechanical properties of paper. HC wing defibrator treatment increased the elongation of paper but had only a minor effect on the tensile strength. With the subsequent Valley beating, the load-bearing ability of the fibres and extent of fibre-fibre bonding was greatly enhanced, which is indicated by the increased paper density and considerably improved strength.

Table 6. Properties of paper (restrained drying and unrestrained drying) prepared from the HC wing defibrator (WD) treatment and subsequent LC Valley beating (VB). RSTR – restrained, UNRSTR – unrestrained, TI – Tensile index, TEAI – Tensile energy adsorption index, TS – Tensile stiffness.

| Drying type | Samples | Density, kg/m ³ | TI, Nm/g | Elongation, % | TEAI, J/g | TS, Nm/g | Shrinkage, % |
|-------------|---------|----------------------------|----------|---------------|-----------|----------|--------------|
| RSTR | Unref. | 513 | 18.1 | 2.15 | 0.31 | 3098 | - |
| | WD | 446 | 21.5 | 3.88 | 0.59 | 2620 | - |
| | WD+VB | 598 | 65.0 | 4.5 | 1.92 | 5883 | - |
| UNRSTR | Unref. | 500 | 15.9 | 4.23 | 0.51 | 1939 | 2.52 |
| | WD | 383 | 18.0 | 7.47 | 0.91 | 1162 | 5.35 |
| | WD+VB | 466 | 51.3 | 9.91 | 2.83 | 1599 | 5.8 |

SEM images of the paper surfaces prepared from pulps subjected to the different mechanical treatments can be found in Fig. 26. The SEM image of paper prepared from untreated pulp (A) suggests that the fibres were relatively stiff, less collapsed and less conformable, but some fibres had extensive dislocations. The images of wing defibrator treated fibres (B and C) reveal a denser fibre network with slightly more deformed fibres than the untreated ones. It is possible to observe damage and deformations in the fibres that had been treated with the wing defibrator at 170°C (Fig. 26 D). The morphology of E-compactor treated fibres (Fig. 26 E) differs from the morphology of untreated and wing defibrator treated fibres significantly. E-compactor treatment had caused fibre cutting and fibre damage in addition to extensive fibre deformations. The paper prepared (Fig. 26 F) from the combined HC and LC treated pulp shows relatively straight and collapsed fibres with a high degree of fibre bonding and also larger dense areas in the sheet.

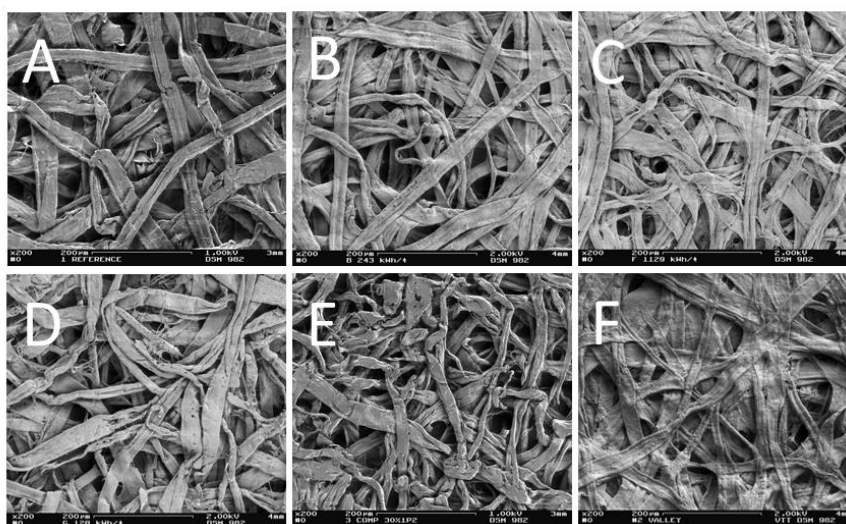


Figure 26. SEM images of paper prepared from fibres modified by different mechanical treatments; (A) untreated reference; (B) wing defibrator treated with SEC of 243kWh/t, 110°C; (C) wing defibrator treated with SEC of 1129kWh/t at 110°C; (D) wing defibrator treated with SEC of 128kWh/t at 170°C; (E) E-compactor treated (30%1P2mm); (F) combined HC wing defibrator and LC Valley beater treatment (150g/m²).

Shrinkage makes a significant contribution to the elongation of the paper prepared from the treated fibres. The shrinkage potential of paper depends on fibre swelling and subsequent fibre shrinkage, on the number of fibre bonds where the fibre shrinkage is converted to axial shrinkage of “neighbour” fibres, and on the axial stiffness of the neighbour fibres (Retulainen *et al.* 1998). A linear correlation between shrinkage and elongation can be observed for wing defibrator treated fibres (HC) and Valley beaten fibres, shown in Fig. 27. Fibres treated using the

combined treatment seem to combine the effects of HC and LC treatment on shrinkage. When the paper is dried without any restraint, shrinkage potential is the crucial factor determining the elongation of sheets. However, it could be speculated that HC wing defibrator treatment contributes to increased shrinkage through a different mechanism than Valley beating. Valley beating probably increases the shrinkage and increasing bonded area and compliance of bonds, whereas wing defibrator treatment reduces the axial stiffness of the fibres.

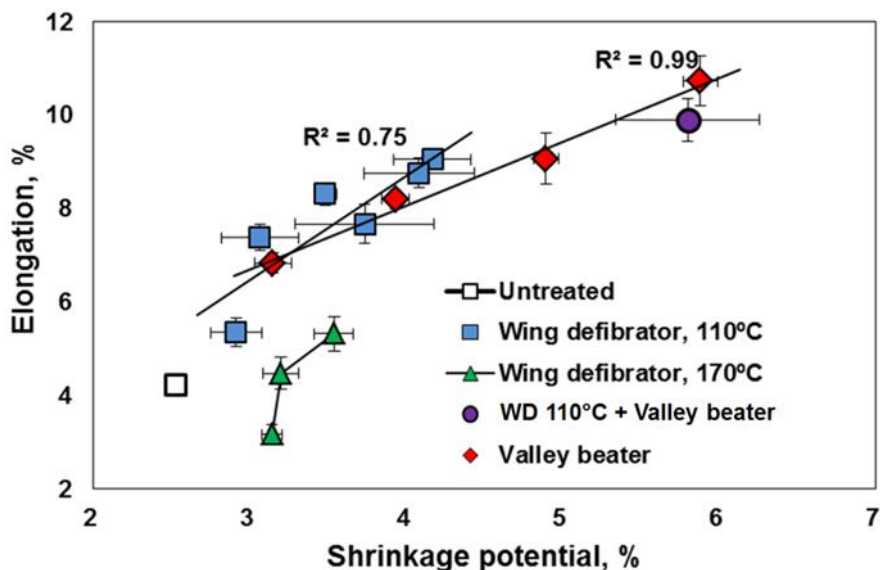


Figure 27. Correlation between the shrinkage potential and elongation of unrestrained dried paper, error bars represent 95% confidence limits. Figure taken from Publication IV.

The results indicated that HC wing defibrator treatment caused curl, kinks, dislocations and microcompressions in the fibres. Among these, microcompressions have an important role in the elongation potential of fibre and paper and can be preserved in subsequent Valley beating, which in turn tends to straighten the fibres and release kinks and dislocated zones. Increasing fibre curl does not necessarily lead to improved paper elongation due to the reduced load bearing ability of curly fibres in the fibre network. The elongation of the freely dried and restrained dried paper is dependent on different factors. In the case of freely dried paper, the shrinkage potential is the dominant factor; while in the case of restrained dried paper, the fibre wall morphology has a crucial role. The combined HC wing defibrator treatment and subsequent LC Valley beating was found to be the best strategy to produce paper with a high level of elongation while maintaining high tensile strength and good drainage.

4.2.1 Summary

Mechanical treatment of fibres is a well-known method to improve the mechanical properties of paper; however, it has rarely been examined in relation to the improvement of the extensibility of paper. It was shown that the combination of HC and LC refining yields paper with significantly improved extensibility while drainage and strength were maintained at a reasonably good level. Improvements in extensibility are the consequence of fibre deformations: dislocations and microcompressions, which reduce the axial stiffness of fibres, while strength is obtained via a relatively straight shape of fibres. Mechanical modification of fibres is an essential part of the strategy for the production of paper with high formability.

4.3 BONDING: Effect of addition of biopolymers on the extensibility and formability of paper

Interfibre bonding and the mechanical properties of fibre joints are the other essential factors that influence the formability of paper. If extensible fibres are not connected via compliant, strong and deformable bonds, they will not yield extensible paper. The character of fibre bonding can be modified via the numerous methods described in the relevant chapter (2.8.2) of this thesis. Among the available options for the modifying of fibre bonding, the addition of biopolymers was selected in this thesis work. The use of polymers for the modification of fibre bonding has been applied in papermaking for centuries, but the primary aim has been to increase the dry or wet strength of paper, while improvement of extensibility via the same method was not observed. A wide array of natural polymers were added to wet paper by spraying; agar (Publication V), gelatine (Khakalo *et al.* 2014), and a combination thereof (Publication VI) were found to be the most viable options.

Agar and gelatine are likely to have different mechanisms in respect to the improvement of extensibility. This difference might provide a synergetic or additive effect if these two polymers are used together. It has been shown that the mechanical properties of gelatine-based films can be improved by the addition of a relatively small amount of carbohydrate polymers such as gellan gum and k-carrageenan (Pranoto *et al.* 2007); the action of agar is somewhat similar to that of carrageenan, so it can be assumed that the performance of gelatine in paper would also be improved.

The influence of the addition of agar and gelatine and the combined addition of these two polymers on the extensibility and tensile strength of restrained and unrestrained dried paper is shown in Figs. 28 and 30.

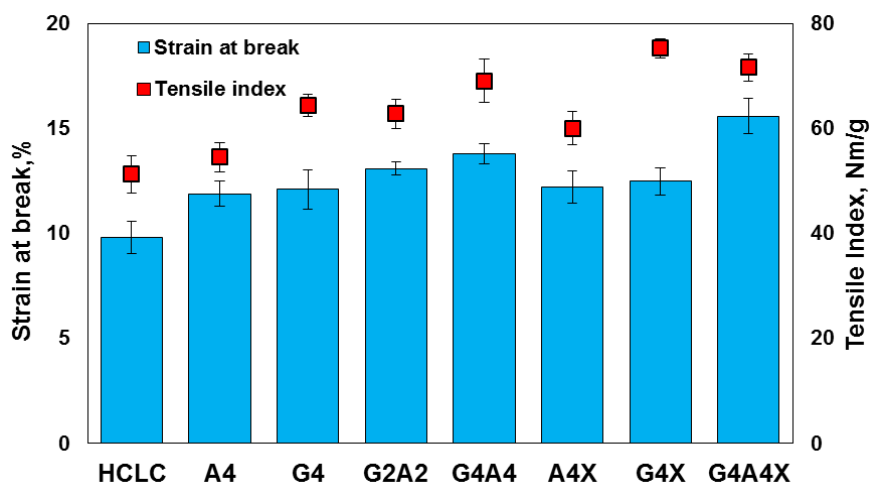


Figure 28. The influence of agar and gelatine addition in the presence and absence of a crosslinker on the tensile strength and extensibility of unrestrained dried paper. HCLC stands for high and low consistency treated pulp; A, G and X stand for agar, gelatine and crosslinker, respectively; the numbers represent the amount of addition (in %) to fibres. Error bars represent 95% confidence limits.

As can be seen from Fig. 28, an addition of 4% of either agar or gelatine improves the extensibility of paper from around 9.5% to around 12%. However, when these two polymers are added together, the extensibility increases to 13.5% (G2A2). The addition of a crosslinker to polymer solutions increases the extensibility from 14% to around 15.5%. It is suggested that agar increases the extensibility of paper mainly by increasing the drying shrinkage while gelatine modifies the character of interfibre bonding. This suggests a certain synergy or at least absence of negative interaction between the polymers in respect to the improvement of extensibility when these two polymers are used together. Additions of agar and gelatine also have different effects on the stress-strain curves, and for example on tensile stiffness.

These changes are also indicated in the changes of the shapes of the stress-strain curves (Fig. 29).

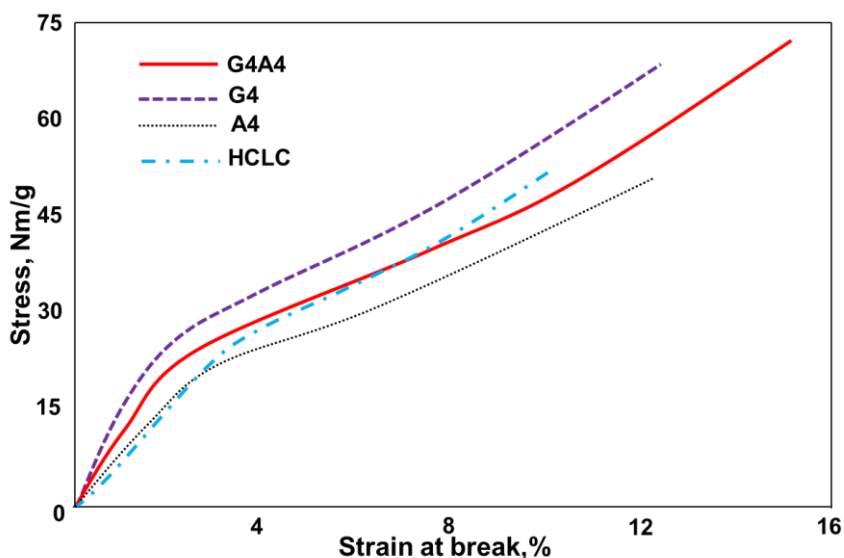


Figure 29. The selected stress-strain curves of unrestrained dried paper sprayed with different polymers, HCLC – high and low consistency refined – pulp, A4 – 4% agar added to fibres, G4 – 4% gelatine added to fibres, A4G4 – 4% of agar and 4% of gelatine added to fibres.

The addition of agar to paper somewhat decreases the tensile strength of the paper, although it provides a somewhat extended elongation, which can be explained by the significantly increased drying shrinkage of paper. The addition of gelatine increases the stiffness and tensile strength but the extensibility of such paper is very close to that of the agar-treated paper. This might indicate more deformable and strong bonding and a higher compliance of bonds (Borodulina *et al.* 2012). The stress-strain behaviour of gelatine-agar treated paper seems to include both; the effect of improved bonding and the region of extended elongation brought about by increased drying shrinkage of paper. Drying shrinkage might also originate from the increased shrinkage of the polymer, or improved transmission of the shrinkage forces (due to good wet adhesion) during the drying of the fibres.

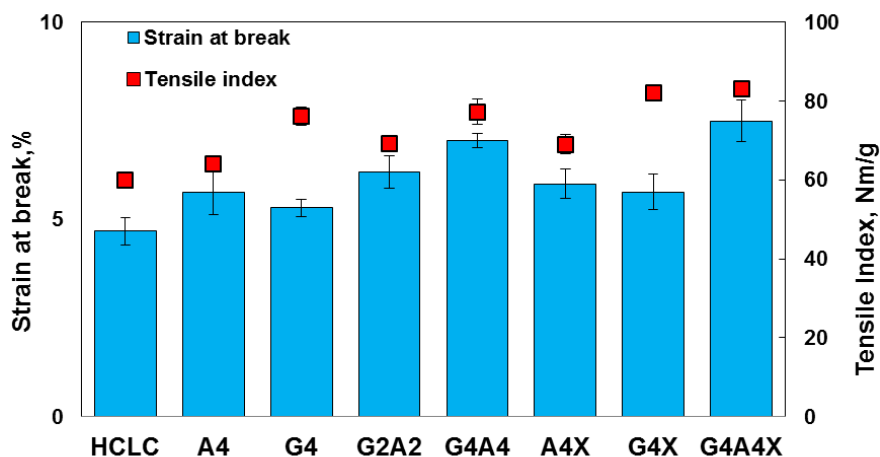


Figure 30. The influence of the addition of agar and gelatine in the presence and absence of a crosslinker on the tensile strength and extensibility of restrained dried paper. HCLC stands for high and low consistency refined pulp; A, G and X stand for agar, gelatine and crosslinker, respectively; the numbers represent the amount of addition (in %) to fibres. Error bars represent 95% confidence limits.

Generally, the same trends can be observed in the development of tensile strength and extensibility as with unrestrained dried paper, due to the addition of agar and/or gelatine in the case of restrained dried paper (Fig. 30). Agar and gelatine are equally effective here in the improvement of extensibility, which suggests that agar improves extensibility not only by increasing the drying shrinkage. The speculated mechanism of agar action in improving the extensibility of restrained dried paper may also be related to its hygroscopicity. Under standard conditions (25 °C, 50% RH), agar-containing paper has a fairly high moisture content (10–11% vs. 8–9% for paper without agar), which has a positive effect on extensibility. The highest extensibility (approx. 7%) and tensile strength (approx. 80 Nm/g) for restrained dried paper were achieved with the simultaneous addition of agar and gelatine and crosslinker. The possible mechanisms of the action of agar and gelatine in respect to the improvement of extensibility should be considered more in detail.

The distribution of polymers and the structure of paper treated with agar and gelatine were studied using SEM imaging. It was shown that the agar forms a film (Publication V) on the surface of the paper, while gelatine somewhat densifies the paper structure (Khakalo *et al.* 2014). The cross-sectional SEM images of the untreated, agar-treated, and agar- and gelatine-treated paper are shown in Fig. 31.

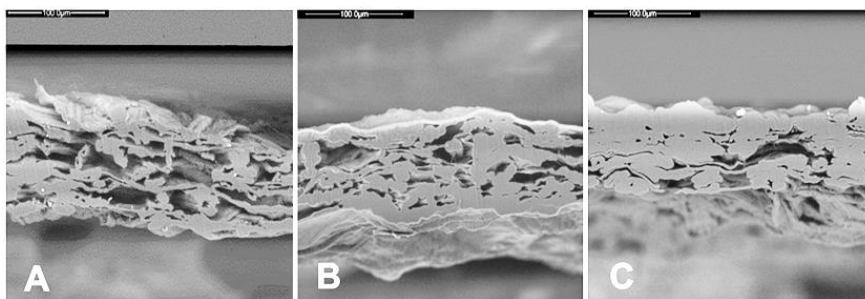


Figure 31. Cross-sectional SEM images of unrestrained dried paper without any additives (A), unrestrained dried paper sprayed with 4% of agar (B), and unrestrained dried paper sprayed with 4% of gelatine and 4% of agar (C).

The structure of untreated paper does not present any particularities, except for a somewhat rough surface, which is due to unrestrained drying. As might be expected, the mildly refined softwood pulp formed a relatively porous and bulky network. Agar forms a film (Fig. 31, B) that evenly follows the surface of the paper without any signs of agglomeration or thinning in any particular place. Also, a certain degree of adhesion between the agar layer and fibres can be noticed which supports the hypothesis of shrinkage transfer. The paper treated with agar and gelatine appears on the SEM images to be somewhat densified and more consolidated in the surface layer. Previously, the densification of paper treated only with gelatine was observed in Khakalo *et al.* (2014) and in Publication VI of this thesis. The lighter agar layer on the surface is distinguishable but not as sharp as in the case of single agar addition on the whole surface of the paper. Perhaps some mixing of agar and gelatine took place, which resulted in the poorer contrast of the agar film in SEM. It seems that the agar and gelatine are intermixed in the surface layer and the formation of the agar film is not so evident. It could be suggested that agar mixed with gelatine has a higher potential to diffuse into paper, which might significantly strengthen the surface layer of the paper, providing more significant improvements in the mechanical strength of the paper.

The effects of the joint addition of agar and gelatine are not so easily visible using only cross-section SEM. Thus, plane-view SEM was performed to further clarify the effect of the polymer additions. The SEM images of the unrestrained dried paper (A), unrestrained dried paper sprayed with agar (B), gelatine (C), and a combination thereof (D) are shown in Fig. 32.

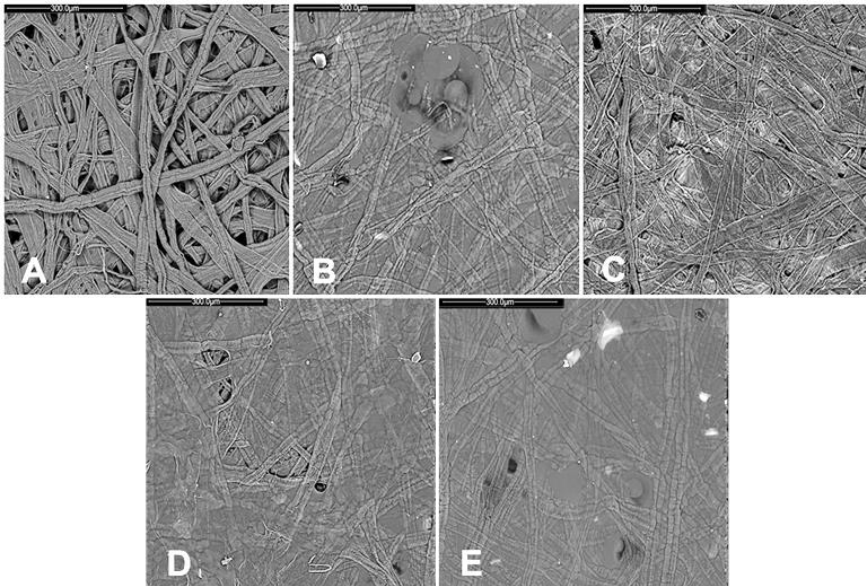


Figure 32. The surface SEM images of unrestrained dried untreated paper (A), unrestrained dried sprayed with 4% of agar (B), unrestrained dried paper sprayed with 4% of gelatine (C), unrestrained dried paper sprayed with agar and gelatine (4% of each) (D), unrestrained dried paper sprayed with agar and gelatine (4% of each) and AmZrCarb (E).

As might be expected, the non-fibrillated softwood pulp fibres formed a relatively porous and bulky network. Also, quite a large number of deformations in the fibres can be observed, probably due to the HC treatment and drying shrinkage.

The addition of agar leads to the formation of a film on the surface of the paper. The fibres under the agar layer appear to be somewhat “swollen” which might be a consequence of the high hygroscopicity of the agar film. Due to this fact and possibly because of high drying shrinkage, axial deformations in the fibres appear to be more profound than in the untreated paper.

The surface of the paper treated with gelatine appears to be denser and less porous than the surface of the untreated paper. This might be a consequence of the improved bonding and larger fibre contact area provided by gelatine. Unlike agar, gelatine penetrates into the paper and accumulates at the fibre crossings, thus providing a reinforcing effect to the paper (Khakalo *et al.* 2014).

The film on the surface of the paper treated with agar and gelatine is interrupted by voids, which could originate from the intermixing of agar and gelatine, which prevents agar from forming a continuous film on the surface or by weakening it. The evenness of the film was improved by the addition of a crosslinker to polymer solutions (Fig. 32 E). The evenness of the film is probably improved due to the depression of the molecular mobility and the increasing viscosity of the agar

solution. It should be noted that the order of addition is extremely important in the case of agar and gelatine spraying. Gelatine should be strictly sprayed first, followed by the addition of the agar solution. In the inverse case, agar may form a difficult-to-permeate gel layer on the surface of the paper that prevents the gelatine from penetrating the paper, thereby preventing the potential positive effects on extensibility. On the other hand, when gelatine is added first, it readily penetrates the paper and is adsorbed by cellulose; the subsequent addition of agar closes the surface with a gel layer, which might also positively affect the retention of gelatine in the paper.

In order to further confirm the absence of negative interactions between agar and gelatine, the influence of these two polymers on drying shrinkage and tensile stiffness (Fig. 33) should be addressed.

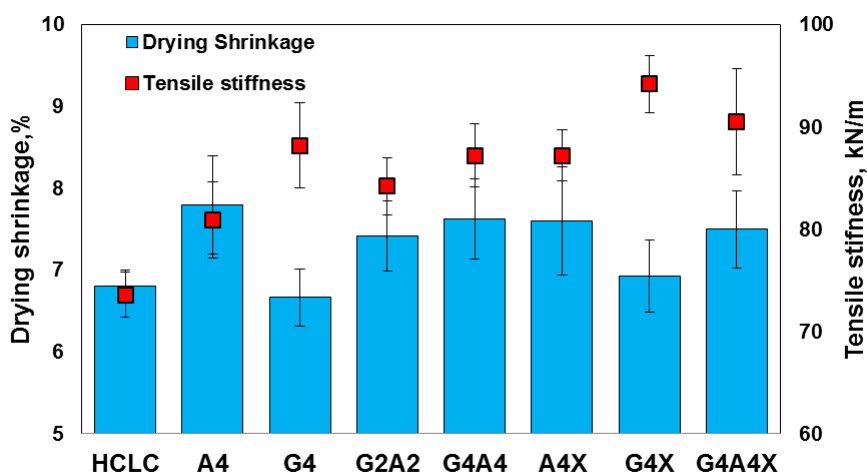


Figure 33. The influence of agar and gelatine addition in the presence and absence of a crosslinker on the tensile strength and extensibility of unrestrained dried paper. HCLC stands for high and low consistency refined pulp A, G and X stand for agar, gelatine and crosslinker, respectively; the numbers represent the amount of addition (in %) to the fibres.

It can be seen that the stiffness of treated paper is directly dependent on the extent of drying shrinkage. Agar-treated paper shrinks most, which is reflected in the lower tensile stiffness of such paper. However, the addition of gelatine has only a minor effect on the drying shrinkage of paper but increases the density and number of interfibre contacts. In the case of gelatine and agar used together, stiffness is somewhere in between that of the samples treated separately either with agar or gelatine. This suggests the presence of an additive effect of applying these two polymers.

4.3.1 Study of the interaction of agar, gelatine and cellulose using QCM-D and AFM

Gelatine should be applied onto the paper surface before agar in order to gain improvements in paper extensibility over the separate addition of this polymer. In order to elucidate this phenomenon, gelatine and agar interactions were studied via the QCM-D method. The Langmuir–Schaefer (LS) cellulose films (Tammelin *et al.*, 2006) were used as the model cellulose surface since they correspond well to native cellulose.

The adsorption of agar and gelatine and adsorbed amounts in different addition sequences onto the LS cellulose film are presented in Fig. 34.

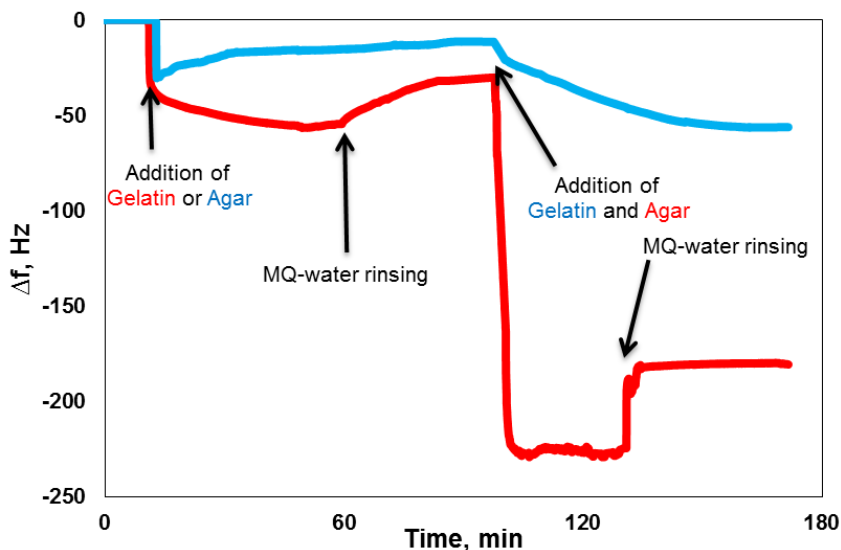


Figure 34. The consequent adsorption of agar and gelatine/gelatine and agar on an LS cellulose film measured using QCM-D.

Gelatine at pH 7.8 has a negative surface net charge (the isoelectric point of gelatine is 5.8) as does the cellulose LS film. However, gelatine adsorption is fairly irreversible as no significant desorption is observed after rinsing with the MilliQ-water (red line in Fig. 34). The same observation was reported by Khakalo *et al.* (2014), who speculated that hydrogen bonding and other non-specific interactions are more important than the electrostatic forces in cellulose-gelatine interaction. Moreover, gelatine adsorption can be promoted by its flexible configuration at the interface, so that the surface of cellulose can accommodate a large amount of protein molecules, *i.e.*, by suitably changing their structural orientation at the polysaccharide interface (Halder *et al.*, 2005).

Gelatine adsorption on a pre-adsorbed agar layer (blue line in Fig. 34) demonstrated the same pattern as in the case of adsorption onto cellulose. Moreover, the amounts of gelatine adsorbed on the cellulose and agar are very

close. The agar adsorption on the cellulose is fairly negligible as indicated by the almost immediate detachment of agar with the solvent flow (blue line in Fig. 34). However, when the agar is adsorbed on a pre-adsorbed layer of gelatine, the situation is completely different, as indicated by the large polymer amount deposited even after the rinsing step. This could be associated with electrostatic interactions between the gelatine and agar. In general, upon introduction of agar solution (pH 5.6), most of the amino groups of the gelatine acquire a positive charge (pKa of arginine is 9.0), meaning that the pre-adsorbed layer of gelatine is positively charged under these conditions. Agar, in turn, consists of a mixture of agarose and agaropectin that is heavily modified with acidic side groups, such as sulphate, pyruvate and glucuronate groups, which are negatively charged at a pH of 5.6.

In addition, it should be noted that the adsorption kinetics of agar and gelatine are different, namely a self-assembled layer formation of gelatine proceeds slower than that of agar. Both agar and gelatine are prone to form gel-like structures via the formation of a hydrogen-bonded cross-linked network in water. However, an agar gel sets faster than a gelatine gel due to its higher molecular weight. Hence, under these experimental conditions, agar might interact with the substrate surface already in the form of a gel, as indicated by the sharp drop in QCM-D oscillating frequency, thus rapidly covering the whole surface. In contrast, the gelatine, being still in a dissolved state, slowly undergoes structural orientation at the interface.

The irreversible adsorption of agar on gelatine improves the retention of gelatine in paper during wet pressing and may provide improved interaction in the fibre-polymer contact zone. These phenomena increase the compliance of fibre bonds, reflected in the increased strength and extensibility of paper (Borodulina *et al.* 2012).

The changes in the nanoscale surface morphology of LS cellulose films modified with gelatine and agar also provide certain insights into the interaction of these polymers with each other and cellulose. The AFM images of pristine LS cellulose film as well as cellulose surfaces modified sequentially with gelatine and agar are shown in Fig. 35.

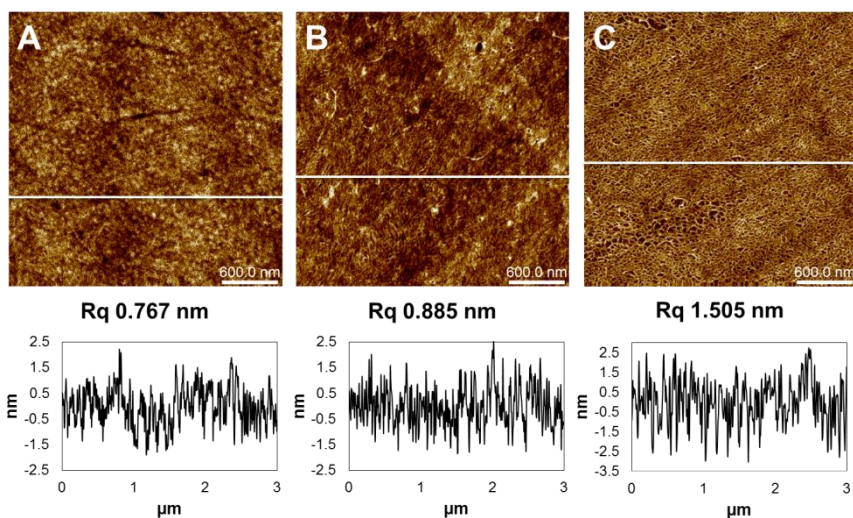


Figure 35. AFM height images and corresponding roughness profiles of unmodified cellulose (A), cellulose modified with gelatine (B) and agar modified cellulose pre-treated with gelatine (C). The z-range of all the images is 5 nm.

As can be seen from the AFM images, gelatine forms a thin layer on the cellulose surface which follows the slightly increased surface roughness without a major change in surface morphology. Subsequent addition of agar leads to the formation of a cross-linked polymer network on the cellulose surface. Agarose may coil into a double helix and join together, thus forming a cross-linked gel. The AFM images were taken in air, which could mask the actual size of the polymer structures in water. The pronounced cross-linked nature of the agar gel is the major distinguishing feature in contrast to the gelatine. These observations are in agreement with the changes observed by SEM in the surface structures (Fig. 32).

4.3.2 Formability strain of the agar- and gelatine-sprayed samples

The influence of the elevated temperature on the formability strain of the untreated, agar-, gelatine-, and gelatine-agar treated paper can be seen in Fig. 36.

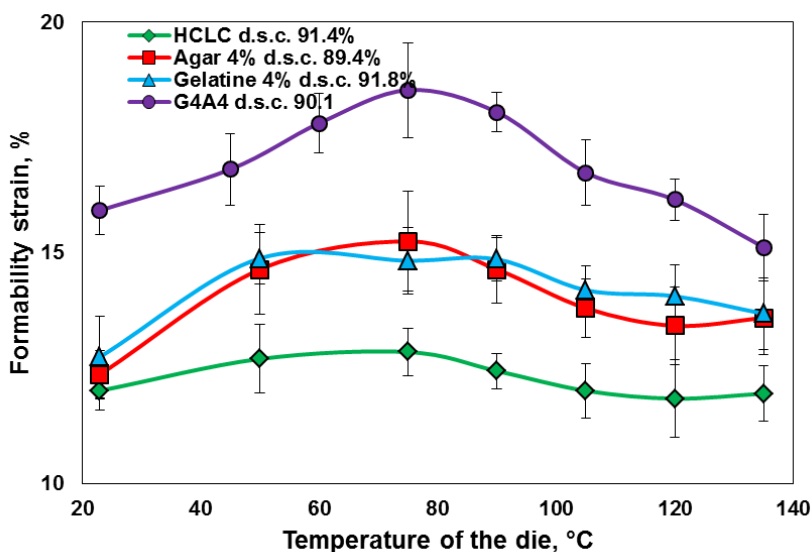


Figure 36. The influence of temperature on the formability strain of untreated paper and paper sprayed with agar, gelatine, and gelatine-agar.

The temperature response of the formability of the paper treated with both agar and gelatine is similar to that of papers treated only with agar or gelatine (Publication V and Khakalo *et al.* 2014). The maximum formability strain of agar- and gelatine-treated paper is around 18%, which is equal to the shapes with depth of around 2–3 cm (depends on curvature) produced using a fixed blank process.

4.3.3 Summary

The fibre bonds and structure of paper can be modified to benefit extensibility by using suitable polymers. Two polymers, agar and gelatine, were used in this study. Agar forms a gel layer on the surface of paper and upon drying, this gel layer shrinks and forms a film; the shrinkage potential of agar gel is greater than that of paper and thus additional drying stress is transferred to the paper, increasing its extensibility (Fig. 37). In addition to increasing shrinkage, the agar film reinforces the surface layer of the paper, thus providing more even stress distribution upon straining.

Unlike agar, gelatine is adsorbed by cellulose and, thus it probably modifies the fibre-fibre bonding, by strengthening and changing the viscoelastic properties of the fibre joints (Fig. 38).

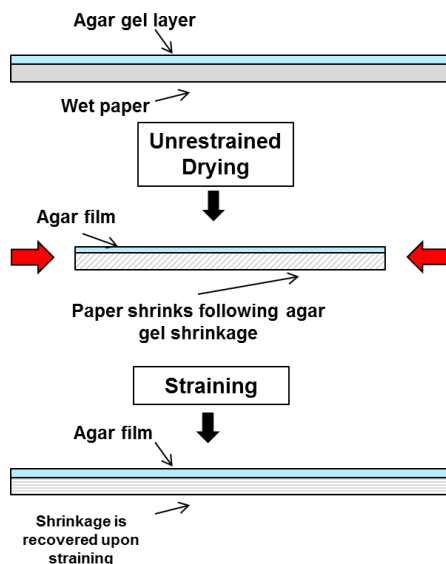


Figure 37. A schematic representation of the mechanism of the action of agar addition to wet paper towards improving the extensibility of paper.

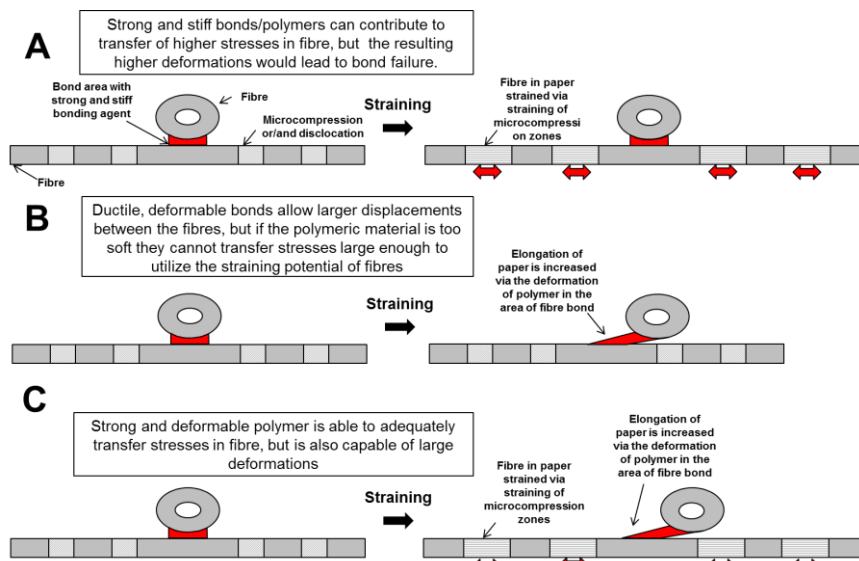


Figure 38. Schematic representation of different mechanisms of the ways in which polymers can improve extensibility of paper, A – strong and stiff polymers, B – deformable polymers with weak adhesion to cellulose, C – suggested mechanism of gelatine action.

The mechanism of gelatine action (Fig. 28) is also supported by the change in the stress-strain curve of paper treated with gelatine (Fig. 29), where both the increased initial stiffness and region of extended elongation indicated modified fibre bonding. Thus, polymers that supposedly improve the extensibility of paper should have both strong adhesion to fibres to fully utilize their extensibility potential as well as a certain deformability upon applied stress.

The consecutive addition of these two polymers to paper provides an additive effect for the improvement of extensibility since the action mechanisms do not interfere with each other. However, this additive effect is only observed when gelatine is added first, followed by the addition of agar. The separate effects of agar and gelatine addition are summarized in Table 7.

Table 7. Suggested effects of agar and gelatine in respect to fibre bonding and the respective consequences in the mechanical properties of paper.

| Effect | Result |
|---|---|
| Gelatine | |
| Increased strength of bonds | Higher strength and extensibility |
| Increased number of bonds (density) | Higher strength and extensibility |
| Agar | |
| Increased drying shrinkage | Higher extensibility |
| Formation of a film on the surface of paper | Reinforcing and evening out of stress distribution in paper |
| Agar and Gelatine | |
| Modified mechanical deformation behaviour (increased ductility) of the bond areas | Higher extensibility |

The elongation of paper can be improved by polymers in several ways: by improving the strength of fibre bonds, modifying the deformation behaviour of the bonds, affecting the density (number of bonds) and increasing the drying shrinkage of the structure. By controlling the location of the polymers the actions can be further diversified.

4.4 NETWORK: Mechanical treatment of fibre networks for improved formability and extensibility

In addition to the fibre structure and fibre bonding, the structure of the fibre network (density, number of fibre contacts, and shape of the fibres in the network) is another essential factor contributing to the formability of paper. The structure of the fibre network can be modified towards the improvement of extensibility by in-plane compaction, creping and drying shrinkage. This chapter considers the effects of laboratory and pilot compaction on the properties of paper. Detailed information about this treatment can be found in Publication VII of this thesis.

4.4.1 Laboratory compaction

Compaction is one type of compressive treatment that is used for the production of extensible sack and bag paper grades (Lahti *et al.* 2014, Ankerfors and Lindström 2011, Poppel *et al.* 2000). However, there is a lack of theoretical knowledge of how this process affects the mechanical properties of paper. In general, compaction increases extensibility (by up to 15 % -points) but, with an increase in extensibility, losses in tensile strength and stiffness are inevitable (Lahti *et al.* 2014, Poppel *et al.* 2000). Compaction is associated with a reduction in the linear length of paper, increase in density and roughening of the surface due to the formation of micro-buckles. Roughening is more profound when the treatment is performed at a high dry solids content of paper and low z-pressure. The effect of compaction can be adjusted by varying several process parameters such as the overall speed of the compaction unit, the speed difference between the compaction rolls, the extension of the rubber blanket, nip pressure, and the adhesion properties of the rubber. Apart from the process parameters, the result of compaction can be controlled by varying the moisture content of paper when it enters the compaction nip. The influence of the dry solids content on the mechanical properties of laboratory compacted paper is shown in Fig. 39.

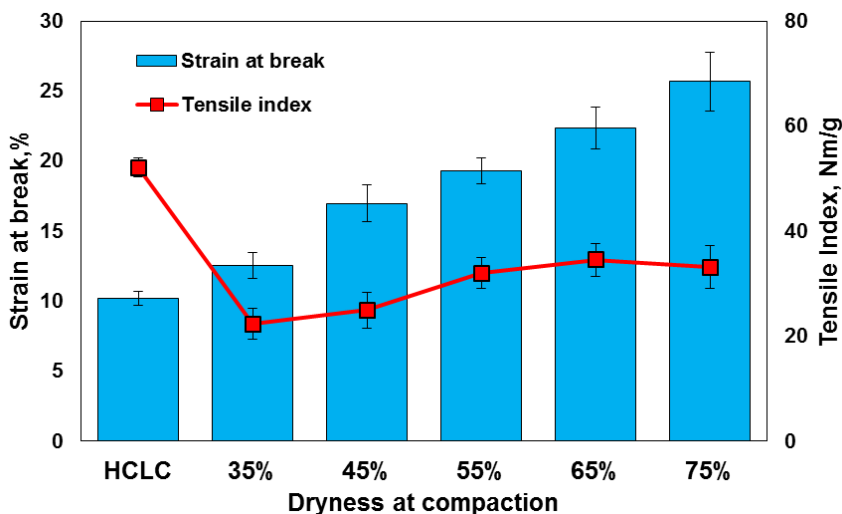


Figure 39. Influence of the dry solids content of paper in compaction on the extensibility and tensile strength of unrestrained dried paper (no agar, compaction at 45% dry solids) HCLC: high and low consistency refined pulp.

The increasing dryness of paper in compaction improves the extensibility, as well as the tensile strength, of paper. On the other hand, paper compacted at a high dry solids content has a wrinkly appearance and extremely low elastic modulus (83 N/mm² vs. 221 N/mm² for 75% DS and 45% DS, respectively).

The decrease in the tensile strength of paper at low dryness can be associated with the sliding of fibres in the network, leading to debonding and subsequently to a loss in tensile strength. At a higher dry solids content, the bonds between fibres are strong enough to withstand in-plane compression without sliding, and the deformation in paper is mainly due to the micro-buckling of the fibres and the fibre network itself. Another option to control the outcome of compaction is to adjust the z-pressure during the process (Fig. 40).

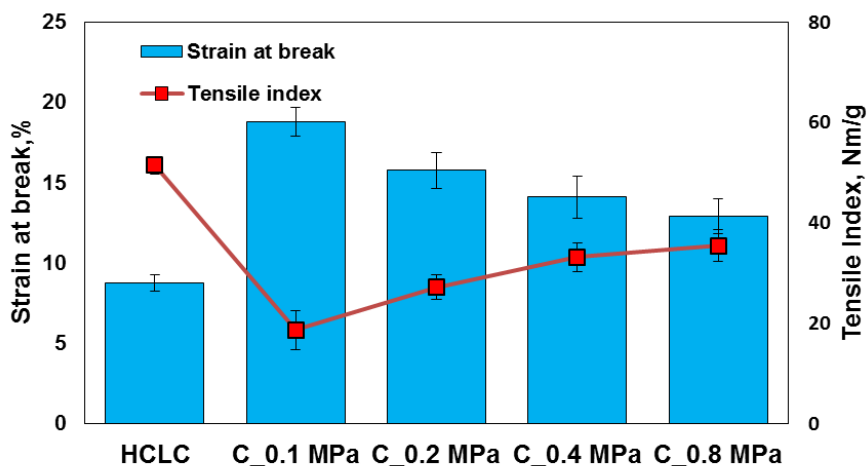


Figure 40. Effect of increasing z-pressure in compaction on the extensibility and tensile strength of unrestrained dried paper (compaction at 45% dry solids HCLC: high and low consistency refined, pulp C: compaction at a certain z-pressure).

The higher the z-pressure in compaction, the higher the tensile strength and the lower the extensibility of paper. High pressure prevents fibres from sliding past each other and thus preserves tensile strength. Additionally, the increase in the z-pressure improves the visual appearance of compacted paper by minimizing the size of the micro-buckles. Controlling the z-pressure together with the adjustment of dryness of paper in compaction allows the fine tuning of the tensile properties of compacted paper for a particular area of application.

The decrease in the tensile stiffness of compacted paper is one major factor that limits its utilization in packaging applications. However, this might not be the case for 3D forming in the fixed blank forming process due to its strain hardening effects. The stiffness of paper increases upon straining. The increase in the tensile stiffness of laboratory compacted handsheets is shown in Fig. 41.

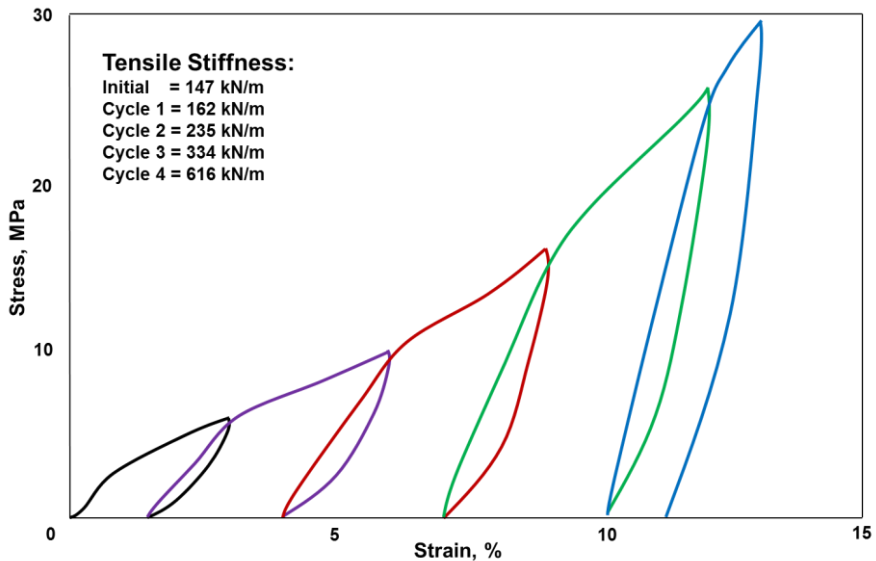


Figure 41. Strain hardening effect demonstrated with a laboratory compacted handsheet sample strained to 15, 30, 45, 60, and 75% of the strain at break value.

When the compacted sample was strained to a 75% of the maximum strain value, tensile stiffness had increased over 4 times from its original value. In 3D forming, paper is strained to values which are close to the maximum strain values and thus additional stiffness can be obtained via the strain hardening effect. This provides good potential for compaction as the process step in the production of paper with high formability. On the other hand, it also means that the local stiffness varies according to the amount of applied strain; thus, shapes should be designed in such a way that straining would take place evenly.

4.4.2 Pilot compaction

The relevance of the results obtained with laboratory compaction was verified using the pilot compactor of Clupak AG. Compaction was performed using typical conditions and at 60% dry solids content (obtained by the rewetting of paper) of paper. A commercial paperboard sample (sample 4) and a handsheet prepared from mechanically treated fibres (200g/m² basis weight) were used for the experiments.

In general, the results of pilot compaction are in line with those obtained with the laboratory compaction device, as well as with the results available in the literature. The effect of pilot compaction on the tensile strength, extensibility and stiffness of the samples is shown in Table 8.

Table 8. Influence of pilot compaction on the tensile strength, elongation and elastic modulus of commercial paperboard (sample 4 from Materials section) and handsheet samples. BC – before compaction, AC – after compaction.

| Sample | Tensile Index, Nm/g | | | Elongation, % | | | Elastic Modulus, Mpa | | |
|---------------|---------------------|------|----------|---------------|------|----------|----------------------|------|----------|
| | BC | AC | % change | BC | AC | % change | BC | AC | % change |
| Commercial MD | 91.9 | 64.2 | -30.1 | 2.1 | 15.9 | 657 | 5921 | 509 | -91.4 |
| Commercial CD | 41.4 | 35.2 | -14.9 | 5 | 7.1 | 42 | 2227 | 1554 | -30.2 |
| Handsheet MD | 46.4 | 33.8 | -27.1 | 10.5 | 27.9 | 165 | 1081 | 575 | -46.8 |
| Handsheet CD | 46.4 | 38.4 | -17.4 | 10.5 | 11.2 | 6.6 | 1081 | 877 | -18.8 |

The most notable change in the properties had occurred in commercial paperboard where MD elongation was increased by 657%. On the other hand, tensile stiffness was decreased by 91.4%. The handsheets experience less severe changes percentage-wise, although the MD extensibility of the handsheets after compaction was around 28%, which is extremely high. It should be noted that in both cases MD compaction had also increased the CD extensibility by 42% and 6.6%, for commercial and handsheet samples, respectively.

4.4.3 Summary

Compaction is an effective tool for the production of extensible paper. It can also be used for the production of paper with high formability, since the losses in stiffness can be regained in the forming process. It can also be applied to paperboard with relatively high grammage and stiffness. The effect of compaction can also be varied on a broad scale using relatively simple methods such as adjustment of the moisture content of paper and nip pressure. The primary limitation is the fact that traditionally compaction is performed in the MD only, which leads to the high anisotropy of paper, even though recent developments in compaction units also allow improvements in extensibility in the CD.

4.5 Combined approach for the improvement of formability

After careful consideration of the factors contributing to the extensibility and formability of paper and projecting the actions needed to utilize these factors on the conditions of modern paper machines, the conclusion drawn is to combine treatments on different structural levels. The 'combined approach' for the

improvement of the formability of paper in the fixed blank forming process is here suggested on the basis of these considerations. It is schematically outlined in Fig. 42.

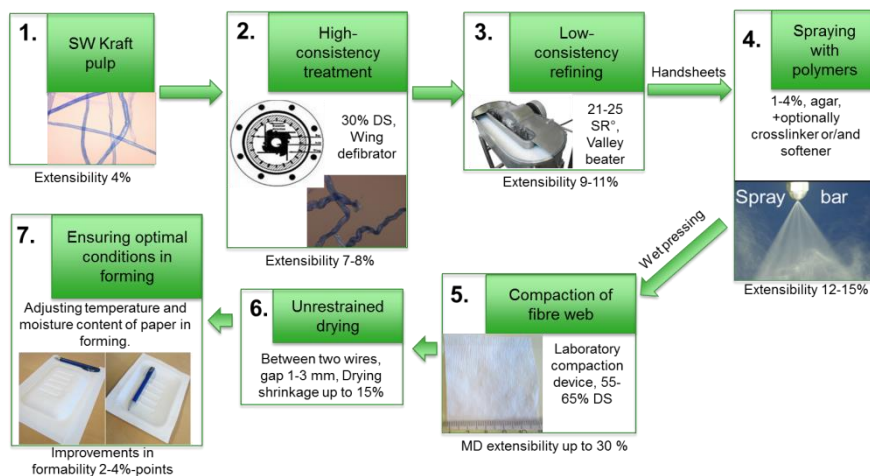


Figure 42. Outline of the suggested combined approach for the production of paper with high extensibility and formability in the fixed blank forming process.

The starting raw material used in the combined approach for the production of extensible paper is softwood kraft pulp, which has been further subjected to combined high- and low-consistency mechanical treatment. This fibre material has been selected due to its higher fibre length, which allows the creation of more deformations per fibre in high-consistency mechanical treatment and relatively high network strength. Once the paper is formed, it is sprayed with water-soluble polymers such as agar and gelatine to promote shrinkage and bonding. Subsequently, this paper is compacted and dried without restraint. The final stage in this approach is to ensure adequate softening of the paper in forming. The conditions, namely the moisture and temperature, are adjusted in accordance with the type of forming equipment, basic properties of the board, and visual appearance of the shapes after forming.

It should be noted that this approach is general and has a certain degree of flexibility, *i.e.* some of the treatments can be modified or even replaced. For instance, instead of using water-soluble polymers, thermoplastic could be applied in thermosetting polymers.

As a result of the treatment in the combined approach, paper with an extensibility of around 18% (without in-plane compaction) and 30% (compaction MD) can be obtained. With further adjustment of the forming conditions, 3D shapes with a depth of around 2.5 cm can be obtained (Fig. 43).



Figure 43. An example of a 3D shape produced using paper manufactured according to the combined approach (without in-plane compaction, grammage of paper is approx. 250 g/m^2).

5. Conclusions

Paper which can be used in thermoforming lines for the production of packaging is no longer a myth but a reality. However, in order to enable this, fibre bonds and fibres should be revisited and modified accordingly.

The primary objective of the present thesis was to produce extremely deformable paper material for the manufacture of 3D shapes. Hypothetically, it was stated that extensibility is the foremost important mechanical property that enables 3D forming. It can be improved by modifying the fibres, fibre bonds and fibre network structure. These hypotheses were verified, and the majority were found to be correct.

The results of the present work indicate that extensibility does control formability, but only in fixed blank 3D forming processes. In the sliding blank 3D forming processes, the requirements for good formability are different: namely, low compressive strain and strength, low paper-to-metal friction coefficient and low elastic recovery.

The research was focused on the fixed blank processes, and thus on improving the extensibility of paper. The key features in producing paper with high extensibility are formulated in following three paragraphs.

Fibres should be extensible, and thus they should be axially deformed or have naturally high extensibility. But not every type of deformation is favourable for extensibility. Conventionally, kink and curl are considered to have a positive influence on extensibility, although dislocations and microcompressions have a much more drastic positive effect on the extensibility of fibres and paper. The formation of dislocations and microcompressions is always accompanied by the kinking and curling of fibres; unfortunately, this phenomenon cannot be reliably quantified using current analytical methods. The amount of kinks and fibre curl can be used for the evaluation of fibre deformations but it should be checked whether these values correlate with the number of dislocations and microcompressions.

Fibre bonding should be sufficiently strong yet deformable, especially under the action of elevated temperature and moisture. This can be achieved by selecting a highly deformable polymer with a chemical affinity to cellulose and by locating it at the point of the fibre-fibre contacts. The polymer can be added either to the pulp suspension or added by spraying before wet pressing. Fibre bonding also affects drying shrinkage, and the polymers which provide strong wet adhesion and denser

fibre bonds significantly contribute to the drying shrinkage of paper. The formation of a separate polymer layer on the surface of the paper is also beneficial to extensibility through the reinforcement of the weakly bonded surface layer of fibres. However, this is only possible in the case of sufficient adhesion of the polymer layer to the paper.

The fibre network can also be modified for a higher extensibility potential using in-plane compressive treatment and drying shrinkage. This leads to the buckling and compressing of the fibres, which can be eventually transferred to additional elongation upon straining. The strength, stiffness and extensibility of paper after compaction can be adjusted to a certain extent by varying the moisture content of the paper entering the compaction unit and the z-pressure in compaction. A low moisture content and high z-pressure decrease improvements in extensibility but on the other hand positively affect stiffness and strength, and vice versa. The negative effects of the losses in tensile strength and stiffness can be mitigated by the strain hardening phenomenon that takes place in 3D forming with the fixed blank process.

As a result of the mechanical modification of fibres and addition of gelatine and agar, paper with an extensibility of 15–18% was produced. Extensibility can be further improved up to 30% using compaction. The formability of the paper produced was better than that of any of the commercially available materials; tray-like shapes with a depth of 2–3 cm (depending on curvature) can be produced with this paper using the fixed blank process. The formability of the developed paper allows it to be used in existing thermoforming lines, which is complementary to the main objective of the thesis. The manufacturing method (i.e the combined approach for improved formability) is compatible with the environment of modern paper and board machines.

In addition to the development of a method for the production of formable paper, and definition of requirements of good formability, important knowledge about the role of moisture and temperature in formability was obtained. The key action of moisture and temperature is to increase the deformation of paper, especially plastic deformation. Softening is a key phenomenon enabling the shape to keep the newly obtained dimensions after forming. The optimal deformability in the fixed blank process is reached at a paper temperature of 70–90 °C and moisture content of 7–9% by weight.

In summary, the work done in the present thesis provides fundamental knowledge about the deformability of paper under different conditions and elucidates the role and potential of several factors in formability and 3D forming. Moreover, the suggested treatment for the improvement of formability is expected to be compatible with a modern paper machine environment and thus presumably can be scaled up without major technical or financial restraints.

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PUBLICATION I

**Deep-drawing of paper and paperboard:
the role of material properties**

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DEEP-DRAWING OF PAPER AND PAPERBOARD: THE ROLE OF MATERIAL PROPERTIES

Alexey Vishtal* and Elias Retulainen

Fibre-based packaging materials are widely utilized all over the world. They have several important advantages in comparison with fossil-based packaging: biodegradability, recyclability, and renewability. However, fibre-based packaging cannot fully compete with plastic in its barrier properties. Also there are limitations regarding its shapes due to poorer formability. The deep-drawing forming process can be used for the production of advanced three-dimensional shapes from paper-based materials. Formability and related characteristics are essential for deep-drawing of paper-based materials. This paper aims to give an overview of the deep-drawing of paper-based materials with the emphasis on the experienced deformations, on the role of mechanical properties of materials in deep-drawing, and on the typical defects found in the shapes after the forming. Additionally, strategies are proposed to help mitigate common problems in deep-drawing.

Keywords: Deep-drawing; Formability; Paper; Mouldability; Deformation; Properties; Elongation

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INTRODUCTION

Paper and paperboard together are the most widely used consumer and industrial packaging materials in the world (Rhim 2010). Paper-based packaging materials appear in the form of wrappings, sacks, boxes, cups, bags, trays, and tubes. These packages have already proven their applicability and have occupied a solid position in the market. The important advantages of paper-based packaging materials in comparison with petroleum-based products are biodegradability, recyclability, good printability, “green” image, and renewability. On the other hand, paper-based materials have characteristic features that limit their use in some applications. Among those features are: poor barrier properties, sensitivity to elevated moisture levels, and inferior formability in comparison with plastics. While the barrier and moisture resistant properties can be improved by introducing different coatings and additional layers, the formability of paperboard cannot be significantly improved without chemical and mechanical modifications to fibres and the fibre network structure.

Formability is the ability of material to undergo plastic deformation without damage, *i.e.* the “ease of forming” (Bhattarychya *et al.* 2003). Formability is especially important for paper-based materials that are subjected to a deep-drawing type of forming process. This process has been conventionally used for production of various products from plastics and metals (Hosford and Caddell 2007). Deep-drawing of paper-

board can be used for production of such products as paper trays, cups, paper plates, containers for food, and various consumer packages. Deep-drawn paper-based products are intended to compete with petroleum-based materials on the market for packages for ready meals, picnic dishes, and foodstuffs such as cheese and sliced meat products. The specific properties of fibre-based materials set significant limitations regarding the obtainable shapes compared to plastics and metals. These limitations are caused by certain insufficient deformation characteristics of paper. They cause defects in deep-drawing such as surface and complete fractures, appearance defects, and shape inaccuracies.

This paper aims to provide an overview of the deep-drawing process and the deformations experienced by paper-based materials in the deep-drawing process. The second objective is to identify the mechanical properties of materials that have an essential role in deep-drawing. Additionally, typical defects in end-products will be reviewed and possible reasons for these defects will be suggested. Finally, solutions to avoid or mitigate the problems will be proposed.

DEEP-DRAWING OF PAPERBOARD: PROCESS, MATERIALS, PRODUCTS, AND LIMITATIONS

There is a lack of information in the literature regarding modern techniques, equipment, materials, and conditions used for deep-drawing of paperboard. German authors (Scherer 1932; Heinz 1966, 1967) have done some fundamental research in this field. Only a few works have been published in recent times (Uggla *et al.* 1988; Kunnari *et al.* 2007; Hauptmann and Majschak 2011; Östlund *et al.* 2011; Post *et al.* 2011). A patent review shows that industry has had an interest in this topic since the 1940s.

Patents are mostly associated with process design features, such as pre-creasing, lubrication, and special coatings for paperboard (Cross and Bernier 1967; Morris and Siegele 1975; Schlesinger *et al.* 1982; Ingraffea 1983), and with the development of new highly-extensible materials (McClurg and Dulmage 1942; Cariolaro and Trani 2000; Nobuhiro *et al.* 2004; Reitzer 2007; Ankerfors and Lindström 2011).

The aim of this section is to overview the current process for deep-drawing of paperboard, materials which are used for it, and common defects and problems in deep-drawing.

Process

The deep-drawing type of the forming process for paperboard is already being applied at the industrial scale. The equipment for deep-drawing and the forming procedure can vary in details from one producer to another; however, the principle is the same: a paperboard blank is drawn into the cavity of a predefined shape by using a moving die (Hauptmann and Majschak 2011; Östlund *et al.* 2011; Post *et al.* 2011). The schematical representation of the deep-drawing process can be found in the Fig.1

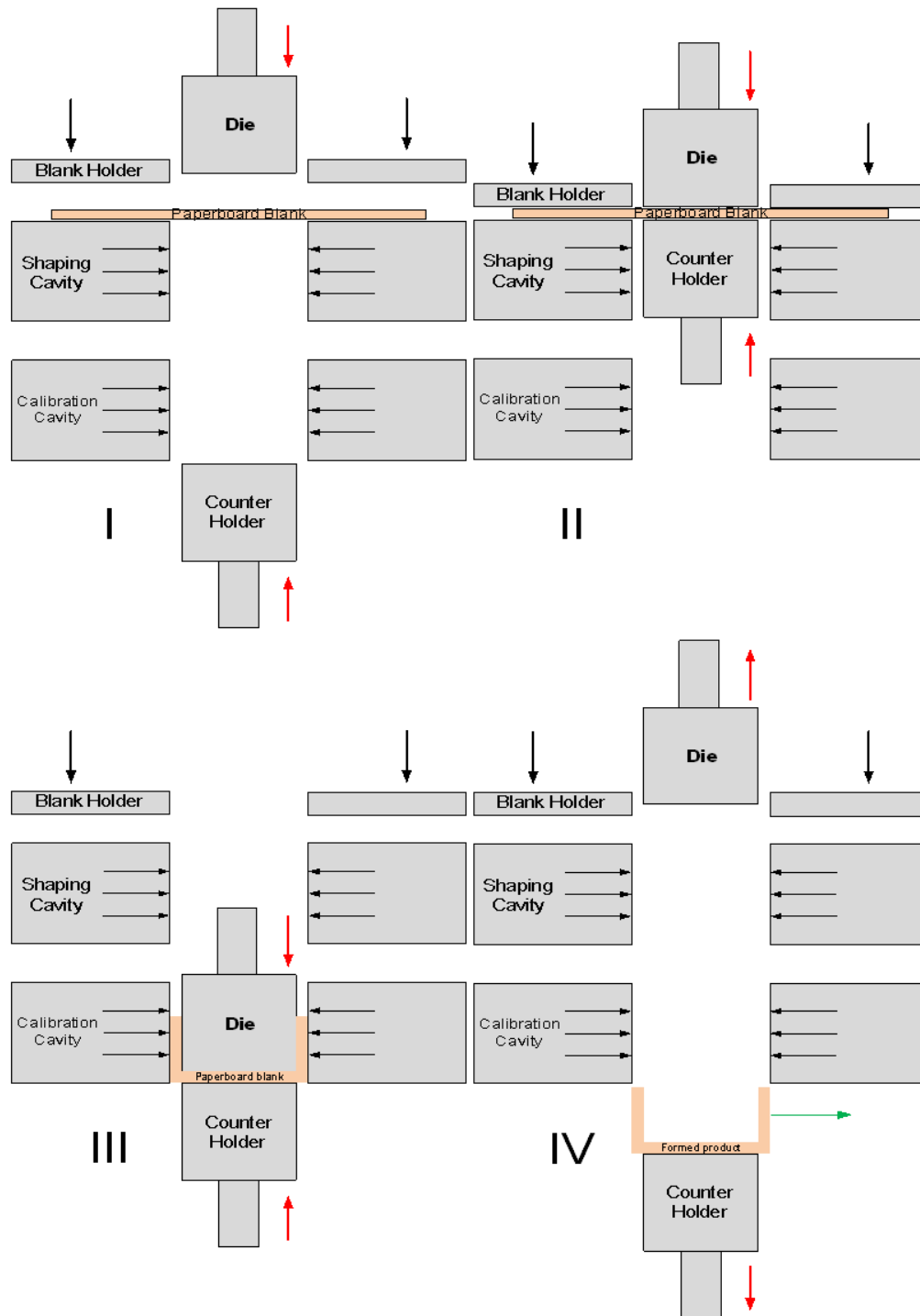


Fig. 1. Stages of the deep-drawing process of paperboard (I: initial stage, II: blank is fixed and heated, III: drawing itself, IV: formed product is released) (adopted from: Hauptmann and Majschak 2011)

As can be seen from Fig.1, the deep-drawing process of the paperboard consists of four phases. The first phase is where the blank is transferred to the forming press. The second is where the blank is fixed by blank holders, heated and optionally moisturized, in

order to soften the paper. The third stage is the forming, when the blank is formed to the designed shape against a forming cavity and counter holder. Finally, in the fourth stage, the formed part is cooled in order to “freeze” the shape and regain stiffness. The timescale of the process is rather short; the forming time varies in the range from one to several seconds.

The typical conditions in the forming process of paperboard are as follows: the temperature of the paperboard is around 100°C and the moisture content is around 6 to 11% (Peltonen 2006, Kunnari *et al.* 2007). The ingoing moisture content of the paperboard can vary because it is not usually controlled prior to forming. A moisture content of above 15% in the blank can lead to the formation of small fractures in the edges of a formed tray (Peltonen 2006).

Materials

The paperboard grades used in the forming are typically of relatively high grammage (200 to 450 g/m²), non-coated, and made of chemical pulp, *e.g.* kraft pulp. However, polyethylene-coated and mechanical pulp containing grades are also available. Among the commercially available paperboard grades used in deep-drawing, some notable ones are: Trayforma® (Stora Enso) and FibreForm® (Billerud) (Stora Enso 2012; Billerud 2012).

Other fibre-based products, such as vulcanized fibres, saturating kraft, latex-fibre, and other fibre composites, have been reported to have high elasto-plastic deformation characteristics in comparison to conventional paper grades (Waterhouse 1976; Alince 1977; Nezamoleslami *et al.* 1998; Suzuki 2004). Recently, vulcanized fibres were utilized in the deep-drawing process for the production of automotive interior parts (Künne *et al.* 2011; Künne and Dumke 2012). The sack and bag grades of paper can have elongation in the cross direction (CD) of around 6 to 8% and in the machine direction (MD) of 2 to 3%. One type of extensible paper, so-called “compacted” or “Clupak” paper, may have elongation of up to 12% in MD (Hernandez and Selke 2001; Holik 2006). Recent developments in the compaction of paper, by the addition of CD compaction, have yielded strain values of 20% and 16% in MD and CD, respectively (Cariolaro and Trani 2000; Cariolaro.com 2011). The aforementioned materials have a great potential to be used in deep-drawing.

Additionally, fibres or paper can be subjected to chemical modifications, impregnation with plasticizers, or blending with thermoplastic polymers such as polypropylene, *etc.* The elongation at break of such materials can be as high as 30% (Waterhouse 1976; Alince 1977; Salmen *et al.* 1984; Rezai and Warner 1997; Borges *et al.* 2001; Wang *et al.* 2007; Cyras *et al.* 2009). Another perspective paper-based material for deep-drawing is the hydroxypropylated pulp, which shows high elongation levels (up to 16%) and partial transparency (Vuoti *et al.* 2012). Hydroxyethylation of pulp has also been shown to be beneficial for strength and stretch of paper; stretch was improved from 3% to almost 8% (Didwania 1968).

Products

Advanced 3D-shapes from paperboard can be produced by deep-drawing process, and the examples of such products are shown in Fig. 2.



Fig. 2. 3D-Shapes obtained from the current industrial forming process

In principle, in deep-drawing, paperboard can be formed to the shape of any geometry. However, the depth, curvature, and side wall angle are limited by the deformation characteristics of paperboard.

Limitations and Defects in the Formed Shapes

The maximum depth of the deep-drawn shape is always a compromise between the appearance, runnability in the forming process, and depth itself; since the more that the blank is drawn, the more the material is contracted in a lateral direction and the more compressive deformation it should have to tolerate. Compression and drawing stresses are also increasing the probability of the breaks and other defects. As for the current state of art, there are generally no defined limitations of the maximum depth to which shapes can be drawn, because products are varying in the shape, curvature, side wall angle, presence or absence of the flange, and creasing lines; however, one might take the trays shown in Fig. 2 as the reference for the current limits in the extent of deep-drawing.

Appearance of defective shapes is the actual indicator that is setting the limitations for the deep-drawing process. The most common defects in the deep-drawn shapes are cracks, fractures, buckles, different types of wrinkles, and dimensional instability reflected as springing back and deflexion.

Cracks and Fractures

Fractures lead to unsuitable outcomes of the process, *i.e.* product with fractures cannot fulfil to its end-purpose, while the surface cracks worsen the shape appearance; *i.e.* material may still keep the shape of the formed product. Moreover, fibres in the crack zone can partially re-consolidate through the action of applied moisture, temperature, and pressure. The main explanation for a surface crack is the difference in the extent of experienced stresses between the inner and outer surfaces of the paper. The inner surface stresses and strains (where the die has been applied) are smaller than those on the outer surface; this difference becomes larger with an increase in the thickness of the material (Bhattacharyya *et al.* 2003). The actual fracture occurs due to a failure of bonds between fibres and a failure of the fibres themselves. Thus, compressive and tensile strengths, and the corresponding strain values, determine the possibility of a fracture (Niskanen *et al.* 1996). Fractures are initiated by the breakage of bonds rather than by fibre breakage (Van Den Akker 1950; Van Den Akker *et al.* 1958). The layered structure of paperboard is an additional factor because the layers may be composed of different pulps, with distinct behaviours under straining and compression. There is naturally a considerable difference between the MD and CD directions in paper and paperboard. Straining behaviour in the CD is more plastic and ductile than in the MD (Salminen 2003). Typically, fractures in deep-drawing occur between the flange and side wall and between the side wall and the

bottom of the shape, since these zones are experiencing higher stresses in comparison with other parts of the shape. Examples of fractures of the deep-drawn shapes are shown in the Fig. 3.

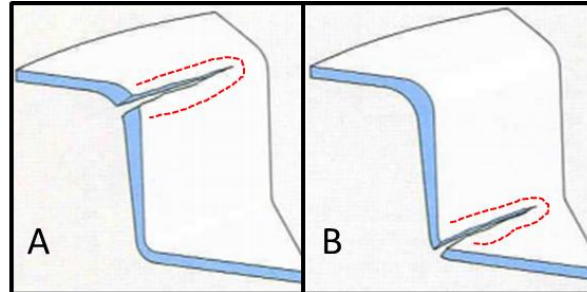


Fig. 3. Two common types of fractures in deep-drawing: A – between flange and side wall; B – between bottom of the shape and side wall

Wrinkling and Buckling

Wrinkling and buckling occur mainly due to the action of compressive forces oriented in a transverse direction (Johnson and Urbanik 1987; Urbanik 1992; Bhattacharyya et al. 2003; Arcelomitall 2011; Hosford and Caddell 2007). Wrinkling leads to uneven height on the upper surface of the package (flange wrinkling), so that it cannot be effectively sealed to protect the aroma and freshness of the product. It is possible to define two principal types of wrinkling: flange wrinkling and draw wrinkling (side wall of the shape) or puckering. The formation of wrinkles and buckles can be controlled by adjusting the blank holder force: the higher the force, the lower the probability of formation of wrinkles and buckles (Bogaerts *et al.* 2001; Hauptmann and Majschak 2011). However, high blank holder force leads to increased tension and compression loads, which increase the possibility of a fracture. One way to control formation of wrinkles is by pre-creasing; this approach creates controlled weaker zones with locally reduced stiffness and elastic modulus in compression (Kunnari *et al.* 2007). Thus, in the forming process, wrinkles are formed in a controlled way. The location of the creasing lines for each type of blank is defined experimentally (Giamperi 2011). One other way to deal with the wrinkles is to use material with low compressive strain and strength, which would lead to the formation of a huge amount of shallow and small wrinkles; thus the surface of material would look rather smooth. The side wall wrinkling of the cylindrical deep-drawn shape is shown in the Fig. 4.

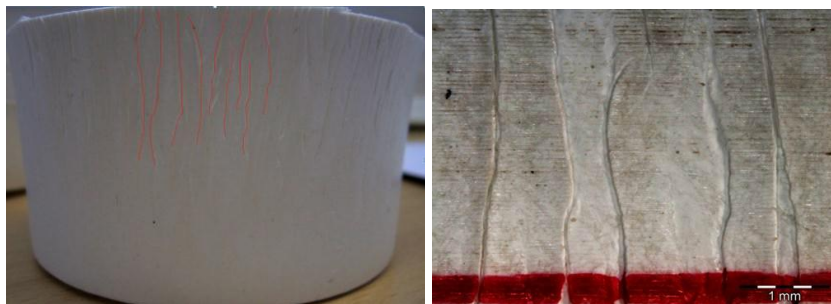


Fig. 4. Side wall wrinkling of the deep-drawn shape (left), at higher magnification (right)

Spring Back and Deflexion

Spring back and deflexion are the defects related to the shape accuracy of the formed product. Spring back describes a change in the angle between the walls and bottom of the formed shape when an applied force is released, while deflexion is the distance between the bottom edge of the shape and the angular line of the spring back measurement (Hauptmann and Majschack 2011). Spring back and deflexion can be attributed to elastic recovery and relaxation effects (Waterhouse 1985; Whitsitt 1987). A spring back effect occurs within one second after the load being removed (Vomhoff 1998). Springing back can be sufficiently decreased by the selection of a proper temperature and moisture profile in forming, in order to rapidly “freeze” the shape (Östlund *et al.* 2011; Golzar and Ghaderi 2009). These defects are furnish-dependent; due to its rigidity, mechanical pulp tends to spring back more rapidly and to a higher extent than the chemical pulp. A schematical illustration of spring back is shown in the Fig. 5.

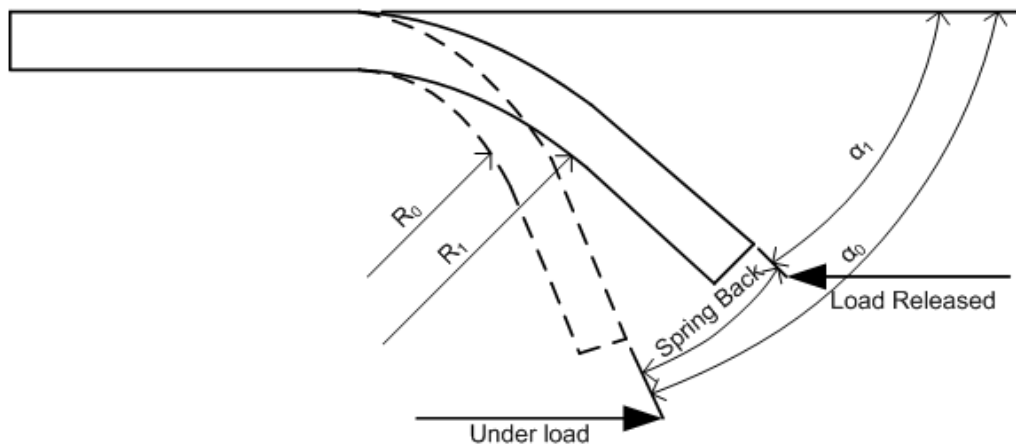


Fig. 5. The illustration of spring back effect

Earing

Earing is the waving of the upper part of a deep-drawn shape. This defect is caused by the anisotropy of the material (Tajally *et al.* 2011), *i.e.* by the difference in the straining of paper in the drawing direction and lateral direction, and also by the difference in the paper properties in MD and CD. An example of earing is shown in Fig. 6.

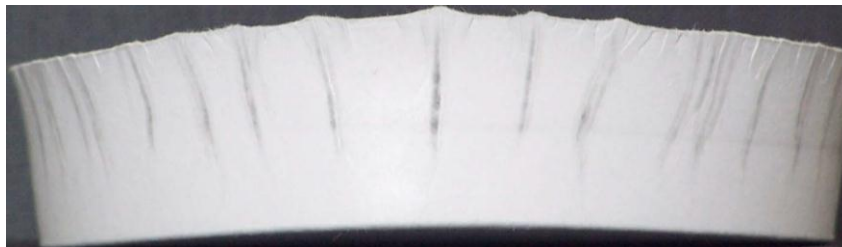


Fig. 6. Earing of deep-drawn shape (courtesy of M. Hauptmann TU Dresden)

Blistering

When using elevated temperature and moisturizing in deep-drawing, one should remember that this may cause blistering in the paperboard. Blistering of the paperboard is a defect in appearance that may also reduce its sealability. It is caused when the water vapour cannot evaporate out of paper fast enough, and it creates internal vapour pressure that is higher than the cohesion of the surface layer. This defect is especially common in coated and/or multilayer paper grades where the density of the outer layers is higher than the density of a middle layer, and air permeability is low, which can lead to excessive internal steam pressure. An illustrative example of blistering in coated paper is shown in the Fig. 7.

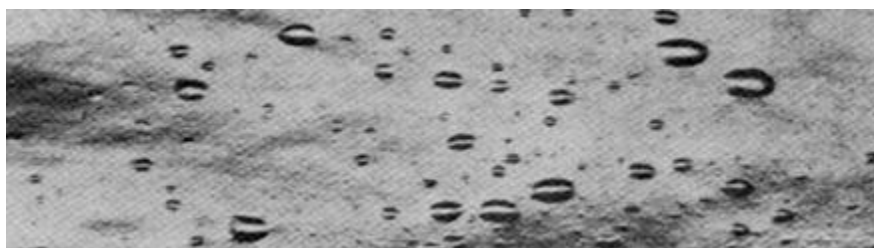


Fig. 7. An example of blistering on coated paper (Paperonweb.com 2012)

STRESSES ARISING IN PAPER-BASED MATERIALS IN THE DEEP-DRAWING PROCESS

Paper-based materials have a stochastic structure in comparison with other materials (plastics, metals) used in deep-drawing. Nevertheless, common aspects in the mechanisms of deformation can be found for these materials. The behaviour of paper-based materials in deep-drawing is based on the properties of single fibres and fibre bonds, and on the structure of the paper web formed during consolidation and drying. Moreover, there are built-in compressive and tensile stresses in paper, formed during the manufacturing process. These stresses have a significant influence on the straining deformation of paper (Niskanen 1998; Alava and Niskanen 2006; Östlund *et al.* 2005). In the case of paperboard, adhesion forces between layers, thickness, chemical composition of layers, and type of coating are of specific importance when considering its behaviour in deep-drawing. Unevenness of the strength and stress distribution in the MD and CD of paper-based materials is the common reason for failure under a load (Xia *et al.* 2002).

Deep-drawing of paperboard means that the material will be compressed, sheared, and strained at the same time (Waterhouse 1985); the extent of these stresses determines the possibility of fractures and defects such as wrinkling, abnormal thinning, buckling, and earing. The main reason for defects in fibre-based composites and paperboard in deep-drawing is the limited ability of the material to withstand plastic deformations, because the softened matrix of wood polymers has a limited ability to flow; it is lower than for truly ductile materials. For instance, elongation at the break of the typical commercial paperboards is in the range of 2 to 5%, while some metals can be strained up to 90%, and certain foams and rubbers up to 1000% (Cada 1996; Bogaerts *et al.* 2001; Anonymous 2011).

The Deformations of Fibre and Fibre Network

Five general modes for fibre and fibre network deformations can be observed: fibre stretching, fibre straightening, intra-ply rotational shear, shear slip, and buckling (Long *et al.* 1996). These deformations have been found in the draping of textile fibres. This process has a certain similarity to the deep-drawing of paper. Thus, models of textile fibre deformation can also be applied to paper fibres without major reconsideration. The modes of fibre deformations for a single layer of fibres are shown in Fig. 8.

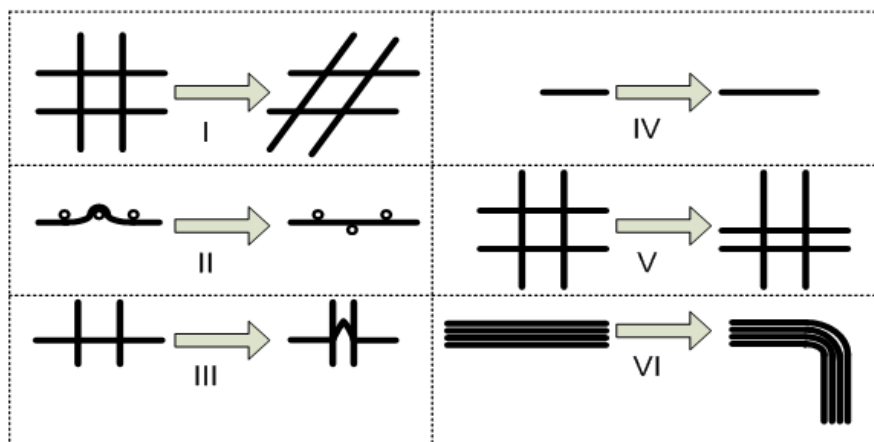


Fig. 8. Schematic Illustrations of fibre and fibre network deformations during draping of textile fibres (I: shear, II: straightening, III: wrinkling, IV: stretching, V: slip, VI: interlay slip) (adopted from Long *et al.* 1996)

Shear stress (I) in fibres occurs when the direction of the tensile load does not match the orientation of the fibres in the plane of paper (Skelton 1980; Stenberg *et al.* 2001). Fibres under tensile load can experience straightening (II), yielding an increase in the linear length. The straightening of fibres is higher in the CD, due to the higher built-in tension in the MD caused by restrained drying, and due to contraction and shrinkage of the sheet in the CD, so that more curled fibres in the CD have a better potential for increasing the linear length due to straightening. Stretching (IV) of fibres is caused by the moving die (Long *et al.* 1996). In paper, due to variations in fibre orientation, shape, cross-sectional area, and dislocations, the stresses within a fibre and between fibres vary (Page and Seth 1980). For natural wood fibres, irregular in thickness, the strain experienced by the different segments of the fibre under extension is different (Page *et al.* 1973). The thinnest segment experiences the maximum strain. The strain difference between regular fibre and a fibre with a 50% variation in diameter can be as high as 45% (Wang and He 2003). Inter-ply rotational or parallel shear (VI) can occur in between two layers (Long *et al.* 1996; Bogaerts *et al.* 2001). The inter-ply slip can be counted as one of the main factors contributing to a change in the shape of a product (Bogaerts *et al.* 2001).

The Deformation of Paperboard

The stresses arising in paperboard during deep-drawing can be compared to those stresses with creasing and embossing. Regarding creasing, paperboard is pressed to the

cavity by the moving die, while the edges of the paperboard sheet are kept under tension. However, the stresses and deformations caused by drawing occur over a larger area than creasing, which is a local process. A schematic representation of the stresses that occur in paperboard during creasing is shown in Fig. 9.

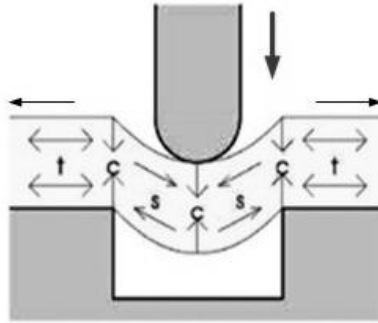


Fig. 9. The deformations and stresses caused by creasing of paperboard (*t*-tension, *c*-compression, *s*-shear), (adopted from Hine 1964, Beex and Peerlings 2009)

The stress model shown in Fig. 9 can be partly applied to the deep-drawing of paperboard. Compression, bending, and shear stresses are caused by the moving die and the walls of the cavity, while tension is mainly due to the in-plane holding force applied on the paperboard sheet. The direction of the tensile and compressive stresses in the deep-drawing of fibre composites is shown in Fig. 10.

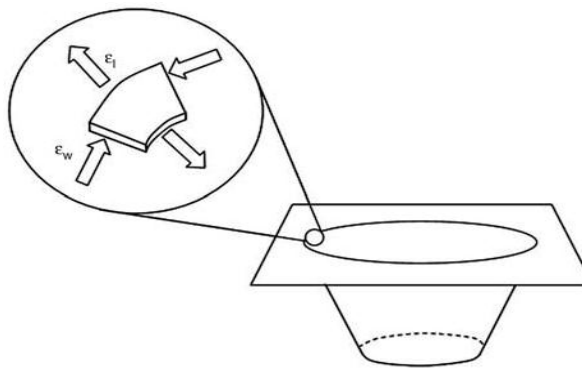


Fig. 10. Scheme of the directions of tensile and compressive strain in deep-drawing of fibre composites (adapted from Nakamura *et al.* 2009)

As can be seen in Fig. 10, the deep-drawing of a cup-like shape yields positive longitudinal strain (ϵ_l), in addition to radial tensile stress, and negative (compressive) transversal strain (ϵ_w), which is a common reason for wrinkling (Nakamura *et al.* 2009; Seo *et al.* 1992; Marynowski 2008). One method of studying the deformation of a material during drawing is grid strain analysis. This method has been applied to fibre composites (Martin *et al.* 1997; Bhattacharyya *et al.* 2003) and recently to paperboard (Östlund *et al.* 2011).

It can be summarized that the most important and commonly occurring modes of deformation for materials used in deep-drawing are tensile strain, shear strain, and compressive strain. The friction between the moving die, the forming cavity, and the

paperboard causes a notable amount of these stresses. When the paperboard cannot withstand these stresses, it leads to the formation of defects in the shape. The deep-drawing process should be performed in a way to avoid excessive stretching in the drawing direction, in order to prevent formed shape from the defects. However, this matter becomes challenging considering the advanced shapes with high depth.

UNDERSTANDING THE DEEP-DRAWABILITY OF PAPER-BASED MATERIALS

There is a need for the development of a systematic approach for evaluation of the applicability of paper-based materials for the deep-drawing process based on the mechanical properties of paper. At present, evaluation is based on empirical methods, which provide results only for a given shape under given conditions (Östlund *et al.* 2011; Post *et al.* 2011). The foremost basic property of paper, which is now used for the evaluation of mouldability, is elongation at a break; additionally compressive strength, shear strength, and metal paper friction are also important (Kunnari *et al.* 2007; Hauptmann and Majchak 2011; Östlund *et al.* 2011; Ankerfors and Lindström 2011; Post *et al.* 2011). The consideration of these properties with respect to the deep-drawing of paper would allow better understanding of which properties should be improved toward better performance in process.

Tensile Behaviour of Paper in Deep-Drawing

A considerable amount of knowledge of the tensile and fracture behaviour of paper is available, because the strength and fracture properties of paper have been an object of close attention in science and industry since the start of modern papermaking (Niskanen 1998; Mark *et al.* 2001; Uesaka *et al.* 2001; Uesaka 2005; Alava and Niskanen 2006; Ek *et al.* 2009). Stress-strain curves are used for the characterization of the behaviour of paper under tension. Most commonly, interest has been concentrated on tensile strength, while extensibility of paper has attracted less interest. The tensile behaviour of wet paper can demonstrate interesting aspects in plastic deformations of paper. The stress-strain curve for paper at 55% dryness is shown in Fig. 11.

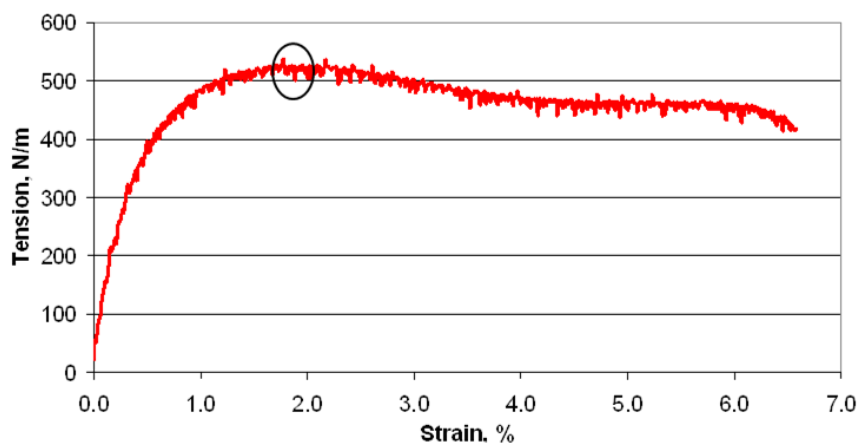


Fig. 11. The stress-strain curve of wet paper at 55% dryness, * the black circle on the figure refers to the point of highest tension, which is conventionally considered as the breaking point

The stress-strain curve of paper, however, depends on several factors related to the straining situation. As Fig. 11 shows, the catastrophic failure of paper is not necessarily imminent when the highest tension, that is, tensile strength, is reached (Robertson 1959; Kurki *et al.* 2004). The fracture behaviour of paper under tensile stress depends on the amount of elastic energy stored in the test sample and the energy needed for the propagation of the fracture line. If the amount of elastic energy stored in the test strip is low or the energy needed for the propagation of the fracture line is high, for example, due to a short testing span, or due to high fracture toughness or high moisture content, additional energy has to be brought into the sample by straining the sample further. Figure 11 shows that paper can be strained a considerable amount before the load-bearing ability of the sample is completely lost. This also indicates that the strain at break value is not always a suitable measure of the deformability of paper. The elongation should be measured at the point at which an essential portion of the tension has been lost.

Tensile strength does not play a crucial role in deep-drawing. Elongation potential is more important, and elongation should be recorded at a point where material still shows a considerable resistance to tension. The amount of tension that can be lost and the amount of the lost tension and stiffness that can be healed during the final stage of deep-drawing have not been studied yet. Another parameter that can be obtained from the stress-strain curve is tensile energy absorption (TEA). This can be used as an estimate of the amount of energy that the sample can absorb before fracture (Hernandez and Selke 2001). However, fracture toughness would be more specific for an evaluation of the energy needed for fracture propagation.

The combined effect of temperature and moisture on the elongation behaviour of paper

The presence of moisture softens the material and changes the character of the stress-strain curve of fibres and paper by reducing the elastic modulus and tensile strength. It increases the elongation due to increased plastic deformation. Increased temperature has a similar effect (Salmén and Back 1977; Back and Salmén 1989). By varying the moisture and/or temperature of paper-based materials, it is possible to get gains in elongation of around 2 to 2.5% points (Kunnari *et al.* 2007). The effect of the increased temperature is mainly related to the softening of the material. Water acts as a plasticizer, decreasing the softening temperature of cellulose and lignin, however, for the latter only to a minor extent (Goring 1963; Back and Salmen 1982; Waterhouse 1984; Shiraishi 1991; Haslach 2000; Alava and Niskanen 2003). The data on the softening of wood polymers (Salmén *et al.* 1982 and 1984; Salmén and Back 1989) allow the assertion that most paper-based materials are fully softened at a moisture content of around 6 to 8% and at temperature of 150 to 180°C. These conditions can be suggested as the reference points when choosing the temperature and moisture for deep-drawing. The effect of moisture and elevated temperature on elongation depends on the structure of the paper-based materials; the higher the density of the material, the lower the increase in elongation (Rhim 2010). Moisture and temperature also have an increasing effect on the stress relaxation rate of paper. Roughly 50% of the tension in wet paper can be released within 0.5 seconds (Kurki *et al.* 2004; Retulainen and Salminen 2009).

Effect of chemical composition on the tensile behaviour of paper

The chemical composition of pulp affects the tensile behaviour of paper-based materials; elongation and tensile strength of paper made from mechanical pulp are lower than for sheets made from chemical pulp (Seth 2005). Chemical composition also influences the amount of absorbed moisture. A high content lignin, which has relatively low ability to absorb moisture, and a low content of hemicelluloses reduce the positive effect of moisture on the elongation (Scallan 1974; Kunnari *et al.* 2007). Moisture at high levels also affects other mechanical and end-use properties of paper-based packaging materials (Sørensen and Hoffman 2003). In addition to deformation properties, it also affects the coefficient of friction. The moisture content of paper is often controlled in printing and converting in order to ensure quality of product (Johnson *et al.* 1983; Alava and Niskanen 2006). In deep-drawing, moisture and temperature adjusting can be used to improve formability and shape stability (Kunnari *et al.* 2007; Hauptmann and Majschak 2011).

Effect of fibre properties and fibre network structure on the tensile behaviour of paper

Curly fibres have a positive influence on the elongation of paper, but at the same time, they moderately decrease tensile strength (Page and Seth 1980; Mohlin *et al.* 1996; Gurnagul and Seth 1997; Joutsimo 2004; Joutsimo *et al.* 2005; Seth 2005; Kunnari *et al.* 2007). Curly and kinky fibres have the ability to distribute induced stresses onto a larger area better than straight fibres (Joutsimo *et al.* 2005). Page and Seth (1980) have indicated different states of curl-like fibre deformations that affect the stress-strain behaviour of fibres: dislocated and micro-compressed fibres, gently curled fibre, and notably curled and crimped fibres. Gently curled fibres most suit deep-drawing processes because they provide paper with the highest straining ability and can withstand high tensile loads. In the case of crimped fibres, the tensile strength is significantly decreased, and in the case of micro-compressed fibres, strain at break is very low (Page and Seth 1980). High-consistency refining (HCR) or a combination of HCR with low-consistency refining (LCR) are strategies to induce the desired curl in fibres and improve elongation (Page 1966; Jackson 1967; Averheim 2004; Gurnagul *et al.* 2009). The fibril angle of fibres is of significant importance for elongation; high fibril angle in fibres provides better elongation and the ability to withstand shearing deformation (Satyanarayana *et al.* 1982; Page and El-Hosseiny 1983; Lindström *et al.* 1998; Bledzki and Gassan 1999; Nishino *et al.* 2004; Ljungqvist *et al.* 2005; Donaldson 2008; Hänninen *et al.* 2011).

The drying phase can, to a significant extent, affect the paper properties. Shrinkage of fibres and paper during drying induces negative strain on paper, which can be further recovered to increase overall elongation of paper (Dumbleton 1972; Wahlström *et al.* 1999; Htun *et al.* 1989; Waller and Singhal 1999). Shrinkage causes axial compression of fibres, which occurs in the interfibre crossings, where it causes micro-compressions that are further transferred to the whole paper web (Page and Tydeman 1966; Nanko and Wu 1995; Seth 2005). Even though drying shrinkage is favourable to the elongation of paper, one should remember that it might lead to poor appearance due to a rough surface. Combined HC/LC refining, together with low-

restraint or unrestrained drying, is the state-of-the-art technology for producing highly extensible papers nowadays (Ankerfors and Lindström 2011).

Ability to Comply with Compressive and Shearing Deformation

Materials used in deep-drawing should have sufficient ability to withstand compressive and shearing deformations without damage (Bhattacharyya *et al.* 2003; Nino *et al.* 2007; Nakamura *et al.* 2009; Huang 2011). Shearing deformation can occur in the paper blank when it is sliding into the moulding cavity, while the edges of the blank are restrained by clamps. The ultimate value of the shear strength is not essential for deep-drawing; the ability to strain under shear deformation is more important (Stenberg 1999 and 2001; Nygård *et al.* 2009; Nygård and Malnory 2010). Shearing stress arises from friction, bending, tensile, and compressive stresses.

Under compressive stress, paper-based materials can experience negative straining. Compression of the sheet in the in-plane direction can release the tension stresses in the sheet, which were formed during restrained drying (Habberger and Whitsitt 1983; Considine *et al.* 2005). In order to avoid defects caused by compressive stress, fibres and fibre layers in the blank should be able to slide against each other without significant self-microbuckling (Cavlin and Fellers 1975; Cavlin 1988; Considine *et al.* 2005). Moisturizing of the blank decreases the compressive strength and resistance to compressive deformation of the material; however, at the same time compressive strain is increased (Kellicutt 1961; Considine *et al.* 1994; Van Eperen and Robbins 1994).

Friction

Friction is of significant importance for deep-drawing, since material is sliding under the certain pressure along the forming cavity. Even though the friction-induced stresses can be relatively low, they may couple with tensile, shear, and compressive stresses and increase the possibility of surface cracks and fatal fractures (Schwarzmann and Illig 2001; Westeneng 2001; Bhattacharyya *et al.* 2003; Peltonen 2006). The friction of paper-based materials originates from two main components: structural – surface topography and rigidity; and chemical – the nature of compounds in the layer and their moisture content (McDonald *et al.* 1996; Fellers *et al.* 1998; Johansson *et al.* 1998). For instance, metal-paper friction can be significantly decreased by residual fats and waxes contained in the paper (Back and Salmén 1989; Back 1991). It has been found that the surface roughness does not determine friction; for smooth paper, friction can be increased by a higher contact area (Fellers *et al.* 1998). Friction coefficient is affected by temperature, velocity, pressure in forming, smoothness, possible lubrication, coating type, chemical composition of the surface layer, filler content, filler type, and fibre orientation (Bhattacharyya *et al.* 2003; Akkerman and ten Thije 2009; Back 1983). In the case of the deep-drawing of paper-like material, static and dynamic paper-metal friction is important.

ESSENTIAL FACTORS IN THE DEEP-DRAWING OF PAPERBOARD

Deficient mechanical properties of the paperboard are reasons for the failures in deep-drawing. However, one should remember that the positive results depend not only on the selection of the material for the process, but also on equipment design and tailoring of the process parameters. A summary of the factors that affect deep-drawing process of paperboard is given in Table 1.

Table 1. Essential Factors in the Deep-Drawing of Paperboard

| Process Conditions | Paperboard Properties | Equipment Design |
|---------------------------|--|--------------------------------|
| Temperature | Tensile behaviour | Shape of the die and cavity |
| Retention time | Fracture toughness | Material of the die and cavity |
| Blank holder force | Shear deformation | Type of the drawing process |
| Drawing sequence | Metal-paper friction | |
| Moisturizing of the blank | Compressive strength and negative elongation | |
| Possible lubrication | Density | |

Process variables such as temperature, blank holding force, and moisturizing of the blank, can be varied for controlling the quality of the final product (Hauptmann and Majschak 2011). Retention time is the time when the paperboard is retained in the forming cavity; this parameter can be used to adjust shape stability and springing back. The sequence of operations in deep-drawing can be adjusted for the optimal distribution of temperature and moisture within the material. High friction in process may lead to the decolouration of the shapes and increase the probability of the fractures, lubrication agents can be used for decreasing the friction in forming (McClurg and Dulmage 1942; Ingraffea 1983).

The variables originating from the paperboard properties are determined in the major extent probability of fractures and appearance of the shape. For instance, fracture toughness of materials determines the propagation of cracks (Fellers *et al.* 1991). Elongation at break, and shear, tensile, and compressive properties are considered to be among the most important material properties in deep-drawing. Bulky materials tend to be more suitable for deep-drawing (Uggla *et al.* 1988).

Equipment and motion design variables are used for adjusting the process for a certain shape of the product and, at some point, for the design of stress distribution in the material during forming. Also, the type of the deep-drawing process can be varied according to the material used and the required shape of the product. One well known variation of classic deep-drawing is the hydroforming process, which has been already applied to paper (Post *et al.* 2011)

It is important to have a criterion or criteria, which would reflect the applicability of fibre-based materials in deep-drawing. Unfortunately, the criteria developed at the present time only deals with the shape of products versus the relative difficulty level of their manufacture. Such an approach does not incorporate material properties in the equations and therefore lacks practical usability. Among the existing criteria for the applicability of fibre-based materials in the deep-drawing process, the most notable are: forming degree (Scherer 1932) and mouldability factor (Haataja *et al.* 1991).

The mouldability of metals and plastics can be expressed by a limiting drawing ratio (LDR). This term means the largest ratio of blank to cup diameter that may be successfully drawn (Hosford and Caddell 1983). In the deep-drawing of metals, the surface area of the blank increases simultaneously with a decrease in the thickness of the material (Bogaerts *et al.* 2001). In contrast to metals, paperboard has a very limited ability to thin without a fatal failure in the structure; the surface area is mainly increased due to stretching of the fibres and the bonds between them. Thus, equations and formability criteria used with metals and plastics cannot be applied to paper-based materials.

POSSIBLE SOLUTIONS TO COMMON PROBLEMS IN DEEP-DRAWING OF PAPER-BASED MATERIALS

The primary problems in the deep-drawing of paper-based materials at present are: surface cracks and fractures, wrinkles, buckles, and shape inaccuracy. These problems are caused either by insufficient mechanical properties of materials or by the non-optimal process design and conditions. By knowing the reasons, it is possible to suggest the solutions for overcoming these problems. The suggested methods on how to avoid or reduce current problems in deep-drawing of paper-based materials can be found in Table 2.

Table 2. Suggested Solutions to Current Problems in the Deep-Drawing of Paper-Based Materials

| Problem | Possible reason(s) | Solution | Description | Effect |
|---------------------------------|--|---|--|--|
| Fracture of material in forming | Insufficient tensile elongation of material ^{1,2,3,4} | Adjusting of moisture and temperature in forming process ^{1,2} | Optimal Temperature of paperboard of 100 °C, and moisture content of 6 to 8% ^{1,5,6,7} | By the selecting optimal conditions, elongation can be increased up to 2-2.5% points ¹ |
| | | Induction of curl and microcompressions to fibres ⁴ | High-consistency refining, combination of high and low-consistency refining ^{6,8,9,10,11,12} | Curl and axial compression increase elongation potential of the single fibre, thus also elongation of fibre network ^{6,9} |
| | | Refining to higher SR number ^{2,4} | Drying shrinkage is increased and bonding in paper is improved ⁷ | Elongation can be as high as 10 to 15% in case of free drying ³⁵ |
| | | Compaction of fibre web ^{13,14,15,16} | Elongation is improved in the CD and MD due to compression of web ¹⁴ | Elongation of compacted paper can be as high as 15% in MD and 10% in CD ^{15,16} |
| | | Creping of fibre web ¹³ | Contraction and in-plane compression and crinkling of paper by means of the doctor blade ¹³ | The elongation of creped paper can be as high as 15 to 300%, in the direction of creping ¹³ |

| | | | | | |
|--|---|---|---|--|--|
| | | Vulcanization of fibres ^{17,18} | Crosslinking of cellulose chains by gelatinization ^{17,18} | Elongation can be as high as 12% ^{17,18} | |
| | | Hydroxypropylation and hydroxyethylation ^{19,20} | Improving flexibility, WRV, and bonding potential of fibres ^{19,20} | Elongation of restrained dried paper up to 8%, for the free dried paper up to 18% ^{19,20} | |
| | | Addition of latexes ^{21,22} | Replacement of fibre-fibre bonds with fibre-latex and latex-latex bonds ^{21,22} | Effect depends on the amount of added substance and its distribution, elongation can be as high as 40% ^{21,22} | |
| | | Other chemical modifications ²³⁻²⁶ | Impregnation, blending, grafting of cellulose with the different chemicals such as methylacrylate, diisocyanates, diesters etc. ²³⁻²⁶ | Up to 30% of elongation ²³⁻²⁶ | |
| | Insufficient deformation characteristics under combined shear, compression, and tensile loads | Using strong fibres with better bonding ability ²⁷ | More bonds between fibres provide better distribution of stresses in forming ^{7,27} | Cannot be quantified | |
| | | Motion and shape design ^{2,3} | Forming sequence and shape of the product can be adjusted so that stresses would be distributed evenly, preventing formation of zones where stresses are critical for given material ^{2,3} | Individual in each case | |
| | | Utilization of paper, where mechanical properties are not significantly affected by formation and anisotropy ^{2,3,4} | Even distribution of fibres within 3D structure of paper provides even distribution of stresses ^{2,3,4,28} | Laboratory handsheets without orientation perform better in deep-drawing ² | |
| | Wrinkling | Compressive deformation ^{2,30,31} | Increasing blank holder force ^{2,3,4} | Tensile load caused by blank holders is affecting the orthogonal compression of the blank, improving distribution of the wrinkles and reducing its size ^{2,3,4} | It was possible to decrease distance between wrinkles up to 80%, thus size and depth of wrinkles were also decreased ² |
| | | | Pre-creasing of the paper blank ¹ | Pre-creasing of blank is locally reducing stiffness and elastic modulus of the material ^{1,29} | This method is not reducing amount of wrinkles but force them to form in the designed points, thus amount of random wrinkles is minimized. |

| | | | | |
|------------------|------------------------------------|--|---|---|
| Shape inaccuracy | Elastic Recovery ^{2,3,33} | Utilization of flexible fibres in furnish (less amount of dried-in stresses) | Flexible fibres store less elastic energy, thus chemical pulp fibres have less spring back effect than rigid fibres of mechanical pulp ³² | Cannot be quantified. |
| | | Finding of an optimal forming temperature and moisture content of paper and adjusting of drawing sequence ² | Adjusting of the temperature to the given moisture content and drawing sequence, would allow to "freeze" shape better by the end of forming ^{2,34} | Conditions and effect are individual in each case |

*References: 1-Kunnari et al. 2007; 2-Hauptmann and Majschak 2011; 3-Östlund et al. 2011; 4-Post et al. 2011; 5-Peltonen 2006; 6-Seth 2005; 7-Alava and Niskanen 2006; 8-Page et al. 1985; 9-Joutsimo et al. 2005; 10-Le Ny and Messner 2007; 11-Ankerfors and Lindström 2011; 12-Sjöberg and Höglund 2007; 13-Hernandez and Selke 2001; 14-Holik 2006; 15-Cariolaro and Trani 2000; 16-Cariolaro.com 2011; 17-Künne et al. 2011; 18- Künne and Dumke 2012; 19- Vuoti et al. 2012; 20- Didwania 1968; 17-Waller and Singhal (1999); 21-Waterhouse 1976; 22-Alince 1977; 22-Salmen et al. 1984; 23-Rezai and Warner 1997; 24-Borges et al. 2001; 25-Wang et al. 2007; 26 - Cyrus et al. 2009; 27-Seth (1995); 28-Bhatarachyya et al. 2003; 29-Beex and Perlings 2009; 30-Arcelomitall, 2011; 31-Hosford and Caddell; 32-Waterhouse (1985); 33-Whitsitt 1987; 34-Golzar and Ghaderi 2009; 35-Gates and Kenworthy (1963)

As can be seen from Table 2, the suggested solutions to overcome problems in deep-drawing of paper-based materials are simple, but they are not generally easy to realise. However, all of them can be implied in the current papermaking process without cardinal changes. By varying process conditions and inducing mechanical treatments of fibres, it is possible to improve the formability of paper-based materials to an extent that would suit the deep-drawing process. The chemical modification of fibres is another strategy, but it may require the introduction of new stages in the current papermaking process.

SUMMARY

Content of the paper can be summarized as follows:

1. In the deep-drawing process, the paperboard is subjected to a combination of tensile, shear, and compressive stresses. However, the tensile, shear, and compressive strengths are not crucial for deep-drawing; more important is the ability of the material to deform under these stresses without failure.
2. A notable part of the tensile, shear, and compressive stresses in deep-drawing is caused by frictional forces between the blank, die, and forming cavity. This is an indication of the important role of frictional properties of the surfaces.
3. An inadequate combination of stresses and material properties causes flaws in the formed product. Typical defects are surface cracks and fractures, wrinkles, ears, and buckles of the formed shapes. Additionally, deflexion of the formed shapes can be caused by spring-back due to excessive elastic recovery.

4. The deep-drawing conditions (including the time, temperature, and moisture conditions) and the required shape of the product determine, to a significant extent, the applicability of certain paperboard materials to the process.
5. The formability of the paper-based materials originates from the properties of fibres, fibre bonds, and the structure of the fibre network formed in the papermaking and converting process. Thus formability can be improved by introducing suitable changes to any of those factors.

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PUBLICATION II

**Boosting the Extensibility Potential
of Fibre Networks: A Review**

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Boosting the Extensibility Potential of Fibre Networks: A Review

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Production of paper-based packaging is growing at the present moment and has great future prospects. However, the development of new packaging concepts is creating a demand for an improvement in the mechanical properties of paper. Extensibility is one of these properties. Highly extensible papers have the potential to replace certain kinds of plastics used in packaging. Extensibility is also important for the sack and bag paper grades and for runnability in any converting process. This paper reviews the factors that affect the extensibility of fibres and paper, and discusses opportunities for improving the straining potential of paper and paper-like fibre networks. It is possible to classify factors that affect extensibility into three main categories: fibre structure, interfibre bonding, and structure of the fibre network. Extensibility is also affected by the straining situation and the phase state of the polymers in the cell wall. By understanding the basic phenomena related to the elongation, and by combining different methods affecting the deformability of fibre network, extensibility of paper can be raised to a higher level.

Keywords: Extensibility; Fibres; Bonding; Network; Deformation; Polymers; Papermaking

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INTRODUCTION

Extensibility is one of the undeservedly disregarded properties of paper. It is considered to be important mainly for sack and bag paper grades (Hernandez and Selke 2001). Typically, papermakers and converters mainly operate with tensile strength, bending stiffness, tear strength, *etc.* However, recent trends in the development of paper-based packaging materials indicate that, in the production of advanced 3D shapes, extensibility of paper is gaining a new, key role that trumps the importance of other mechanical properties (Kunnari *et al.* 2007; Östlund *et al.* 2011; Post *et al.* 2011; Vishtal *et al.* 2013; Svensson *et al.* 2013; Larsson *et al.* 2014). In 3D-forming processes with fixed paperboard blank, extensibility is the main parameter determining the depth of the shapes produced and the formability of such paper in general (Vishtal *et al.* 2013). Novel paper-based materials with high extensibility are broadening the area of utilization for paper, and may help to bring the paper industry back onto a growth trajectory in some grade categories.

Despite the importance of extensibility, most of the paper-based materials that are produced at present have poor extensibility. Most paperboards have extensibility in the range of around 1 to 4% and 3 to 6% in MD and CD, respectively. Such values are obviously too low for the development of many new applications. The question is how far and by which means the extensibility potential of paper can be further boosted?

The extensibility of paper has been specifically addressed by only a few researchers (Stenberg 1947, 1949; Brecht and Erfurt 1960; Dodson 1970; Seth 2005). It has been commonly studied together with the other stress-strain properties of paper. Therefore, an extensive summary of the previous fundamental research together with the analysis of the methods for the improvement of extensibility can be a useful addition to the current knowledge in this field.

This paper aims to review extensibility as a mechanical property of paper, and discusses the factors that control it. The influence of the straining situation is also considered. The overarching goal is to find tools to increase the extensibility of paper to a qualitatively new level. The methods that can be used for the improvement of extensibility are comprehensively reviewed, with the focus on the industrial applicability of such methods.

GENERAL OUTLOOK ON THE EXTENSIBILITY OF PAPER

Stress-strain Behaviour of Paper

The extensibility of paper can be defined as the ability of paper to increase its linear length, due to elastic, viscoelastic, and plastic deformations under the action of external mechanical forces. The most widely studied type of mechanical deformation in paper is tensile deformation, where extensibility is determined as the strain at break value of the stress-strain curve (Fig. 1.).

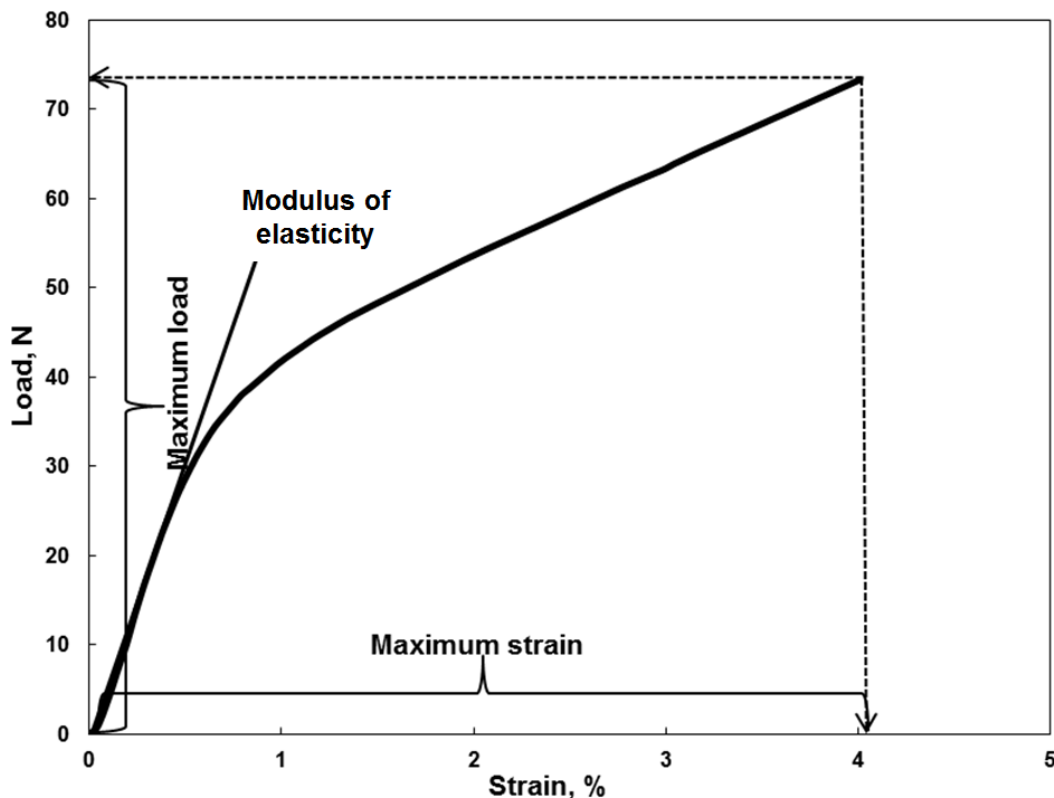


Fig. 1. A typical stress-strain curve for isotropic restrained-dried paper made from softwood pulp

The strain at break value of paper is determined at the point of maximum tension of the stress-strain curve (Fig. 1). Usually, at this point fracture of paper occurs. In this

respect, strain at break value is closely associated with the tensile strength of paper, and factors that affect the tensile strength are likely to control the strain at break value as well. However, strong paper may be brittle, while extensible paper usually exhibits a decrease in tensile strength with increase in extensibility.

The extensibility of paper is defined by the fracture point. By considering the stress-strain curve of paper it is possible to suggest that extensibility is dependent on the same factors that are in charge for the shape of the curve and the fracture point of paper. However, the shape of the stress-strain curves may vary to a great extent in accordance with the fibre network properties and the straining conditions (sample dimensions, temperature and moisture content, strain rate, *etc.*). The influence of the straining conditions can be demonstrated via the stress-strain curve for non-immediate rupture of paper depicted in the Fig. 2.

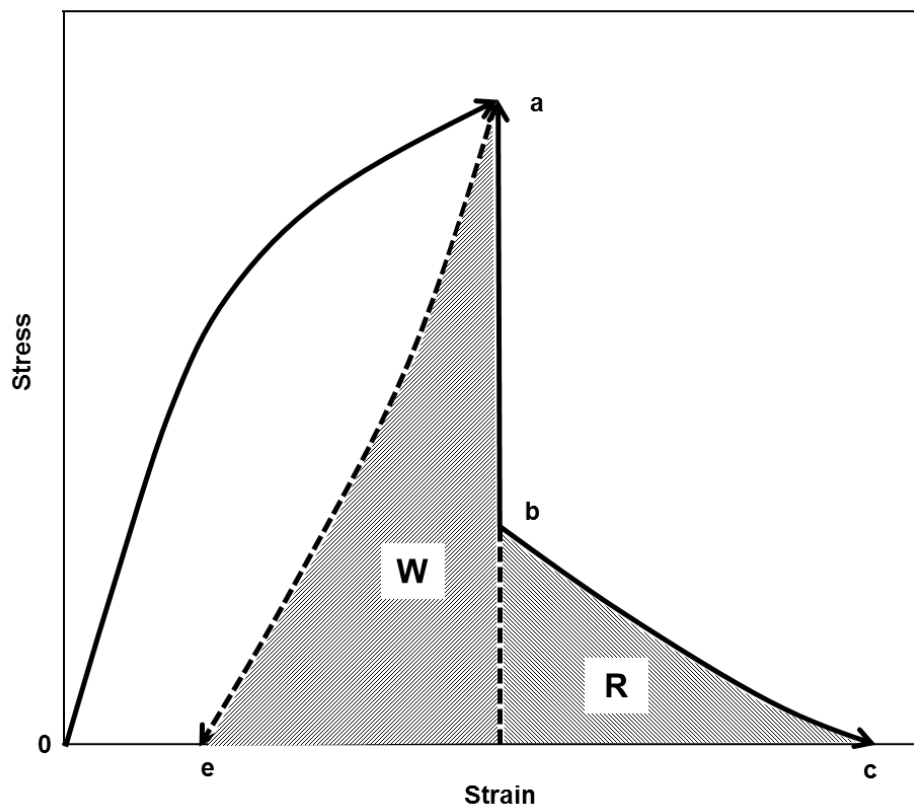


Fig. 2. A stress-strain curve of paper with a non-immediate rupture (redrawn from Goldschmidt and Wahren 1968)

The development of fracture in paper under tensile stress depends on the amount of elastic strain energy stored in the test sample (area W in Fig. 2), and the amount of energy needed for the propagation of the fracture line to complete the break. If the test specimen is sufficiently long and the elastic strain energy is large, then a brittle, catastrophic failure occurs. If the amount of elastic energy stored in the test strip is low or the energy needed for the propagation of the fracture line is high, for example, due to a short testing span, high fracture toughness or high moisture content, additional energy (area R) has to be delivered into the sample by further straining so as to complete the break (Robertson 1959; Goldschmidt and Wahren 1968; Kurki *et al.* 2004). It can be assumed that, in many converting and forming processes, the apparent testing span is actually shorter than in the standard tensile test.

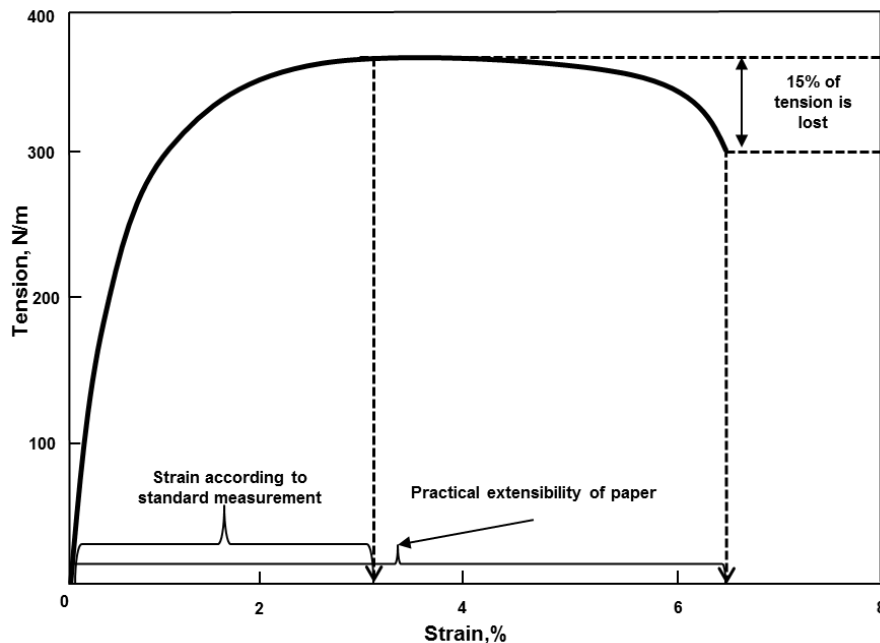


Fig. 3. A stress-strain curve of rewetted paper (55% dryness) prepared from hydroxypropylated pulp (material produced in Vuoti *et al.* 2013)

From the example in Fig. 3, we can observe that the fracture of paper does not always occur at the point of maximum load. For example, wet paper can often be strained much further, and only a part of the tension is lost. Such behaviour is close to that of truly ductile materials.

This raises the question of how the extensibility of paper should be defined – at the point of maximum tension or at the point where a significant part of the tension is lost?

This is especially relevant for various converting processes, including 3D-forming. In these cases, extensibility should not be evaluated only through the maximum tensile strength of paper, but rather through the typical loading situation in accordance with the end-use of the paper. For the sack paper grades, extensibility is usually evaluated in connection with TEA (Tensile Energy Adsorption) *i.e.* gain/loss in strength or strain is compared with gain/loss in TEA.

The deformation of paper is usually divided into elastic, viscoelastic, and plastic components. In forming 3D structures, a large plastic deformation is preferred in order to avoid the springing back and deflexion of shapes (Vishtal and Retulainen 2012). With increase in overall deformation, the extent of all strain components also increases. However, the relative share of plastic deformation increases and the relative share of elastic deformation decreases with increase in overall deformation (Brecht *et al.* 1971; Skowronski and Robertson 1986). The development of the plastic and elastic components in overall deformation of paper is shown in Fig. 4, where *x*-axis represents overall strain in %-points and *y*-axis is for %-points of elastic or plastic deformation. Elastic deformation is defined as the immediately recovered component while plastic deformation component is approximated to be the rest of the deformation.

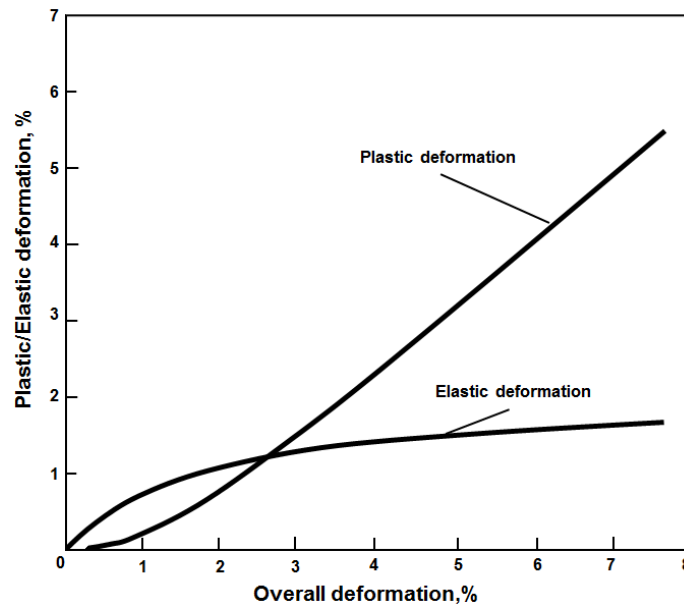


Fig. 4. The amounts of the apparent elastic and plastic deformations in overall tensile deformation of lightly creped paper for both MD and CD (redrawn from the data of Brecht *et al.* 1971)

When using only two components, apparent elastic and apparent plastic deformation (which also includes the viscoelastic deformation), it is possible to see that, at overall strains of 2 to 3% points, the amount of apparent plastic and elastic deformations are equal, and after that the apparent plastic component increases linearly. The elastic strain component is present at all deformation levels, but the plastic component starts to appear only at 0.2 to 0.3% strain. At strains higher than 3% the apparent plastic deformation is the dominating component, and it increases linearly. It is also interesting that, despite the different paper structures and different strains at break, the plastic deformation of several papers grades even in machine and cross machine directions was found to follow the same curve (Brecht *et al.* 1971).

Factors Affecting the Shape of Stress Strain Curve and Final Failure

Qualitatively, the non-linear shape of the stress-strain curve and plastic deformation of paper has been shown to depend mainly on the properties of the fibres in paper. It should be noted that the properties of fibres in paper are different from those of individual fibres because during the papermaking process the fibre properties are modified by wet straining and drying stresses. Ebeling (1976) stated that in well bonded paper “the plastic region in the load/elongation curve is not caused by the breakage of fibre-fibre bonds but is connected to the significant irreversible intra-fibre deformation on molecular and supramolecular level” (Ebeling 1976). The term “efficiency factor” has been used when analysing the shape of the stress strain curve (Seth and Page 1981; Coffin 2009, 2012). When isotropic paper made from a certain fibre material gives higher extensional stiffness, the material has a higher efficiency factor. The efficiency factor is closely related to the load-bearing activity of the material (Lobben 1975). When a fibre network has a higher load-bearing activity, the efficiency factor is also increased and the slope of the stress-strain curve is steeper. Seth and Page (1981) showed with well-bonded sheet that in cases where the slope of stress-strain curve and the initial load bearing activity of the material is changed, for example due to beating, wet pressing, or bonding agent, the stress-strain curves normalised by the efficiency factor (that is calculated from

the elastic moduli) can be transposed to an apparently single curve. Bonding plays only a minor role; this is based on the statement that the stress-strain curve of paper is related to the stress strain curve of fibres through the factors that take into account the orientation of fibres and the efficiency of stress distribution of fibres. This suggests that, with a certain pulp, the straining behaviour of the material that actually bears the load is the same, although the amount of the load bearing material is initially different, and only the end point of the stress-strain curve, *i.e.* the fracture point, varies. The load-bearing activity (and efficiency factor) of the material, however, can change during straining, when the bonding level is low. Then even the stress-strain curves normalised by efficiency factor do not superimpose when transposed (Seth and Page 1981).

Skowronski and Robertson (1983) have concluded that, in addition to elastic, viscoelastic, and plastic behaviour, activation, deactivation, and failure phenomena are also needed in order to explain the tensile behaviour (including stress-strain cycling and relaxation) of paper. Activation of paper under tension can be related to the straightening of fibre segments and re-arrangement of the fibrillar material in the fibre wall, especially in dislocated and microcompressed areas. Straining of wet paper before drying is also known to be an efficient method to activate the load-bearing ability of fibre material (Parsons 1972).

During the straining of paper internal fractures take place. The most fractures are micro-failures and related to debonding. Debonding, *i.e.* partial or complete fracture of fibre-fibre bonds, is known to take place during straining of paper (Page *et al.* 1962). However (Ebeling 1976; Seth and Page 1981), the plastic behaviour of paper is not caused by the debonding, but is related to the irreversible intrafibre deformations. Although fibre bonding and debonding have only a minor effect on the shape of the stress-strain curve with well-bonded papers, in less bonded papers the debonding eventually plays a more important role in reducing the efficiency factor and altering the shape of the stress-strain curve. Debonding creates stress concentrations that may lead to the initiation of the final failure (Helle 1965). The first mechanism initiating the final macroscopic failure of paper is either a burst of bond failures or fiber failures (Alava and Niskanen 2006). This conclusion has also gained support from recent stress-strain simulations of paper (Borodulina *et al.* 2012). Additionally, other factors such as structural heterogeneity or unevenness (bad formation, holes, *etc.*) can also cause uneven stress distributions and lead to premature initiation of the final fracture (Nazhad *et al.* 2000).

To conclude this section, it can be claimed that especially in well-bonded sheets the general shape of the stress-strain curve is mainly determined by the properties of fibres in the network and their activity to bear load; but the end point of the curve is also determined by factors that trigger the final failure. Therefore the factors that affect the extensibility of paper are related to properties of fibres, fibre bonds, and network structure.

FACTORS THAT CONTROL THE EXTENSIBILITY OF PAPER

Numerous factors affect the extensibility of paper. In his excellent review paper Seth (2005) stated that the extensibility of paper depends on two principal components: fibres and interfibre bonding. However, from the point of controlling the extensibility of paper, we should also include the network structure as a separate factor.

It is known that the fibre network and properties of individual fibres in the fibre network are modified by wet straining and drying stresses (Retulainen *et al.* 1998, Wahlström and Fellers 2000). But factors that modify the fibre network also affect the properties of fibres and bonds. Extensible fibres might be connected by strong bonds, but yet the paper would not be extensible due to restrictions arising from the fibre network structure. This fact is illustrated by conventional papermaking process in which the wet draws, fibre orientation anisotropy, and restrained drying limit the extensibility in MD (machine direction) to the range 1 to 3%, while in CD (cross direction) paper can be strained two times more than in MD. The straining conditions have a major impact on the overall elongation of paper as well as on the share of elastic and plastic components of deformation.

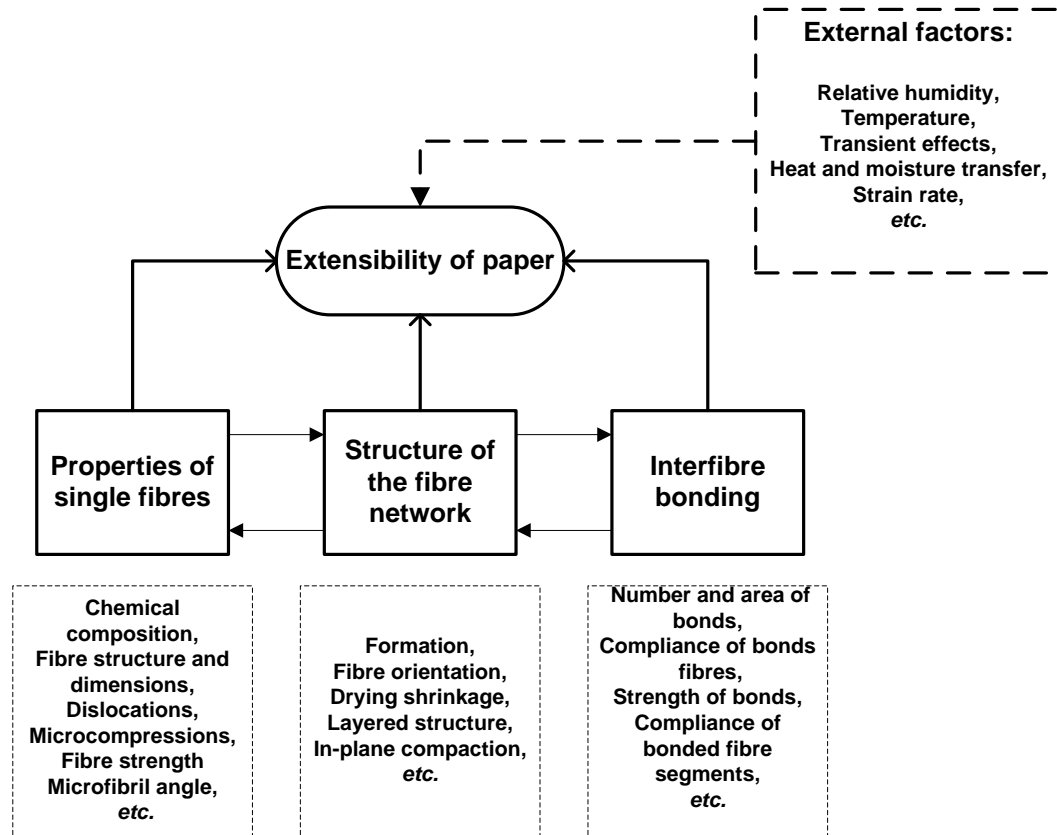


Fig. 5. Factors that affect the extensibility of paper

The scheme in Fig. 5 shows the three factors that affect the extensibility of paper. This scheme emphasizes the role of straining conditions in the overall extensibility potential of paper. Even though these factors are presented individually, they are in close interaction with each other in papermaking and converting processes. For instance, changes in the structure of single fibres due to high-consistency treatment (causing curl, kinks, dislocations, and axial microcompressions) affect the formation of paper and properties of interfibre contacts and the deformation behaviour of the whole network. And, on the other hand, drying shrinkage of the fibre network affects individual bonds and fibres.

In order to boost the extensibility potential of paper to a maximum level, one should design and adjust treatments in such way that they would complement each other.

Properties of Single Fibres that Affect Extensibility

Fibres are the primary constituents and load-bearing elements of paper. They have a strong influence on all the mechanical properties of paper, and its extensibility is not an exclusion from this rule. Wood fibres are generally axially stiff and non-extensible. The typical strain of wood pulp fibres is about 3 to 6%, but juvenile wood fibres may have extensibility up to 20%-points (Hardacker and Brezinski 1973; Bledzki and Gassan, 1999). Also, certain non-wood and synthetic fibres have extensibility varying over a broad range, *i.e.* 50 to 800%. However, extensible fibres are not necessarily able to form an extensible paper. In order to fulfil this requirement, fibres should be able to form sufficiently strong bonds and network structure with even stress distribution (Seth 2005; Zeng *et al.* 2013). The bonding potential of fibres depends on morphological, chemical, and mechanical properties. The features of single fibres, which are of high importance for extensibility, are discussed below.

Fibrillar angle

The morphological features of fibres are the key factors determining their mechanical properties. Cellulose, the main chemical component of fibres, is stiff in an axial direction, with a theoretical modulus of the chain around 250 GPa (Vincent 1999). When the individual cellulose chains form a cellulose I β crystallite structure, the stiffness decreases to 140 GPa (Cintron *et al.* 2011). The stiffness is further decreased to around 55 to 65 GPa, when the cellulose I β nanostructures are assembled into microfibrils (Sun *et al.* 2014), and finally to 20 to 40 GPa for fibres (softwood latewood) (Page and El-Hosseiny 1983; Altain 2014). It should be noted that the different cellulose crystalline allomorphs have different stiffness; it is decreasing in the order of Cel I (140 GPa) > Cel II (88 GPa) > Cel III (87GPa) > Cel IV (58GPa) (Nishino *et al.* 1995).

The decrease in stiffness and the corresponding increase in the extensibility of fibres in comparison with the cellulose molecule is partially attributed to the spring-like alignment of the microfibrils in fibres. This alignment is described by the microfibrillar angle (MFA) that is determined as the angle between the axis of fibre and the direction of the cellulose fibrils in the S2 cell wall layer (Barnett and Bonham 2004) (Fig. 6). The increase in elongation of fibres due to high MFA is explained by the untwisting of the spring-like structure, sliding of fibrils under shear forces, and higher flexibility of such fibres (Horn 1974; Page and El-Hosseiny 1983; Gurnagul *et al.* 1990; Martinschitz *et al.* 2008).

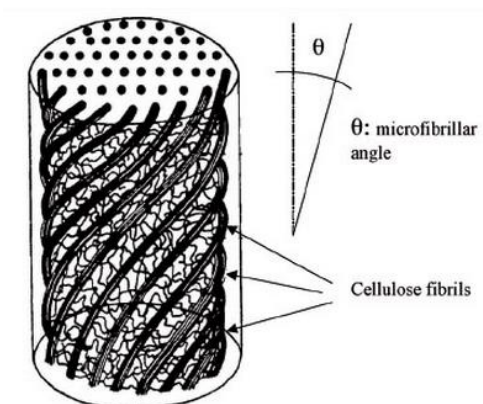


Fig. 6. Graphic representation of the MFA in fibre (Hearle 1963)

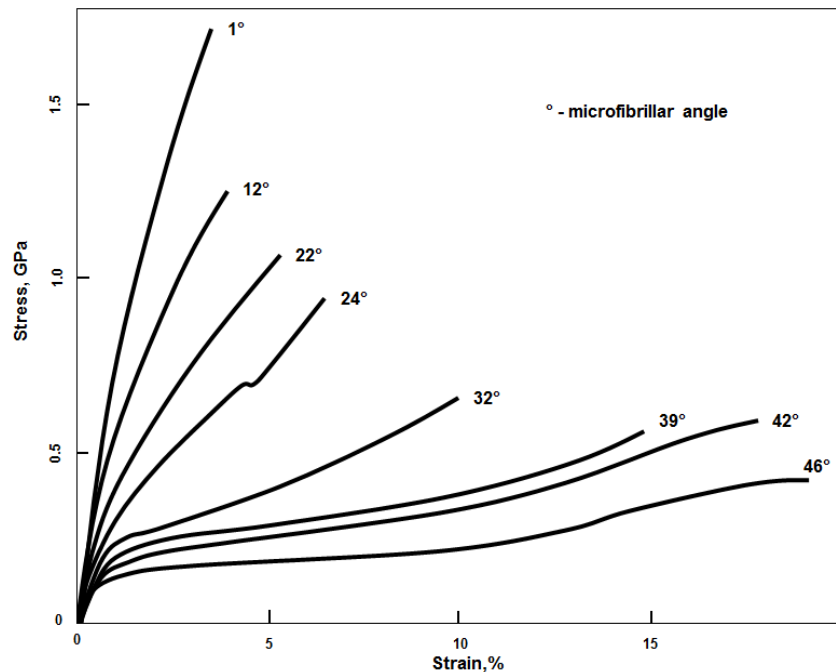


Fig. 7. The relation between MFA and extensibility of chemical pulp fibres of black spruce (redrawn from the data of Page and El-Hosseiny 1983)

Fibres with high MFA tend to have higher extensibility and lower stiffness than fibres with low MFA (Fig. 7), which is explained by unwinding of the structure of fibres with high MFA under the action of shear forces (Page and El-Hosseiny 1983). Juvenile softwood fibres have higher extensibility than latewood fibres, which is explained by the higher fibrillar angle of juvenile fibres (Wimmer 1992; Lindström *et al.* 1998; Reiterer *et al.* 1999; Ljungqvist *et al.* 2005; Donaldson 2008; Hänninen *et al.* 2011). For instance, extensibility of latewood fibres of *Picea Abies* is around 2%-points (MFA 5°), while for springwood fibres it is around 13%-points (MFA 50°) (Reiterer *et al.* 1998). It was also shown that the fibres with high MFA in *Acacia mangium* have lower glass transition temperature, which indicates certain differences in the composition and arrangement of wood polymers in the cell in comparison with latewood fibres (Tabet and Aziz 2013).

An additional factor contributing to the higher extensibility of paper made from springwood fibres is the higher longitudinal drying shrinkage (Dong 2009). Although fibres with a high fibril angle have generally lower axial stiffness, they do have better resistance to the shear forces than fibres with a low fibril angle (Satyanarayana *et al.* 1982; Page and El-Hosseiny 1983; Bledzki and Gassan 1999; Nishino *et al.* 2004). Interestingly, a trend analogical to the MFA of wood fibres can be observed with viscose fibres, in which the molecular orientation in major extent determines the elongation of the fibres (Lenz *et al.* 1994).

Fibre fraction with high MFA can be obtained by hydrocyclone separation, which allows separation of springwood and latewood fibre in an efficient way. This treatment was applied and found to be efficient both for softwood (Paavilainen 1992; Vomhoff and Grundström 2003) and hardwood pulps (Blomstedt and Vuorinen 2006). However, this method separates fibres according to their hydrodynamic properties, which are not always correlated with MFA. Utilization of the first-thinning wood (Kärenlampi and Suur-Hamari 1997) or tree species such as *Juniperus communis* (Hänninen *et al.* 2011) for pulping is also an option for obtaining extensible fibres with relatively high MFA. Recently, a method for production of cellulose nanofibrils filaments with controlled fibril

alignment along the filament axis was proposed (Håkansson *et al.* 2014). In this case fibrillar alignment is artificially adjusted by process parameters such as flow velocity, flow acceleration and deceleration, *etc.*, which makes it possible to obtain fibres with desired stress-strain properties. Mechanical properties of the artificial fibres are in line with the natural wood fibres with the same degree of alignment (*i.e.* MFA) (Håkansson *et al.* 2014). This is an interesting approach allowing the design of mechanical properties of fibres for a certain applications.

Chemical composition of fibres

Chemical pulp fibres are composed of cellulose and hemicelluloses; lignin is present in very small amounts (less than 0.5%). However, unbleached (2 to 5%) and especially mechanical pulps (5 to 25%) have significantly higher lignin content (Alén 2000). The alternation in the relative share and internal structure of different natural polymers which constitute fibres is of great influence for the mechanical properties of paper (Spiegelberg 1966).

Cellulose is the stiffest chemical component of fibres. Basically, the elongation of cellulose takes place through two mechanisms: by elastic axial elongation of the cellulose molecules and by irreversible, time-dependent slippage between cellulose molecules (Altaner *et al.* 2014). The axial elongation of the cellulose molecule is, in addition to covalent bonds, also dependent on the intramolecular hydrogen bonds and intermolecular hydrogen bonds. The slippage between molecules is dependent on the intermolecular hydrogen bonds. In fibres, slippage is more likely to occur between fibrils and fibril bundles, which are held together by amorphous cellulose and hemicellulose.

Cellulose in papermaking fibres is present in two states, crystalline and amorphous, with a respective ratio of around 3:1 for bleached wood pulp (Ward 1950; Fiskari *et al.* 2001). In addition to fully amorphous and crystalline cellulose, the regions with not fully amorphous cellulose can be found, and they are typically regarded as the paracrystalline regions (Kulasinski *et al.* 2014).

Crystallinity of cellulose in fibres depends to a great extent on the origin and type of the processing utilized for fibres. Increase in the crystallinity of cellulose increases the strength and stiffness of the fibres; at the same time, it negatively affects their extensibility and flexibility (Ward 1950; Lee 1960; Parker 1962; Thygesen 2006). High stiffness and respective low extensibility of crystalline cellulose regions is likely to originate from the O3'H...O5 and O2H...O6' intermolecular hydrogen bonds and their interaction with the covalent bonds (Altaner *et al.* 2014). The hydrogen bonds are also responsible for the moisture sensitivity of the cellulose molecules and their extensibility. The mechanical properties and structure of the amorphous cellulose is known to a much smaller extent than that of crystalline cellulose. Generally amorphous cellulose is characterized by the absence of long range order and greater disorder in the orientation of the cellulose chains (Fink *et al.* 1987; Muller *et al.* 2000). The stiffness of the crystalline and amorphous parts of the cellulose differs significantly (220 GPa for crystalline vs. 10.4 for amorphous) (Sun *et al.* 2014). This great difference means that the softer amorphous part mainly determines the extensibility of cellulose (Fig. 8).

An increase in the proportion of amorphous cellulose in pulp is accompanied by an equivalent increase in extensibility and a decrease in elastic modulus, as is schematically depicted in Fig. 8. The same assumption is valid for the regenerated cellulose fibres. For instance, a decrease in the degree of crystallinity of regenerated cellulose fibres (Lyocell®) from 0.63 to 0.5 improves the extensibility of the fibres from 11 to 17% (Lenz *et al.* 1994). It is important to note that the actual nature of crystallinity is different

for cellulose I (native fibres) and cellulose II (regenerated cellulose). In the Cel I cellulose, chains are aligned parallel, meaning that the reducing ends are all facing the same direction. However, upon swelling and dissolution, resulting in the transformation to the Cel II form, they develop an antiparallel arrangement, which is more thermodynamically stable (Kim *et al.* 2006). The anti-parallel arrangement of the cellulose chains leaves more space for alignment upon straining, and thus explains the higher elongation and lower stiffness of regenerated cellulose in comparison with the native form.

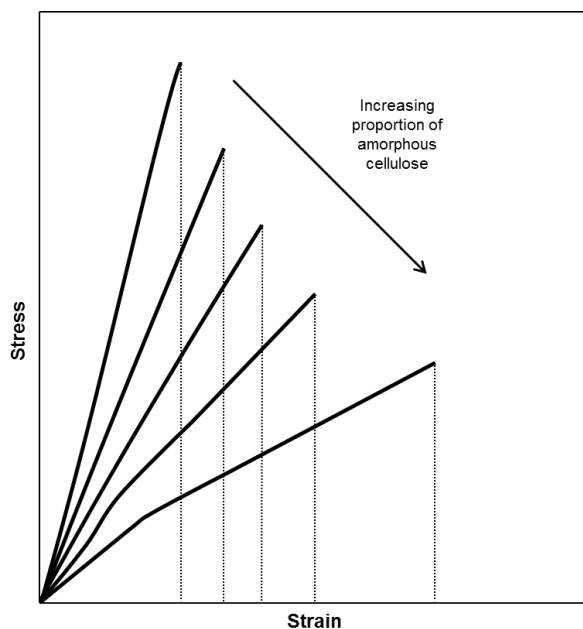


Fig. 8. Schematic representation of the influence of the increase in amorphous cellulose content on the extensibility and strength of pulp relation between fibres (redrawn from the data of Page 1983)

The crystallinity of the cellulose can be reduced by means of several chemical treatments; for example, concentrated acid treatment (Ioelovich 2012), ZnCl_2 impregnation (Patil *et al.* 1965), or ethylamine decrystallization (Parker 1962). Also, the structure of crystalline cellulose can be transferred to a less-ordered one by treatment in water under severe conditions (320°C, 25 MPa) (Deguchi *et al.* 2006, 2008). Electronic beam irradiation also can be used to reduce crystallinity of cellulose. For instance a dose of irradiation of 200 kGy has been found to reduce crystallinity of MCC, flax, cotton, and viscose by up to 12% (Alberti *et al.* 2005). At the same time, degradation of hemicelluloses and condensation of lignin is observed (Chung *et al.* 2012). The amount of energy needed to decrease the crystallinity by a certain value greatly varies in accordance with sample origin, type of the pre-treatment applied, moisture content, *etc.* (Driscoll *et al.* 2009). Irradiation has a considerable effect on the structure of cellulose; it causes chain scission and thus decreases DP (Saeman *et al.* 1952) and oxidizes cellulose by introduction of carboxyl and carbonyl groups (Morin *et al.* 2004; Bouchard *et al.* 2006; Henniges *et al.* 2013). Decrease in crystallinity is likely to be caused by substitution of hydroxyl groups with the oxidized ones, along with a consequent weakening of intramolecular and intermolecular hydrogen bonding (Henniges *et al.* 2013).

However, reducing the cellulose crystallinity cannot be regarded as a feasible method for obtaining of highly-extensible fibres due to the associated costs of chemical treatments and rather poor selectivity in case of irradiation.

Xylans and mannans are the most common hemicelluloses in hardwood and softwood pulp fibres, respectively (Alén 2000). Hemicelluloses are amorphous polymers with a relatively low degree of polymerization (50 to 300) and elastic modulus (7 GPa) and significantly lower softening temperature. This is also reflected in the extensibility of hemicellulose; for instance strain at break of films prepared from arabinoxylan can be as high as 15% (Mikkonen *et al.* 2012).

Hemicelluloses improve the bonding potential of fibre and thus the extensibility of paper. According to Spiegelberg (1966) and Leopold and McIntosh (1961), high hemicellulose content in chemical pulp fibres is favourable to the extensibility and strength, while Helmerius *et al.* (2010) have not observed any decrease in the elongation of paper even after removal of 60% of the xylan from birch pulp. Obermanns (1934) in his pioneering work has claimed that there is a certain optimum for hemicellulose content in respect to the strength of paper, which then depends on the origin of pulp. Henriksson *et al.* (2008) showed that the MFC films with high hemicellulose content had the highest tensile strength and strain, which was attributed to decreased porosity of such films. Hemicellulose removal has also been found to relate to hornification (loss of the swelling ability due to drying) of fibres (Oksanen *et al.* 1997). The extensibility of fibres is often related to their swelling ability (WRV) and the corresponding shrinkage potential of fibres. Hemicellulose-rich pulps have a higher swelling ability. However, hemicellulose removal by hot water extraction has been shown to increase the WRV of fibres and the elongation of paper (Saukkonen *et al.* 2011). The explanation may be that, in this case, the fibres were not hornified and dried after the hemicellulose removal. Removal of the hemicelluloses makes dried and rewetted fibres stiffer, which results in a reduced amount of fibre-fibre contact and lowers the density of dry paper (Spiegelberg 1966). At the same time, the tensile elastic recovery of alkaline-extracted birch fibres decreases with the removal of xylan, *i.e.* deformation of fibres tends to be more plastic and come from rearrangements of cellulose microfibrils (Spiegelberg 1966). Cottrall (1954) reported that the mannan is more effective in the strength improvement of pulp than xylan, which is explained by higher amount of available non-acetylated hydroxyl groups per unit of mannose.

However, when it comes to the question of how low or high content of hemicelluloses in fibres affects the extensibility of fibre, there is no straightforward answer. It is likely that the hemicelluloses do not directly influence the elongation of fibres themselves but favour the elongation of paper.

The influence of lignin content on the extensibility of fibres and paper is of concern with mechanical, chemomechanical, semichemical, and unbleached pulps. It was found that selective removal of lignin from wood fibres improved their elongation by around 20%; notably this effect was obtained already when 25% of total lignin was removed from fibre (Zhang *et al.* 2013). Further delignification did not improve extensibility or the tensile strength of fibre. The effect of lignin removal might be associated with the rearrangement of the microfibrillar structure due to slippage of fibrils in fibres, besides the fact that lignin is actually a stiff and non-extensible polymer in dry state (Zhang *et al.* 2013). High lignin content also negatively affects the extensibility of paper; mechanical pulps have much lower elongation than chemical pulps (Hatton 1997). In mechanical pulps, lignin is still present in the cell wall of fibres, which also negatively affects the fibre-fibre bonding and flexibility of fibres, and as a consequence the density

of fibre network. Unbleached chemical pulp fibres (both kraft and sulphite) are capable of forming fibre-fibre bonds as strong as bleached ones (Mayhood *et al.* 1962; McIntosh 1963; Fischer *et al.* 2012). Hartler and Mohlin (1975) claimed that the maximum bond shear strength between fibres occurred at lignin contents of 7% for unbleached kraft and 10 to 12% for unbleached sulphite. In the practice of sulphite cooking, it is sometimes observed that lignin may adsorb on the surface of fibres restricting the formation of effective bonds, and thus negatively affect extensibility (Paasonen and Koivisto 1970; Koljonen *et al.* 2004). Additionally, the area of bonding and the strength of bonds should be considered. Stiffer fibres tend to make bonds with a smaller area; however, when fibres are pressed together with sufficient force, the specific strength bond can be as high as the more flexible bleached fibre.

Lignin as well as the hemicelluloses and the amorphous part of the cellulose soften under the action of elevated temperature, and the temperature-induced component of extensibility is thus higher in lignin- and hemicellulose-rich pulps (Waterhouse 1985; Salmén 1979; Back and Salmén 1989). However, water is not an effective plasticizer for the kraft lignin and thus it is not softened by moisture alone. The lowest softening temperature of moist lignin is around 80 °C, and it is reached at around 10% moisture content (Scallan 1974; Kunnari *et al.* 2007). To summarise, fibres with high lignin content are not likely to demonstrate high extensibility.

Fibre length and fibre strength

The length, microfibrillar angle, strength, and coarseness of individual papermaking fibres have been found to correlate with each other (Kärenlampi and Suurhamari 1997). Therefore, these properties may affect extensibility of fibres and the extensibility of paper prepared from such fibres. The effect of the fibre strength on extensibility is much greater than the effect of fibre length (Kärenlampi and Yu 1997). These effects are illustrated in Fig. 9.

The higher the strength of the fibres, the higher its extensibility paper (Fig. 9 “A”). In this case the fibre strength was varied by weakening them by acid vapour treatment. Therefore, this assumption is valid only in the case of strong bonds between weak fibres. In the case of strong fibres, the strength and extensibility of paper would be determined by the strength of the fibre bonds. The influence of fibre length on the extensibility of paper in zero-span test (Fig. 9 “B”) is almost negligible; the strain at break is increased only slightly. But, on the other hand, there is a considerable increase in the work needed to complete the fracture after the stress maximum. The influence of the fibre length on the extensibility of paper is likely to be more evident in the case of wet paper or weakly bonded fibres. The simulation study of Kulachenko and Uesaka (2012) showed that increase in the fibre length from 1.5 to approximately 3 mm doubled the elongation to breakage of the paper.

Mechanical treatments and fibre morphology

Fibres experience mechanical stresses and deformations in many operations on their way from the wood yard to the paper machine (Rauvanto 2010). These stresses may cause both positive and negative changes in fibre morphology, in relation to fibre extensibility (Ljungqvist *et al.* 2003). High-consistency (*ca.* 30% dry solids content) mechanical treatments are known to create deformations in fibres. The deformations are local structural changes in the fibre wall and MFA. Visually, they appear in the form of dislocations, microcompressions, curls, twists, folds, kinks, *etc.*

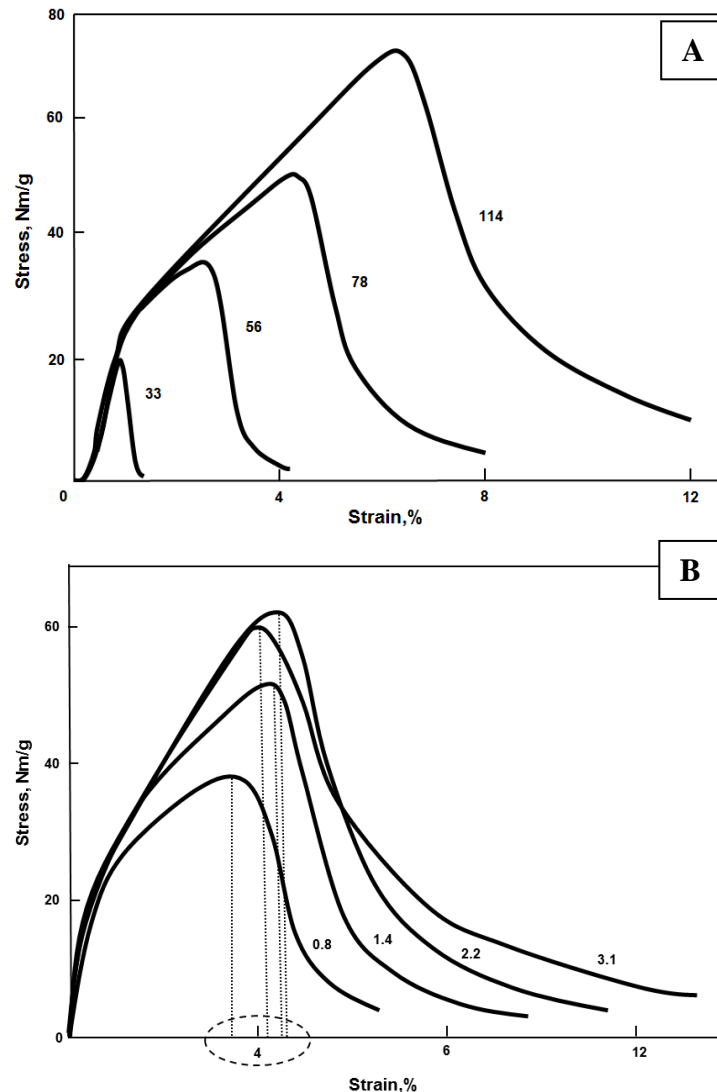


Fig. 9. The influence of the fibre strength of spruce pulp (measured as zero-span tensile strength of paper, number stands for Nm/g) on the elongation of paper (A) and the influence of the fibre length (number stands for the length in mm) of spruce fibres on its elongation (B) (redrawn from the data of Kärenlampi and Yu 1997).

Microcompressions (telescoping axial buckling along the fiber axis), curls, and dislocations (irregularities in fibres origination from the jams or bends of fibre) contribute to the improvement of extensibility of fibres. They have a definite effect on the elongation of wet paper (Barbe *et al.* 1984) and they may increase the elongation of dry paper (but they reduce the tensile stiffness and elastic modulus). These deformations occur due to the action of compressive forces oriented in the axial direction of the fibre (Dumbleton 1972; Page *et al.* 1976; Page and Seth 1980b; Barbe *et al.* 1984; Mohlin *et al.* 1996; Gurnagul and Seth 1997; Joutsimo *et al.* 2005; Seth 2005; Kunnari *et al.* 2007). Kinks in fibres have not been observed to have any effect on extensibility of paper. However, they impair the tensile strength (Kibblewhite and Kerr 1980). The influence of different fibre deformations on the shape of stress-strain curve of fibre is illustrated in Fig. 10.

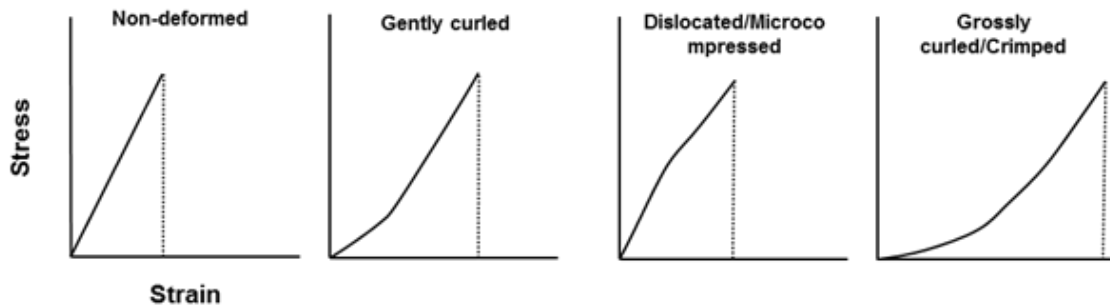


Fig. 10. The stress-strain curves of the fibres with different deformation types (redrawn from the data of Page and Seth 1980)

Page and Seth (1980) have stated that gently curled fibres impart high extensibility to paper, maintaining the stiffness. The influence of fibre deformations on the extensibility of paper have been discussed in more detail elsewhere (Mohlin *et al.* 1996; Seth 2005; Zeng *et al.* 2012, 2013).

High consistency treatments are known to cause deformations that reduce the straightness and increase the extensibility of single fibres. However, extensible fibres do not necessarily result in improved extensibility of paper, and in addition they usually lead to a decreased elastic modulus and tensile strength of paper (Seth 2005). Low consistency refining straightens fibres and does not increase fibre level extensibility, but induces fibre swelling that increases paper shrinkage, which can have a considerable effect on the extensibility of paper, as shown later.

Combined high- and low-consistency mechanical treatment is a well-known method for improving the extensibility of paper. It unites creation of fibre deformations in the high consistency treatment with the straightening of curled fibres in low-consistency refining that improves the stress transfer ability of the fibre network and promotes bonding between fibres. This combination provides high extensibility to paper, while at the same time maintaining the dewatering resistance of the furnish at low level (Arlov and Hauan 1965; Jackson 1967; Ljungqvist *et al.* 2005; Sjöberg and Höglund 2007; Pettersson *et al.* 2007; Gurnagul *et al.* 2009).

Axial microcompressions can be observed in fibres that still appear to be straight (Fig. 11). Changes in fibre morphology are caused by deformations occurring to some extent in all pulp and papermaking processes in which shear and compressive forces are involved (Forgacs and Mason 1958, 1959; Seth 2005; Salmén and Hornatowska 2014). Industrially produced pulp generally gives paper with higher elongation than laboratory-cooked pulp, due to the higher amount of deformations in the industrially made pulp (Ljungqvist *et al.* 2003; Duker *et al.* 2007).

Comparison of different natural and synthetic fibres

Based on the previous discussion, it is clear that chemical and structural properties of fibres have a definite effect on the rupture elongation of the fibres. In natural fibres, the content of cellulose, hemicelluloses, and lignin varies, but what is even more important is that they have a different cell wall structure and dimensions, which may have a detrimental influence on extensibility of fibres.

Synthetic fibres are generally more homogeneous in terms of morphology, but their chemical composition and mechanical properties can vary over a wide range in accordance with the origin of such fibres. The mechanical, structural, and chemical properties of selected natural and synthetic fibres are shown in Table 1.

Table 1. Mechanical, Structural, and Chemical Properties of Selected Natural and Artificial Fibres

| Morphology | | | Mechanical properties | | Chemical composition | | | Ref. |
|-----------------------------|------------|----------------------------|-----------------------|----------------------------|--|----------------------|--------------|--------------|
| Origin | MFA, ° | Length, mm | Elongation, % | Elastic Modulus, GPa | Cellulose, % | Hemicelluloses, % | Lignin, % | |
| <i>Pinus sylvestris</i> | 5–20 | 3–3.5 | 1.5–3.5 | 40 | Varies significantly according to the defibrillation and delignification method and conditions | | | 1,2 |
| <i>Betula pendula</i> | 10 – 19 | 1–1.2 | 2–5.5 | – | | | | 1,2,3, 16 |
| <i>Juniperus communis</i> | 30–40 | 0.83 | 5.4 | – | | | | 4,5,6 |
| <i>Eucalyptus Grandis</i> | 8-20 | 0.8-1.1 | 2-6 | 4-11 | | | | 17,18 |
| Coir | 40–49 | 20–150 | 20–50 | 4–6 | 46 | 0.3 | 45 | 1,2,7,8 |
| Cotton | 25–35 | 20–40 | 7.0–8.0 | 5.5–12.6 | 83 | 6 | ~1 | 1,9 |
| Flax | 8–11 | 20–50 | 2.7–3.2 | 20–30 | 64 | 12 | 12 | 1,11,10 |
| Viscose | – | Varies | 8–13 | 11 | 98–100 | 0.1–4 | Traces | 2,12 |
| Micro-fibrillated cellulose | – | Varies, in nm and µm scale | 6.7–10 | 90–150 | 99.9 | Traces | Traces | 13 |
| Spandex | - | Varies | up to 800 | 0.025 | Polyurethane-based | | | 14,15 |
| Wool | - | 25-400 | 25-50 % | 3.4 | Protein-based | | | 9 |

1-Peel 1999; 2-Bledzki and Gassan 1999; 3-Peura *et al.* 2008; 4-Hänninen *et al.* 2011; 5-Satyanarayana *et al.* 2009; 6- Satyanarayana 2010; 7-Martinschitz *et al.* 2008; 8-Mahato *et al.* 2009; 9-Haudek and Viti 1978; 10-Bos 2004; 11-Bourmaud *et al.* 2013; 12-Lenz *et al.* 1994; 13-Eichhorn *et al.* 2010; 14-Singha 2012; 15-Sun *et al.* 16-Spiegelberg 1966,17- Hein and Lima 2012, 18-Downes *et al.* 2003

Some synthetic (spandex) and natural (coir) fibres have a notably high extensibility potential. These fibres, however, are not capable of creating a strong bonded network due to their limited ability to form hydrogen or covalent bonds. The differences in mechanical behaviour between natural and synthetic fibres are more evident when the stress-strain curves are compared (Fig. 12).

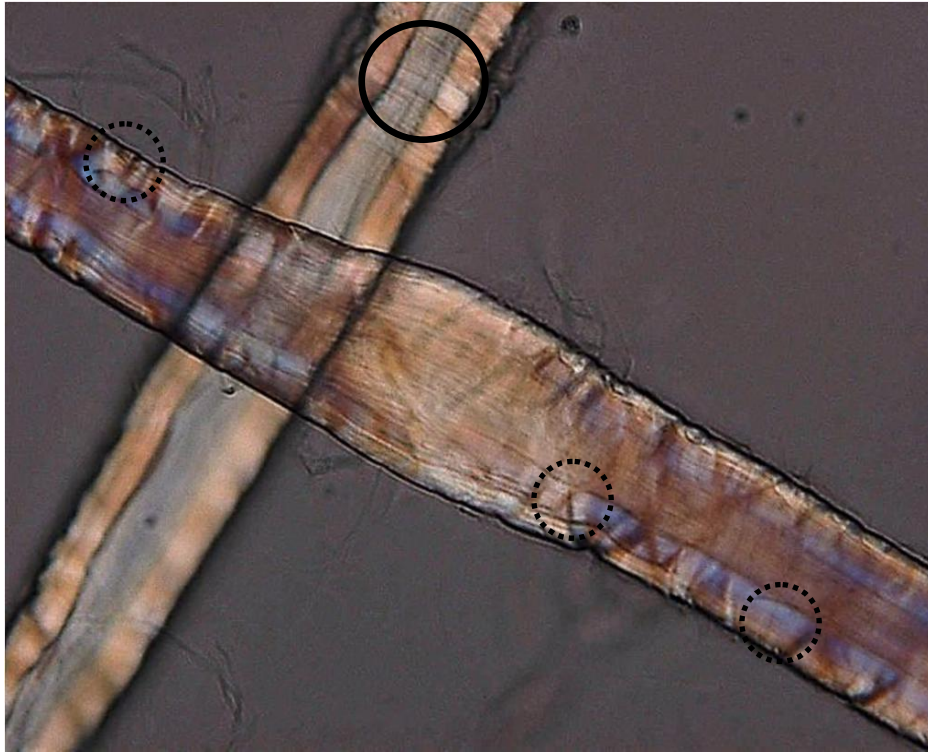


Fig. 11. Variations in the fibrillar orientation due to microcompressions (solid line circle) and dislocations (dashed line circle) in softwood latewood fibres after combined high and low consistency refining. Image taken with polarized light microscopy (courtesy of S. Heinemann, VTT)

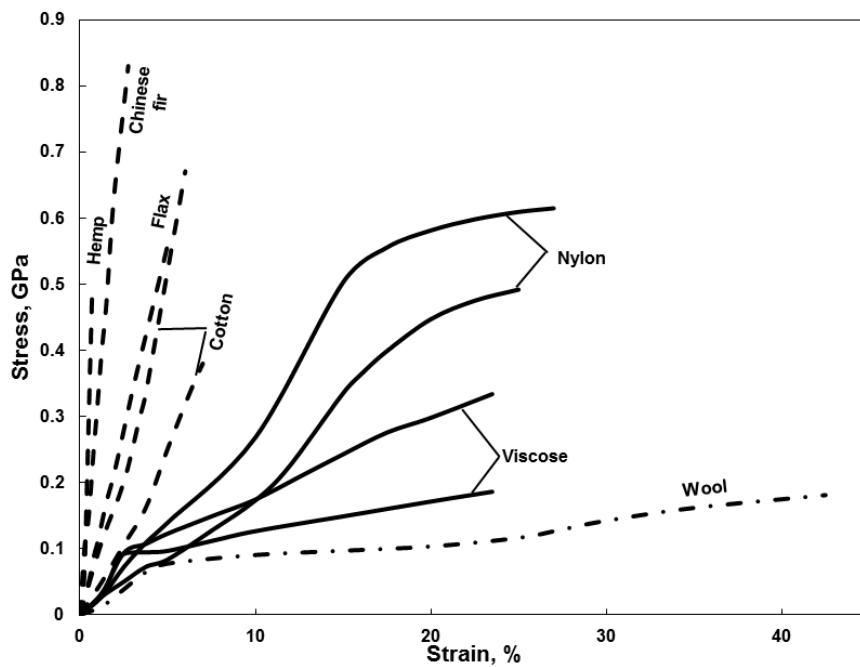


Fig. 12. The stress strain curves of different natural and synthetic fibres (redrawn from the data of Haudek and Viti (1978))

Figure 12 shows that the stiff and strong fibres seem to have low elongation, and natural fibres are obviously less stretchable than synthetic ones. However, viscose fibres, which are made of basically the same material as natural fibres, have much greater extensibility, which is likely due to lower crystallinity and less-pronounced microfibrillar structure (Dlugosz and Michie 1960). This emphasizes the importance of the internal structure of fibres over other factors affecting extensibility of fibres.

It is clear that extensible fibres are not the only prerequisite for the formation of strong and extensible paper; bonding and structure are equally, if not more important than extensibility of single fibres.

Improvement of Fibre-Fibre Interaction towards Increased Extensibility of Paper

In order to be able to form an extensible paper, fibres should have sufficient bonding and load-bearing activity to evenly distribute the load within the paper sheet. The effectiveness of the interfibre bonding can be improved by establishing more and/or stronger molecular bonds and by modifying the viscoelastic nature of the adhesive joints (Zhao and Kwon 2011). Such effects can be obtained either by means of chemical modification of the fibres, or by the addition of various compounds (strength agents) to the paper furnish. Both approaches are discussed in below.

Chemical modifications on the fibre level

Generally speaking, improvement of the extensibility via chemical modification of fibres comes through decreased crystallinity of cellulose and the secondary effects of increased swelling, drying shrinkage, improved bonding, improved compliance of bonds, *etc.*, which are difficult to differentiate. In order to yield a paper with high extensibility, the fibres can be modified in a number of ways, including: grafting with various polymers, etherification, esterification, physicochemical adsorption of polyelectrolytes, blending with polymers, introduction of functional groups, *etc.* Some of these treatments (*e.g.* etherification, esterification) are quite tedious and require a waterless medium so as to perform the chemical reaction, which limits their usability in conventional pulp and papermaking processes.

Grafting (chemical or physical coupling of polymers on the surface of cellulose) of softwood fibres with methyl acrylate has been found to improve elongation of paper from 1.1% to 5.9%-points. This treatment also provides better water absorbency, and improvements in wet and dry strength and extensibility are expected to come via increased swelling of fibres and drying shrinkage of paper. Grafting of cellulosic fibres with methyl acrylate increased the amount and strength of effective bonds in the paper (perhaps via increased interdiffusion), which yielded better utilization of extensibility potential of the paper (Rezai and Warner 1997a,b). Grafting copolymerization of hydroxypropylmethylcellulose (HPMC) with ethylacrylate (EA) can significantly improve extensibility of paper-like material made from HPMC. Elongation of paper increases with the increasing percentage of EA grafted onto HPMC. The highest value of elongation, 40%-points, has been recorded when 100% of HPMC was grafted; however, at the same time tensile strength decreased significantly (from 80 MPa to 20 MPa). The effect is likely to come via the changes in the bonding, caused by modification of the interface (Wang *et al.* 2007). Paper can also be grafted with acrylamide; such treatment has been reported to increase extensibility by 150% in comparison to untreated pulp (Neimo *et al.* 1967).

Hydroxyethylation and hydroxypropylation are beneficial for the strength and elongation of paper. The improvements in extensibility have been attributed to the improved fibre bonding, and increased drying shrinkage. Etherification of cellulose to a relatively low degree of substitution (DS) (<1) increases flexibility and swelling of fibres, which provides additional interfibre contacts with a higher contact area, and thus increases the drying shrinkage and improves bonding (Didwania 1968; Vuoti *et al.* 2013).

Hexanoation of cellulose to a relatively high DS of 1.7 allows thermoformable and water resilient cellulose materials to be obtained, which after being compressed into sheets show strain at break values of around 30%-points. The structure of the hexanoated cellulose sheet was found to represent a continuous cellulose ester matrix reinforced with the unmodified cellulose I. High extensibility values of such structures are likely to originate from the properties continuous matrix formed by cellulose ester upon hot pressing (Matsumura *et al.* 2000).

The selective oxidation of the C2-C3 hydroxyls of cellulose by periodate oxidation with sodium periodate to dialdehyde cellulose and further reduction of aldehyde groups with sodium borohydride to form dialcohol cellulose has been found to be effective in the improvement of extensibility of fibres and paper. The stretch of single fibres in zero-span test increased from 60 μm to 180 μm . The increase in the extensibility of paper made from such fibres was more pronounced; the elongation of paper was increased from 4% (non-modified) to 23%-points (oxidised and crosslinked). This indicates that the changes occur not only in the fibre structure but also in the character of interfibre bonding. The changes in the elongation of individual fibres are associated with the different core-shell structure of fibres, which increases the mobility and flexibility of the nanofibrils in the fibre wall (Larsson *et al.* 2014a). The same approach was applied for preparation of the films from surface-oxidized cellulose nanofibrils representing the crystalline core structure “wrapped” in the dialcohol cellulose; such films have extensibility of around 37%-points (measured at 90% RH) (Larsson *et al.* 2014b). Wu *et al.* (2014) have observed that oxidation causes formation of the coil-like curved structures in fibrils and decreases thickness of the fibrils.

Partial dissolution of the cellulose fibres can be used to produce extensible all-cellulose composites with superior to original material strength, strain, and stiffness. Treatment of filter paper with (LiCl)/DMAc increased the strain at break by 50% and decreased crystallinity of cellulose from *ca.* 80 to 20% (Nishino and Arimoto 2007). Swelling of the bacterial cellulose in 8% (LiCl)/DMAc for 60 minutes drastically changed the deformability properties of the resulting material; the strain at break was increased from 3.5%-points to around 30%-points. Such a shift was attributed to loss of fibrous structure of bacterial cellulose and decreased crystallinity, at the same time the pattern of hydrogen bonding is expected to change to a much more extensive one (Soykeabkaew *et al.* 2009).

In general, there is no clear understanding of which chemical modifications of fibres are especially effective in the improvement of the extensibility of paper, since the improvement often comes through the secondary effects of increasing strainability of fibers, swelling/drying shrinkage, improved bonding, and bond compliance.

Different additives for improving the extensibility

The specific strength of the bonds relies on the stereotopochemistry of the fibres and the type of binder present in the paper, if any (Akagane *et al.* 1979). In additive-free paper, the interactions between fibres are mainly assumed to be due to the hydrogen bonding and adhesion formed by the van der Waals forces (Stratton and Colson 1993).

Also other mechanisms such as interdiffusion, mechanical interlocking, and Coulomb bonding cannot be excluded (Lindström *et al.* 2005; Hirn and Schennach 2014). A high degree of interfibre bonding allows distribution of tensile stresses in a more uniform way, utilizing the straining potential of the fibres in the paper more efficiently. Interfibre interactions during the distribution of the shrinkage stresses during drying also affect the fibre structure in the web. Stronger interfibre interactions in the wet state make it possible to transmit higher forces in wet paper, to modify the fibres, and to increase the shrinkage potential of the fibre network.

Introduction of various additives to the furnish or to the already formed paper is commonly used to enhance the dry and wet strength of paper as well as to provide certain functional properties. This approach dates back to the 19th century, when paper was sized with a mixture of caustic, wax, turpentine, and fat so as to enhance stretchability (Nonnenmacher 1898).

Pelton (2004) in his excellent review provided interesting hypotheses regarding how polymeric compounds affect the fibre-fibre bonding. Apart from the general hypothesis that additives improve adhesion, he has considered three other possibilities. The first possibility is the *lubrication* – the presence of slippery surface polymer layer allow fibre-fibre slippage in drying, and thus reducing the built stress of the fibre network and possibly increasing drying shrinkage without the introduction of microcompressions to fibres. The second possibility is the *viscous dissipation* in which a polymer layer can form stretchable domains between the fibres; in this case significant energy needs to be brought in before fibres would separate from each other. This was found to be the case for the latex-impregnated paper and thick polymer multilayer systems; polymer monolayers are still likely to have brittle behaviour in this case. The third mechanism is the *crack stopping*, which is the inclusion of small stretchable domains between brittle ones (fibres in this case); this mechanism stops cracks from propagating. Thus, in order to increase extensibility one should consider whether the added polymer is promoting deformability of the fibre-fibre joints, and not only the adhesion itself. Several methods known to improve extensibility of paper using different additives are summarized in below.

Fines are readily available at the paper mill and are known to improve paper strength; the addition of fines increases RBA (relative bonded area) and drying shrinkage. The simultaneous addition of starch and kraft fines is especially beneficial for tensile strength improvement, and thus for extensibility, but also for drying shrinkage (Retulainen *et al.* 1993; Taipale *et al.* 2010). Films made from nanofibrillated cellulose (NFC, and the same applies to MFC-microfibrillated cellulose), have higher extensibility than paper made from chemical pulp fibres. MFC can be added to the paper furnish for the improvement of the strength and extensibility in a same way as fines (Klemm *et al.* 2011). The addition of 10% MFC to the bleached hardwood pulp increases the strain at break of the paper by 5%-points, for the sheets dried under restraint. MFC increases RBA as fines do, but due to the higher specific surface area, MFC is even more effective in binding and modifying the stress distribution and in increasing drying shrinkage (Madani *et al.* 2011; Manninen *et al.* 2011). Addition of carboxymethyl cellulose (CMC) to unbeaten softwood kraft pulp may, in addition to the strength, also improves the elongation of the paper. For instance the addition of 7.3 mg/g of CMC (FinnFix WRH) has raised the strain at break of paper from 3.6% to 5.8% (Laine *et al.* 2002). Blending of cellulose fibres with poly (3-hydroxybutyrate-co-3-hydroxyvalerate)(PHBV) results in plastic-like materials with improved elongation. The addition of 40% of PHBV was found to improve the strain at break value from 4 to 5.2%-points (Hameed *et al.* 2011).

Starch is a well-known dry strength additive for the papermakers and its addition either to wet end or by surface sizing positively affects not only strength but also extensibility of paper. Lindström *et al.* 1985 claimed that wet end addition of cationic starch (4.2% to fibres) improves extensibility of both filled (from 1.2% to 2.1%-points) and unfilled (from 2.1% to 3.2%) paper by improving sheet consolidation (bonded area) increasing specific bond strength and evens the stress concentration in paper (Lindström *et al.* 2005). The surface addition of starch also improves extensibility by *ca.* 1% for restrained dried paper and by *ca.* 4% for unrestrained dried paper; in the latter case the effect comes *via* increased shrinkage of paper (Lipponen *et al.* 2005).

Surface carboxymethylation of pulp may also be applied for the improvement of extensibility (Duker *et al.* 2007). The surface sizing of paper with methylcellulose has improved extensibility of base paper by 23% without deterioration in stiffness (Akim and Telysheva 1991). Recently, coating of paper with sodium caseinate was found to be effective in the improvement of extensibility; application of 5 g/m² caseinate coating on paper improved extensibility by approx. 2%-points (Khwaldia *et al.* 2014). Spray addition of gelatine to the surface of wet paper can increase extensibility up to 8%-points; the effect comes from the enhanced bonding caused by gelatine adsorbed on the surface of fibres and increased drying shrinkage of paper (Khakalo *et al.* 2014). In general, surface addition of the extensible material on the surface of paper, even in relatively small amounts, improves overall extensibility, because surface layers were found to be in charge of failure initiation in paper (Stockmann 1974). Thus by strengthening and increasing of extensibility of only the surface layer of paper one might postpone fracturing and thus improve overall extensibility.

The formation of polyelectrolyte multilayers from polyacrylic acid polyallylamine hydrochloride on the surface of fibres can significantly improve the tensile strength and extensibility of paper (from 4 to 8%-points) (Gustafsson 2012). Polyethylene imine/NFC and polyallylamine hydrochloride/hyaluronic acid multilayer systems were also found to be effective in the improvement of extensibility (Marais *et al.* 2014). By introduction of the several consequent layers of deformable polymers on the cellulose, it is possible to modify the viscoelastic nature of the fibre joints and thus fibre bonding. This concept was previously verified with materials other than cellulose (Ankerfors *et al.* 2014).

Fibre-based composites

Due to their relatively high strength and stiffness, natural fibres have been used for decades for preparation of composite materials. Even small (0.5 to 10% by weight) amounts of fibrous materials can increase the strength and reduce the elongation of a composite. With an increasing amount of fibres in composites there is a certain point when the fibres are contacting each other and a kind of percolation threshold is reached. For a papermaking approach, the situation is the inverse. The target is to increase the elongation of fibre network with as small an amount of added polymeric material as possible so that the added amount is applicable in a papermaking process. There are two principal ways to introduce polymers to the paper: wet-end addition and impregnation of pre-formed fibre network. In the first case the effectiveness of the treatment is bordered by the limited adhesion of polymer (usually hydrophobic) to fibres in the aqueous medium, interference with the formation of hydrogen bonds between fibres, and by the retention of polymer upon dewatering. When the polymer is added to an already formed fibre network, the low extensibility of the network will limit the extensibility of the composite, but with increasing amounts of polymer, composites with higher extensibilities can be obtained.

The addition of natural and synthetic latexes and resins can be used for the improvement of the elongation and strength of the paper. The addition of styrene-butadiene latex in the amount of 30 mg/g to kraft pulp has improved the elongation of paper from 1.8 to 4%-points (Alinec 1977). Addition of PLA latex dispersion in the amount of 20% to paper is capable of improving the elongation by 5 to 10%-points, and such paper has also demonstrated convertibility in the 3D-forming process (Svensson *et al.* 2013).

Elastomeric polymers added in the amount of 20 to 40% to a fibre network can improve the extensibility of such material by up to 30 to 40%-points (Waterhouse 1976). By coating paperboard with polyhydroxybutyrate, it is possible to obtain a material with high strain at break values. Materials made of 80% pulp and 20% PHB have elongation at break around 36% (Cyras *et al.* 2009). The changes in the stress-strain behaviour of the cellulosic materials caused by addition of the thermoplastic polymers are shown in Fig. 13.

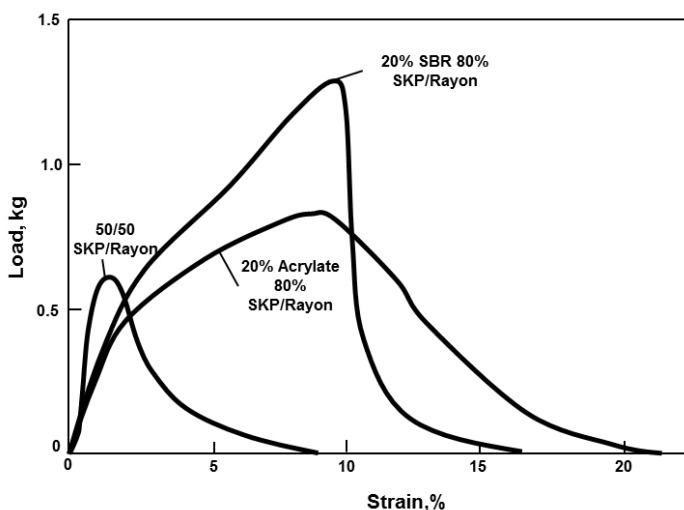


Fig. 13. The stress-strain curves of the non-woven type paper composed of 50% softwood kraft pulp (SKP) and 50% rayon impregnated with 20% of acrylate and 20% styrene-butadiene resin (SBR) emulsions (redrawn from the data of Fredricks 1971)

It is clear that the addition of polymers considerably improves elongation of the non-woven type of fibre network. It was found that the addition of polymers changes the character of the fibre bonding in such a way that the fracture of fibre network is caused by fibre failure; *i.e.* acrylate and SBR addition provides strong polymer-fibre and polymer-polymer bonds (Heyse *et al.* 1960). In addition to the elongation, also the work needed to complete the fracture after reaching the maximum tensile strength value is often increased. Another interesting class of polymers that may improve the extensibility of cellulosic materials is polyethylene/polypropylene carbonates (Xing *et al.* 2013). For instance, the blend composed of 90% of polypropylene carbonate with 10% of cellulose nanowhiskers has an elongation of around 950%-points (Wang *et al.* 2013). However, the effect of the polypropylene carbonate should be still studied at much lower addition levels.

Despite the evident advantages and relative simplicity, the addition of thermoplastic polymers can introduce some unwanted features into the production of paper and its mechanical properties. Conventionally, thermoplastic polymers have a poor compatibility with the cellulosic fibres, and thus require an additional thermal treatment

(curing) in order to amalgamate the polymer within the fibre matrix. In some cases when the film-forming temperature of latex is low, thermal treatment is not needed. Polymer melts and fills the free spaces between the fibres and forms fibre-polymer and polymer-polymer bonds, allowing a larger area for molecular contact between fibres, and thus improving stress distribution within fibre network (Anonymous 1954; Alince 1977, 1979, 1991, 1999). The filling of the free space between the fibres with the polymers reduces drying shrinkage. An addition of 5% of polymer dispersion reduces shrinkage by 50% (de Ruvo 1979). The addition of the highly elastomeric polymers such as Nylon, Dacron, or Spandex can reduce the plastic deformation component of the stress-strain curve and increase the overall strain recovery of paper (Waterhouse 1976).

Utilization of various additives is a straightforward method for improving the extensibility of paper, but they will compromise the paper manufacturing process and some paper properties. The amount of the added substances generally is proportional to the increase in extensibility, which limits the operational window for this method. The efficiency could be improved if a method of depositing the additives precisely at the place of fibre-fibre contacts could be found. A reasonable percentage of addition can be set as 10% of the fibres, in order that the production process and environment are not severely affected by the change in furnish properties (drainage, sticking to roll surfaces, steam consumption, *etc.*).

The Structural Aspects of the Fibre Network Affecting Extensibility of Paper *Drying shrinkage*

The extensibility of paper is to a significant extent dependent on the drying method. Conventionally, the paper web is dried under tension on the heated metal cylinders of the paper machine. Due to the tension in MD, wet paper experiences straining deformations, which are further “frozen” in the paper structure during drying. However, the role of web tension required for smooth runnability is reduced with increasing basis weight and decreasing machine speed. It is also possible to dry paper without restraint or with only a minor restraint, thus allowing drying shrinkage and preventing the formation of built-in strains in the paper. Impingement, IR (infrared), and air float (*e.g.* Fläkt) drying can be used in combination with cylinder drying for such purpose. Float drying is most efficient for the development of drying shrinkage when applied to paper with a solids content of between 60 and 85% (Flyate 1988; Steenberg 2006).

It is well known that the higher the drying shrinkage, the higher the elongation of the paper (Fujiwara 1956; Page 1971; Htun and de Ruvo 1981; Htun *et al.* 1989; Waller and Singhal 1999; Wahlström *et al.* 1999). Wet draw of the paper web and subsequent restrained drying reduces the extensibility of paper. High extensibility of unrestrained dried paper is attributed to the “release of shrinkage” in fibres during straining of the paper.

The mechanism of drying shrinkage of paper is believed to be the following: fibres shrink laterally, which in turn causes axial shrinkage of the single fibres bonded to it, and eventually shrinkage of the whole web by means of interfibre crossings. Fibres shrink anisotropically; fibres can shrink up to 30% in a transverse direction, though the axial shrinkage is limited to 1 to 3%. Such a low value of longitudinal shrinkage can be attributed to the low microfibrillar angle and stiffness of crystalline microfibrils, which prevents lengthwise shrinkage (Page and Tydeman 1966; Page 1969, 1971). Drying shrinkage also causes axial microcompressions in fibres (Page and Tydeman 1966). The extent of the drying shrinkage of paper in unrestrained drying varies greatly, and can be between 3 and 10%. This value is governed by lateral shrinkage of the single fibres,

which depends on the initial swelling of fibres, the area, number and adhesion in fibre contacts that transmit the shrinkage forces from one fibre to another, and the axial stiffness of the fibres, which resists axial shrinkage. Swelling and shrinkage of fibres can be easily controlled by the extent of refining. The lower the freeness value, the higher the swelling of fibres, which primarily depends on the extent and type of refining (Zeng *et al.* 2012, 2013).

Apart from refining, swelling of fibres is also dependent on electrolyte concentration in white water, the type of counter ion on the carboxylic group (swelling of fibres and strength of paper increase in a row of Al^{3+} , H^+ , Mg^{2+} , Ca^{2+} , Li^+ , Na^+), pH, and amount of carboxylic groups in pulp (Scallan and Grignon 1979; Scallan 1983). The surface charge of the cellulose is very important for the deformability and strength of the fibre joints. The higher the surface charge, the higher will be the strength and deformability of fibre joints. However, at the same time critical strain of the fibre is reduced. It was suggested that the effect of surface charge comes via surface softening of the fibre, which is increasing molecular contact and promoting a better interdiffusion of polymers (Torgnysdotter and Wågberg 2003). The swelling induced to the fibre by transferring into the Na^+ ionized form improves extensibility of paper by around 0.5%; however this effect is further amplified by the refining (Bäckström *et al.* 2009). Increase in swelling is usually accompanied by improvement in bond strength, and thus might positively affect the extensibility of paper.

The axial stiffness of fibres can be reduced by certain high-consistency treatments, which create dislocations and microcompressions. Axially flexible fibres create smaller resistance to sheet shrinkage than do stiff ones. Also, at similar fibre diameters, fibres with a thick cell wall tend to shrink less than thin-walled fibres (Page and Tydeman 1962). Other methods that can be used to increase shrinkage of paper include addition of fines and micro- and nanofibrillated cellulose (Lobben 1977, 1978; Sampson and Yamamoto 2011) and the addition of agar (Vishtal and Retulainen 2014).

Paper shrinks more in CD due to a lower restraint and a higher shrinkage potential due to fibre orientation. Moreover, MD tension creates a Poisson contraction in CD. Fibres in MD are also subjected to wet straining during manufacturing, which reduces the elongation of paper in this direction (Nanko and Wan 1995; Seth 2005). On modern paper machines, paper is stretched by 2 to 3% on its way from the forming to the drying section. However, historically these values were as high as 6 to 8% (Halme 1967). The relation between the wet draw (extent of straining in a paper machine in MD), drying shrinkage, and strain at break of paper can be seen from Fig. 14.

Strain at break of paper is shown to have an almost linear dependence on the wet draw and drying shrinkage. At higher shrinkage, the relationship may become exponential. The dryness at which the drying restraint has been applied or the shrinkage has taken place may also play a role in the extensibility of paper (Htun and De Ruvo, 1981). However, Mäkelä (2009) has stated that strain at break of paper is only controlled by total drying strain and that the dryness level at which draw has taken place does not have much influence on it. However, recent results of Kouko *et al.* (2014) suggest that although the strain at break depends linearly on the draws, the dryness at which the draws take place have some effect. A draw performed at dryness over 80% is more harmful for the MD strain at break than a draw of same size performed immediately after wet pressing at dryness below 60% (Kouko *et al.* 2014). This difference might originate from the furnishes that were used (Hardwood pulp vs. LWC (lightweight coated)-furnish) and the testing procedures applied. The influence of the wet straining on the stress-strain properties of paper has also been studied in detail, for example by Schulz (1961).

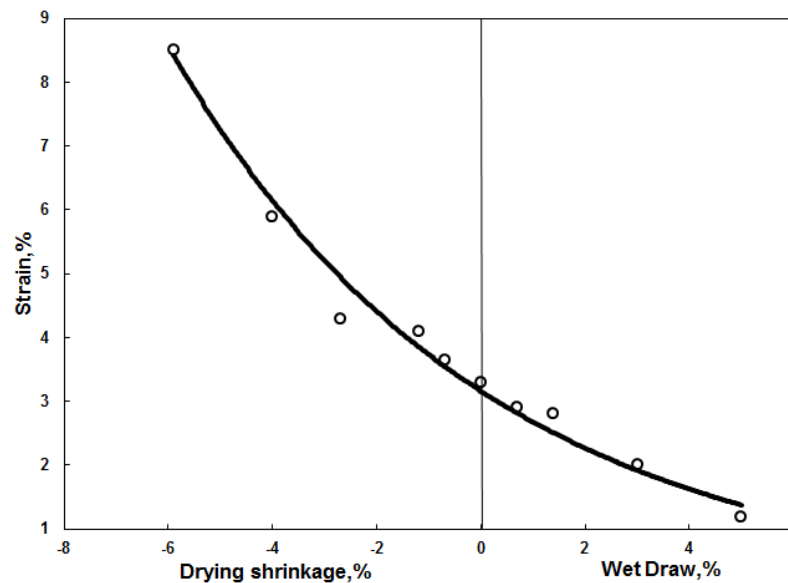


Fig. 14. The relation between the strain of paper and drying shrinkage and wet draw in a paper machine in MD (redrawn from the data of Silvy 1971)

Based on the findings just discussed, it is possible to conclude that unrestrained drying or low-restrained drying is a viable option for production of extensible paper products.

Modification of the fibre network by in-plane compression: compaction and creping

Paper can be compressed in-plane on a paper machine in order to improve extensibility. Compaction and creping are the best known methods of in-plane compression of the paper web.

Improvements in elongation obtained by in-plane compression have a linear correlation with a decrease in geometrical length and increase in the basis weight of the paper after treatment. Increase in extensibility is always accompanied by a decrease in tensile strength, and especially the elastic modulus of paper.

Creping

In creping, paper is attached to the drying cylinder (most often a Yankee cylinder), and dried until certain dryness (this varies based on the creping process, typically 70 to 85%). Then it is released from the cylinder by means of a creping blade, which causes folding of the paper web, partial fibre-fibre bonds breakage, fibre rearrangements, and sheet buckling (Welsh 1965; Oliver 1980; Stitt 2002). Creping yields in highly-extensible papers with an elongation in range of 10 to 200%, and it is mainly utilized in tissue products requiring a high softness of paper (Hollmark and Ampulski 2004). However, creped paper has a limited utilization in packaging applications due to the wrinkly surface, low stiffness, and significantly decreased tensile strength. It is mainly used for cushioning and decorative purposes (Hernandez and Selke *et al.* 2001; Welsh 1965). Straightening of the buckles in creped paper does not require much mechanical energy, and thus the stiffness and TEA of the creped paper is several folds lower than for compacted paper. As a result of creping, paper obtains a buckled structure with the length of each buckle around 1 mm. However, no principal changes in the internal structure of paper can be found (Ramasubramanian 2011). The cross-

sectional images of the creped and uncreped kraft paper, depicting the wrinkly appearance of creped paper, are shown in the Fig. 15.



Fig. 15. The cross-sectional images of uncreped and creped paper (Welsh 1965)

The creping processes can be distinguished as having two main types: moist (wet) creping and dry creping. Moist creping (performed at 60 to 85% dry solids) provides a smaller decrease in tensile strength and stiffness; however, the increase in extensibility is lower in comparison with dry creping. This is explained by the ability of fibres to form hydrogen bonds after creping during the drying process. Among creping methods, dry creping (performed at 93 to 97%) produces the greatest increase in elongation and the greatest decrease in strength and stiffness (Ramasubramanian 2001). The results of creping are mainly controlled by the percent crepe, the value that expresses the difference in speed between the Yankee cylinder and the reel. The higher the percent crepe, the higher is the extensibility of the resulting paper. Additional factors include crepe blade angle, temperature of cylinder and creping blade, chemical composition of pulp, application of adhesive, and adhesive release onto the Yankee cylinder (Boudreau and Germgård 2014, Boudreau and Barbier 2014).

In-plane compaction of paper

The compaction of paper is an in-plane compressive treatment of moist paper in MD. This process is also applied with wet-laid non-woven fibre networks. Paper is compacted either between the moving rubber blanket, steel roll, and non-rotating nip bar (Clupak®), or between the steel roll covered with a rubber blanket and the heated steel roll (Expanda®). Modifications of the compaction process do exist; however, the principle is the same. Compaction improves extensibility, but reduces tensile strength, elastic modulus, and bending stiffness of paper to a lesser extent than in the creping. Compaction is mainly used in the production of sack and bag paper grades in order to increase the tensile energy absorption of such papers (Ihrman and Öhrn 1965; Welsh 1965; Hernandez and Selke 2001; Poppel *et al.* 2000; Ankerfors and Lindström 2011). The schematic principle of operation of the Clupak® compaction unit for paper is shown in Fig. 16.

At the beginning of the compaction process, the rubber blanket (Fig. 15) is stretched in front of the nip before it adheres to the paper fed into the nip. Once the paper with rubber blanket passes the nip, the rubber blanket recoils because the straining force is released. Due to adhesion, the paper shrinks together with rubber blanket. The typical dryness of paper entering the nip is 60 to 65%, and the dryness is increased once the paper leaves the Clupak® unit. The influence of compaction on the mechanical properties of paper can be demonstrated with the stress-strain curves (MD and CD) of paper before and after compaction, as shown in the Fig. 17.

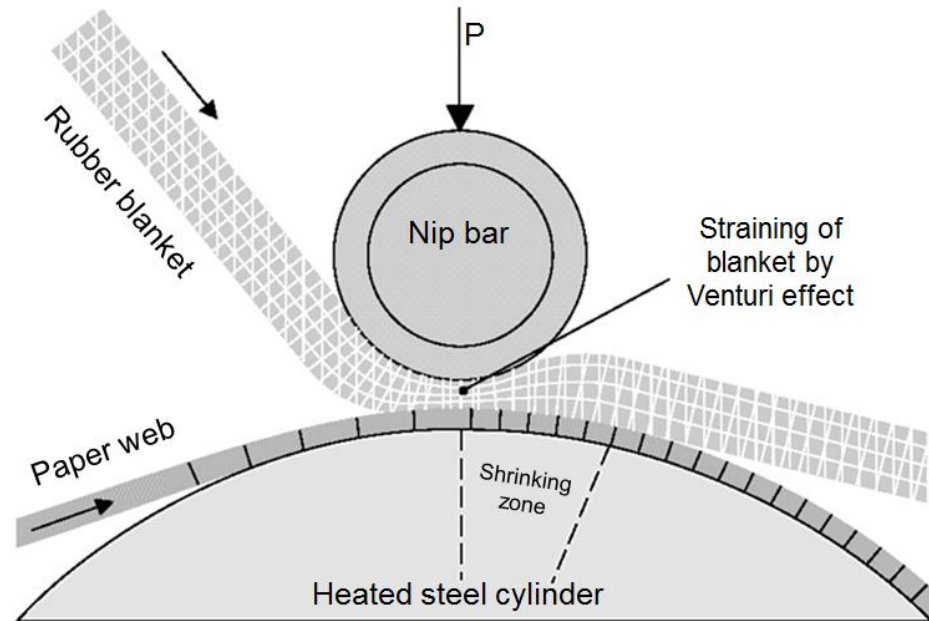


Fig. 16. The outline of Clupak® compaction process

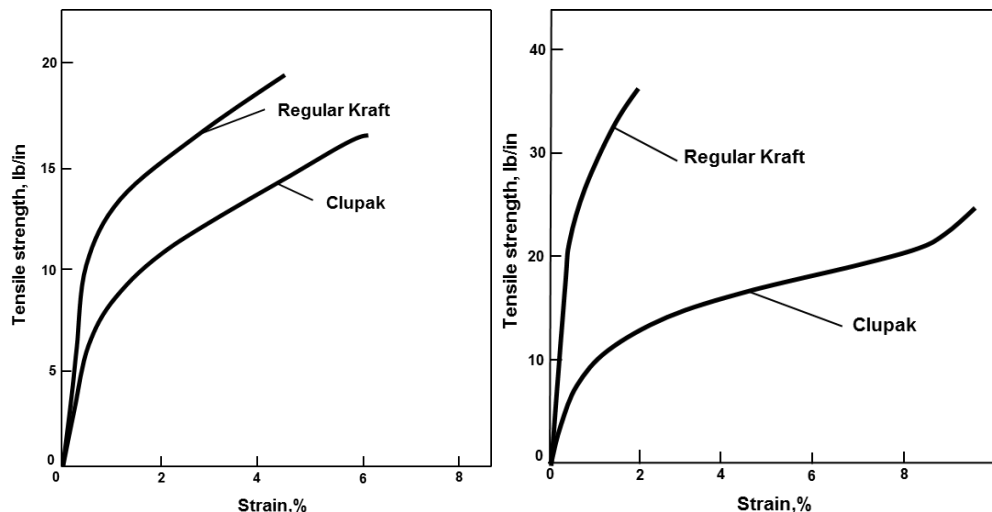


Fig. 17. The comparison of the stress-strain curves of the Clupak and Kraft sack paper in CD (left) and MD (right) (redrawn from the data of Shoudy 1959)

As can be seen from Fig. 17, compaction is an effective tool for the improvement of extensibility in MD, in exchange for a decreased ultimate tensile strength; however TEA (Tensile energy adsorption) is increased. In addition to the improvement in MD elongation, the extensibility also slightly increases in the CD. A 10%-point gain in MD strain provides a 1 to 2% points increase in CD strain (Shoudy 1959; Welsh 1965). Paper can be compacted in both directions to produce paper with more isotropic properties. This can be achieved by controlling the recoiling of the rubber blanket in CD and by utilization of circumferentially grooved or inclined rolls (Welsh 1960; Cariolaro and Trani 2000; Kawasaki and Nagai 2003; Saitaka *et al.* 2006). The gain in elongation, a decrease in tensile strength caused by compaction, can be adjusted by varying the stretch of the rubber blanket, Z-pressure, and moisture content of the paper entering the nip. A

high strain on the blanket leads to a higher gain in elongation, but to a major decrease in stiffness of paper. High z-pressure reduces the gain in elongation, but maintains stiffness at a higher level. Moisture content can be varied in the range of 40 to 75%. Typically, the higher the moisture content of paper, the higher the elongation can be; however, it is accompanied by decreased stiffness (Welsh 1965; Ihrman and Öhrn 1965; Chen 1991; Lahti *et al.* 2014).

The elongation of paper is increased primarily due to the buckling of fibres and incorporation of microcompressions to fibres. A fine wrinkle pattern can be observed on the surface of paper. A decrease in the tensile strength is explained by the partial disruption of the fibre-fibre bonds (Chen 1991). The cross-sectional images of the double-roll compacted paper before and after compaction are shown in the Fig. 18.

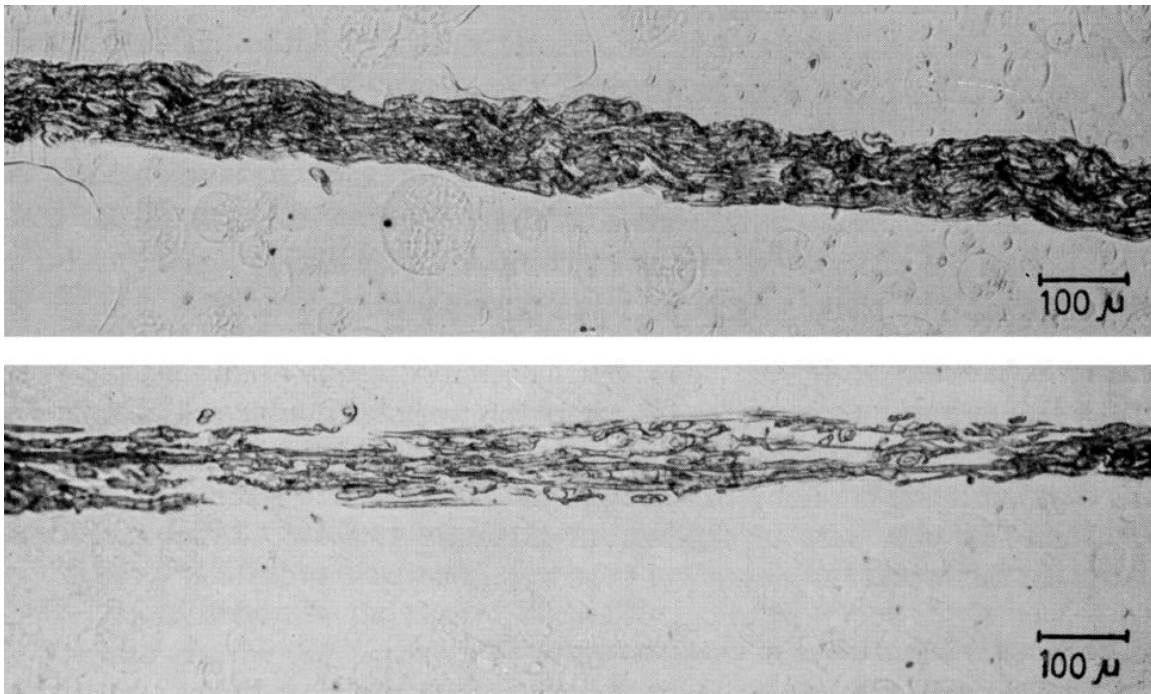


Fig. 18. The cross-sectional microscopic images of double roll compacted paper before (upper) and after straining (lower) Ihrman and Öhrn (1965)

Steenberg (1949) has proposed that the extensibility of compacted paper comes through the extension of the creases in fibres between the fibre joints, which also can be observed in Fig. 18. The decrease in ultimate tensile strength of paper is explained by damage to the fibres and by partially disrupted fibre-fibre bonds. Another possible reason is the reduced efficiency in stress distribution of the network due to reduction or absence of activation (*i.e.* prestraining). Fibres after compaction appear to be curled, bent, and buckled, and they have higher plastic deformation and high-impact resistance due to high energy absorption of curled fibres (Dumbleton 1972; Page and Seth 1980b), which is also reflected in the decreased stress relaxation of compacted paper in comparison to uncompact (Gregorova *et al.* 2013). However, after the straining, compacted paper appears to be quite smooth and no compaction marks can be observed in it (Fig. 18). Compaction results in densification of the paper, while its surface still appears to be rather planar (Shoudy 1959). In the case of paper with a relatively high basis weight (>100 g/m²), the density of the surface and bottom layer of compacted paper may differ.

The surface layer facing the rubber blanket may have a higher density (Kawasaki and Nagai 2003).

An additional benefit of compaction for the increased elongation of the paper is the reduced axial stiffness of the fibres, which can enhance the drying shrinkage of the paper (Dumbleton 1972). The use of the thermoplastic additives together with compaction may lead to formation of sticky deposits on blankets and rolls. Compaction of paper seems to be a feasible option for the production of extensible paper, it is widely used in manufacturing of sack paper and was recently applied for production of so-called “formable” paper for 3D-forming (Hado *et al.* 2001; Billerud 2012).

Fibre orientation

Most of the papers produced on modern paper machines have their fibres aligned more towards the MD than CD due to the flow patterns in wet end. The fibre orientation has a great influence on the tensile properties of paper. However, despite the common difference in strain at break in MD and CD, the effect of fibre orientation on the strain at break of restrained-dried paper was not observed, which can be noted from Fig. 19.

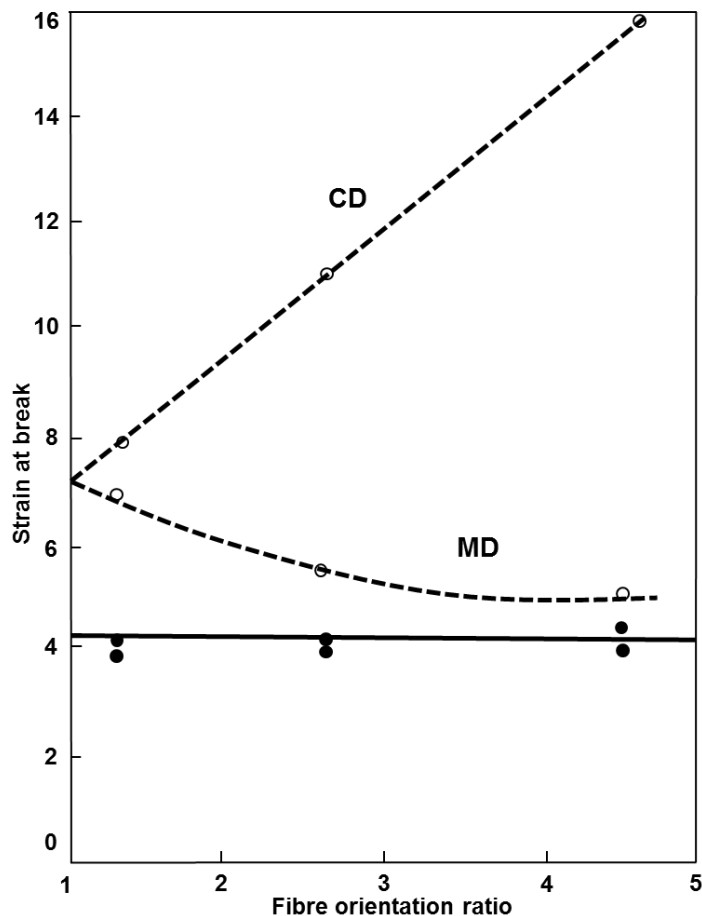


Fig. 19. The relation between the strain at break and fibre orientation ratio for the restrained (filled circles MD and CD) and unrestrained dried paper (empty circles), difference in orientation was obtained by varying the speed of the handsheet former (redrawn from Htun and Fellers 1982).

It is clear that the strain at break of the paper is determined by the extent of drying shrinkage and not directly by the fibre orientation in the sheet (Fig. 19), which is also in line with observations of Setterholm and Kuenzi (1970). Moreover, the relation between

strain at break of paper and drying shrinkage is also not dependent on the fibre orientation (Gates and Kenworthy 1963). Nevertheless, large fibre orientation anisotropy leads to limited MD-shrinkage potential and thus strain, no matter how low the draw during drying is, which makes the question about influence of fibre orientation somewhat confusing.

Influence of External Effects and Straining Conditions on Extensibility Of Paper

In addition to the interfibre bonding, the structure of single fibres and network, the extensibility of paper is influenced by the straining situation and conditions at which straining is occurring. This section discusses the influence of strain rate and softening of polymers in the paper on its extensibility.

Influence of the strain rate on the extensibility

Individual fibres behave viscoelastically, and the strength and elastic modulus increase with the strain rate (Hardacker 1970). Therefore, it is no wonder that the same phenomenon occurs with paper (Andersson and Sjöberg 1953; Davison 1972). However, the influence of the strain rate on the extensibility of paper is not that straightforward and depends on the type of paper and other factors (Andersson and Sjöberg 1953). According to Okushima and Robertson (1979), the extensibility of blotting paper decreases with increasing strain rate. This effect is especially marked at high relative humidity, at which the share of plastic deformation is higher (Fig. 20).

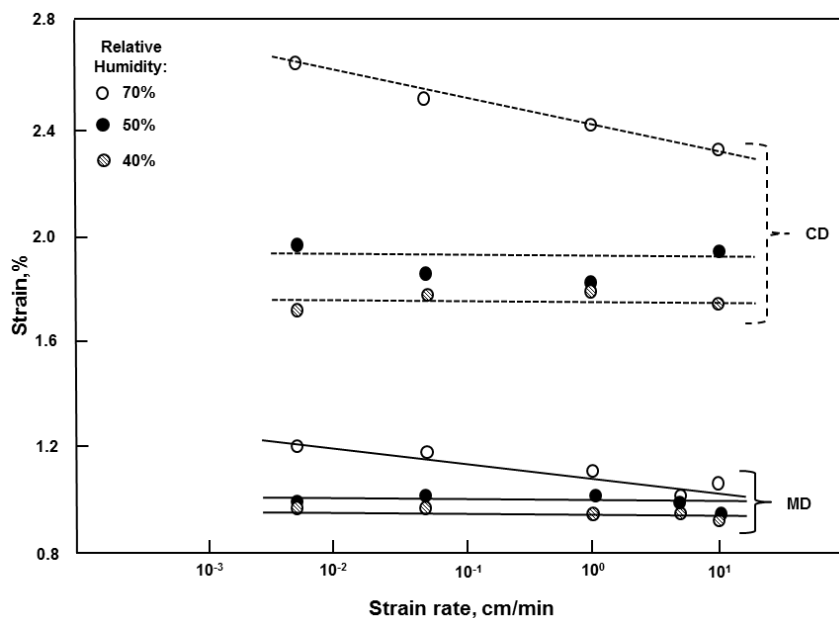


Fig. 20. The influence of strain rate on the extensibility of blotting paper conditioned at different RH levels (redrawn from the data of Okushima and Robertson 1979)

The decrease in overall strain with increasing strain rate is probably related to the reduction of the visco-elastic and plastic deformations of paper, which result in a reduced redistribution of stresses, higher stress concentrations at the rupture zone, and increased failure of the fibres themselves. With the increase in strain rate, the number of fibre breakages at the rupture zone has been found to increase and the number of failed bonds decreases (Helle 1965). Davison (1972) has shown that there is a certain optimum strain

rate, 10000%/min, which gives the maximum extensibility for a given paper sample. The straining span length might also affect the overall extensibility; in general, with a decrease in span length, the strain increases slightly (Andersson and Sjöberg 1953), which could be explained by the lower probability of having weak spots.

To summarise, the strain rate does not generally affect the extensibility of the paper, but in certain cases and at extreme strain rates the extensibility decreases with increased strain rate. The decrease in elongation may be related to the difference in the structure and stresses, and the shorter time available for redistribution of stresses. Higher stress concentrations and higher elastic energy may lead to an earlier initiation and propagation of the fracture line.

Influence of temperature and moisture on the extensibility of paper

Straining of paper under elevated temperature or/and moisture level commonly occurs in production and converting processes. Temperature and moisture effects are not independent since at elevated temperature the equilibrium moisture content of paper changes. When paper is heated and/or moistened, the polymers in the fibre wall soften. Softening of paper as a phenomenon is related to the changes in the mechanical properties of paper, and can be characterized as the reduction in fibre stiffness, reduced strength of H-bonds, and increase in the mobility of polymeric components of fibres.

The chemical pulp fibres are mainly composed of hydrophilic polymers – cellulose and hemicelluloses – and therefore they are susceptible to the action of moisture and elevated temperature. Lignin, the third constituent of paper, is not significantly affected by the action of moisture, but it softens under elevated temperature. However, lignin plays an important role only in the case of mechanical and chemomechanical pulps. The chemical composition of fibres and the internal structure of polymers to a great extent determine the softening behaviour of paper.

The effect of the increased temperature is mainly related to the reduction in the axial stiffness of the fibres, when the water acts as a plasticizer by interacting with intramolecular and intermolecular hydrogen bonds in cellulose and intermolecular bonds between fibres and fibrils, and thus allows the deformation and rearrangement of the cellulosic microfibrils (Tsuge and Wada 1962; Goring 1963; Crook and Bennet 1962; Salmén and Back 1977; Back and Salmén 1982; Waterhouse 1984; Caulfield 1990; Shiraishi 1991; Haslach 2000; Alava and Niskanen 2003). The data on the softening of wood polymers from the references (Andersson and Berkyto 1951a; Goring 1963; Ogiwara *et al.* 1970, Salmén and Back 1977a and 1982; Salmén *et al.* 1984; Back and Salmén 1989; Waterhouse 1984; Salmén 1990; Shiraishi 1991) allow the prediction that most wood polymers in paper at moisture content around 6 to 8% soften at a temperature in the range 150 to 180 °C. However, the crystalline part of the cellulose does not soften under elevated temperature/moisture, and starts to degrade at a temperature of around 240 °C (Beyler and Hirschler 2001; Szcześniak *et al.* 2008). The optimal temperature for the improvement of extensibility is highly dependent on the heating situation. In an open system, in which water can evaporate from the paper upon heating, the maximum improvement in extensibility can be observed at temperature ranges of 60 to 70 °C and 80 to 100°C for chemical and mechanical pulps, respectively (Kunnari *et al.* 2007). The dependence of softening temperatures of the wood polymers on the moisture content is shown in Fig. 21.

The softening temperatures of wood polymers in paper depend largely on the moisture content of the polymers. In the absolutely dry state cellulose, lignin, and hemicelluloses have softening temperatures of 230 °C, 205 °C, and 180 °C, respectively.

These values are significantly lower already at 6% moisture content, which is typical for air-dry paper. However, lignin cannot absorb more than 10% moisture content due to its network structure and limited amount of the exposed hydroxyl groups.

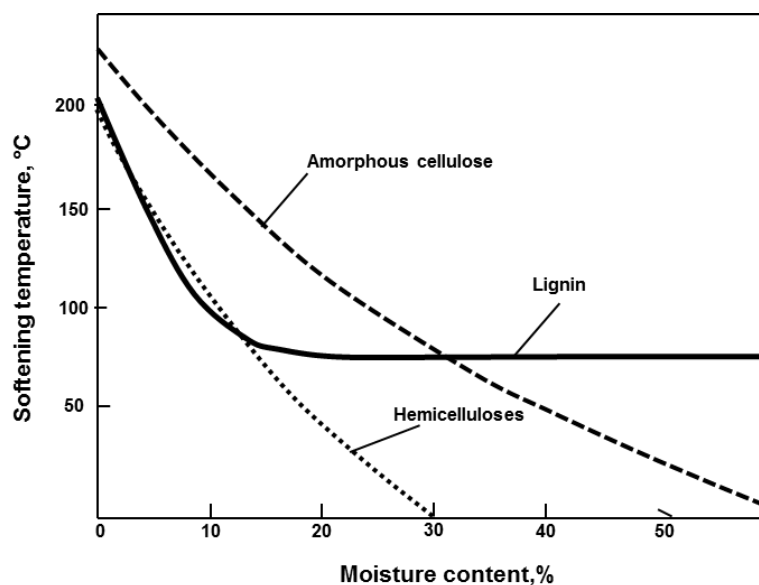


Fig. 21. A schematic representation of the relation between softening temperature of lignin, hemicelluloses, and amorphous cellulose and the moisture content (redrawn from the data of Salmén 1990)

Once paper is heated or moistened, the stiffness of the fibre wall decreases and interfibre bonds are weakened. Higher moisture amount also breaks fibre bonds, allowing a certain degree of sliding between the fibres. This changes the stress-strain behaviour of paper towards higher extensibility and less stiffness. This leads to the occurrence of an extended elongation region after the point of ultimate tensile strength (Brecht and Erfurt 1960; Johnson *et al.* 1983; Back and Salmén 1989; Retulainen *et al.* 1998; Uesaka *et al.* 2001; Sørensen and Hoffman 2003; Uesaka 2005; Alava and Niskanen 2006). Increased extensibility of paper in the softened state is primarily attributed to increased plastic deformation, while the elastic component is mitigated and ultimate tensile strength is reduced (Caulfield 1990). The amount of softening (reduction of elastic modulus) is higher, the higher the amount of amorphous cellulosic material. The elastic modulus of different cellulose-based materials decreases by around 0.18 to 0.64% for every 1 °C increase in temperature in a range of -25°C and 175°C (Nissan 1977; Caulfield 1990). The effect of a change in moisture content from 0 to 25% is even more pronounced (Fig. 22).

From Fig. 22, NSSC fluting paper experiences a decrease of 60% of elastic modulus at a moisture content of around 23%, while kraft sack paper and cotton linter paper experience the same decrease at 16% and 12%, respectively. Such behaviour can be explained by the different content of crystalline material in these samples. Water is only absorbed in the amorphous regions, and therefore for the materials with lower crystallinity, drastic changes in the mechanical properties would occur at higher overall moisture content. Additionally, higher lignin content in kraft and NSSC paper may mitigate the effect of the elevated moisture content on the softening of the paper, which might be attributed to the inaccessibility of the cellulose surface covered by lignin to water vapour.

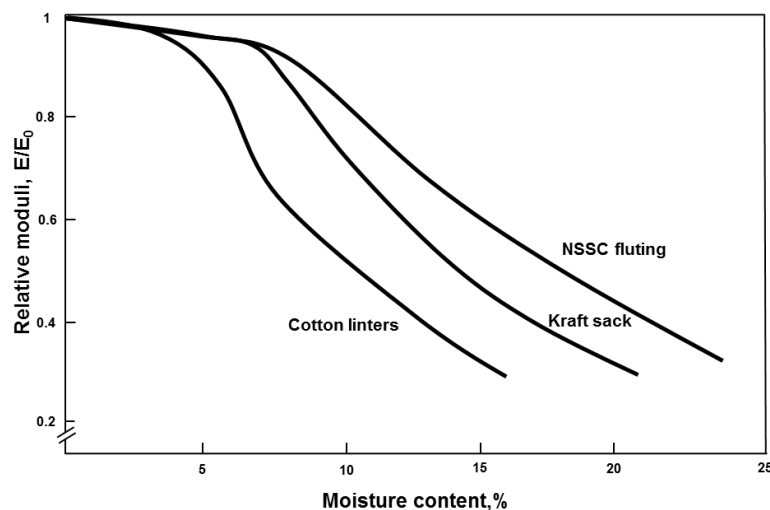


Fig. 22. The influence of the changes in the moisture content of cotton linter, kraft sack, and NSSC (Neutral Sulfite Semi Chemical) fluting paper on the relative moduli of paper (E_0 is the dry modulus), the crystallinity of samples was 85%, 70%, and 65%, respectively (redrawn from the data of Salmen and Back 1980)

The sole effect of moisture on the extensibility of paper is much stronger than that of temperature (Salmén and Back 1980; Kunnari *et al.* 2007). In the recent study by Linvill and Östlund (2014) the authors claimed that the increase in temperature only decreases the strain at break value, in the temperature range of 23 °C to 170 °C, while a gradual increase in moisture content of paper from *ca.* 6% to 14% improves the strain at break of paper on 20%. Negative action of elevated temperature in this case might be explained by insufficient amount of experimental points in the 23 to 100 °C temperature range and the mode of heating applied.

The changes in mechanical behaviour of paper exposed to a humid environment are related to transitions within the fibre wall and fibre bonds. As long as the interfibre bonding is strong enough, the fibre properties, especially of the bonded segments, probably explain the behaviour. With increasing moisture and especially when free water is present, the fibre bonds are weak, or are just based on frictional and capillary forces, and this explains a major part of the straining behaviour. Wet paper, although much weaker, can elongate much more than dry paper. This can be thought to be related to the properties of fibre contacts. In dry paper, the fibre contacts are bonded by H-bonds, and once broken they do not reform. In wet paper the fibre-fibre hydrogen bonds have not developed yet, the web strength is created by capillary forces and friction between the fibers, which does not disappear upon slippage between the fibers (van de Ven 2008). Unrestrained dried highly refined sulphite pulp (SR 88°) can have elongation of around 22%-points at a dryness of 40%, but the elongation gradually decreases to 8% when dryness increases to 90% (Brecht and Erfurt 1959). The characteristic change in the paper stress-strain curve of kraft paper occurs after it reaches around 50% dry solids content; then the elastic component of the curve starts to increase, while plastic component decrease (Retulainen *et al.* 1998). The joint effect of the temperature and moisture can be demonstrated by failure envelopes for paper at different temperatures and moisture levels (Fig. 23).

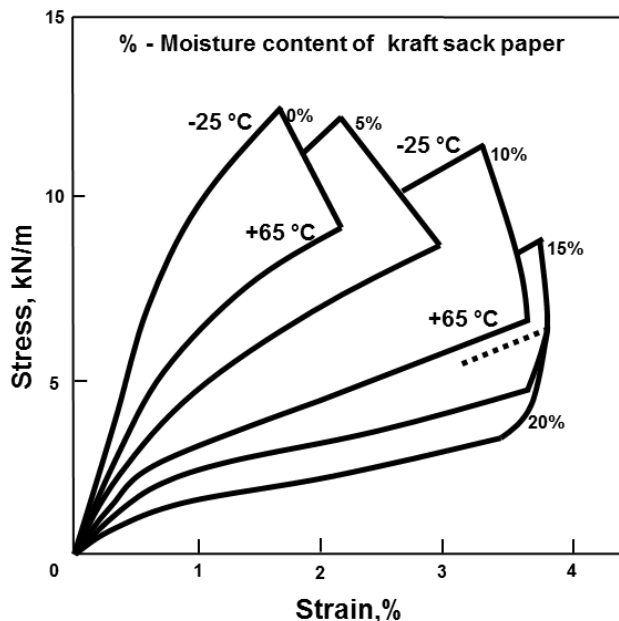


Fig. 23. Failure envelopes for a kraft sack paper in the machine direction at temperatures from minus 25 to plus 65°C and moisture contents of 0, 5, 10, 15 and 20% (redrawn from the data of Salmen and Back 1980).

The response of paper to elevated moisture content is different in remoistening. The maximum extensibility can be observed already at 85 to 90% dryness (Andersson and Berktyo 1951b). There is a clear difference in response to the high moisture content between unrestrained dried and restrained-dried paper. Extensibility of unrestrained dried paper is not affected by an increase in moisture content, while restrained dried paper, once moistened to 83% dryness, can be strained twice more than original value for dry paper (Kunnari *et al.* 2007). Part of this may also be associated with the partial relaxation of the drying stresses in paper (Kimura 1978).

The moisture and elevated temperature are of great importance for the 3D-forming of paper in such processes as hot pressing, vacuum forming, and deep-drawing. In these processes, paper is heated to reach an adequate formability, which enables straining or compressive folding (deep-drawing), and eventually production of the 3D-shapes. The typical temperature of the metal tools used in these processes is around 140 to 180 °C, which corresponds to the softening temperature of amorphous cellulose at a given moisture content of 6 to 8%. However, in the fast forming process, the temperature of the paper itself does not necessary reach values over 100 °C (Vishtal and Retulainen 2014). In several cases, the role of temperature is to dry the paper, create dried-in strains, and to “freeze” the formed shape.

CONCLUSIONS

The analysis presented in this paper has elucidated the nature of extensibility of fibre networks with a focus on paper and board. The aspects of fibre structure, bonding, network structure, fracture, and external conditions were considered in order to establish a solid basis for analysis. It can be concluded that the extensibility of the paper relies on three major factors: deformability of the single fibres, the ability of fibres to form a

strong and flexible bond which delays the onset of fracture, and the three-dimensional structure of fibre network created during the manufacturing process. In addition to this, straining conditions, including the temperature, moisture content, strain rate, *etc.* directly affect the extensibility of paper. In order to maximise the extensibility, measures in all these areas should be undertaken. Also for several practical applications the strain at break (according to standard procedure) is not a correct measure of the extensibility of paper, because in many cases paper can be strained beyond the point of maximum tension without a major loss in tensile stress.

The aim of this paper was to identify methods for the improvement of the extensibility of fibre networks. The answer to this question depends on target extensibility values for paper. Extensibility of paper can relatively easily be increased in the range of 5 to 10%-points by using high-consistency mechanical treatment and minimizing the wet draw on paper machine. However, if one is targeting values above 20%-points or even above 30%, then the solution would not be as easy. In order to boost extensibility of paper to such high levels, one would definitely require modifying the structure of paper by an in-plane compaction treatment, in addition to utilization of extensible fibres and modifying the character of the stress transfer between fibres by the addition of highly-extensible material. A common drawback with increased extensibility is that the tensile stiffness tends to decrease. It is essential that treatments should comply with each other and should correspond to the final use of the paper product. The approach to the production of highly-extensible paper can be compiled using the list of methods presented in Table 2.

Table 2. Methods for the Improvement of Elongation of Paper

| Treatment | Description of the effect | Advantages | Disadvantages | Increase in elongation | Ref * |
|---|--|---|--|--|------------|
| Treatments on the fibre level | | | | | |
| Utilization of fibres with high fibrillar angle | Fibres with the high fibril angle have better elongation potential. | Easy to apply. No need for additional treatments. | Poor availability of such pulp. | Up to 2–3% percent. Depends on the added amount of fibres and fibrillar angle. | 1,2,3 |
| Utilization of fibres with optimum hemicelluloses content | Hemicelluloses provide better bonding, increase swelling and drying shrinkage. | Easy to apply. Increased strength of paper. | Special cooking conditions might be needed to preserve the hemicelluloses. | Minor effect, Difference is clear when compared to hemipoor pulp. | 4,5, 30 |
| Mechanical treatment of fibres | Creation of dislocations and microcompressions which decrease axial stiffness of fibre and promote shrinkage and extensibility. | Can be applied using current equipment at paper mill. Refining may also improve other paper properties. | Inferior tensile strength and stiffness (for HC treatment). Increased energy consumption. | 2–8% points. The effect is more significant in case of unrestrained drying. | 6,7,2,8,9 |
| Grafting of fibres with polymers | Chemical grafting with acrylate polymers. This treatment increasing elongation potential by stronger and more extensible bonds in the paper web. | Great improvements in the extensibility. Biodegradability and recyclability of paper is preserved. | High cost. Complex chemical reaction. At high grafting levels, strength is impaired significantly. | 2–6%, depends on grafting level. | 10, 11, 12 |

Table 2 (continued). Methods for the Improvement of Elongation of Paper

| Treatment | Description of the effect | Advantages | Disadvantages | Increase in elongation | Ref * |
|---|---|--|---|---|----------------|
| Amorphisation of cellulose or utilization of cellulose with low crystallinity | The extensibility of amorphous cellulose is higher than for crystalline. Fibres have lower axial stiffness which would increase shrinkage. | Relatively high improvements in extensibility. Effect is scalable. | Amorphisation might require expensive chemical or harsh physical treatment. Associated with decrease in strength and some side effects. | Up to 20%-points. Proportional to decrease in crystallinity or/and amount of amorphous cellulose added. | 32,33,34 |
| Hydroxypropylation and hydroxyethylation of fibres | Direct etherification or addition of etherified fibre material improves bonding. Drying shrinkage is increased. | Great improvements in the extensibility. The physical and chemical nature of fibres is preserved. | High cost of chemical synthesis. Impaired dewatering. | 5–25%, depends on degree of substitution and drying method. | 13 |
| Oxidation of fibres | Periodate oxidation of C2-C3 hydroxyls in cellulose. Improved bonding, decreased crystallinity, changes in microfibrillar arrangement in the cell wall. | Significant improvements in extensibility even in case of restrained dried paper. The physical and chemical nature of fibres is preserved. | Decreased MW of cellulose. Cost associated with chemical treatment. Increased susceptibility to moisture. | 2–10%, depends degree of oxidation | 14 |
| Hexanoation | Esterification of cellulose to DS 1.7 leads to formation of continuous cellulose ester matrix with inclusions of unmodified cellulose. | Thermoformable. High improvements in extensibility. | Chemical modification associated cost. Not compatible with papermaking process. | Up to 30%-points | 31 |
| Treatments on the fibre network level | | | | | |
| Unrestrained or low restraint drying | Effect comes from drying shrinkage. | Greater extensibility and tensile energy adsorption. | Lower tensile strength and elastic modulus. | Gains in the extensibility are proportional to the amount of the shrinkage. | 8,15, 16 |
| Compaction | In-plane compression of wet paper web. Fibres after compaction appear curved, bended and buckled. | Significant improvements in MD elongation. CD elongation can be also improved. Easy to apply. | Decrease in tensile strength and stiffness. Need additional equipment. | Gains up to 10–30% in MD. CD elongation can be improved with advanced equipment. | 17,18,19,20,29 |
| Creping | Paper web is buckled against the doctor blade. By this web is buckled, wrinkled and compressed. | Significant improvements in MD elongation. Easy to apply. | Wrinkly and rough surface. Very low tensile strength and stiffness. | Elongation of crepe paper is in range of 35–200%. | 18 |
| Addition of latexes and rubbers | Latexes and rubbers after curing can form a polymer matrix within paper. | Easy to apply. Strength and extensibility are improved. Recyclability is questionable. | Needed to be cured. High cost of latexes. High addition amount. | At 10–40% addition to fibres, extensibility increased to 20–40%-points. | 21, 22,23 |
| Addition of NFC, CMC, | Improved bonding and increased drying shrinkage | Easy to apply. Cellulosic material | Impaired dewatering. Poor availability and high cost to produce. | Up to several %-points. | 24,25,26,27,28 |

Notes for Table 2 are given on the following page.

* NOTES for Table 2.

1-Hänninen *et al.* 2011; 2-Joutsimo *et al.* 2005 3-Donaldson 2008; 4-Spiegelberg 1966, 5-Scallan 1974, 6-Dumbleton 1972, 7-Page *et al.* 1976, 8-Seth 2005, 9-Ljungqvist *et al.* 2005, 10-Rezai and Warner 1997a, 11-Rezai and Warner 1997a, 12-Wang *et al.* 2007, 13-Didwania 1968, 14-Larsson *et al.* 2014a and 2014b, 15-Htun *et al.* 1989, 16-Page and Tydeman 1966, 17-Ihrman and Öhrn 1965, 18-Welsh 1966, 19-Poppel *et al.* 2000, 20-Cariolaro and Trani 2000, 21-Waterhouse 1976, 22-Alinec 1977 and 1979, 23-Svensson *et al.* 2013 24-Klemm *et al.* 2011, 25-Henriksson *et al.* 2008, 26-Duker *et al.* 2007, 27-Laine *et al.* 2002, 28-Madani *et al.* 2011, 29-Lahti *et al.* 2014, 30-Obermanns 1934, 31-Matsumura *et al.* 2000, 32-Page 1983, 33-Lenz *et al.* 1994, 34-Parker 1962.

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3D Forming of Paperboard: The Influence of Paperboard Properties on Formability

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Paper and paperboard are widely used in various types of packaging. Paper-based packaging is a recyclable, biodegradable, renewable and sustainable product, which gives it certain advantages over most plastic-based packaging materials. Although paper-based packaging, in some areas, lacks attractiveness in terms of visual appearance, 3D forming is an important method for producing advanced shapes from paper and paperboard, suitable, for instance, for modified atmosphere packaging. That said, very little is known about the deformations experienced by paper-based materials in 3D forming. Understanding the role played by the mechanical properties of paper and paperboard in the 3D forming process is key to improving performance. This paper presents experimental results obtained using three different forming devices designed to be used with paper-based materials and links the formability data with specific mechanical properties of the paperboard samples. Paperboard properties that were found to correlate with formability were as follows: compressive strength and strain, tensile strain, paper-to-metal friction and out-of-plane stiffness. The requirements for formability are different for the fixed blank forming process and sliding blank forming process. Copyright © 2013 John Wiley & Sons, Ltd.

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INTRODUCTION

Paperboard and other paper-based materials are the most widely used food packaging materials in the world, and their use has the potential to increase in the future.^{1–3} Paperboard is a recyclable, biodegradable and renewable packaging material possessing certain advantages over plastic-based materials. However, paperboard packaging cannot compete with packaging made of plastics in terms of the attractiveness of package design. Paper-based packaging appears in rather simple geometrical forms, whereas plastics can be formed into a wide variety of shapes. The main limiting factor for the production of advanced 3D shapes from paperboard is its poor formability, or rather its limited ability to withstand certain types of plastic deformations without damage.⁴

Formability can be defined as a complex mechanical property that determines the performance of a material in the forming process. The formability of paper depends on several mechanical properties related to aspects of formability: elongation, compressive strain, compressive strength and paper-to-metal friction.⁵ However, the actual role played by each mechanical property in respect to the maximum depth of shapes, their appearance and their runnability in the forming process has hitherto

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not been clear. Moreover, the relative importance of these aspects of formability varies according to the forming equipment and the forming conditions.⁶

In this study, the results of experiments with three different forming devices were analysed against the mechanical properties of the paperboard. The formability of seven different commercial paperboard samples was evaluated using variables reflecting the maximum depth of the shapes and their visual appearance after forming. These variables were as follows: formability strain, maximum drawing limit (MDL) and the frequency of compression wrinkles on the side wall of the cylindrical shapes. These variables were obtained from a 2D formability tester, a 3D spherical forming device and 3D deep-drawing equipment, respectively. Next, the paperboard samples were analysed for tensile strain, compressive strength and strain, paper-to-metal friction coefficient, thickness and density. The influence of elevated moisture and temperature levels was also considered. The results provide experimental knowledge of three different forming processes for paper-based materials and the aspects of formability involved.

EXPERIMENTAL

Materials

Seven different samples of commercial paperboards were used in this study. Samples were kindly supplied by Stora Enso Oy, Finland. The properties of the paperboard samples can be seen in Table 1.

As can be seen from Table 1, the properties of the paperboard varied over a broad range, thus providing a solid basis for the comparative evaluation of the performance of typical commercial paperboards in the forming process.

Methods

Experimental design. The experiments were aimed at shedding light on the relationship between the forming of paperboard and its mechanical properties. As such, only observed correlations are included in this paper. A primary difficulty is the fact that all three forming devices used in the study follow different forming principles. Thus, correlations between the formability and the mechanical properties of paperboard are device specific and should be treated separately in each case. A further study aim was to investigate the influence of temperature and elevated moisture content on the process of forming, whenever it was possible to do so. For example, the influence of temperature was studied with the 2D formability tester and 3D spherical forming device.

Forming the paperboard. Three forming devices were used to investigate the formability of paperboard: a 2D formability tester (supplied by VTT, Jyväskylä, Finland), a 3D spherical forming device (supplied by Stora Enso Research Centre, Imatra, Finland) and a 3D deep-drawing device (supplied by Technische Universität, Dresden, Germany). A scheme showing the forming principles and formed shapes for the 2D formability tester, 3D spherical forming device and 3D deep-drawing device can be seen in Figures 1 and 2.

Table 1. Properties of the commercial paperboard samples used in the experiments.

| Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|----------------------------------|-------|-------|-------|-------|-------|-------|-------|
| Grammage, g/m ² | 189.9 | 198 | 210.3 | 250.2 | 256.8 | 263 | 314.4 |
| Thickness, μm | 242 | 268 | 280 | 395 | 346 | 363 | 406 |
| Density, kg/m ³ | 784 | 738 | 752 | 644 | 743 | 725 | 774 |
| Tensile index MD, Nm/g | 87.8 | 83.3 | 73.3 | 91.9 | 70 | 77.9 | 98 |
| Tensile index CD, Nm/g | 35.1 | 35.8 | 37.5 | 41.4 | 37.3 | 32.2 | 48.9 |
| Strain at break MD, % | 2.2 | 2.3 | 2.6 | 2.1 | 2.5 | 2.1 | 2.3 |
| Strain at break CD, % | 6.3 | 6 | 5.6 | 5 | 5 | 6 | 6.2 |
| Moisture content 50% RH, 23°C, % | 6.39 | 6.34 | 6.27 | 6.99 | 6.23 | 6.44 | 6.55 |
| Moisture content 75% RH, 23°C, % | 10.73 | 10.43 | 10.12 | 11.29 | 10.44 | 10.53 | 10.62 |

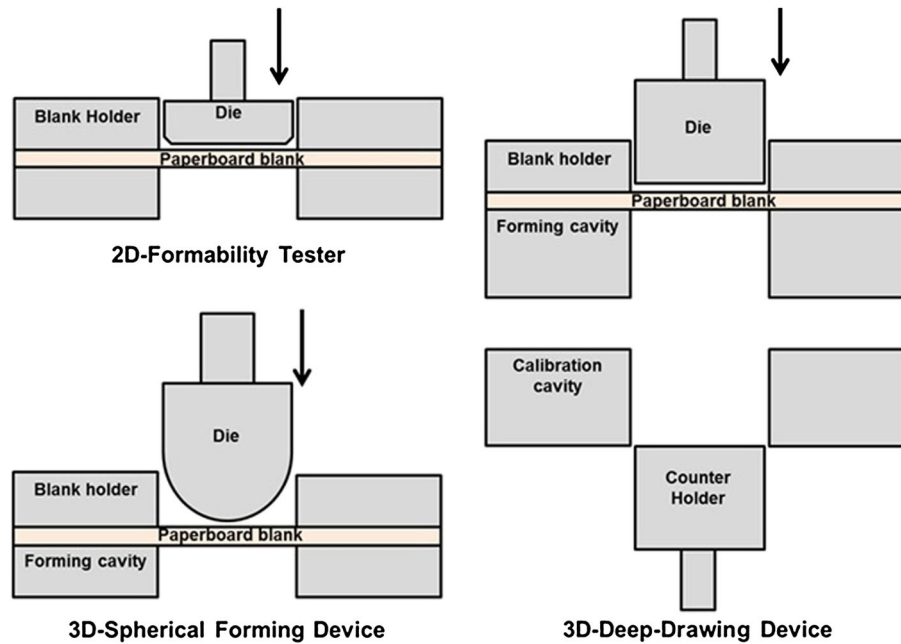


Figure 1. Schemes of operation for the 2D formability tester, 3D spherical forming device and 3D deep-drawing device.

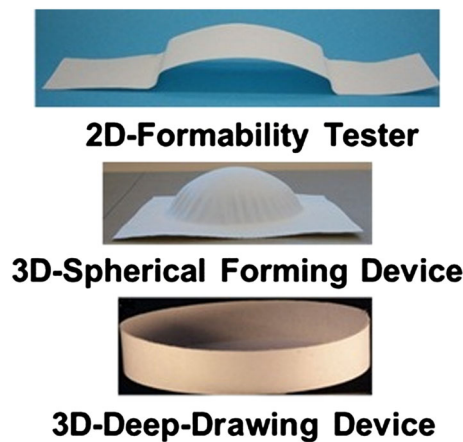


Figure 2. Examples of shapes obtained with the 2D formability tester, 3D spherical forming device and 3D deep-drawing device.

The 2D formability tester is equipped with a double-curved, heated press (reaching temperatures up to 250°C), blank holders and an infrared sensor (Omega® OS36, Stamford, Connecticut) to measure the temperature of the paper. The forming procedure works as follows: a paperboard sample (20 mm wide × 65 mm long) is clamped by the blank holders. The press is then moved into contact with the sample and kept in place for 0.5 s in order to heat the sample. The press then continues in a downward movement until breakage. The velocity of the forming press was 10 mm/s.⁷ The formability strain of the samples was then measured as an average value of 10 samples at 23°C, 70°C and 130°C in the press.

The 3D spherical forming device is similar in operation to the 2D formability tester, with the exception of the shape of the die and the method of heat transfer. In this device, only the forming cavity is heated, while the forming die is not. The temperature of the forming die was adjusted by conditioning it at maximum possible proximity to the forming cavity until it reached a stable

temperature. The value of the multidimensional strain that the paper could tolerate without breakage was the variable measured in these experiments. This variable is referred to hereafter as the MDL. The parameters used in experiments with the 3D spherical forming device can be found in Table 2.

The 3D deep-drawing equipment utilizes a different forming principle from the other devices. In this case, a paperboard blank of a predefined shape and size is fed into the device where it is clamped with blank holders set at a particular force. It is then drawn through the shaping and calibration cavities until it comes into contact with a counter holder. The formed shape is then released from the device.⁶ The process parameters and dimensions for the blank and formed shape can be found in Table 3.

Among the parameters listed in Table 3, the forming gap needs further explanation. The forming gap is the distance between the edge of the forming cavity and the edge of the die. This distance can be varied according to the thickness of the materials. When the thickness is too small, the forming gap increases the out-of-plane shear and in-plane compressive forces. This can lead to fractures and cracks in the formed shape.⁶ When the thickness is too large, a forming gap on the other hand leads to a poor appearance of the shape because of wrinkles, whose formation is less restricted.

Friction measurements. Friction tests were carried out using a custom-built friction measurement device at VTT. The device is composed of a heated steel plate (grade TOOLOX33®, Stockholm Sweden) and electric drive with a voltage sensor (Kyowa® LVS – 100 GA, Chofugaoka, Chofu, Tokyo, Japan) connected to a moving sledge via an inextensible cord. The paper sample is placed under the sledge, and a voltage sensor is set to 1000 scans/s. Voltage in this case refers to the sliding resistance. The weight of the moving sledge was 892 g. A photograph of the friction measurement device can be seen in Figure 3.

Static friction was recorded as the voltage value at the moment when the sledge started to move. Dynamic friction was measured as the average value of force needed to move the sledge with the paper sample (65 mm wide × 65 mm long) for a path of 80 mm at a velocity of 19 mm/s. The Coulomb friction model was assumed to be valid in this case.

Measuring the distance between wrinkles. In the deep-drawing process, where a paper blank is allowed to slide into the forming cavity, wrinkles are the most important quality indicator in the shapes produced. They affect both the appearance and the functionality of the final product, influencing the shape's accuracy, stability after forming and possibility of sealing for modified atmosphere packaging. The frequency of wrinkles is a reflection of the uniformity of the mechanical load distribution on the

Table 2. Parameters used in experiments with 3D spherical forming device.

| Parameter | Set 1 | Set 2 | Set 3 | Set 4 | Set 5 | Set 6 |
|---------------------------------------|-------|-------|-------|-------|-------|-------|
| Size of the sample, m ² | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Blank holding force (hydraulic), kPa | 4000 | 4000 | 4000 | 4000 | 4000 | 4000 |
| Speed of the die, mm/s | 50 | 50 | 50 | 50 | 50 | 50 |
| Relative humidity in conditioning, % | 50 | 50 | 50 | 75 | 75 | 75 |
| Temperature of the forming cavity, °C | 23 | 110 | 165 | 23 | 110 | 165 |
| Temperature of the die, °C | 23 | 67 | 83 | 23 | 67 | 83 |

Table 3. Process parameters in deep drawing.

| Parameter | Set 1 | Set 2 | Set 3 |
|---------------------------------------|-------|------------------------|-------|
| Temperature of the die, °C | 60 | 70 | 80 |
| Temperature of the forming cavity, °C | 100 | 120 | 160 |
| Die force, kN | | 20 | |
| Blank holding force, kN | | 2 | |
| Counter holder force, kN | | 2 | |
| Forming gap, mm | | 0.7*thickness of board | |
| Blank diameter, mm | | 160 | |
| Shape diameter, mm | | 110 | |
| Height of the shape, mm | | 25 | |
| Type of the shape | | Cylindrical | |

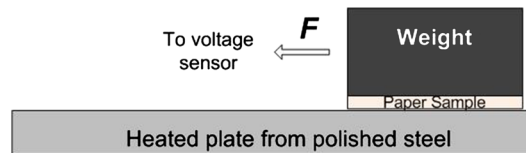


Figure 3. The friction measurement device.

side wall of the shape. Paperboard blanks were drawn into cylindrical shapes with a 25 mm high wall. The wrinkles were measured in the machine direction (MD) of the paper along a straight line parallel to, and 5 mm from, the edge of the shape. This method is discussed earlier.⁶ The frequency of the wrinkles was measured using a light microscope. The mean value of the distances between wrinkles was taken as the result. An image of the cylinder wall and wrinkles is shown in Figure 4.

An evaluation of the visual appearance of the shapes was based on the following hypothesis: A short distance between wrinkles means a high number of small, shallow wrinkles. This indicates a satisfactory appearance for the shape while a greater distance means that there are fewer wrinkles, highly irregular in their dimensions, indicating a poor appearance of the shape.

Measuring the stress–strain and compressive properties of the paperboard. The stress–strain properties of the paperboard were measured in accordance with SCAN-P 38:12. The compressive strain and strength were measured using the ring crush test by Zwick/Roell (Zwick GmbH & Co. KG). The size of sample was 8 mm wide \times 152 mm long. A spherical indentation test to measure the z-directional stiffness was made using a 1 mm diameter steel ball in a modified tensile tester. The test tip is shown in Figure 5. A pile of four sheets was used in the test. The test comprised a loading–unloading cycle in which the highest load was 25 N. The speed of loading and unloading was 25 and 1 mm/min, respectively. The recoverable elastic compressive strain was measured from the unloading curve. The loading and unloading stiffness values were estimated at the 10 N.

RESULTS

The forming devices for paperboard used in this study belong to two principal types: a 2D formability tester and a 3D spherical forming device for machines using a fixed paper blank, while a 3D



Figure 4. The formed shape with wrinkles and microscope image of the wrinkles.

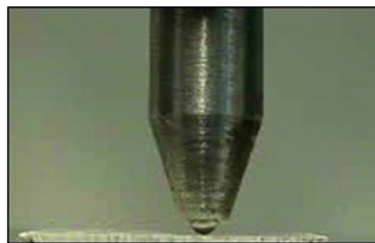


Figure 5. Test tip used in spherical indentation measurements.

deep-drawing device was used where paperboard is allowed to slide into the forming cavity. Such a divergence in the forming procedure sets completely different requirements on the mechanical properties of paperboard. Thus, the formability of paper and the properties that govern it depend on the type of deformations experienced in each particular forming process.

The role of elevated temperature in forming

Paper-based materials are strongly affected by the action of elevated temperature and changing moisture levels.⁸ In general, elevated temperature and high moisture content lower the elastic modulus and tensile strength but increase elongation.⁹ The improvements in elongation can be as high as 2.0 to 2.5 percentage points.⁷ In 3D forming, paper is heated in order to improve its plasticity, as well as to 'freeze' the shape after forming.⁶ The influence of elevated temperature on the formability of paperboard in the 2D formability tester and the 3D spherical forming device is shown in Figure 6. The formability values are expressed as the percentage change in the parameter in relation to the values measured at 23°C.

The data represented in Figure 6 show that elevated temperature has a positive influence on the formability of paperboard in both cases. In the 2D formability tester, heat transfer occurs through the continuous contact of paper with the heated forming die. It was found that paper with a grammage of 80–250 g/m² can be preheated to the die temperature within 0.5–0.7 s. This means that the temperature of the paper at the moment of forming is close to the temperature of the die. Additionally, the forming cavity of the 2D formability tester is not 'sealed' from the outer atmosphere, and moisture can escape from the board by evaporation. The optimal temperature of the paperboard is clearly below 100°C, and the softening effect of the elevated temperature (at levels above 80°C) is mitigated by the decrease in the moisture content of the sample.⁷

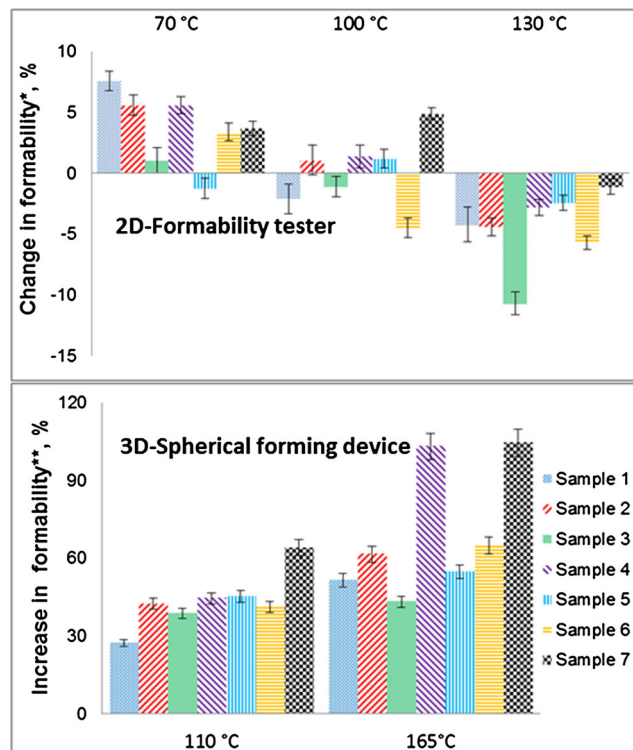


Figure 6. The influence of elevated temperature in the forming die (2D formability tester) and forming cavity (3D spherical forming device) on the formability of the samples. *formability strain and **maximum drawing limit.

In the 3D spherical forming device, the paperboard is heated via convective heat transfer and via direct contact with the forming die. It is probable that the temperature of the paper was far lower than the temperature of the forming cavity and was close to the temperature of the forming die, that is, 67°C and 83°C for cavity temperatures of 110°C and 165°C, respectively. In this case, the temperature of the paperboard did not exceed 80°C. Increase in the formability at the temperature of cavity of 165°C for the samples 4 and 7 may be related to the significantly higher thicknesses of these samples. In thick samples, heat transfer generally takes more time, and thus thick paperboards require higher forming temperature in order to soften the paperboard. Additionally, the paperboard blank in the 3D spherical device is better isolated from the outer atmosphere, which reduces any drying of the paperboard and promotes a softening of the material.

In the 3D deep-drawing equipment, the role of temperature cannot be compared with that in the other forming devices. The parameter studied with this device (the frequency of wrinkles) may not be directly affected by any softening of the material caused by temperature. Furthermore, forming was not possible at cavity temperatures below 100°C, probably because of high paper-to-metal friction. A possible alternative reason for the unsuitability of forming temperatures lower than 100°C is the lack of any softening of the material.

The influence of the temperature of the metal plate on the paper-to-metal friction of the paperboard samples can be found in Figure 7.

As can be seen from Figure 7, paper-to-metal friction decreases with elevated temperature. This is the case for both static and dynamic friction. This may be explained by the lubricating action of evaporating moisture.⁹ A slight increase in friction at a temperature of 130°C can be explained by excessive drying of the paperboard by the end of the measurement.

In general, the optimal forming temperature in the 3D deep-drawing device was in the range 140–180°C (cavity temperature) and 60–100°C (die temperature), depending on the thickness of the paperboard.

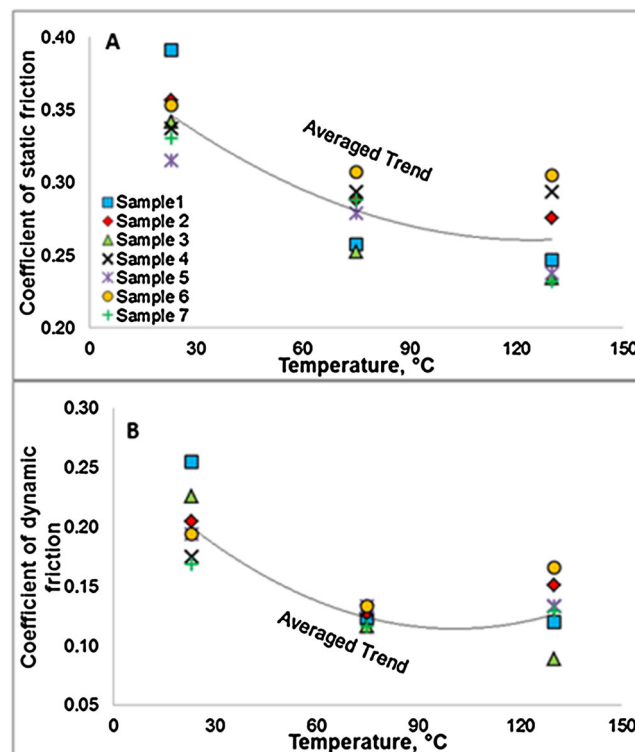


Figure 7. The influence of temperature on the static (a) and dynamic (b) paper-to-metal friction coefficient.

It is possible to conclude that the temperature in forming should be adjusted in a way that the paper will soften and reduce friction, while at the same time avoiding excessive drying. Thus, factors such as the heat transfer rate within the paperboard, the moisture evaporation rate, the softening properties of the fibre web and the effect of elevated temperature on friction should all be taken into account in the forming process.

Influence of moisture on the maximum drawing limit of commercial samples

Elevated temperature and moisture in paper act in synergy, promoting a softening of the material. Thus, moistening the paperboard prior to forming is one aid to improving its deformability characteristics and increasing the depth of shapes. The influence of conditioning the samples in a humid environment (75% RH, 23°C) on the formability of the samples is shown in Figure 8. Values on the graph are expressed as a comparison of the results with those for the samples conditioned at 50% Relative Humidity (RH), 23°C.

As can be seen from Figure 8, the elevated moisture level of samples results in improved formability of the paperboard, and an increase in formability of up to 70% can be observed at room temperature. With the increase in temperature, the effect of elevated moisture decreases. This indicates that at elevated temperatures, the water evaporates rapidly from the paper. Therefore, the moisture content decreases and approaches the moisture content of the samples conditioned at 50% RH, 23°C. Alternatively, extensive softening of the paper may impair fibre bonding, thus making the paper weaker. It may be the case that moistening the samples enhances their formability. However, it is important to note that high moisture content decreases the strength of the paperboard, increases the paper-to-metal friction and may increase the probability of fractures and breaks. It may also lead to such defects as blistering.^{5,10}

Stress–strain properties versus formability

2D formability tester. The elongation of paper is considered to have a primary importance for the formability of paper-based materials.^{7,11,12} It is assumed that the input materials are strained in forming; they therefore need to have sufficient elongation. The resulting tensile elongation measurements taken during experimentation correlate with the forming results in the 2D formability tester (formability strain) and the 3D spherical forming device (MDL).

The correlation between the formability strain (in the 2D formability tester) measured at 70°C and the elongation of the commercial samples is shown in Figure 9.

The data shown in Figure 9 indicate that the formability strain correlates well with the strain at break value, for the paperboard samples. The same correlation can be observed for the MD of paperboard and at other tested temperatures. This correlation is quite obvious because the stresses experienced by paper in the 2D forming device are similar to the stresses in conventional stress–strain

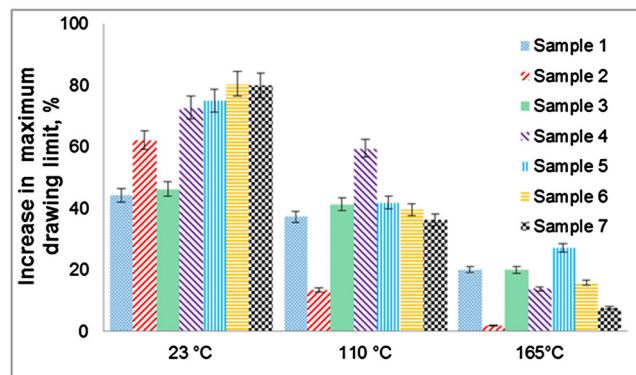


Figure 8. The effect of elevated moisture level (conditioning at 75% RH, 23°C) on the maximum drawing limit at different forming cavity temperatures. Results shown as percentage change in comparison with the corresponding values obtained at 50% RH, 23°C. *Moisture content of samples was 6–7% (50% RH, 23°C) and 10–11% (75% RH, 23°C).

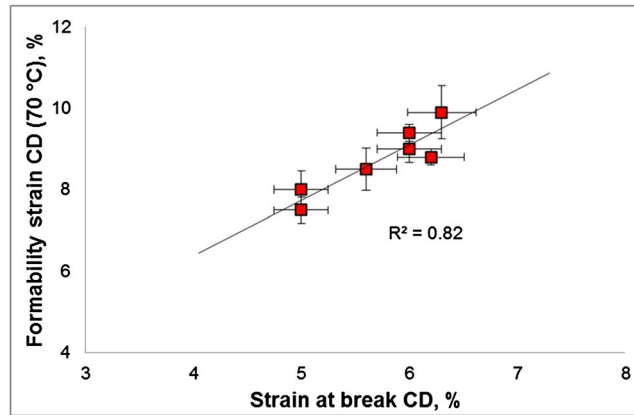


Figure 9. The correlation between the formability strain in CD measured at 70°C and the strain at break value (CD) of commercial samples.

measurement, with the exception of the frictional stresses, which can be found in tests with the 2D formability tester. Additionally, in 2D forming, stresses on the outer surface of the paper die are higher than those on the inner surface of the paper.

3D spherical forming device. Formability in the 3D spherical forming device was also found to correlate with the elongation of paper in the cross direction (CD). The correlation between the strain at break value of the paperboard and the MDL can be found in Figure 10.

As can be seen from Figure 10, there may be correlation between the MDL and the elongation in CD, but the value of R^2 is not as high as for the 2D formability tester. No correlation between MDL and elongation in MD exists. This fact can be explained by the type of straining deformation in the 3D spherical forming device (the straining in this case is close to the biaxial straining). Because of this fact, the MDL is also determined by the elongation in the CD of the paper. The straining deformation is clearly higher in the CD than that in the MD when the paper is strained in a hemispherical shape.¹¹

3D deep-drawing device. The forming principle with the 3D deep-drawing equipment is different from the two other devices. The elongation of paper plays only a minor role in the formability of paper in the sliding blank forming process, because the paper blank is allowed to slide in the forming cavity, preventing significant straining of the paper. In this device, paper is subjected to a combination of shear, tensile, frictional and compressive stresses.⁵ Therefore, no statistically significant correlation was found between the elongation of the paperboard and the distance between wrinkles.

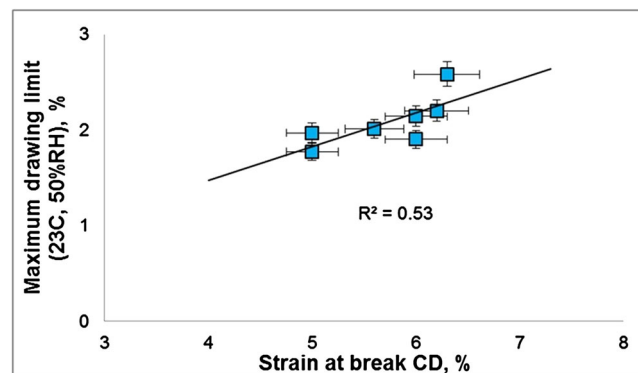


Figure 10. The correlation between the maximum drawing limit at 23°C, 50% RH, and the strain at break value (CD) of commercial samples.

Influence of frictional properties of paperboard on formability

When the metal tools of the forming device come into direct contact with the paper, the formation of frictional forces between the two surfaces (metal–paper) is inevitable. High friction in forming increases tension and the probability of fractures and thus has a negative influence on the depth of the shapes. The influence of friction on formability was studied using the three forming devices. It is important to notice that no difference in coefficient of friction was observed between the MD and the CD of the paper samples.

2D formability tester and 3D spherical forming device. The relation between the formability strain, the MDL and the coefficient of static friction is shown in Figure 11.

As can be seen from Figure 11, there is a correlation between the MDL measured at 165°C (50% RH, 23°C) and the coefficient of static friction at 130°C. The correlation between the formability strain measured at 130°C and the coefficient of static friction at 130°C is conditional, probably because of a relatively high deviation in formability strain. High friction negatively affects the formability of the paperboard in the forming processes using the fixed blank. This can be explained by the fact that high static friction may lead to ‘stick and slip’ of the die–paperboard interface and to uneven straining stress distribution in the sample during the initial phase of forming. The same trend can also be observed for the correlations measured at lower temperatures, although the correlations are weaker. It should be noted that friction is sensitive to the changing moisture content and temperature of paper. High temperature decreases paper-to-metal friction, while high moisture content increases it. This behaviour is valid in the case of both static and dynamic friction.

3D deep-drawing device. In forming, the paperboard is forced to slide against the forming cavity under a certain amount of force caused by the narrow slot tightening the paper between the die and the forming cavity (forming gap $\leq 0.7 \times$ thickness of the material). The transverse compressive deformation is resisted by the frictional forces. The coefficient of dynamic friction has a higher influence on the formation of wrinkles than the coefficient of static friction.

The relationship between the frequency of the wrinkles on the side walls of the shapes and the coefficient of dynamic friction is shown in Figure 12.

As can be seen from Figure 12, the high coefficient of dynamic friction has a positive influence on wrinkle distribution; that is, there are more wrinkles, but they are more uniform. It can be suggested that the frictional forces prevent displacements caused by compression deformation, which decreases the area in which wrinkles can form. This improves the uniformity of the wrinkles and, in fact, the appearance of the shapes. It is quite probable that friction forces might act in synergy with the blank holding force and thus affect wrinkle distribution. Despite the fact that the high coefficient of dynamic

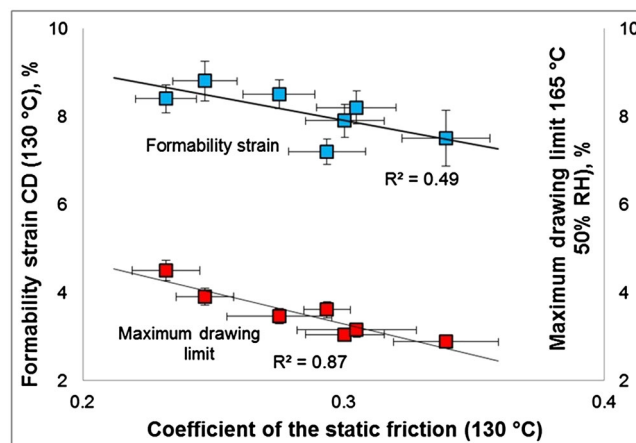


Figure 11. The correlations between the formability strain (70°C), the MDL (165°C) and the coefficient of friction (130°C).

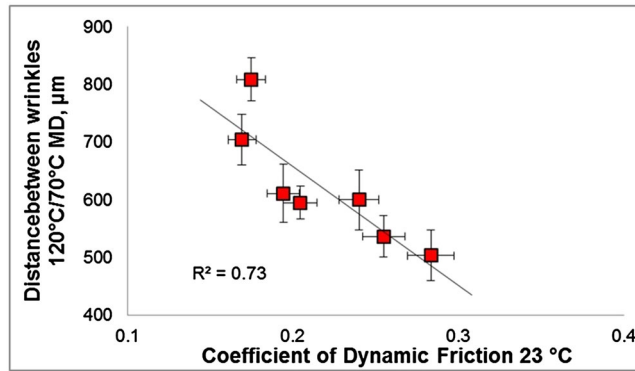


Figure 12. The relationship between the coefficient of dynamic friction measured at 23°C and the distance between wrinkles 120/70°C.

friction may improve the visual appearance of the shape, it can also increase the probability of fractures and may contribute to discolouration (darkening) of the material at high temperatures.⁶

Influence of compressive strain and strength of paperboard on the formation of wrinkles

The relationship between the compressive strength (a) and strain (b) and the frequency of wrinkles can be found in Figure 13. The compressive strength and strain of paper appear to have a significant impact on the character of wrinkle distribution.

The data in Figure 13 shows compressive strain to be a crucial determining factor for the frequency of wrinkle formation, while the influence if the compressive strength is not as clear. Wrinkles are formed because of compressive stresses, and the lower the compressive strain on the

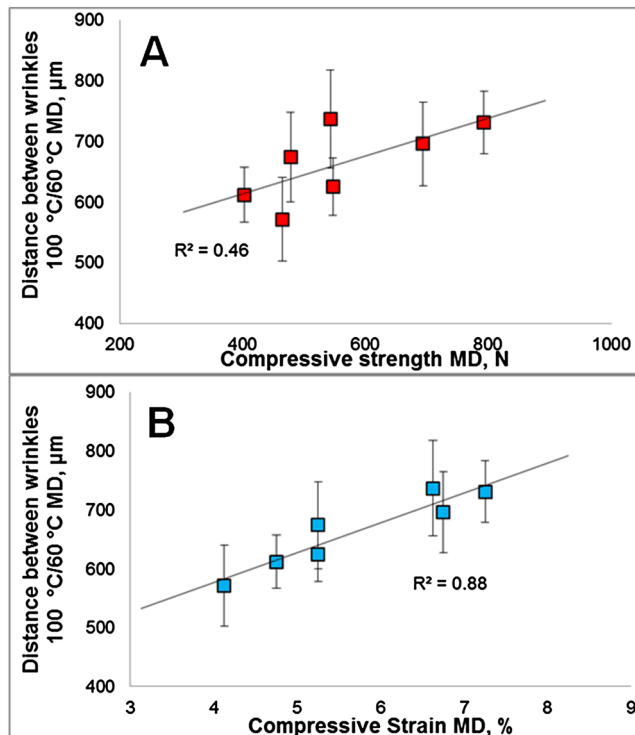


Figure 13. Correlations between compressive strength in MD (a), compressive strain in MD (b) and distance between wrinkles.

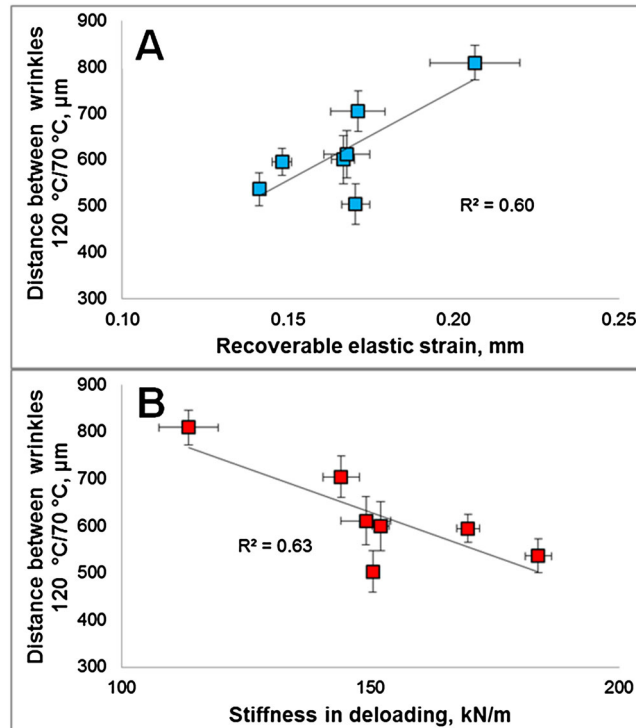


Figure 14. Correlations between recoverable elastic strain in the z-direction (a), stiffness in unloading (b) and distance between wrinkles.

paper, the shorter the distances between wrinkles. The appearance of the shapes is therefore better. Compressive strength itself does not seem to have a direct influence on the formation of wrinkles because material in deep drawing is subjected not only to compressive stresses but also to a combination of shear, tensile and compressive stresses and frictional forces. Thus, the R^2 values for this correlation are below significant limits.

The out-of-plane compressive properties of the paper were measured using a modified spherical indentation test. The relationship between the frequency of wrinkles, the recoverable elastic strain and the unloading stiffness is shown in Figure 14.

As can be seen from Figure 14, the more elastic the paperboard is, the worse an appearance it has, and the stiffer the material is, the better an appearance it has. Based on this hypothesis, in order to yield shapes with best possible appearance, paperboard should be stiff and have a low elastic recoverable strain component.

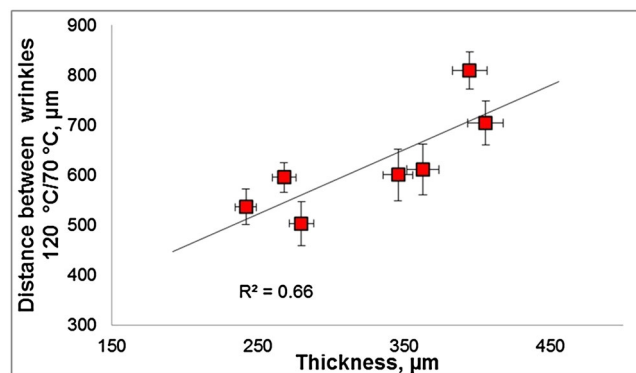


Figure 15. The relationship between the thickness of paper and the distance between wrinkles.

Table 4. The summary of the experimental work in this paper.

| | | | |
|---|---|--|---|
| Category | 2D formability (no sliding) Paperboard blank is fixed firmly. Formability strain Maximum depth of the shape Insufficient elongation | 3D spherical forming (no sliding) Paperboard blank is fixed firmly. Maximum drawing limit Maximum depth of the shape Insufficient elongation/high metal–paper friction Moisture content of the paper, temperature of the forming cavity | 3D deep drawing (sliding) Paperboard blank is sliding. Distance between wrinkles in MD Visual appearance, printability, sealing Formation of wrinkles due to compressive contraction of the blank Temperature of the tools, thickness, density, grammage of the paper, metal–paper friction (dynamic) Compressive strain and strength, thickness and density of material, paper-to-metal friction (dynamic) |
| Type of the process | | | |
| Measured parameter | | | |
| Practical meaning | | | |
| Primary limitation | | | |
| Additional factors, affecting the investigated parameter | Paper-to-metal friction (static), temperature of the die | | |
| Mechanical and basic properties to be considered while selecting paper-based material for the forming process | Tensile strain and strength, paper-to-metal friction (static) | Tensile strain and strength, paper-to-metal friction (static) | |

The influence of the basic properties of paperboard on formability

In the deep-drawing process, lateral contraction of the paper is inevitable, resulting in the formation of wrinkles. The basic properties of paper, such as grammage, thickness and density, affect the appearance of shapes. The relationship between the thickness of paper and the frequency of wrinkles can be found in Figure 15.

As can be seen from Figure 12, an increase in the thickness of paperboard leads to a decreased frequency of wrinkles. It was also found that density correlates (weakly) with the frequency of wrinkles, although in the opposite manner (higher density = better appearance). These basic properties correlate with the compressive properties of paper¹³ and thus affect wrinkle formation. The increase in thickness is commonly associated with the increase in the bulk of the material, which in turn lowers the density and leads to a greater distance between wrinkles. These basic properties also affect heat and mass (water) transfer within the paper and thus affect the optimal temperature for forming.

SUMMARY

Three different forming devices, each with different forming principles, were studied. It was found that the paperboard properties that contribute to its formability are different in each process. The information regarding the forming principles, limitations and other factors that affect formability can be found in Table 4.

Based on the results of this study, it is possible to draw the following conclusions:

The requirements placed on the paperboard depend strongly on the forming process that will be applied to it. The maximum depth of shape in a forming process in which the paperboard blank is firmly fixed depends on elongation and the coefficient of static friction. In this case, elongation should be as high as possible while the paper-to-metal friction should be low in order to obtain the maximum possible depth of shape.

In the deep-drawing process, in which sliding takes place, the appearance of the shape depends on the coefficient of dynamic paper-to-metal friction, compressive strain, z-directional stiffness and elasticity, and the basic properties of the paperboard. Ideally, the paperboard should be stiff and show plastic behaviour in compression (z-direction), with low compressive strain. High dynamic friction is favourable to appearance but may lead to fractures and discolouration.

The temperature and moisture levels of paper, as well as process parameters such as the forming gap, blank holding force and temperature of the metal tools, are also of high importance in the forming processes as discussed earlier.

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PUBLICATION IV

**The Elongation Potential of Paper –
How should fibres be deformed
to make paper extensible?**

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The Elongation Potential of Paper – How Should Fibres be Deformed to Make Paper Extensible?

Xiling Zeng,^{a,*} Alexey Vishtal,^b Elias Retulainen,^b Eino Sivonen,^c and Shiyu Fu^a

Elongation at failure is an important but underrated functional property of paper. Traditionally, elongation has been of specific importance for sack and bag paper grades. Mechanical treatments at high consistency are known to induce fibre deformations that contribute to the elongation of paper. However, it is not clear to what extent different fibre deformations can improve the elongation of paper. The aim of this work was to investigate the influence of three mechanical treatments on fibre and paper properties. The wing defibrator, the E-compactor, and the Valley beater were used for treating chemical softwood pulp. It was found that the type and intensity of mechanical treatments significantly affect the formation of fibre deformations, and thus the resulting properties of paper. The combination of high-consistency wing defibrator treatment and subsequent low-consistency valley beating provided paper with high elongation potential and good strength properties without impairing the dewatering properties.

Keywords: Elongation; Fibre deformations; Microcompressions; Shrinkage; Tensile strength

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INTRODUCTION

The mechanical properties of paper have been the subject of research since the rise of modern papermaking. Conventionally, tensile strength has been the primary target of improvement, while the other properties have been somewhat underrated. The elongation of paper is one of these underrated properties. In principle, elongation is the ability of material to increase its linear length under the action of external mechanical forces; the increase in the linear length is attributed to elastic and plastic deformations (Levlin and Söderhjelm 1999). This property increases the tensile energy absorption (TEA) potential of paper, which is defined as the integral of the tensile force and specimen elongation up to the point of failure, and is important for runnability of the web on the paper machine and in the printing house (Hristopulos and Uesaka 2002; Uesaka 2005; Deng *et al.* 2007), and for converting operations of paper and paperboard (Gärd 2002; Post *et al.* 2011; Östlund *et al.* 2011). Elongation of paper is also one of the central components of formability of paper-based materials (Vishtal and Retulainen 2012). The elongation potential of paper relies on three principal factors: properties of single fibres, the character of interfibre bonds between them, and the structure of the fibre network formed in the papermaking and converting processes (Dumbleton 1972; Page *et al.* 1985; Seth 1996; Welsh 1965). However, when the fibres have sufficient bonding, the elongation of a typical fibre network is primarily dependent on the single-fibre properties

(Seth 2005). Mechanical treatments of fibres at high consistency are known to induce fibre deformations that contribute to the elongation potential of the paper (Page *et al.* 1985, Seth 2005). Gentle laboratory beating at low consistency tends to straighten and lengthen fibres, reducing fibre deformation (Mohlin *et al.* 1996; Seth 2005; Seth 2006). The combination of the high- and low-consistency refining is also known as a method to improve the elongation and tensile energy absorption of the paper at low airflow resistance (Sjöberg and Höglund, 2005 and 2007). This approach is used for production of sack and bag grades of paper in the industry. Also, compressive treatment at high consistency has been shown to be a potential fibre treatment to improve strength properties of paper. It causes different types of deformations in axial and transverse dimensions of fibres (Hartman 1985; El-Sharkawy 2008). However, there is still a lack of information in scientific literature on the subject of how mechanical treatments of different type and intensity affect the fibre deformations and the stress-strain properties of paper, and how the other essential paper properties are affected.

The influence of the mechanical treatments with three different devices, the wing defibrator (high consistency, HC), a compressive E-compactor (HC), and a Valley beater (low consistency, LC), on fibre and paper properties was investigated in this work. The combination of HC wing defibrator treatment and subsequent LC Valley beating was also studied. The effect of these treatments on fibre properties and zero-span tensile strength has been reported in a recent publication (Zeng *et al.* 2012).

EXPERIMENTAL

Materials

The fibre raw material used in the study was first-thinning bleached pine kraft pulp obtained as pulp sheets from the Pietarsaari mill of UPM-Kymmene. The chemical composition and fibre properties of the first-thinning pulp are quite close to those of conventional once-dried softwood market kraft pulps.

Methods

Mechanical treatments

Three different mechanical devices were used to treat the fibres: the wing defibrator (HC), the E-compactor (HC), and the Valley beater (LC). Figure 1 shows schematic illustrations of the wing defibrator and E-compactor devices.

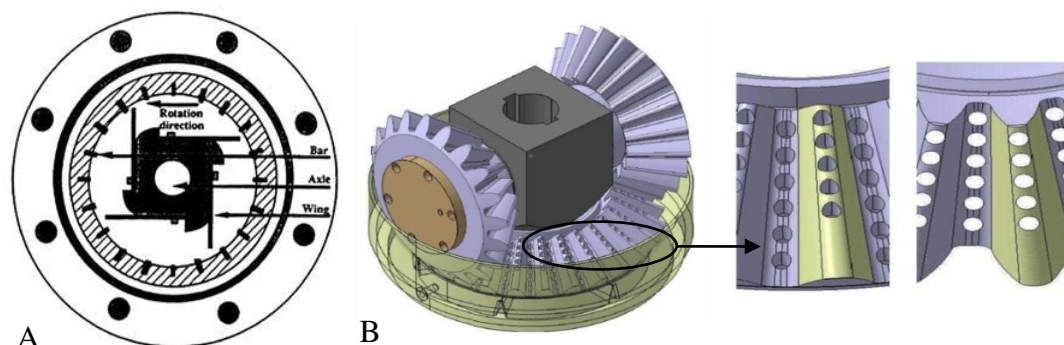


Fig. 1. Schematic illustrations of the wing defibrator (A) (Sundström *et al.* 1993) and the E-compactor (B)

Wing defibrator treatment

The wing defibrator is a high-intensity mixer fitted with four rotating blades; its primary utilization is in the preparation of mechanical pulp (Sundström *et al.* 1993). Each batch of 150 g (oven-dry) pulp was adjusted to a consistency of approximately 35% before the mechanical treatment. The rotation speed was 750 rpm, and the gap between the blades and the stator bars was 1 mm. There was a 20-minute pre-heating period. The jacket and chamber of the wing defibrator were heated by direct streaming. The condensate from the heating steam decreased the consistency of the pulp during the pre-heating phase. The conditions of the wing defibrator treatment are summarized in Table 1. The pure heating treatment without a mechanical treatment took place in an oil bath under similar conditions

Table 1. Conditions in the Wing Defibrator Treatment

| Sample | SEC*, kWh/t | Temp. °C | DS** after treatment, % |
|---------------------------|-------------|----------|-------------------------|
| Untreated/Preheated 110°C | 0 | 110 | 35.6 |
| B | 243 | 110 | 25.6 |
| C | 297 | 110 | 21.4 |
| D | 418 | 110 | 21.6 |
| E | 657 | 110 | 22.1 |
| F | 1129 | 110 | 21.7 |
| Untreated/Preheated 170°C | 0 | 170 | 35.5 |
| G | 128 | 170 | 9.9 |
| H | 612 | 170 | 9.2 |

*Specific energy consumption, **DS-dry solids content

E-compactor treatment

The E-compactor (Fig. 1B) is a device with two rotating cogwheels that employs both compressive and hydraulic forces to press fibres through conical holes. It was developed at VTT Tampere. The fibres were treated at 30% consistency by passing them once or twice through the E-compactor with conical holes of 2 mm in diameter.

Valley beater treatment

The applied beating procedure was in accordance with the SCAN-C 25:76 method. Pulp measuring 360 g (oven-dried weight) was used for one batch in Valley beater and was diluted to the 23 L of total volume, giving a consistency of 1.57 g/L. The pulp was disintegrated in the beater without a load for 30 minutes. The disintegrated sample was defined as the “untreated fibres” sample. Then, pulp samples of 2 L were taken after 15, 30, 45, and 60 min of beating.

Combined high consistency (HC) and low consistency (LC) treatment

The combined HC and LC treatment included a wing defibrator treatment (WD) followed by a Valley beating (VB). The refining conditions for HC treatment are shown in Table 2, and LC beating was performed according to the SCAN-C 25:76. The SR number after the Valley beating was 23. The conditions used in the HC-refining are shown in the Table 2.

Table 2. The Conditions for HC Wing Defibrator Treatment

| Parameter | Value |
|-----------------------------|-----------|
| Refining gap | 1 mm |
| Starting pulp consistency | 30% |
| Temperature in refining | 110°C |
| Preheating time | 5 min |
| Rotation speed | 750 rpm |
| Specific energy consumption | 566 kWh/t |

Fibre and pulp analysis

Fibre samples (approx. 0.1 g oven-dry mass) were taken for the automated fibre analysis with the STFI FibreMaster by Lorentzen & Wettre. Fibre parameters, including fibre length, fibre width, fibre curl, kinks, and fines content were analysed. The dewatering properties were characterised by the Schopper Riegler number (SR number) and the water retention value (WRV) in accordance with the ISO 5267-1 and SCAN-C 62:00 standards, respectively.

The fibre samples were unstained and observed under a light microscope (Olympus BX50) using transmitted light. The polarized mode was used for analysis, in which the angle positions of polarizer and analyser were varied.

A scanning electron microscope (SEM, LEO DSM 982 Gemini FEG-SEM, NORAN Instruments, Inc.) was used for inspecting the surface structure of the handsheets. Paper samples (ca. 10 mm × 10 mm) were attached on carbon adhesive discs (12 mm) pressed on 12.5 mm aluminium stubs. A thin layer (ca. 10 nm) of platinum was sputter coated on each sample surface prior to analysis. The SEM analyses of the samples were conducted using an acceleration voltage of 1.0 keV or 2.0 keV.

Handsheet preparation

Handsheets were prepared according to SCAN-C 26. In addition to standard plate drying, a second set of handsheets were air-dried between two wire fabrics that had a gap of around 1 to 3 mm, which allows free shrinkage of the handsheets without excessive cockling or curling.

Paper properties analysis

The strength properties of the handsheets, including tensile strength, elongation, tensile energy absorption (TEA), and tensile stiffness, were determined using a universal material-testing device (LR10K, LLOYD Instruments) in accordance with SCAN-P38. Light scattering coefficient of handsheets was determined in accordance with ISO-9416.

The procedure applied for shrinkage potential measurement can be described as follows: Handsheets were marked after wet pressing by making holes using a square plate with awls at each corner. The four punched holes defined a square with a known perimeter. After this, the handsheets were allowed to dry and shrink freely. The extent of shrinkage was calculated from the change of the perimeter using a high-resolution scanner and special software. Equation (1) was used for the calculation of the shrinkage,

$$\text{Shrinkage} = \frac{L_w - L_d}{L_w} \times 100\% \quad (1)$$

where L_w is the perimeter of the rectangular perimeter in the handsheet before drying and L_d is the perimeter of the dried handsheet.

RESULTS AND DISCUSSION

Fibre Properties

The effects of the wing defibrator and Valley beater treatment on the fibre properties and dewatering properties of pulp can be found in a previous publication (Zeng *et al.* 2012). The treatment of pulp using the E-compactor device brought about drastic changes in the fibre structure, which can be seen in Table 3.

Table 3. Fibre Parameters, Water Retention Value, and Drainage Properties of E-Compactor Treated Pulp

| Sample | Fibre length, mm | Fibre width, μm | Shape factor, % | Kink/mm | Fines, % | SR number | WRV, g/g |
|-----------|------------------|----------------------------|-----------------|---------|----------|-----------|----------|
| Untreated | 2.05 | 29.6 | 82.1 | 0.69 | 6.0 | 14 | 1.03 |
| 1 pass | 1.25 | 30.6 | 82.8 | 0.93 | 8.5 | 8 | 1.16 |
| 2 passes | 1.13 | 30.9 | 82.9 | 0.97 | 10.5 | 9 | 1.27 |

E-compactor results in Table 3 show that fibre length was reduced by as much as 40% even though the fibres were passed through the E-compactor only once. Fibre width was increased because of the flattening and collapse of fibres. Kinks were induced to fibres during the E-compactor treatment. It can be concluded that E-compactor treatment caused severe fibre deformations and damage, such as fibre flattening, squashing, and fibre cutting.

The influence of HC wing defibrator treatment and subsequent LC valley beating on the fibre properties can be seen in the Table 4.

Table 4. The Effect of HC Wing Defibrator Treatment and Subsequent LC Valley Beating on Fibre Parameters and Drainage Resistance

| Sample | Fibre length, mm | Fibre width, μm | Shape factor, % | Kink/mm | Fines, % | SR number |
|--------------------------------------|------------------|----------------------------|-----------------|---------|----------|-----------|
| Untreated | 2.05 | 29.6 | 82.1 | 0.69 | 6.0 | 14 |
| HC wing defibrator | 1.90 | 30.0 | 79.6 | 0.87 | 8.5 | 14 |
| HC wing defibrator +LC Valley beater | 1.97 | 29.2 | 85.8 | 0.31 | 9.8 | 23 |

In Table 4 it can be clearly seen that the HC wing defibrator treatment created deformations (curl and kinks) in the fibres, while the subsequent LC beating straightened the fibres, released fibre curl and kinks, and increased the swelling of the fibres. Fines content was increased by both of the mechanical treatments.

Polarized light microscopy was used for the evaluation of the fibre deformations caused by the different types of mechanical treatment. The emphasis in this study was on the identification and characterization of microcompressions in fibres. The polarized images allow for better observation of the changes in the fibre structure caused by the mechanical treatments. Figure 2 shows polarized images of the untreated, HC wing defibrator treated fibres, and combined HC wing defibrator and LC valley beater treated fibres.

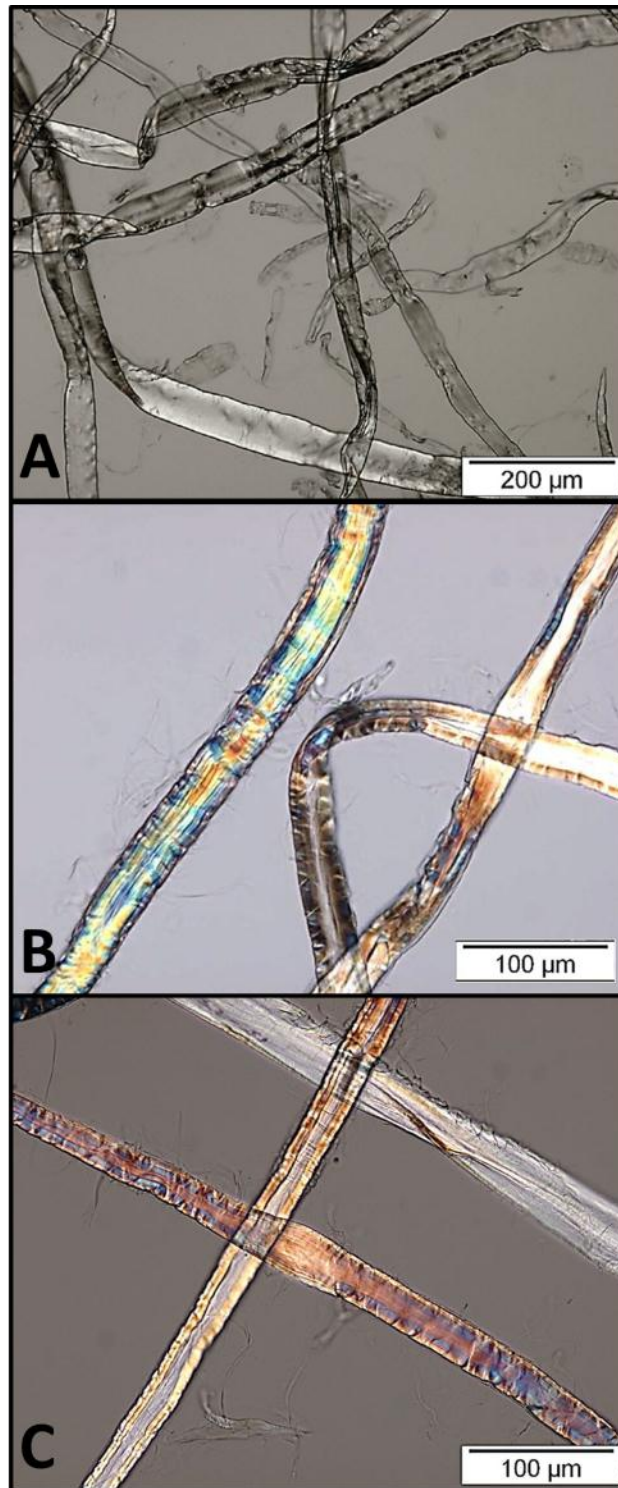


Fig. 2. Polarized (45° polarizer/90° analyser) images (A) untreated fibres, (B) high-consistency wing defibrator treated fibres, and (C) fibres after combined HC wing defibrator and LC Valley beater treatments

The microcompressions and dislocations can be observed as high-contrast lines perpendicular to the axis of the fibre (Thygesen and Ander 2005). Untreated fibres showed only some microcompressions, though dislocation zones, kinks, and curl were

present. HC wing defibrator treated fibres showed more severe dislocations and also microcompressions. The combined HC wing defibrator and LC valley beater treated fibres tend to have less dislocation zones but also a considerable number of microcompressions could be seen. This suggests that microcompressions can be preserved well during the LC beating, even though LC beating is able to straighten fibres and release fibre curl and kinks, as previously mentioned.

Paper Properties

The properties of the restrained-dried and freely-dried handsheets made of wing defibrator treated fibres are summarized in Table 5a and 5b, respectively.

Table 5a. Handsheet (restrained drying) Properties from the Wing Defibrator Treated Pulp

| Temp., °C | SEC, kWh/t | Density, kg/m ³ | Scattering coeff., m ² /kg | Tensile index, Nm/g | Elongation, % | TEA index, J/g | Tensile stiffness, Nm/g |
|-----------|------------|----------------------------|---------------------------------------|---------------------|---------------|----------------|-------------------------|
| 110 | 0 | 527 | 33.9 | 20.4 | 2.76 | 0.45 | 3695 |
| | 243 | 599 | 26.8 | 31.12 | 4.01 | 0.96 | 4008 |
| | 297 | 609 | 25.9 | 35.42 | 4.33 | 1.17 | 4372 |
| | 418 | 610 | 25.9 | 35.77 | 4.35 | 1.17 | 4206 |
| | 657 | 637 | 23.9 | 41.22 | 4.71 | 1.47 | 4937 |
| | 1129 | 644 | 23.3 | 47.14 | 4.83 | 1.70 | 5455 |
| 170 | 0 | 527 | 32.9 | 16.52 | 1.6 | 0.20 | 3512 |
| | 128 | 470 | 36.5 | 11.28 | 2.27 | 0.20 | 1986 |
| | 612 | 486 | 36.1 | 12.13 | 2.42 | 0.23 | 2080 |

Table 5b. Handsheet (free drying) Properties from the Wing Defibrator Treated Pulp

| Temp., °C | SEC, kWh/t | Density, kg/m ³ | Tensile index, Nm/g | Elongation, % | TEA index, J/g | Tensile stiffness, Nm/g | Shrinkage, % |
|-----------|------------|----------------------------|---------------------|---------------|----------------|-------------------------|--------------|
| 110 | 0 | 500 | 17.59 | 5.35 | 0.72 | 2067 | 2.91 |
| | 243 | 538 | 25.43 | 7.38 | 1.35 | 1956 | 3.06 |
| | 297 | 517 | 27.12 | 7.68 | 1.45 | 1875 | 3.73 |
| | 418 | 522 | 29.76 | 8.32 | 1.71 | 1989 | 3.48 |
| | 657 | 539 | 32.94 | 9.05 | 2.02 | 2040 | 4.17 |
| | 1129 | 558 | 37.58 | 8.76 | 2.17 | 2219 | 4.08 |
| 170 | 0 | 502 | 14.12 | 3.17 | 0.34 | 2013 | 2.24 |
| | 128 | 461 | 8.51 | 4.48 | 0.3 | 999 | 3.2 |
| | 612 | 477 | 10.24 | 5.33 | 0.43 | 1120 | 3.54 |

For the handsheets dried under restraint, the density increased and the light scattering coefficient decreased with increasing specific energy consumption in wing defibrator treatment at 110°C. This reduction in light scattering coefficient indicates that there was an increase in the number and area of fibre bonds in the sheets. Tensile index,

TEA, and tensile stiffness all increased with the increase in specific energy consumption (110°C). Preheating of pulp caused a decrease in paper density, probably due to the reduced fibre flexibility caused by hornification type of effect (Zeng *et al.* 2012). Preheating of pulp at 170°C had a clear negative effect on the tensile strength, tensile stiffness, and elongation of the sheet. At 110°C the elongation of freely dried handsheets was as high as 9%. Although a rather high amount of refining energy was needed to reach that level, the SR number was as low as 15 (Zeng *et al.* 2012).

Table 6. Handsheets (restrained drying and free drying) Properties of E-Compactor Treated Pulp

| Drying type | Samples | Density, kg/m ³ | Scattering coeff., m ² /kg | Tensile index, Nm/g | Elongation, % | TEA index, J/g | Tensile stiffness, Nm/g | Shrinkage, % |
|-------------------|-----------|----------------------------|---------------------------------------|---------------------|---------------|----------------|-------------------------|--------------|
| Restrained drying | Untreated | 513 | 34.7 | 18.05 | 2.15 | 0.31 | 3098 | - |
| | 1 pass | 535 | 26.9 | 17.91 | 2.22 | 0.29 | 3038 | - |
| | 2 passes | 516 | 25.3 | 18.77 | 2.25 | 0.32 | 3270 | - |
| Free drying | Untreated | 500 | 34.6 | 15.89 | 4.23 | 0.51 | 1939 | 2.52 |
| | 1 pass | 480 | 26.5 | 14.24 | 4.01 | 0.43 | 1506 | 3.24 |
| | 2 passes | 465 | 25.6 | 14.41 | 4.19 | 0.45 | 1461 | 3.36 |

Mechanical properties of the paper made of fibres that had been treated using the E-compactor can be found in Table 6. The stress-strain properties of the handsheets did not essentially improve with E-compactor treatment, even though the treatment caused severe damage and shortening of fibres as previously mentioned. The negative effects were partially covered by the improved bonding and sheet density caused by the fibre flattening and increased amount of fines in pulp. In general, the increased number of fibre kinks caused by E-compactor treatment did not contribute to any improvements in strength properties of paper. It seems that the applied compressive E-compactor treatment, in addition to weakening fibres, also caused excessive deformations that were not able to improve elongation or bring any other benefits for the paper. Thus, the E-compactor treatment does not warrant any further analysis or discussion.

Table 7. Properties of Handsheets (restrained drying and free drying) Prepared from Valley Beaten Pulp

| Drying type | Refining time, min | Density, kg/m ³ | Scattering coeff. m ² /kg | Tensile index, Nm/g | Elongation, % | TEA index, J/g | Tensile stiffness, Nm/g | Shrinkage, % |
|-------------------|--------------------|----------------------------|--------------------------------------|---------------------|---------------|----------------|-------------------------|--------------|
| Restrained drying | 0 | 513 | 34.7 | 18.05 | 2.15 | 0.31 | 3098 | - |
| | 15 | 625 | 26.0 | 64.08 | 3.77 | 1.75 | 6613 | - |
| | 30 | 664 | 23.3 | 82.44 | 3.73 | 2.16 | 7587 | - |
| | 45 | 700 | 21.0 | 87.59 | 3.55 | 2.18 | 8247 | - |
| | 60 | 734 | 18.5 | 101.65 | 3.64 | 2.45 | 9382 | - |
| Free drying | 0 | 500 | 34.6 | 15.89 | 4.23 | 0.51 | 1939 | 2.52 |
| | 15 | 563 | 25.6 | 53.43 | 6.84 | 2.17 | 2880 | 3.15 |
| | 30 | 568 | 21.8 | 69.17 | 8.21 | 3.13 | 2568 | 3.93 |
| | 45 | 571 | 19.2 | 75.53 | 9.07 | 3.75 | 2637 | 4.89 |
| | 60 | 571 | 17.0 | 78.95 | 10.7 | 4.42 | 2167 | 5.88 |

The mechanical properties of the handsheets prepared from the pulp treated in the Valley beater are shown in Table 7. The density of paper increased and the light scattering coefficient decreased significantly with Valley beating. An increase in the tensile strength of handsheets can be explained by the improved interfibre bonding, as well as by the fact that in addition to the improved straightness, the fibres also have a better load-bearing ability in the fibre network. Extensive beating resulted in elongation of freely dried sheets as high as 10.7%. However, these improvements were associated with the strongly impaired drainage, which is indicated by the considerable increase of SR number. SR number was 79 for the 60 min beaten pulp (Zeng *et al.* 2012).

Table 8. Properties of Handsheets (restrained drying and free drying) Prepared from the HC Wing Defibrator and Subsequent Valley Beater Treated Pulp

| Drying Type | Samples | Density, kg/m ³ | Tensile Index, Nm/g | Elongation % | TEA Index, J/g | Tensile Stiffness, Nm/g | Shrinkage % |
|-------------------|---------------------------------------|----------------------------|---------------------|--------------|----------------|-------------------------|-------------|
| Restrained drying | Untreated | 513 | 18.05 | 2.15 | 0.31 | 3098 | - |
| | HC wing defibrator | 446 | 21.49 | 3.88 | 0.59 | 2620 | - |
| | HC wing defibrator + LC valley beater | 598 | 64.95 | 4.50 | 1.92 | 5883 | - |
| Free drying | Untreated | 500 | 15.89 | 4.23 | 0.51 | 1939 | 2.52 |
| | HC wing defibrator | 383 | 18.01 | 7.47 | 0.91 | 1162 | 5.35 |
| | HC wing defibrator + LC valley beater | 466 | 51.32 | 9.91 | 2.83 | 1599 | 5.80 |

The data in Table 8 show the effects of combined HC wing defibrator treatment and LC Valley beating on the mechanical properties of the handsheets. HC wing defibrator treatment increased the elongation of paper but had only a small effect on the tensile strength. With the subsequent Valley beating, the load bearing ability of the fibres and extent of fibre-fibre bonding was greatly enhanced, which was indicated by the increased paper density and strongly improved strength.

SEM images of the handsheets

The SEM pictures of handsheet surfaces prepared from the pulps, which had been subjected to the different mechanical treatments, can be found in Fig. 3. The SEM-image of a handsheet prepared from untreated pulp (A), suggests that fibres were relatively stiff, less collapsed, and less conformable, but that some fibres had extensive dislocations. Images of wing defibrator treated fibres (B and C) suggest that the fibres were curlier and better bonded than the untreated ones. It is possible to observe damage and deformations in fibres that had been treated with the wing defibrator at 170°C (Fig. 3D). The morphology of E-compactor treated fibres (Fig. 3E) differed remarkably from the morphology of untreated and wing defibrator treated fibres. E-compactor treatment caused fibre cutting and fibre damage in addition to extensive fibre deformations. The handsheets (Fig. 3F) from the combined HC and LC treatment show relatively straight and collapsed fibres with a high degree of fibre bonding and also relatively large dense areas in the sheet.

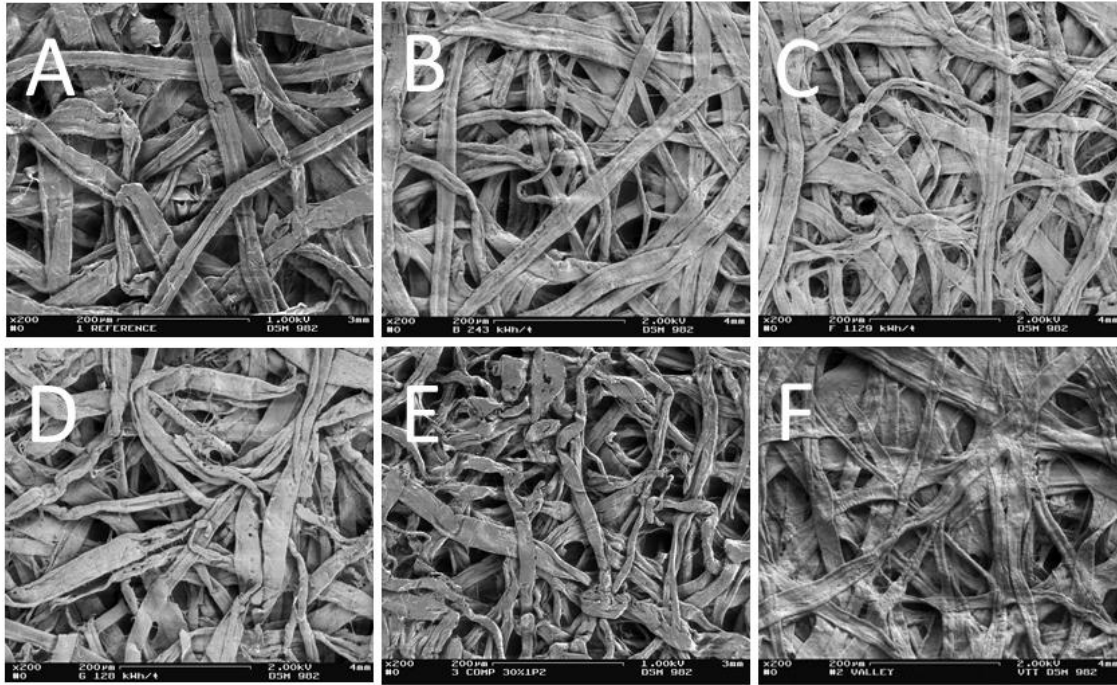


Fig. 3. SEM images of handsheets from different mechanical treatments; (A) Untreated reference handsheet; (B) wing defibrator treated with SEC of 243kWh/t, 110°C; (C) wing defibrator treated with SEC of 1129kWh/t at 110°C; (D) wing defibrator treated with SEC of 128kWh/t at 170°C; (E) E-compactor treated (30%1P2mm); (F) combined HC wing defibrator and LC valley beater treatment (150 g/m²)

Factors affecting the elongation potential of paper

The elongation of paper varied according to the different mechanical treatments. When the handsheets were dried under restraint as shown in Fig. 4, the wing defibrator treatment (at 110°C) provided fibres with the higher elongation potential than Valley beating but paper of lower tensile strength. The combined HC wing defibrator treatment and Valley beating provided high elongation potential, and at the same time, clearly higher tensile strength for the paper, in comparison with wing defibrator treated fibres.

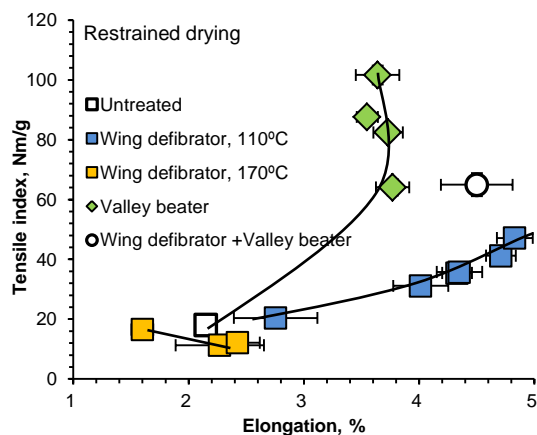


Fig. 4. Elongation versus tensile index of handsheets with restrained drying. The error bars show 95% confidence intervals.

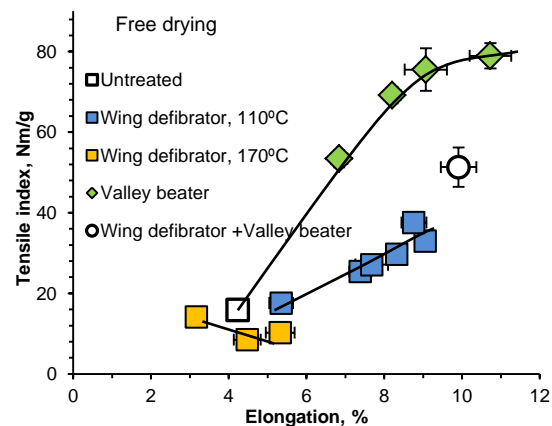


Fig. 5. Elongation versus tensile index of handsheets with free drying. The error bar shows 95% confidence intervals.

In the case of freely dried handsheets (Fig. 5.), Valley beating appeared to be a promising way to obtain high tensile strength and elongation properties of paper. HC wing defibrator treatment followed by Valley beating seemed to have better elongation potential at a certain value of tensile strength, compared with Valley beating.

It was expected that there would be a correlation between fibre deformations and elongation potential of handsheets, since the structure of the single fibres is one of the factors that determine the mechanical behaviour of the paper. However, the correlation between the degree of fibre curl and elongation of paper was found to be scattered (in Fig. 6) in the present work. In the initial stage of mechanical treatment, the elongation of handsheets improved with increasing fibre curl for HC wing defibrator treatment (at 110°C), but even with reducing fibre curl for Valley beating. This result implied that increasing fibre curl is not necessarily leading to improved elongation. The fibre deformations contributing to elongation were probably smaller scale deformations than fibre curl, such as microcompressions. The reduction of fibre curl probably contributes to better stress distribution in paper, which improved both paper strength and elongation.

The density of the paper has a strong influence on the stress-strain properties of paper, since the density is directly related to the amount of fibre-fibre contacts. Figure 7 shows that paper elongation generally increased with increasing sheet density for HC wing defibrator treated fibres (110°C). The extent of fibre bonds determined the elongation potential of paper for HC wing defibrator treated fibres. For Valley beating, paper elongation was increased with the sheet density up to a certain point, after which the sheet density continued to increase, and the elongation stayed constant. These results suggest that fibre flexibility and bonding are, to a certain point, beneficial for elongation of the sheet.

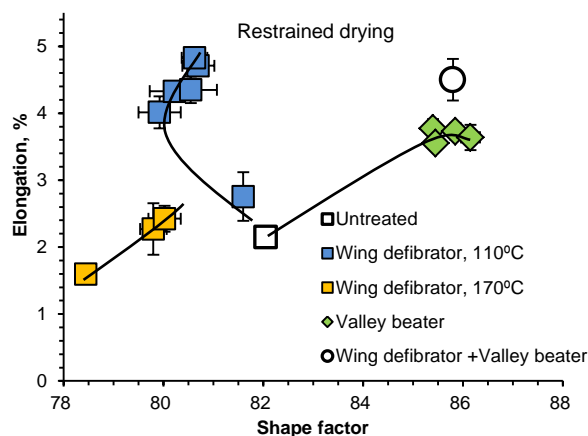


Fig. 6. Effect of shape factor on the elongation of handsheets with restrained drying. The error bars show 95% confidence intervals.

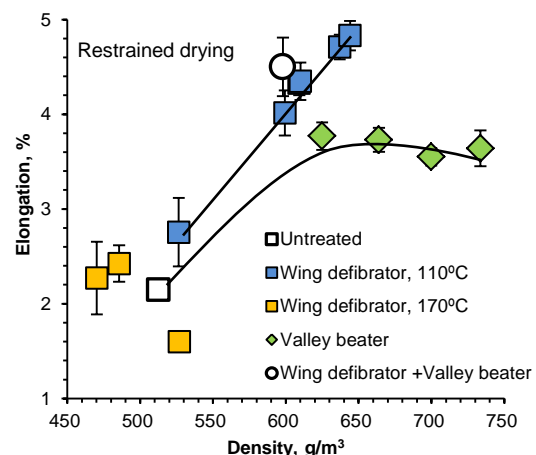


Fig. 7. The effect of the density on the elongation of the handsheets (restrained drying). The error bars show 95% confidence intervals.

The Schopper Riegler number (SR number) can be used for estimation of the dewatering ability of pulp, and it was correlated with the degree of swelling of fibres and also with the fibre flexibility and amount of fines. The relation between the elongation of the freely dried handsheets and SR number of the pulp is shown in Fig. 8. The elongation of handsheets (freely dried) was increased continuously with increasing SR-number due to Valley beating. For HC wing defibrator treatment (110°C), the elongation was

increased even though SR number did not change greatly. Generally, HC wing defibrator treatment provided higher elongation than Valley beating when compared at a certain drainage resistance level. The combined HC wing defibrator and LC Valley beating achieved high elongation and good strength, while drainage resistance and fibre swelling were on a relatively low level.

The degree of swelling affects the drying shrinkage of handsheets due to the higher shrinkage of fibres. Water retention value of the pulp can be used for the estimation of the changes in the swelling of fibres. The influence of the water retention of the pulp on the elongation of restrained and freely dried paper in the case of wing defibrator treatment is shown in Fig. 9. There was a linear correlation between the WRV of pulp and the elongation of handsheets, and this correlation was stronger in the case of the restrained dried handsheets. However, one might say that the WRV was influencing the elongation of freely dried handsheets to a higher extent, since the trend line was steeper. This can be explained by the drying shrinkage effect, because shrinkage of paper during drying is greatly dependent on the degree of swelling of the fibres.

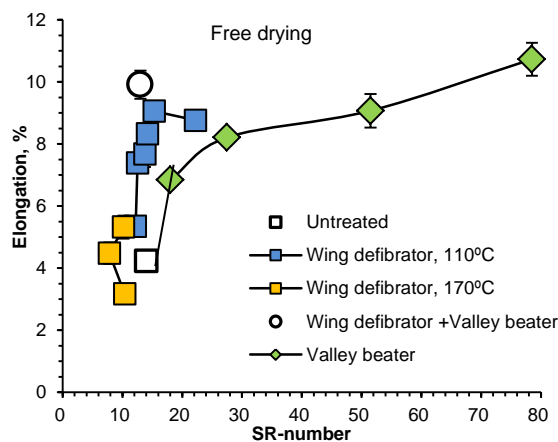


Fig. 8. Effect of drainage property on the elongation of handsheets (free drying). The error bars show 95% confidence intervals.

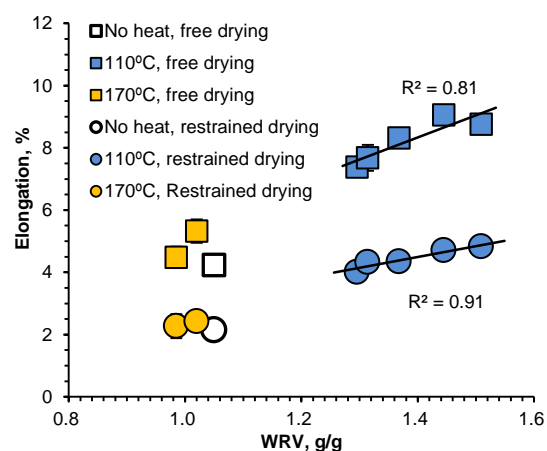


Fig. 9. Effect of water retention value of pulp on the elongation of the handsheets in the case of wing defibrator treatment. The error bars show 95% confidence intervals.

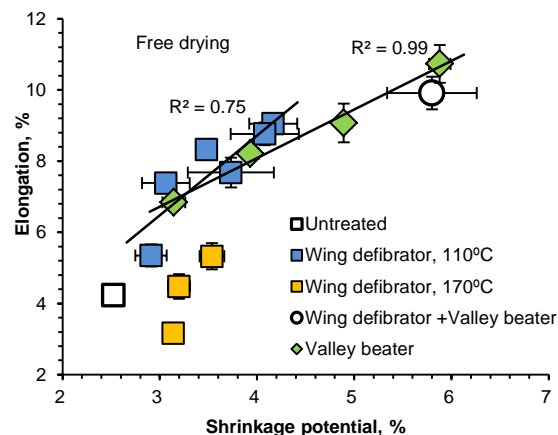


Fig. 10. Correlation between the shrinkage potential and elongation of handsheets (free drying). The error bars show 95% confidence intervals.

Shrinkage potential of the handsheet depends on fibre swelling and subsequent fibre shrinkage, on the number of fibre bonds where the fibre shrinkage is converted to axial shrinkage of neighbor fibres, and on the axial stiffness of the “neighbor” fibres (Retulainen *et al.* 1998). A linear correlation between shrinkage and elongation could be observed for wing defibrator treated fibres and Valley beaten fibres, as shown in Fig. 10. When the handsheets were dried without any restraint, shrinkage potential was the crucial factor determining the elongation of sheets. However, we could speculate that HC wing defibrator treatment contributes to increased shrinkage through a different mechanism than Valley beating. Valley beating probably increases the shrinkage and bonding of fibres, whereas wing defibrator treatment reduces the axial stiffness of the fibres.

CONCLUSIONS

First-thinning bleached pine kraft fibres were treated using selected mechanical treatments. The development of the elongation of freely and restrained-dried paper was evaluated through the fibre and fibre network properties. The results indicated that high consistency wing defibrator treatment caused curl, kinks, dislocations, and microcompressions in the fibres. Among them, small scale deformations, such as microcompressions have an important role in the elongation potential of sheets and can be preserved in subsequent Valley beating, which tends to straighten the fibres and release kinks and dislocated zones. Increasing fibre curl does not necessarily lead to improved paper elongation due to the reduced load-bearing ability of curly fibres in the fibre network. The elongation of the freely dried and restrained dried paper is dependent on different factors. In the case of freely dried paper, the shrinkage potential is the dominant factor; while in the case of restrained dried paper, the fibre wall morphology has a crucial role. The combined high consistency wing defibrator treatment and subsequent low consistency Valley beating was found to be the best strategy to produce paper with a high level of elongation, maintaining high tensile strength and good dewatering properties.

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PUBLICATION V

Improving the extensibility, wet web and dry strength of paper by addition of agar

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PUBLICATION VI

**Improving the extensibility of paper:
sequential spray addition of
gelatine and agar**

Nordic Pulp and Paper Research Journal, 30 (3),
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PUBLICATION VII

**An approach for improved 3D
formability of paper**

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Packaging

An approach for improved 3d formability of paper

By Alexey Vishtal and Elias Retulainen

Paper-based materials constitute a significant share of the world packaging market, successfully competing with plastic packaging¹. Paper is renewable, recyclable, sustainable and biodegradable material. However, it is not as flexible in terms of package design as plastic materials are.

Paper packaging appears in rather simple geometrical forms while plastics can be formed to great variety of shapes. This is due to poor formability of paper. Overcoming of this problem is the key to novel paper packaging applications. Extensibility is considered to be of primary importance for the formability of paper in the processes with fixed paper blanks such as vacuum forming, hydroforming, hot pressing etc. where it determines the maximum depth of the shapes and their appearance^{2,3}.

In earlier publications it has been shown that the extensibility of paper is a complex phenomenon and it is affected by numerous factors. Generally, the extensibility of paper relies on three principal factors: properties of single fibres, character of inter-fibre bonds, and the structure of the fibre network formed in the papermaking process. Certain mechanical treatments on the fibre level improve the extensibility of paper⁴, the bonding can be affected by chemical modification of fibres⁵ and by application of different additives⁷, and the structure of the fibre network can be altered by compaction⁶ or drying shrinkage⁷. However, these methods were not used together in the same approach until now.

The primary objective of this work was to find a set of different methods to increase the extensibility of paper to a qualitatively new level. Mechanical modification of fibres, addition of agar, and in-plane compaction of the fibre web were combined in the approach for improved 3D-formability of paper. The mechanical modification of fibres and spraying of agar was described previously^{7,8}, but in this approach these methods are utilized together with compaction of paper.

Experimental

The fibre raw material used in the study was first thinning bleached pine kraft pulp obtained from Pietarsaari mill of UPM-Kymmene. The morphology of pulp was analysed with L&W Fibermaster equipment. Agar used in this study was typical food grade agar obtained from the Gourmetologia Oy, Finland. Refining was done accord-

ing to the procedure described in⁸. At first, the pulp was subjected to a high consistency (HC) treatment in wing defibrator, and then to a low-consistency (LC) refining in Valley beater.

Handsheets were prepared in accordance with SCAN-C 26, except that the grammage of the handsheets was around 70 g/m² and the sheets were dried unrestrained. After spraying, handsheets were wet pressed and dried between two wire fabrics that have a gap of around 1 to 3 mm, which allows the free shrinkage of the handsheets without excessive cockling or curling. The tensile properties of the handsheets were measured according to SCAN-P 38. The drying shrinkage of paper was measured using procedure described in⁸.

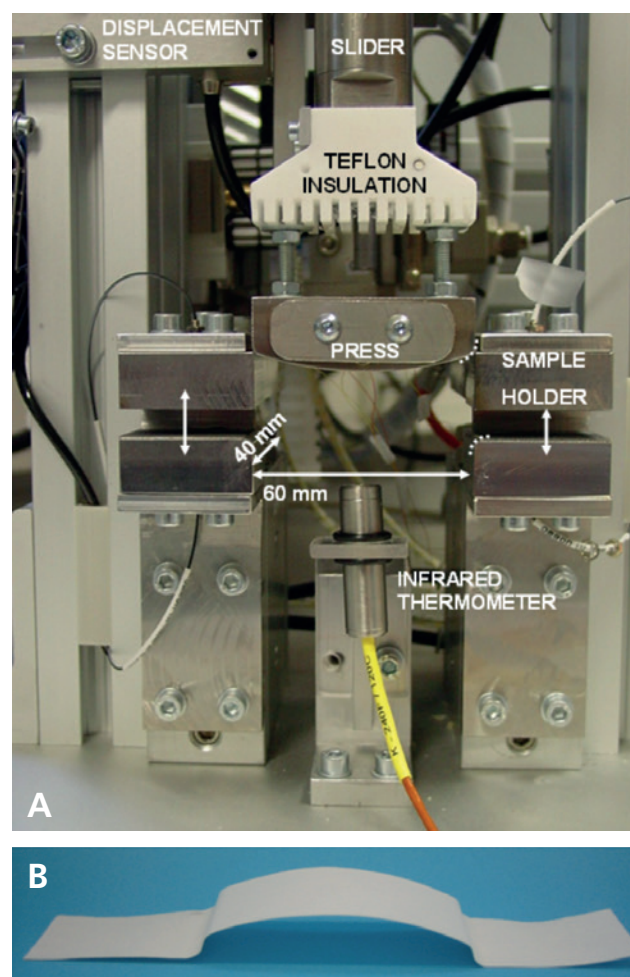


Fig. 1: Outline of the formability tester (A) and formed strip of paper (B)

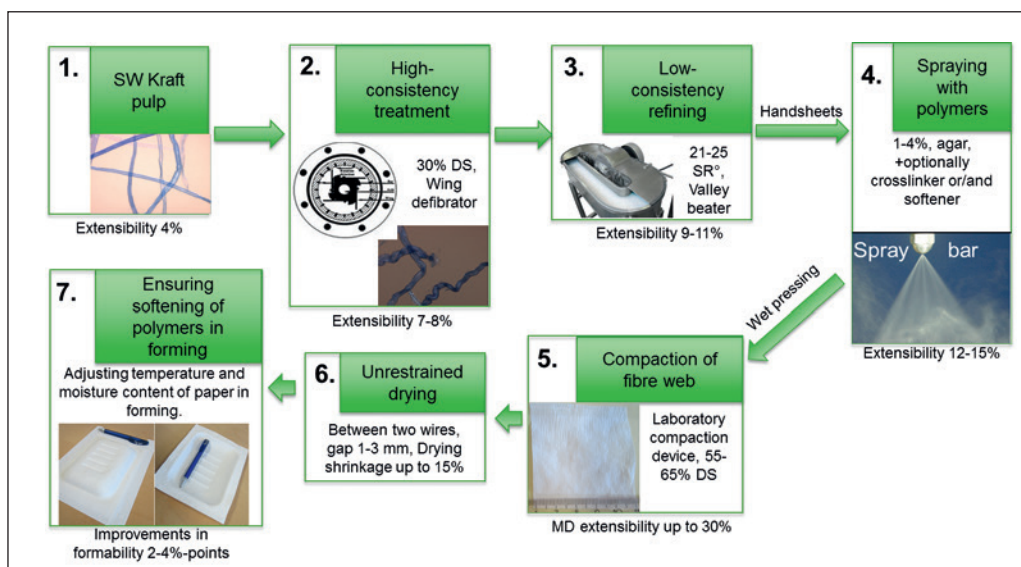


Fig. 2: Combined approach for the improvement of extensibility (SW = softwood, DS = dry solids, SR = Schopper Riegler)

Agar was sprayed on paper before wet pressing as a 2 % (by weight) water solution using electro-spray gun. The amount of added agar was controlled gravimetrically. The temperature of used water solution was around 80 °C. Crosslinker (ammonium zirconium carbonate) was added directly to the carbohydrate solution. Detailed description of the procedure used can be found in⁸.

In-plane compressive treatment was performed using a self-constructed compaction device of VTT Jyväskylä. It was built in a way to replicate the compaction process (Clupak-type of the processes) in laboratory scale. In this device, paper is fed in between of two strained rubber belts and further pressed by a plate with a piston to a pre-determined pressure. Once paper is pressed between the belts, tension was released and the belts start to contract to regain the original length. Paper is contracted following to the contraction of rubber belts. After compaction, paper was dried without restraint. The strain and the consequent strain recovery of the rubber belts was 13 %.

Formability of the samples was evaluated using the 2D-formability tester designed and constructed in VTT Jyväskylä. This device replicates 3D-forming processes with fixed blank in 2D. The formability-reflecting parameter from this device is the formability strain, which is calculated as the extension of the middle plane of paper. 2D-formability tester is equipped with a double-curved heated press (temperature up to 250 °C), blank holders, and an IR sensor to measure the temperature of paper. The forming procedure is as follows: paper sample (length 65 mm, width 20 mm) is tightly clamped by the blank holders. After this, press is moved into contact with the sample and kept still for 0.5 seconds, in order to heat the sample. Then, the press continues downward movement until the breakage of the sample. The downward velocity of the forming press was 10 mm/s⁹. The device and a formed strip of paper are shown in figure 1.

Results & discussion

The extensibility of paper can be improved by affecting the structure of the fibres, fibre bonds, and the resulting structure of the fibre network separately, or as it is shown here, altogether. Certain treatments on the fibre and fibre network levels were found to be additive to each other i.e. they can be applied simultaneously in paper production and this would maximize improvements in extensibility. The combined approach for the improvement of extensibility that was developed based on this assumption is schematically shown in figure 2.

The starting raw material used in the combined approach for the production of extensible paper is softwood kraft pulp which was further subjected to mechanical treatments. The material was selected due to higher fibre length which allows creating more deformations per fibre in high-consistency mechanical treatment and relatively high network strength. Once paper is formed from refined pulp it is sprayed with a water-soluble, film-forming carbohydrate (e.g. agar) and wet pressed to ensure adhesion of the agar gel layer to the paper.

It was found that the addition of agar does not affect the dry solids content (DS) of paper after wet pressing; however, agar decreases DS of paper after drying on average 1 to 2 % due to hygroscopicity⁷. Consequently, paper is compacted with an in-plane compaction device and allowed to dry freely. A combination of previous methods was applied in this work and yielded in paper with extensibility of 20 to 25 % in MD (machine direction) and 15 to 20 % in CD (cross direction). Also, other mechanical properties of paper such as tensile strength, for instance, can be adjusted in relatively broad scale using these methods. The extensibility values are given for unrestrained dried paper, in paper machine unrestrained drying can be performed by using air float dryers. The specific information on certain steps of the combined approach can be found in below.

| Sample | Kink/mm | SR number | Density, kg/m ³ | Tensile index, Nm/g | Strain at break, % | Tensile stiffness, Nm/g | Shrinkage, % |
|---------------|---------|-----------|----------------------------|---------------------|--------------------|-------------------------|--------------|
| Untreated | 0.69 | 14 | 500 | 15.89 | 4.23 | 1939 | 2.52 |
| HC treated | 0.87 | 14 | 383 | 18.01 | 7.47 | 1162 | 5.35 |
| HC+LC treated | 0.31 | 23 | 466 | 51.32 | 9.91 | 1599 | 5.80 |

Tab. 1: Influence of the mechanical treatments on the fibre and paper properties (unrestrained drying)

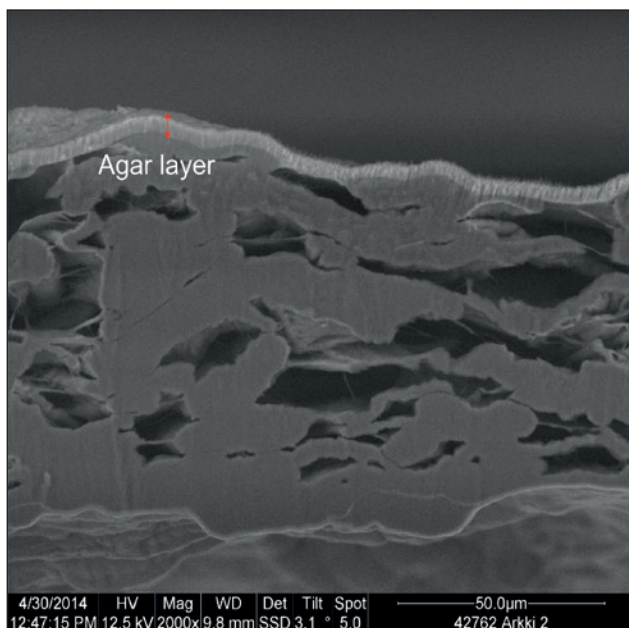


Fig. 3: The cross-sectional SEM Image representing the formed agar film on the surface of dry paper

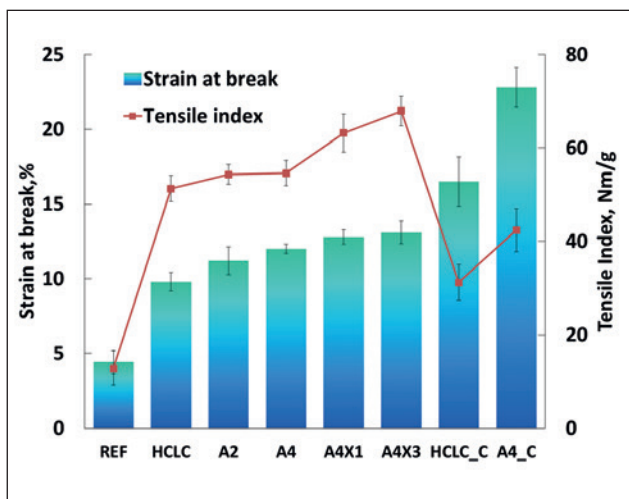


Fig. 4: Influence of the agar addition and compaction on the extensibility and tensile strength of unrestrained-dried paper

REF: unrefined softwood pulp
HCLC: high and low-consistency refined pulp
A2, A4: agar 2% and 4% to fibres
A4X1, A4X3: agar 4% and 1 and 3% of crosslinker
_C: in-plane compressive treated samples (at 45% dry solids content)

Mechanical treatment of fibres

A suitable combination of high- and low-consistency mechanical treatments is a known strategy for the improvement of the extensibility of sack and bag paper grades¹⁰. In high consistency treatment fibre experiences deformations such as micro-compressions, dislocations, kinks, etc. which can positively affect the extensibility of paper⁴. Mild low-consistency refining (to 23°SR) in Valley beater straightens fibres and provides additional strength, while micro-compressions and dislocations in fibres are still preserved and the dewatering of the furnish stays on good level⁴. Extensibility of the paper was improved from 4.23 to 7.47%, as a result of the HC treatment, and to 9.91% for combined HC and LC treatment. Increase in the extensibility was accompanied with increases in drying shrinkage and tensile strength (table 1).

Addition of agar

Spray addition of agar to wet paper can be used for the improvement of the extensibility of paper⁷. Agar forms a film on the surface (figure 3) of paper without penetration into the fibre network structure or adsorption the fibres⁷. The formation of the film on the surface of paper improves agar of the surface layer and strengthens the whole network. However, the improved extensibility induced by the agar addition is mainly explained by the increased drying shrinkage of paper. Wet agar layer has a high shrinkage potential upon formation and drying of the film, this shrinkage is transferred to the moist paper which increases the extensibility⁷.

Apart from the improved extensibility the addition of agar provides to paper also other features, such as decreased air permeability, increased internal bond and tensile strengths⁷. The influence of the agar addition, addition of crosslinker to agar, and combination of agar addition and compaction is shown in figure 4.

The addition of agar has improved both extensibility and strength of the paper. The compaction provided great improvements in extensibility, but at the same time lowered tensile strength of the paper. Addition of crosslinker improved tensile strength of paper by 10 to 12 units, while the extensibility was not much affected. Compacted paper sprayed with agar showed much better tensile strength and extensibility than untreated compacted sample. This can be explained by the ability

of agar to enhance bonding within fibre network, by modifying strength and properties of the fibre joints. Potentially, extensibility of compacted paper sprayed with agar can be over 30 %, in the case when the compaction is performed at higher dry solids content (over 65 %).

In-plane compaction treatment of paper

Compaction is a one type of compressive treatment which is used for the production of extensible sack and bag paper grades^{6,10,11}. However, there is a lack of knowledge of how this process affects mechanical properties of paper. In general, compaction increases extensibility (by up to 15 %) but, with increase in extensibility the losses in tensile strength and stiffness are inevitable^{6,11}. Compaction is associated with the reduction in the linear length of paper, increase in density and roughening of the surface due to formation of micro-buckles. The roughening is more profound when the treatment is performed at high dry solids content of paper and at low Z-pressure. Dryness of paper in the compaction also has a significant impact on the mechanical properties of paper (figure 5).

Increasing dryness of paper in compaction improves the extensibility, as well as the tensile strength of paper. On the other hand paper compacted at high dry solids content has a far too, wrinkly appearance and extremely low elastic modulus. This observation is in line with the study of Lahti et al. done in 2014⁶. The decrease in the tensile strength of paper at low dryness can be associated with sliding of fibres in network leading to debonding and subsequently to a loss in tensile strength. At higher dry solids content the bonds between fibres are strong enough to withstand the treatment without sliding of fibres, and the deformation in paper is mainly due to micro-buckling of fibres and fibre network itself. Another option to control outcome of compaction is to adjust the Z-pressure during process (figure 6).

The higher is the Z-pressure in compaction, the higher is the tensile strength and the lower the extensibility of paper. High pressure prevents fibres from sliding past each other and thus preserving tensile strength. Additionally, increase in the Z-pressure improves visual appearance of compacted paper by minimizing the size of micro-buckles. Controlling the Z-pressure together with the adjustment of dryness of paper in compaction allows to fine tune the tensile properties of compacted paper for particular area of application.

Evaluation of the formability

Formability was evaluated using 2D-formability tester. In practice, formability strain value correlates with the potential depth of the shapes that can be obtained from the material tested⁹. Elevated temperature is used in forming in order to soften the material and improve extensibility, and "freeze" the shape after forming². Agar softens at relatively low temperatures. In order to

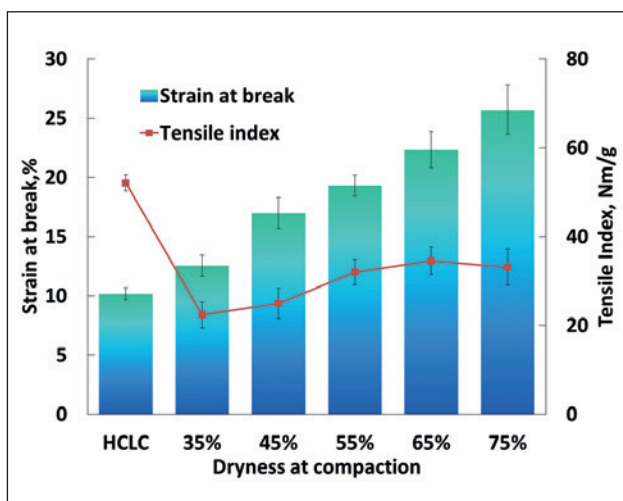


Fig. 5: Influence of the dry solids content of paper in compaction on the extensibility and tensile strength of unrestrained dried paper (no agar, compaction at 45 % dry solids)

HCLC: high and low consistency refined pulp

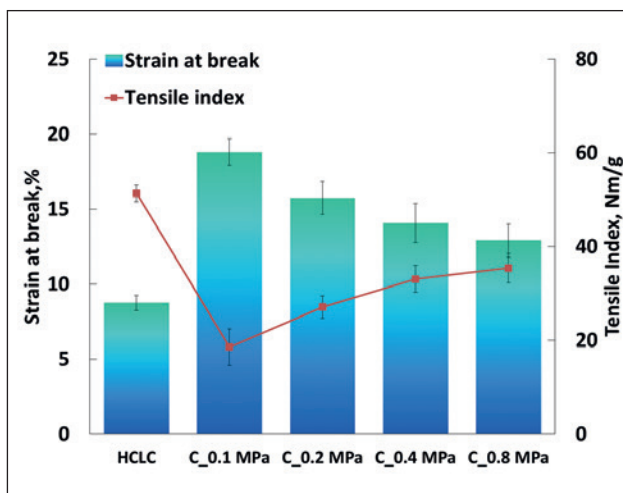


Fig. 6: Influence of the Z-pressure in compaction on extensibility and tensile strength of unrestrained dried paper (no agar, compaction at 45 % dry solids)

HCLC: high and low consistency refined pulp

C_: compaction at certain Z-pressure

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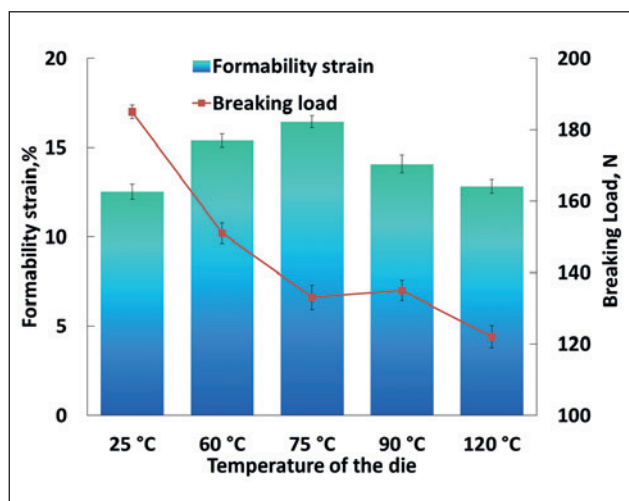


Fig. 7: Influence of the die temperature on the formability strain of unrestrained dried paper prepared from high- and low-consistency treated pulp sprayed with 4% of agar

* In the case of paper with grammage below 100 g/m² the temperature of die equals the temperature of paper

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find optimal forming temperature for the agar sprayed samples a series of forming experiments was performed (figure 7).

The optimal forming temperature for the paper sprayed with agar is between 60 and 90 °C. At this temperature the formability strain was improved by around 4 %. This improvement is most likely associated with the softening of agar and fibre cell wall polymers. Softening is reflected in the decreased breaking load. Decrease in the formability strain at the higher temperatures can be explained by the excessive drying of paper. Adjusting of the forming conditions provides significant improvements to the formability of paper and therefore it should have a significant role in the optimization of the formability of paper.

Conclusions

The data and the treatments presented in this paper allow to make following conclusions:

1. Formability of paper can be improved by modifying the fibre properties, fibre bonding and fibre network.
2. Combined high- and low-consistency mechanical treatment improves extensibility without deterioration of drainage of paper.
3. Agar sprayed on wet paper forms a film that modifies the strength properties of fibre joints in the surface layers and simultaneously increases the strength and extensibility of paper, as well as the drying shrinkage. The effect of agar addition can be enhanced by crosslinker.
4. Compaction is an effective tool to modify the network structure and improve extensibility of paper, though it impairs strength and stiffness of paper.
5. The formability strain of paper sprayed with agar has a maximum at 60 to 90 °C.
6. Mechanical treatment of fibres, addition of agar, free shrinkage, and in-plane compaction can be combined to produce paper with excellent formability and extensibility. ■



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| Title | Formability of paper and its improvement |
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| Abstract | <p>Paper and paperboard are the most utilized packaging materials in the world. This position has been achieved due to several advantageous features of paper such as: renewability, biodegradability, recyclability, and unmatched printability. Paper can be produced anywhere in the world, using local resources and at relatively low cost, which also makes it the most sustainable packaging material. Despite these beneficial features, paper packaging is in tough competition with plastic materials. The competitiveness of paper is mitigated by barrier properties, sensitivity to moisture, and limited ability to be converted into advanced 3D shapes with added functionality. The ability of paper and paperboard to be formed into 3D shapes is described as formability, or sometimes, mouldability.</p> <p>Formability can be defined as the ability of paper to be formed into 3D shapes without defects in appearance and functionality. Formability as a mechanical property represents a group of parameters which vary according to the type of forming process used. The primary objective of this thesis is to improve the formability of paper by increasing its extensibility. An additional objective is the characterization of formability as a mechanical property of paper and the development of a testing platform for the evaluation of formability.</p> <p>It was found that the formability of paper in fixed blank forming processes is governed by the extensibility and tensile strength of paper. On the other hand, in sliding blank forming processes, it is dependent on the compressive properties of paper, elastic recovery, and the paper-to-metal coefficient of friction. The criteria of good formability are also different in these two cases, as fixed blank process formability is evaluated via the maximum depth of the shape, i.e. the deeper the shape, the better the formability. In the sliding blank process, formability is evaluated via the visual appearance of the shapes, i.e. the shapes with less profound compressive wrinkles and defects reflect good formability of paper. These results were established by comprehensive investigation of different forming processes and comparison of the outcome with the mechanical properties of paper.</p> <p>Taking into account the hypothesis that the formability of paper is governed by the extensibility of paper, a set of methods for its improvement was suggested. These methods included combined high- and low-consistency treatment of fibres, spraying of agar and gelatine, in-plane compaction of paper and unrestrained drying. High-consistency treatment of fibres under elevated temperature induces permanent deformations to fibres such as microcompressions and dislocations, which in turn may decrease the axial stiffness of fibres, promoting shrinkage of paper and fibres. The low-consistency treatment straightens the fibres and induces the fibrillation of fibres to promote bonding, while microcompressions in fibres still exist. The spraying of agar and gelatine is likely to modify the character of the fibre joints by making them more deformable, and the drying shrinkage is also increased due to polymer addition. Finally, the fibre network was subjected to in-plane compaction and drying shrinkage which lead to buckling and fibre and network compression.</p> <p>As a result of these treatments, the extensibility of unrestrained dried paper was increased from 4% points (untreated fibres) to 15–18% points (mechanical treatment and addition of polymers). The extensibility can be increased further by up to 30% points in one direction by compaction. This corresponds to tray-like shapes with a depth of 2–3 cm, depending on the curvature. Such values of formability are the highest reported so far in the scientific literature. The approach for the production of formable paper developed in this thesis work allows the production of a paper-based material with unmatched formability, which can replace certain types of plastic packaging. Replacement of plastics with paper improves the sustainability of packaging in general, and reduces the harmful environmental impact of non-degradable and non-renewable packaging.</p> |
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Formability of paper and its improvement

Paper and paperboard are the most utilized packaging materials in the world. This is due to such features as: renewability, biodegradability, recyclability, sustainability and unmatched printability. However, paper packaging is inferior to plastics in respect to moisture sensitivity, and limited ability to be converted into advanced 3D shapes with added The ability of paper and paperboard to be formed into 3D shapes is described as formability, and in the fixed blank forming processes formability is governed by the extensibility of paper.

The primary objective of this thesis is to improve the formability of paper by increasing its extensibility. An additional objective is the characterization of formability as a mechanical property of paper and the development of a testing platform for the evaluation of formability.

The formability (extensibility) of paper was improved using a set of methods which included: mechanical treatment of fibres, spraying of agar and gelatine, in-plane compaction of paper and unrestrained drying. Extensibility of paper was increased from 4% points (untreated fibres) to 15–18% points (mechanical treatment and addition of polymers), and up to 30% (in one direction) after compaction. This corresponds to tray-like shapes with a depth of 2–3 cm, depending on the curvature. Such values of formability are the highest reported so far in the scientific literature.

This approach allows the production of a paper-based material with unmatched formability, which can replace certain types of plastic packaging. Replacement of plastics with paper reduces the harmful environmental impact of non-degradable and non-renewable packaging.

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