

# Boosting the Extensibility Potential of Fibre Networks: A Review

Alexey Vishtal<sup>a,b</sup> and Elias Retulainen<sup>a,\*</sup>

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

*Contact information:* a: VTT Technical Research Centre of Finland, Koivurannantie 1, P.O. Box 1603, FI-40101 Jyväskylä, Finland; b: Tampere University of Technology, Laboratory of Paper Converting and Packaging Technology, P.O. Box 589, FI-33101 Tampere, Finland;

\* Corresponding author: [elias.retulainen@vtt.fi](mailto:elias.retulainen@vtt.fi)

## 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?

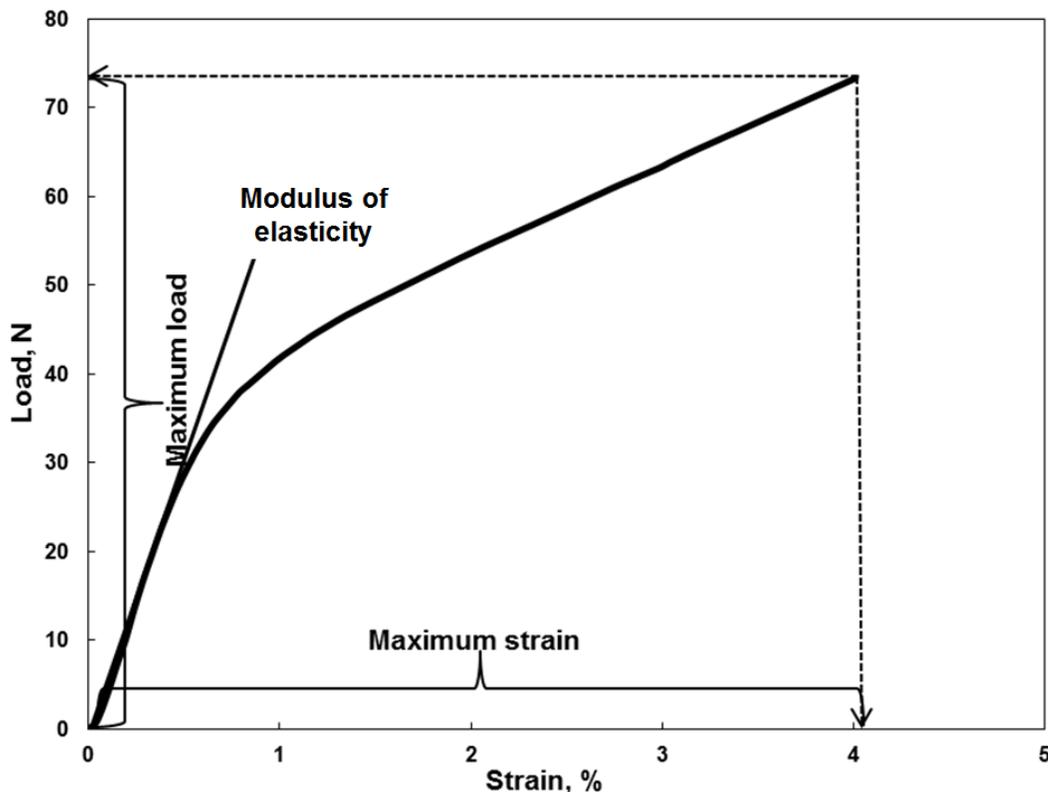
The extensibility of paper has been specifically addressed by only a few researchers (Stenberg 1947, 1949; Brecht and Erfurt 1960; Dodson 1970; Seth 2005). It has been commonly studied together with the other stress-strain properties of paper. Therefore, an extensive summary of the previous fundamental 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.).

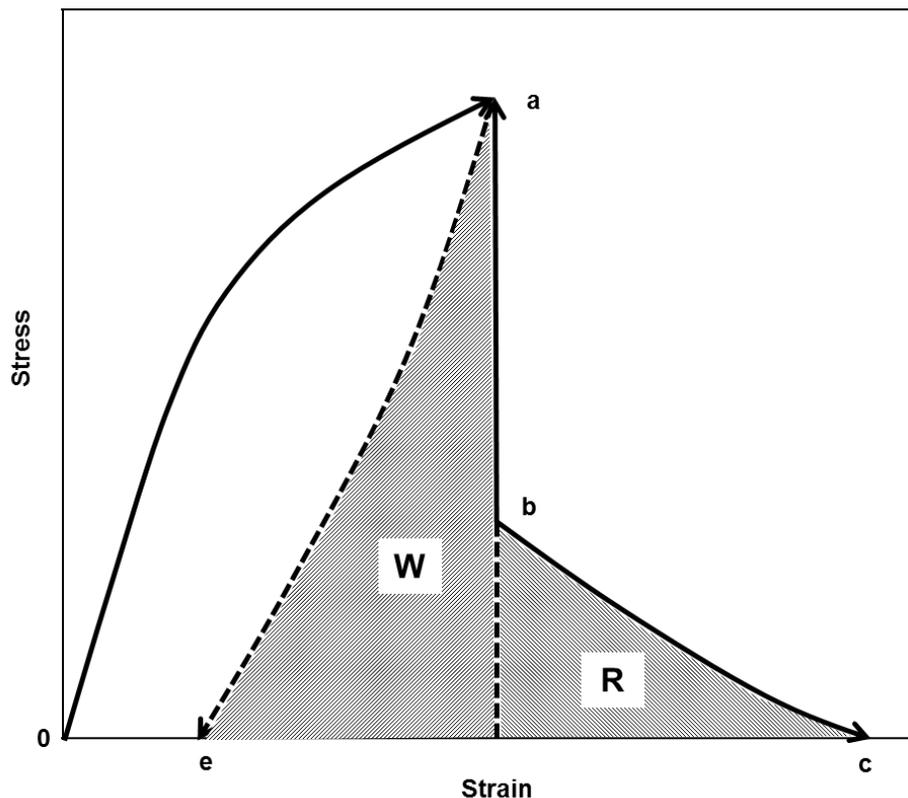


**Fig. 1.** A typical stress-strain curve for isotropic restrained-dried paper made from softwood pulp

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

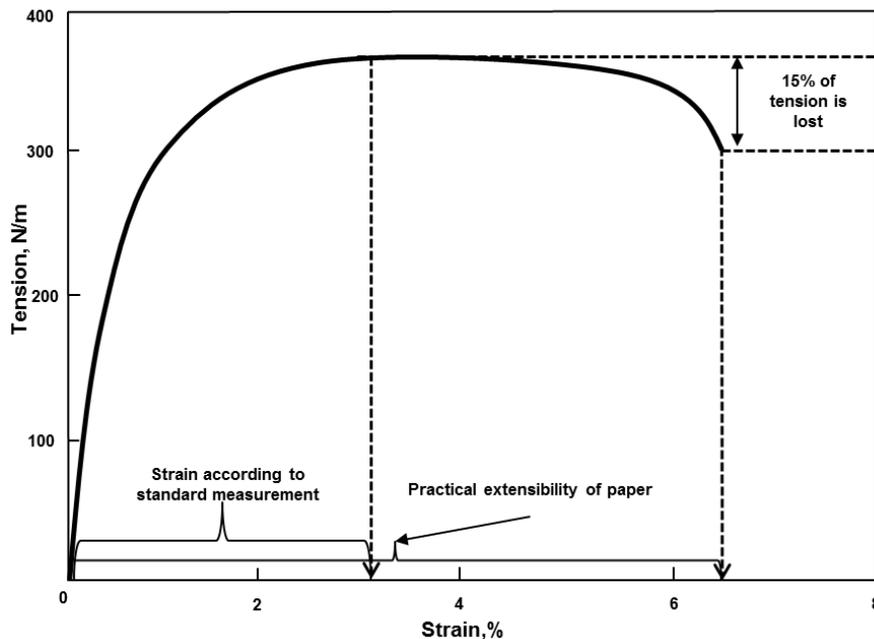
respect, strain at break value is closely associated with the tensile strength of paper, and factors that affect the tensile strength are likely to control the strain at break value as well. However, strong paper may be brittle, while extensible paper usually exhibits a decrease in tensile strength with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



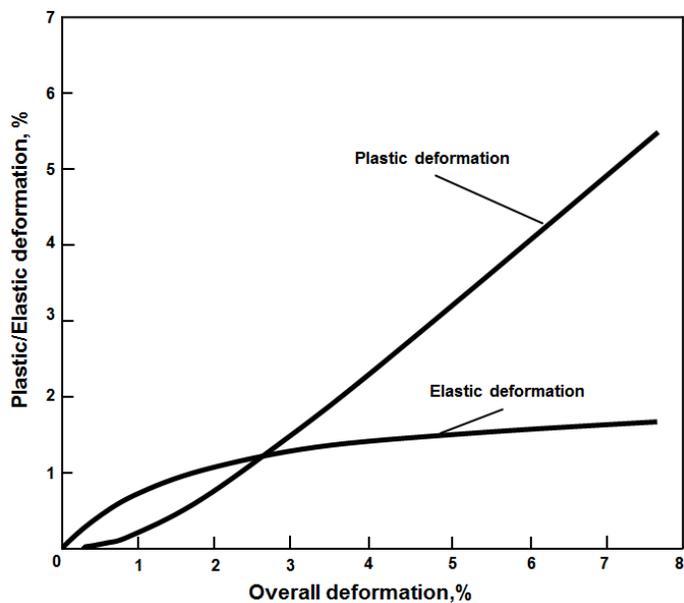
**Fig. 3.** A stress-strain curve of rewetted paper (55% dryness) prepared from hydroxypropylated pulp (material produced in Vuoti *et al.* 2013)

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).

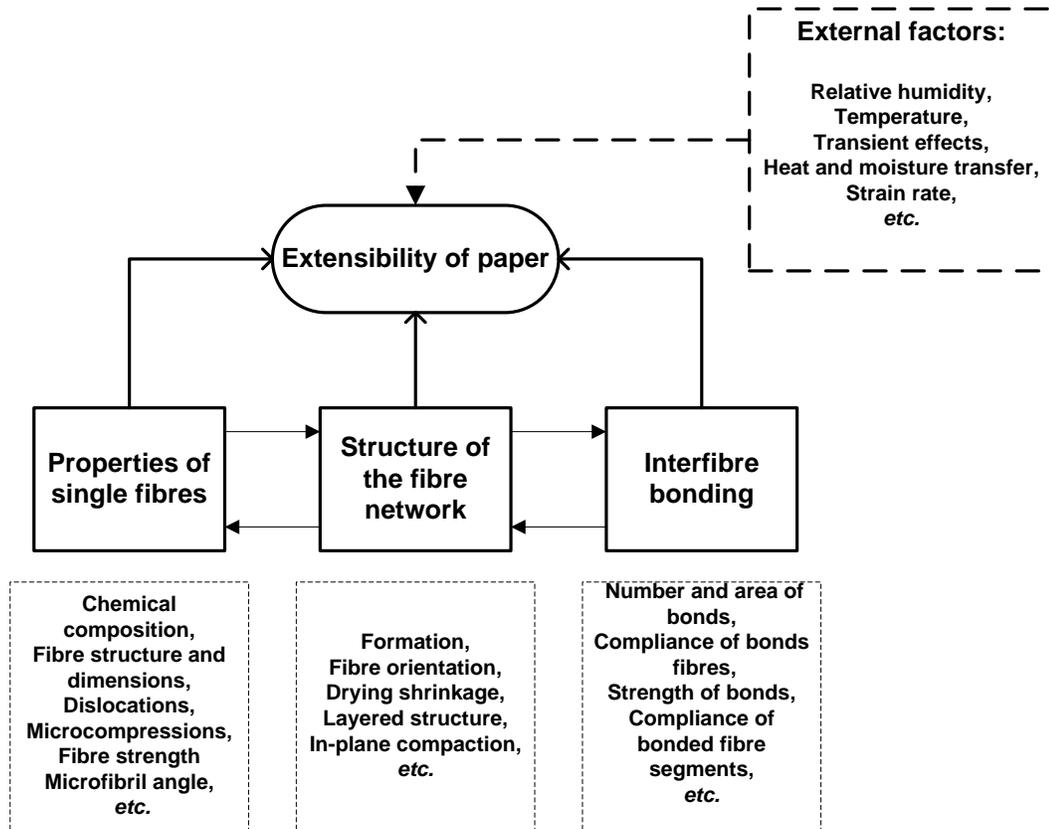
During the straining of paper internal fractures take place. The most fractures are micro-failures and related to debonding. Debonding, *i.e.* partial or complete fracture of fibre-fibre bonds, is known to take place during straining of paper (Page *et al.* 1962). However (Ebeling 1976; Seth and Page 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.

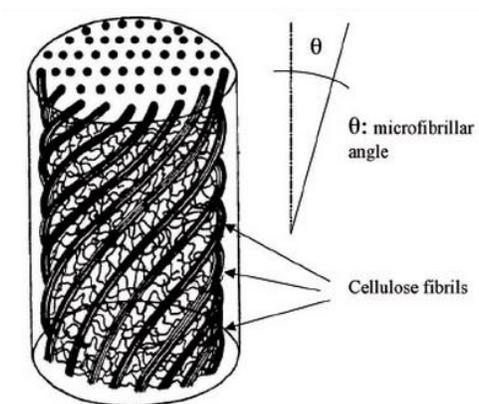
## Properties of Single Fibres that Affect Extensibility

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.

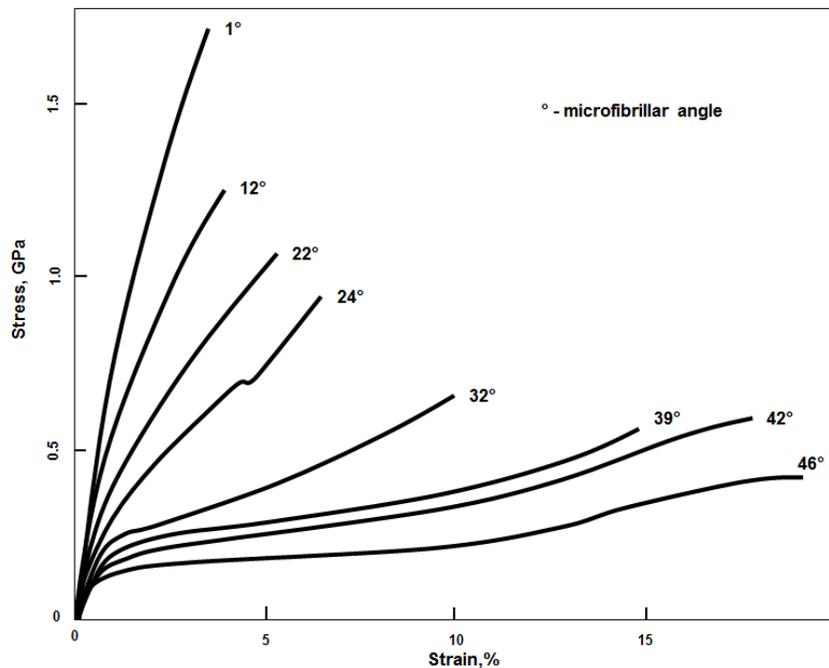
### *Fibrillar angle*

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 $\beta$  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 $\beta$  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).

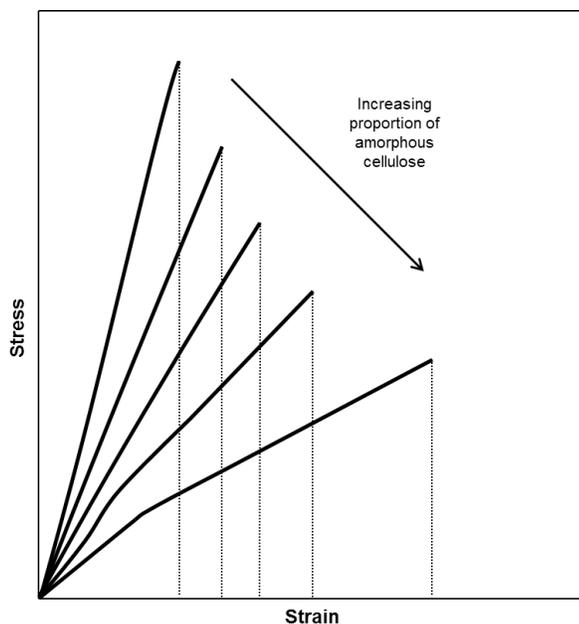
Cellulose is the stiffest chemical component of fibres. Basically, the elongation of cellulose takes place through two mechanisms: by elastic axial elongation of the cellulose molecules and by irreversible, time-dependent slippage between cellulose molecules (Altaner *et al.* 2014). The axial elongation 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),  $\text{ZnCl}_2$  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.

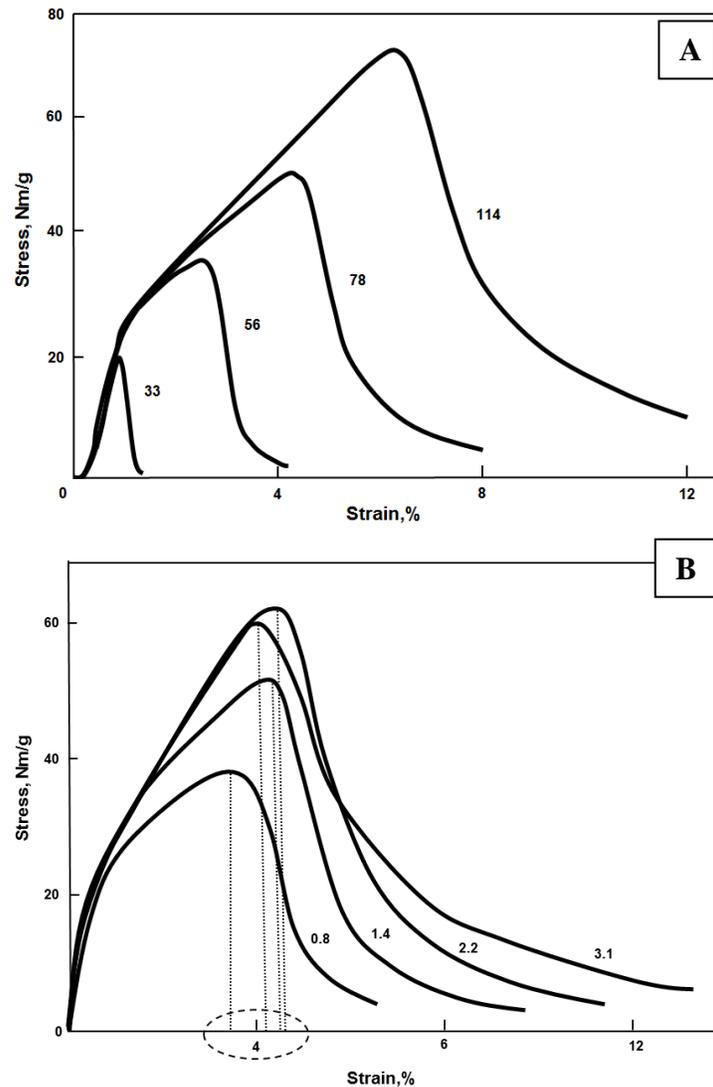
#### *Fibre length and fibre strength*

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.

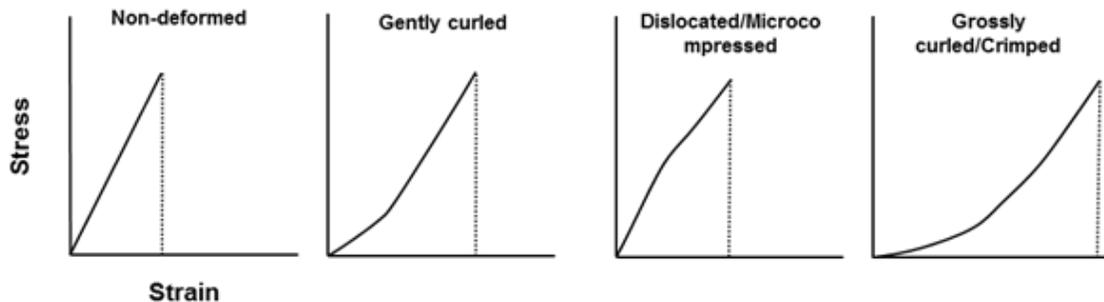
#### *Mechanical treatments and fibre morphology*

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.

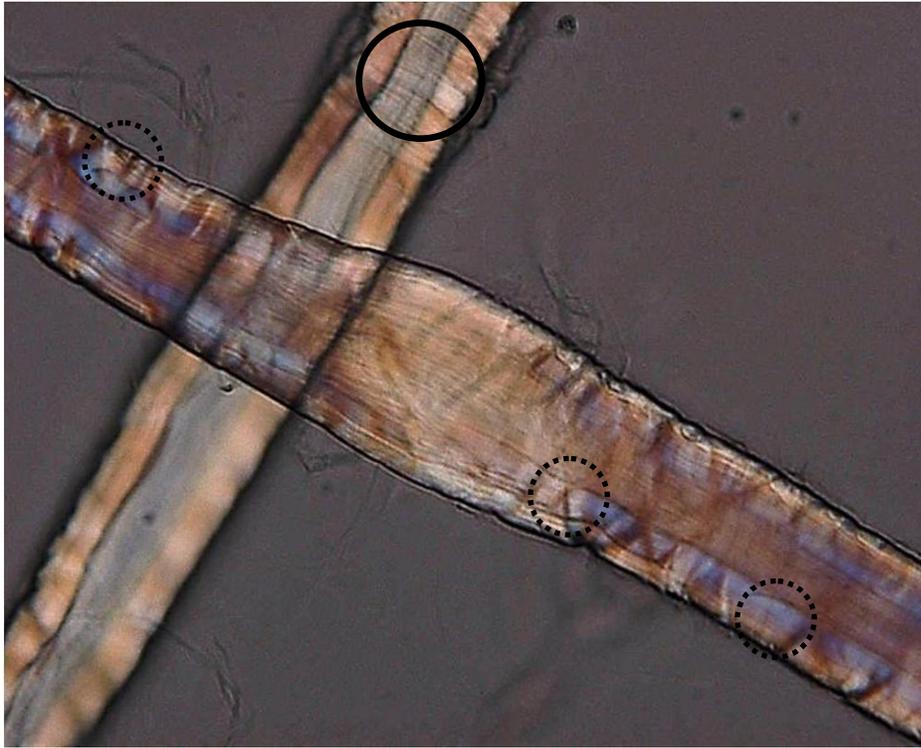
Synthetic fibres are generally more homogeneous in terms of morphology, but their chemical composition and mechanical properties can vary over a wide range in accordance with the origin of such fibres. The mechanical, structural, and chemical properties of selected natural and synthetic fibres are shown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

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

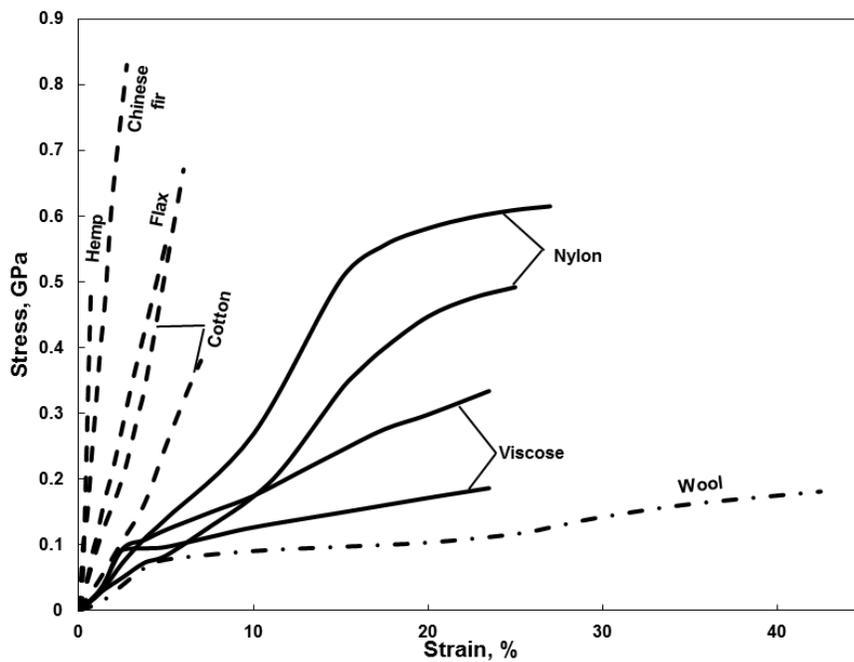
Morphology			Mechanical properties		Chemical composition			Ref.
Origin	MFA, °	Length, mm	Elongation, %	Elastic Modulus, GPa	Cellulose, %	Hemicelluloses, %	Lignin, %	
<i>Pinus sylvestris</i>	5–20	3–3.5	1.5–3.5	40	Varies significantly according to the defibrillation and delignification method and conditions			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  $\mu\text{m}$  to 180  $\mu\text{m}$ . 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 19<sup>th</sup> 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/m<sup>2</sup> 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.

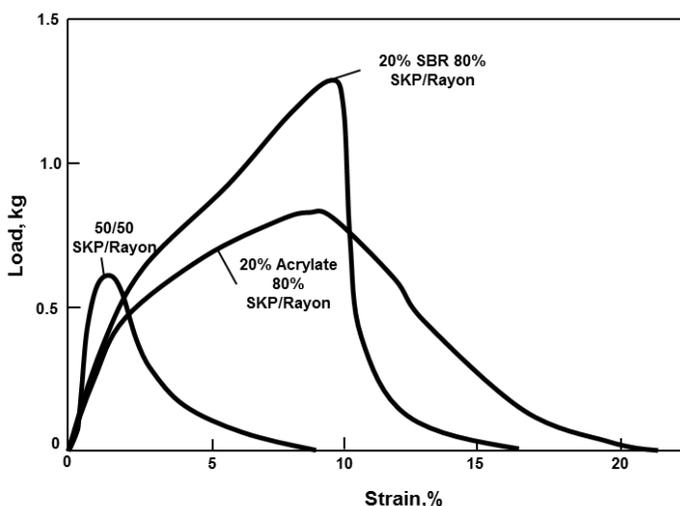
The formation of polyelectrolyte multilayers from polyacrylic acid polyallylamine hydrochloride on the surface of fibres can significantly improve the tensile strength and extensibility of paper (from 4 to 8%-points) (Gustafsson 2012). Polyethylene imine/NFC and polyallylamine hydrochloride/hyaluronic 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; Alinec 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,

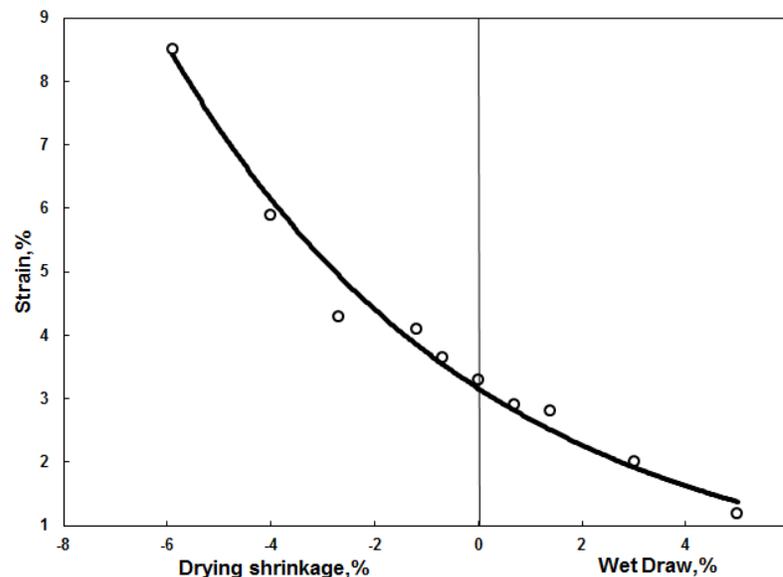
which depends on the initial swelling of fibres, the area, number and adhesion in fibre contacts that transmit the shrinkage forces from one fibre to another, and the axial stiffness of the fibres, which resists axial shrinkage. Swelling and shrinkage of fibres can be easily controlled by the extent 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  $\text{Al}^{3+}$ ,  $\text{H}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ), 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  $\text{Na}^+$  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.

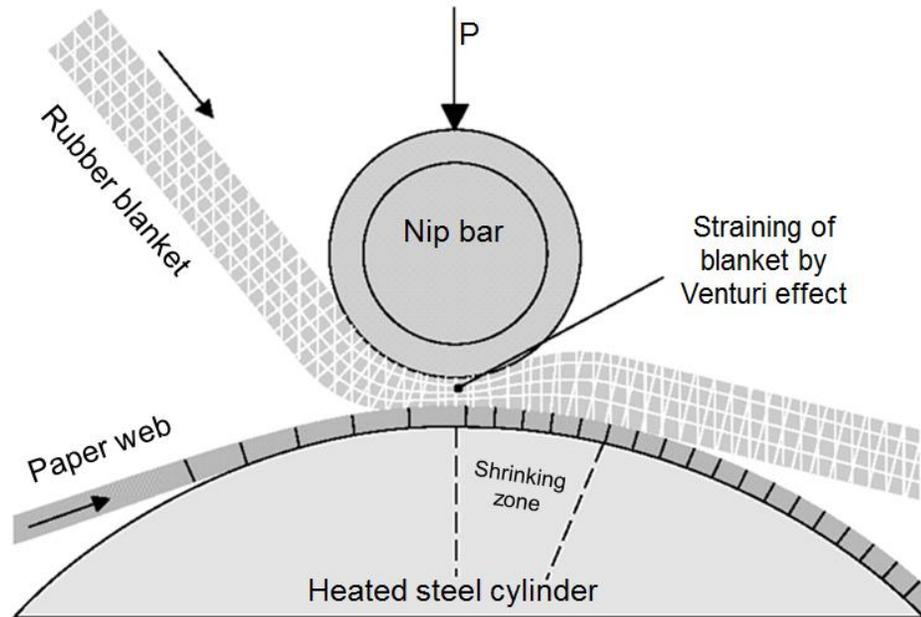


Fig. 16. The outline of Clupak® compaction process

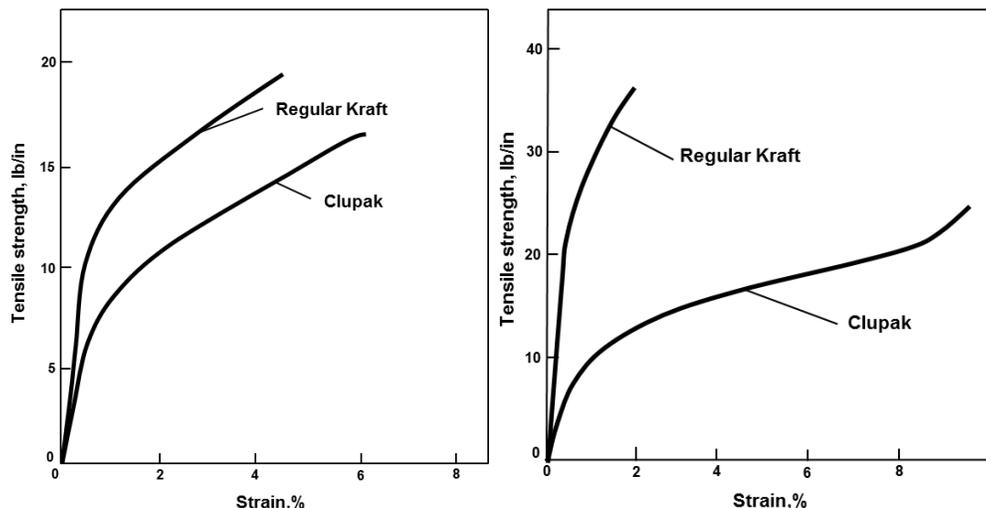
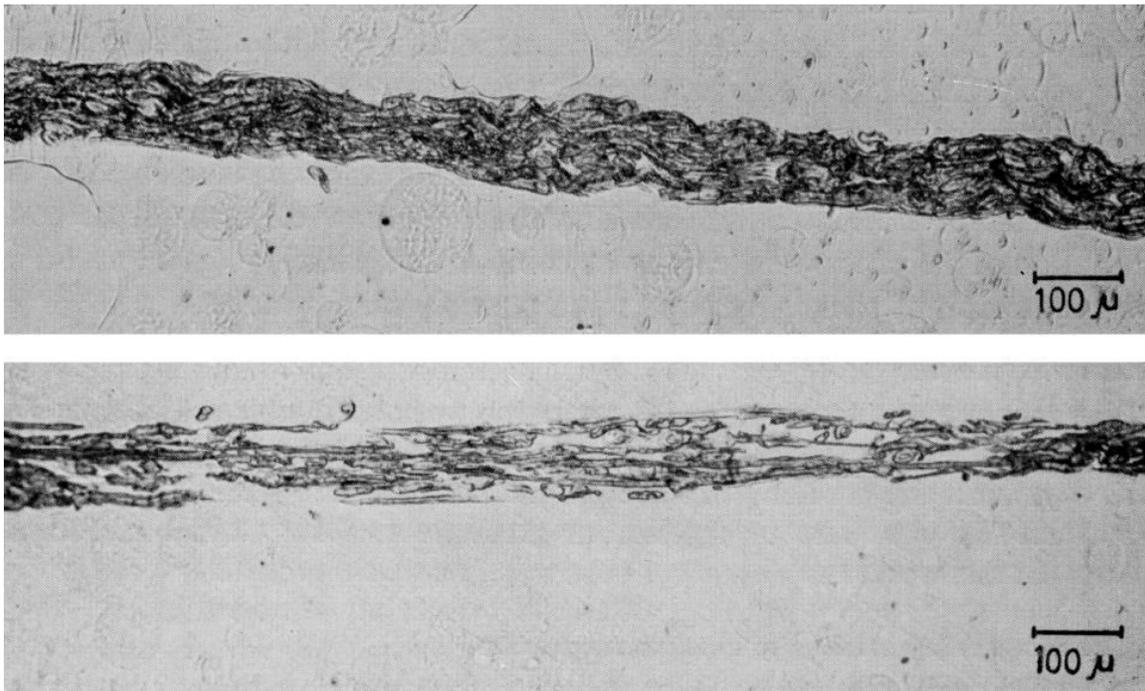


Fig. 17. The comparison of the stress-strain curves of the Clupak and Kraft sack paper in CD (left) and MD (right) (redrawn from the data of Shoudy 1959)

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)

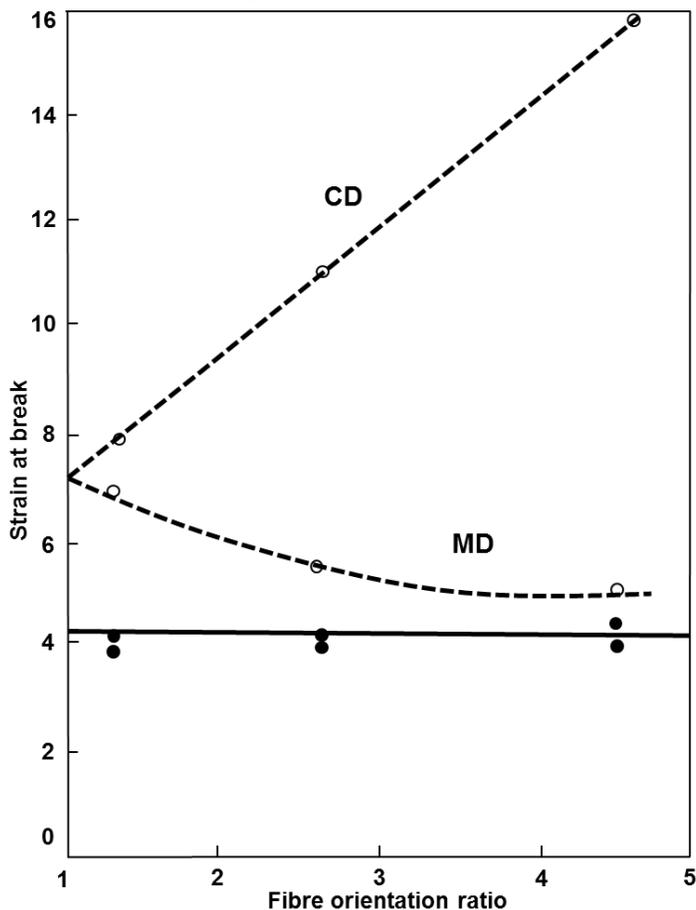
Steenberg (1949) has proposed that the extensibility of compacted paper comes through the extension of the creases in fibres between the fibre joints, which also can be observed in Fig. 18. The decrease in ultimate tensile strength of paper is explained by damage to the fibres and by partially disrupted 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 ( $>100 \text{ g/m}^2$ ), 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

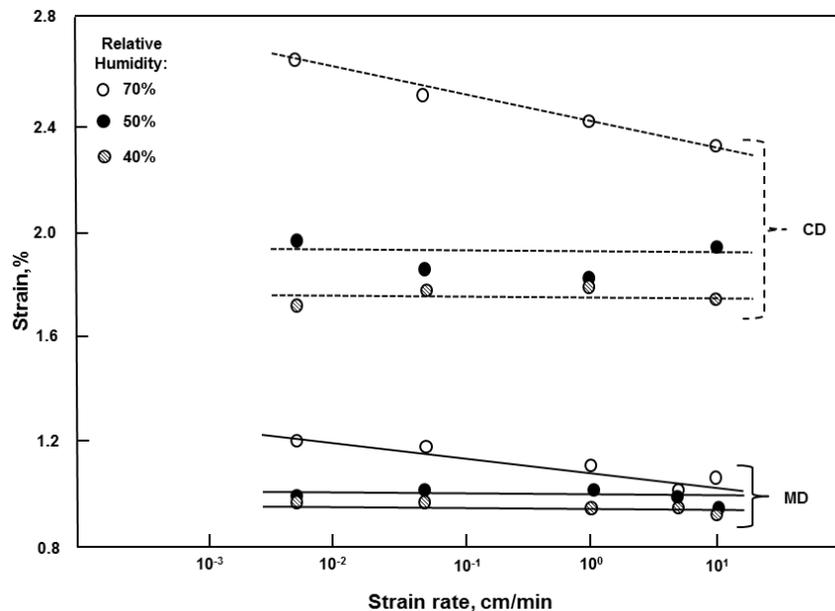
strain at break of paper and drying shrinkage is also not dependent on the fibre orientation (Gates and Kenworthy 1963). Nevertheless, large fibre orientation anisotropy leads to limited MD-shrinkage potential and thus strain, no matter how low the draw during drying is, which makes the question about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

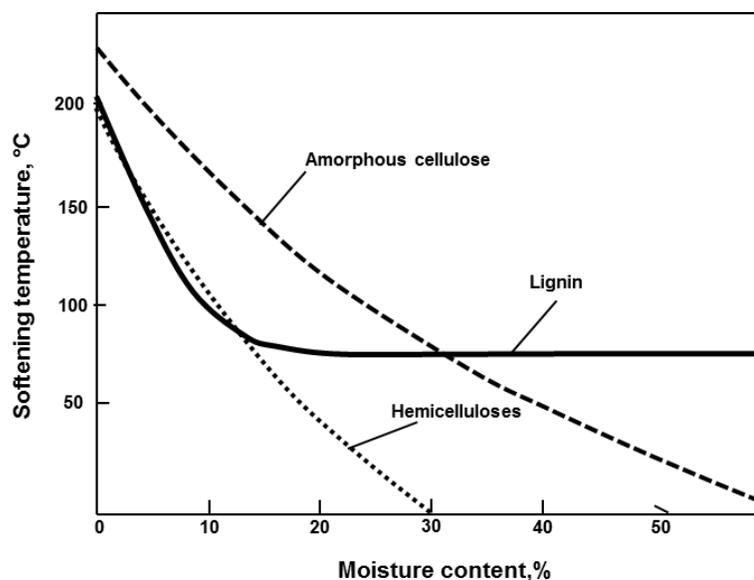
Straining of paper under elevated temperature or/and moisture level commonly occurs in production and converting processes. Temperature and moisture effects are not independent since at elevated temperature the equilibrium moisture content of paper changes. When paper is heated and/or moistened, the 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.

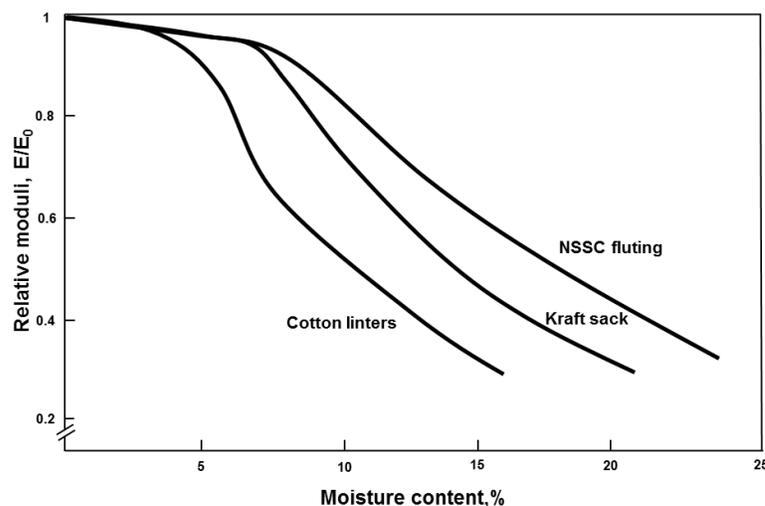
These values are significantly lower already at 6% moisture content, which is typical for air-dry paper. However, lignin cannot absorb more than 10% moisture content due to its network structure and limited amount of the exposed hydroxyl groups.



**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).

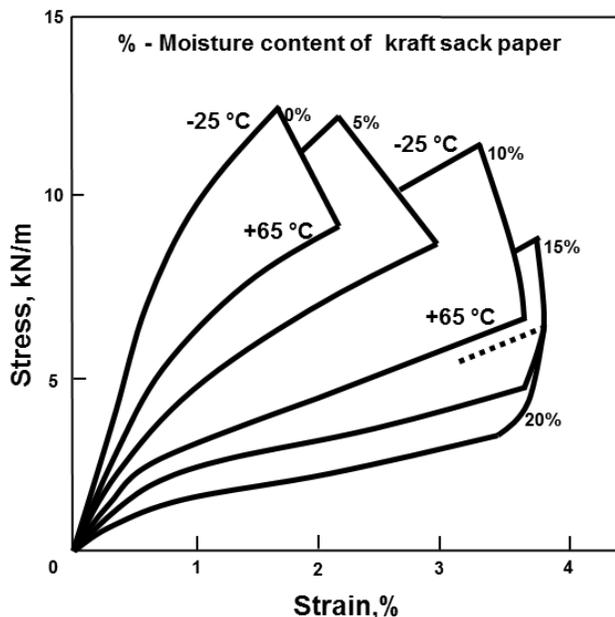
From Fig. 22, NSSC fluting paper experiences a decrease of 60% of elastic modulus at a moisture content of around 23%, while kraft sack paper and cotton linter paper experience the same decrease at 16% and 12%, respectively. Such behaviour can be explained by the different content of crystalline material 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 *
<b>Treatments on the fibre level</b>					
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
<b>Treatments on the fibre network level</b>					
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.

## ACKNOWLEDGEMENTS

The Future Biorefinery Programme and ACel project at Finnish Bioeconomy Cluster Ltd., and VTT Graduate School are acknowledged for providing financial support to this study.

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Article submitted: July 7, 2014; Peer review completed: August 6, 2014; Revised version received and accepted: September 18, 2014; Published: September 29, 2014.