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MANU SOMERKALLIO  
SPRAY APPLICATION OF STRENGTH CHEMICALS  
Master of Science Thesis

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Spray application can bring various benefits when applying chemicals on wet and dry paper or board such as precise adjustability of dosage and good coverage. Special advantage of spray application is in creating a uniform coverage onto irregular surfaces. This thesis is divided into two major sections. In the literary section the basic aspects of spraying are covered. Some of the current applications in paper and board industry, with ongoing research projects included, are reviewed with benefits and problems arising from using spray technology. The aim of the study was to determine the possibilities and restrictions of application of strengthening chemicals via spraying. Based on the literary section, xyloglucan, a water soluble polysaccharide, was chosen as focus.

Xyloglucan (XG) was selected as the main focus as according to previous studies the strength properties, when sprayed onto paper web, increase significantly. Viscosity measurements were carried on a variety of solutions to characterize their behaviour when sprayed. Surface tension, according to general theories, factors in to good sprayability and was therefore included in the measurements – although the results from surface tension measurements were inconsistent. The power of ultrasound was taken in use to determine the effect of deflocculation and shorter molecules on the viscosity of the xyloglucan solution.

The main objective of the experimental part was to study how the sprayed solutions which varied in viscosity and composition affect strength properties. Goal was also to determine whether it is possible to increase the dry weight fraction of sprayed xyloglucan solutions on to the level where the amount of water in the solutions would not require too much energy to be evaporated at drying sections in paper or board machines.

Amount of borax in Tamarind Kernel Powder (TKP) and XG solutions was the most significant factor increasing the strength properties of the handsheets. Borax addition lowered viscosity to a certain point at lower dosages and increased the dry weight proportion of the solutions. XG with an addition of borax had the highest percentage of strain at break by far. Addition of only TKP or XG to the handsheet did not improve the sustained strain notably thus the runnability improving properties of borax seem to be excellent with conjunction of XG.

Introducing ultrasound to higher concentrations of TKP showed a vast decline in viscosity already at short processing times. It can be assumed that sonication reduces viscosity via deflocculation to a certain point. The strength properties were significantly worse when compared to unmodified TKP. The results show that spraying of XG or TKP with borax provides best total increase in almost all strength properties. Borax can also be used effectively to increase the dry weight fraction of the sprayed solution without increasing viscosity too much.

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Spray-menetelmällä voidaan kemikaaleja annostella tarvittaessa hyvinkin tarkasti ja hyvällä peittokyvyllä sekä kuivalle että märälle paperille. Spray-applikoinnin erinomaisuus käy ilmi etenkin epätasaisia pintoja käsiteltäessä.

Tämä työ jakautuu kahteen osaan. Teoreettisessa osassa käydään läpi spray-menetelmän teoreettinen tausta. Lisäksi työssä sivutaan tämän hetkisiä sovellutuksia ja tutkimuksia paperiteollisuudessa. Työn tavoitteena oli selvittää spray-menetelmän soveltuvuus lujituskemikaalien levitykseen. Kirjallisuuden pohjalta valittiin kokeellisen osuuden tutkimuskohteeksi xyloglukaani (XG), joka on vesiliukoinen polysakkaridi.

Aikaisempien tutkimusten mukaan spray-applikoitu XG parantaa paperin märkä- ja kuivalujuuksia. XG-liuoksen ominaisuuksia selvitettiin erityisesti viskositeettimittauksin, jotta pystyttiin ennustamaan XG-vesi-liuosten käyttäytymistä spray-applikoinnissa. Myös liuoksien pintajännitys mitattiin, sillä teorian mukaan pintajännityksen muutokset vaikuttavat sprayn ominaisuuksiin – tutkimuksissa tosin ei havaittu suuriakaan muutoksia pintajännityksissä kuiva-ainepitoisuuksien muuttuessa. Kokeellisessa osassa selvitettiin myös mahdollisuutta vaikuttaa viskositeettiin hajottamalla XG-flokkeja ultraäänien avulla.

Kokeellisen osan tavoitteena oli myös selvittää, kuinka viskositeetiltään ja koostumukseltaan erilaiset liuokset vaikuttavat paperin lujuuksiin, ja pystytäänkö liuosten kuiva-ainepitoisuutta nostamaan, jotta haihdutetun veden määrä esimerkiksi paperikoneen kuivatusosalla olisi mahdollisimman pieni.

Boraxin lisääminen puhtaan XG:n tai tamarindipuun siemenistä tehdyn jauheen (TKP) vesiliuokseen sai aikaan suurimmat kasvut käsiarkkien kuiva- ja märkälujuusarvoissa. Boraxin lisääminen alensi myös viskositeettia tiettyyn pisteeseen asti. Lujuusmittausten pohjalta voitiin päätellä, että boraxin ja XG:n yhdistelmällä saadaan ajettavuuden kannalta paras ratkaisu aikaan.

TKP:n ultraäänikäsitteily alensi korkeamman konsentraation liuosten viskositeetteja huomattavasti. Teorian pohjalta voidaan olettaa, että ultraäänikäsitteily pienensi viskositeettia ensin flokkeja avaamalla ja mikäli käsitteily jatkui tarpeeksi pitkään, myös molekyyliketjut alkoivat katketa. Ultraäänikäsitteilyllä TKP:lla spray-applikoitujen käsiarkkien lujuusarvot olivat selkeästi heikompia kuin natiivilla TKP:lla käsitellyt arkit. Kokonaisuuden kannalta boraxin spray-applikointi XG:n tai TKP:n kanssa sai aikaan parhaimmat lujuusarvot niin kuivilla kuin märillä arkeilla. Boraxin avulla pystyttiin myös nostamaan liuosten kuiva-ainepitoisuutta jopa 10 prosenttiyksiköllä.

## **PREFACE**

The first part of this thesis, the literary report, was made during late winter 2010 in Tampere to broaden the knowledge on basic theory and special applications of spray technology. Based on the information gained from that study the experimental work began in Jyväskylä at early spring of the same year and was finished after the summer of 2010.

With the excellent guidance from thesis' examiner, docent Elias Retulainen, and Mr. Antti Oksanen, MSc, who acted as supervisor to the thesis, the project as a whole was surprisingly smooth and easy to complete. I would also like to thank the laboratory staff of VTT Jyväskylä for the extra information and help they gave me regarding the basic laboratory measurements and also the attributes of the chemicals used in the experimental section of this thesis. Also to my lovely girlfriend, Anni, I want to give huge appreciation for enduring the weeks spent apart and late nights spent writing this thesis.

03 November 2011

MANU SOMERKALLIO

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**Abbreviations**

Borax	Sodium tetraborate decahydrate
CMC	Carboxymethyl cellulose
PAE	Poly(amido-amine)-epichlorohydrin
TKP	Tamarind Kernel Powder
TKP US	Sonicated Tamarind Kernel Powder
UMTF	Ultrasound-modulated two-fluid atomization
XET	Xyloglucan endotransglycosylase
XG	Xyloglucan
XG 15 k / 50 k	Short-chained xyloglucans with molecular weights of 15 kDa and 50 kDa

# 1. INTRODUCTION

Current investment costs when building new paper machines are extremely high and return on investments are historically considered very low, which results in a need for high operating efficiency. In the current market situation modernization of existing machinery is considered often as a better alternative than building a totally new mill or machine and especially in Finland it is the current situation within paper and board industry. [1]

Spraying can bring various benefits when applying chemicals on wet or dry paper or board. Adjustability of spraying systems helps in achieving the right dosage and coverage of sprayed liquid. Chemical spreading can be controlled and if desired, full penetration of the chemical to the inner layers of paper web is achievable. Low space requirement can be considered as a very important factor which favours spraying over conventional technologies when modernizing equipment. [2]

Spraying process in general is well known for example in painting industry. It excels in creating a uniform coverage of paint layer onto irregular surfaces. In paper and board industries spraying technology related to sizing and coating has been under research from early seventies. Spray coating in particular has had big interest in paper industry as machine speeds keep rising and the conventional coating techniques can't keep up with the pace as well as is required. It's yet to see whether spray coating can exceed speeds of 3000 m/min. In the current factory applications it has been shown to perform excellently at speeds of 2500 m/min.[2, 3]

In this thesis the basic theory behind spraying is covered with few examples of typical spraying nozzles. Some of the current applications in paper and board industry, with ongoing research projects included, are reviewed with benefits and problems arising from using spray technology.

The aim of this study was to determine the possibilities and restrictions of application of strengthening chemicals via spraying. Furthermore, based on literary analysis, xyloglucan, a water soluble polysaccharide, was chosen as the main focus. In the literary analysis common factors affecting sprayability are studied and in the experimental part of this study these factors are studied in laboratory scale.

Xyloglucan was selected as the main focus as the strength properties, when sprayed onto paper web, do increase significantly. Viscosity measurements were carried on a variety of solutions to characterize their behaviour when sprayed. Surface tension, according to general theories, does factor in to good sprayability and was therefore included in the measurements. The power of ultrasound was taken in use to determine



the effect of deflocculation and shorter chain lengths on viscosity and surface tension of the xyloglucan solution and on strength properties of paper. The main objective of this thesis was to figure out whether it is possible to increase the dry weight fraction of sprayed xyloglucan solutions to the level where the amount of water in the solutions would not require too much energy to be vaporized at drying sections in paper or board machines.

## **2. LITERARY ANALYSIS**

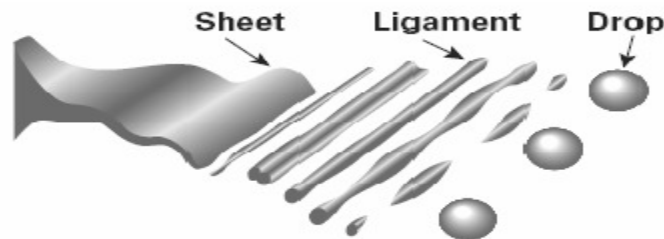
The aim of the literary analysis in chapters 4 - 6 was to set up the basis upon which the experimental section would be grounded on. Main issues were to determine the most suitable spraying equipment, especially regarding possible nozzle types, and to find out the basics behind droplet formation.

Regarding droplet formation it was also necessary to determine the key factors affecting in forming of the most ideal spray pattern so those factors could be controlled when spraying in the experimental section. Spraying being relatively new to papermaking, especially spraying of chemicals, other more common industries were also reviewed in terms of theories behind droplet formation and selecting of optimal nozzles.

### 3. SPRAYING

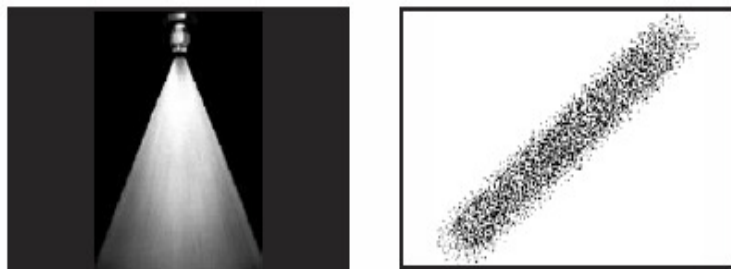
#### 3.1. *Atomization and droplet size*

Spray technology is based on droplet formation due to atomization of the liquid used and to getting these droplets in to contact with the surface of the substrate. Atomization as a process begins by forcing liquid through a nozzle with the help of high pressure. Atomization can be divided in to three major phases describing the form of the liquid as shown in **Figure 1**. [4]



**Figure 1. Three phases of atomization process.** [4]

After exiting the nozzle the liquid is in sheet-like form which progresses into ligaments due to elongational forces affecting in the liquid. Shape of the ligaments depends on geometry of the nozzle used - which for example in spraying chemicals on paper and board is usually a flat spray nozzle illustrated in **Figure 2**. Last phase of the atomization process is droplet forming. This is caused by the same elongational forces which caused the liquid to form ligaments [2]. After few tens of milliseconds the ligaments will break up into droplets due to forces affecting inside the liquid [5]. Droplets will then pursue the form of a sphere because it has the minimum surface energy.



**Figure 2. Flat spray nozzle.** [4]

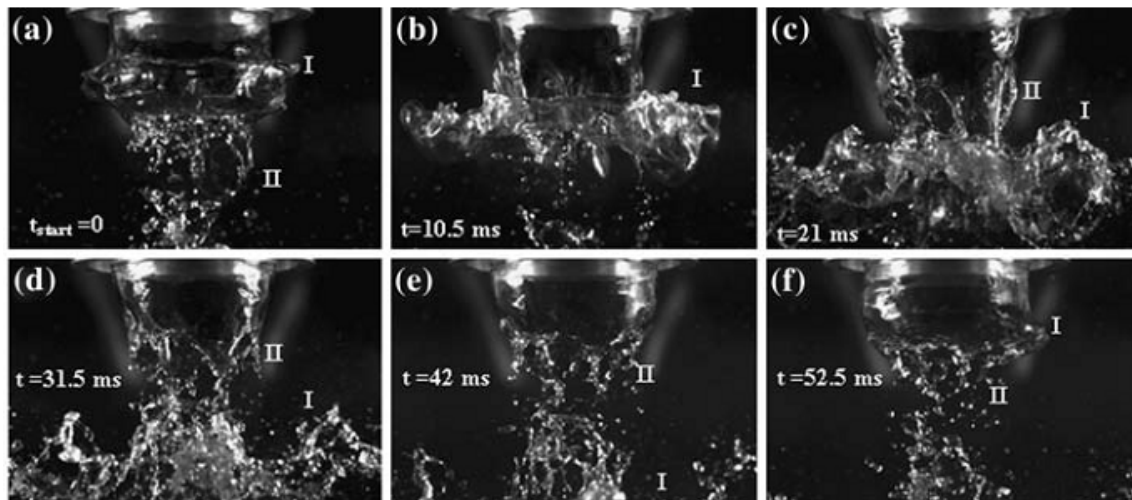
Surface tension, work which is needed to increase area of the liquid, plays a key role: it represents the energy needed for transferring the liquid stream to droplets. Atomization energy needed is then defined by equation 1:

$$E_a = \sigma \Delta A, \quad (1)$$

Where  $E_a$  is the activation energy,  $\sigma$  is surface tension and  $\Delta A$  the increase in surface area of the liquid. In spray system this energy is provided for the most part by pressurizing the liquid. [2]

High viscosity affects the atomization by decreasing the available atomization energy because of high viscous losses. The previous results in a delay in disintegration and increase in the size of the droplets. [2]

The complex theory behind atomization process is called Rayleigh's wave theory which describes the droplet formation with development of waves in the sprayed liquid. High-speed images taken of the rupture phase in a spray formed by typical full cone nozzle can be seen in **Figure 3** which shows sinuous waves in the liquid after it exits the nozzle tip. The shape and size distribution of droplets are dependent on the nozzle type, spraying pressure, spray angle and liquid properties such as viscosity and surface tension as mentioned before, and specific gravity. [4]



**Figure 3. High-speed photographs of ligament formation from typical full cone nozzle. I indicates a sinuous wave in an annular fluid stream, II indicates ligament formation. [5]**

Spreading of the droplet onto the surface depends mainly of the droplet velocity at the time of the impact. In spray coating the impact velocity is typically close to 10 m/s. At this velocity other factors such as surface tension and viscosity become insignificant during the initial stages of the impact. According to Hämäläinen [6] in spray coating the rapid immobilization of coating colour after impact makes surface tension's role negligible in spreading of droplets thus making it driven mainly by inertia of the droplets. Levelling driven by wetting requires more time than occurs in the spraying process [7].

Weber number can be used to explain the importance of impact velocity. With high Weber number values, according to equation 2:

$$We = \frac{\rho u^2 d_0}{\sigma}, \quad (2)$$

where  $\rho$  is the liquid density,  $u$  the impact velocity,  $d_0$  the droplet diameter before impact and  $\sigma$  the surface tension, the kinetic energy of the droplet is able to overcome its resistive forces i.e. surface tension. When Weber number is low, surface tension is able to resist the spreading of the droplet and droplet tends to stay in spherical form. [6]

Correlation between impact velocity and viscosity of the liquid can be seen from Reynold's number. It's defined by equation 3:

$$Re = \frac{\rho u d_0}{\mu}, \quad (3)$$

where  $\mu$  is the liquid viscosity. With high values of Reynold's number kinetic energy is able to overcome the viscous forces resisting the change of form from spherical to flat.

In a study performed by Toivakka [7] values commonly used in spray coating were used in analysing both the Weber and the Reynold's numbers. With values of  $\rho = 1500 \text{ kg/m}^3$ ,  $u = 10 \text{ m/s}$ ,  $d_0 = 50 \mu\text{m}$ ,  $\sigma = 70 \text{ mN/m}$  and  $\mu = 100 \text{ mPas}$ , the numbers will be  $Re = 7.5$  and  $We = 107$ . These both values being larger than the value of one suggests that the impact velocity can overcome the resistive forces applied by both the surface energy and the viscosity of the liquid.

When considering droplet size ideal for even distribution of sprayed liquid, the smaller the droplet the better the coverage will be on the surface. This is explained by the fact that bigger droplets – even though covering more area under them – leave bigger areas uncovered between the droplets. This is assuming that no overlapping of droplets occur. One of the most important factors affecting droplet size is viscosity. For the atomization to be successful in spray coating for example, viscosity has to be around 50 – 100 mPas which limits the use of thickeners and water retention chemicals greatly. According to Hämäläinen [6] higher solids content also increases viscosity of coating colour and accelerates the wear of the nozzles used, hence the maximum solids content in his trials were around 60 % which can be seen as a general maximum in current spray coating applications. Other factors affecting drop size are:

- Flow rate – increase in flow rate will increase droplet size, assuming pressure remains unchanged.
- Pressure – increase in pressure will reduce droplet size.
- Spray angle – increase in spray angle will result in smaller droplets.
- Surface tension of liquid – increase in surface tension will increase minimum operating pressure, decrease spray angle and increase drop size.

To summarize viscosity's effects – increase in viscosity will decrease flow rate, create heavy edges to the spray pattern and increase droplet size. [4] Factors affecting droplet size, spray coverage, and nozzle wear are listed in **Table 1**.

**Table 1. Common factors affecting spray coverage, droplet size and nozzle wear.** [4, 6]

	Nozzle wear	Droplet size	Coverage
<i>Increase in pressure</i>	Increases	Decreases	Increases to a point
<i>Increase in solids content</i>	Increases	Increases	Decreases
<i>Increase in surface tension</i>	Negligible	Increases slightly	Decreases slightly
<i>Increase in Brookfield visc.</i>	Increases	Increases	Decreases
<i>Increase in temperature</i>	Usually negligible	Decreases	Increases

### 3.1.1. Droplet impact pressure

Hämäläinen [6 p. 28] showed in his study that the impact pressure from individual droplets created by normal spray coating nozzle with droplet diameter of 50 to 100  $\mu\text{m}$ , viscosities of 50 to 100 mPas and impact speeds of 10 to 20 m/s affects the base paper with a top pressure of 0,8 MPa. This peak pressure comes to a zero within 10  $\mu\text{s}$  after the impact. The area of impact is very small thus resulting in only a minor average pressure force affecting the web.

Impact pressure varies mostly when the kinetic energy of droplets changes. According to Hämäläinen this should be taken in consideration when optimising the levelling of droplets. The impact pressure does not affect the runnability of the web in normal spray applications - however in washing applications it is considered to be very significant factor affecting performance.

### 3.1.2. Liquid penetration to the substrate

In blade coating, coating colour penetrates the base paper with assistance of hydrodynamic pressure under the blade. Capillary suction plays a role just before and after the blade. In spray coating there is no external pressure present after the initial impact. Liquid penetration to paper web in spray applications has to be therefore controlled mainly with substrate parameters. These parameters are pore size distribution, connectivity of pores and surface energy. Pore size distribution and connectivity can be affected by refining pulp, the use of filler and calendering and surface energy by using different surfactants. [6]

Addition of calcium chloride, normal table salt, to water reduces it's penetration into the base paper due to decreased absorption of water onto the fibres. This is caused by reduction in the osmotic pressure gradient. When added to coating colour salt does in

fact reduce the wetting of the base paper but also increases absorption of coating colour into the base paper. In **Table 2** are listed other factors affecting water solution's transfer rate to paper web in both traditional and spray techniques. [6]

**Table 2.** Factors affecting the penetration of water-like liquid to substrate when external pressure is zero (spray techniques) and when there is an external pressure present (traditional coating techniques). - indicates a reduction in liquid penetration, + an increase and ~ no apparent effect. [6]

	External pressure zero	External pressure non-zero
<i>Viscosity up</i>	-	- -
<i>Water temperature up</i>		
<i>Hydrophobic paper</i>	++	~
<i>Hydrophilic paper</i>	+	~
<i>Salt concentration up</i>	-	~
<i>Water pH up</i>	~	~
<i>Mechanical pressure</i>	- -	- -
<i>Basis weight up</i>	~	+
<i>Pulp refining</i>	~	~
<i>Calendering</i>	-	-
<i>Moisture content of paper up</i>		
<i>Hydrophobic paper</i>	- -	+
<i>Hydrophilic paper</i>	-	~
<i>Filler content up</i>	~	-

### 3.1.3. Ultrasonic atomization

There are few applications in industries that take benefit from ultrasonic atomization of liquids, most common of them being domestic humidifiers. In humidifiers the atomization is controlled by piezoelectric resonator. The droplet size distribution which results from this process is very narrow and can be controlled by adjusting the voltage used. In **Figure 4** can be seen the atomized vapour cloud which has been produced with a piezoelectric resonator. [8]



**Figure 4. Water vapour cloud formed by a piezoelectric resonator. [8]**

In larger scale atomization process induced by mechanical vibration is based on the formation of capillary waves in the liquid which passes through a nozzle tip that is vibrating. The vibration is caused by ultrasonic waves focused on the nozzle. Atomization produced this way occurs when the wave length in the liquid is too great to maintain wave stability. By increasing the frequency of the ultrasound, droplet diameter can be decreased. In current applications a mean diameter of 30  $\mu\text{m}$  can be considered as a normal droplet size. Ultrasonic atomization can provide varying sizes of droplets without altering the flow rate. This can be used to form a spray that falls down gently on the substrate rather than with the high impact velocities that the conventional spray techniques use. In paper machine solutions low impact velocity can't be usually considered since a fine mist with very low velocity will just travel to machine hall or anywhere else but the paper web due to the high velocity of the substrate. [9, 10]

In a study performed by Tsai et al. [9] a new spray technique, ultrasound-modulated two-fluid atomization (UMTF), was developed which utilizes both ultrasonic and air assisted atomization. With UMTF sprayed liquid is first introduced to a nozzle vibrating at ultrasonic frequency and after exiting the nozzle tip the liquid is sprayed to an air flow which amplifies the liquid's capillary waves. This results in atomization process generating much smaller droplet sizes than the mechanical vibration assisted atomization could solely achieve with less energy needed from the ultrasound.

### **3.2. *Nozzle characteristics***

In the following are described the most common nozzle types used in paper and board industries. Materials used in nozzles vary greatly depending on the liquid used. If the



liquid has highly corrosive or erosive characteristics nozzle material has to be chosen with care. [4]

### 3.2.1. Hollow cone nozzle

As the name implies the impact pattern from this nozzle has an area free of droplets at the centre of the spray pattern as is described in **Figure 5**. The pattern is usually formed by putting the sprayed liquid into rotation within the nozzle in a small chamber. Benefits from hollow cone nozzle are that it's self-cleaning and doesn't clog easily. It can also be used to spray liquids that have high solids content. [11]

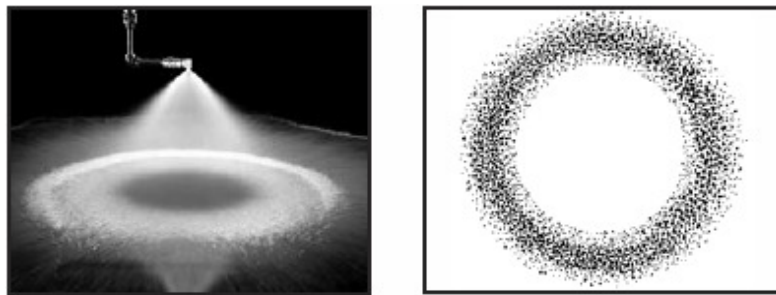


Figure 5. Spray pattern of a typical hollow cone nozzle. [4]

### 3.2.2. Full cone nozzle

Full cone nozzle creates uniform, usually round and full spray pattern described in **Figure 6**. The pattern can be formed by getting the sprayed liquid into a spiral-type motion within the nozzle chamber. The orifice is usually much smaller than in similar sized hollow cone nozzles which causes the pattern to be more of an uniform than hollow. [4, 11]

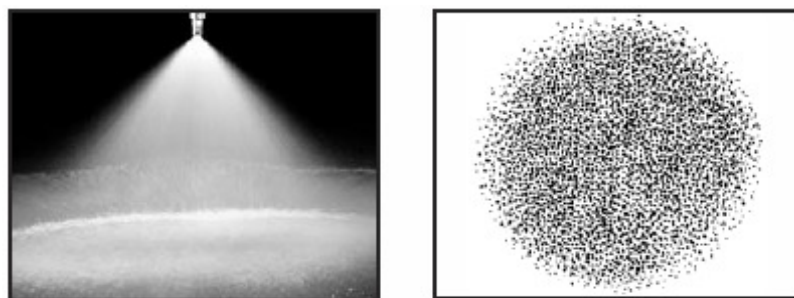


Figure 6. Spray pattern of a typical full cone nozzle. [4]

### 3.2.3. Flat spray nozzle

As illustrated in **Figure 2**, flat spray nozzle creates spray pattern of a thin quadrangle or an ellipse. The pattern can be created by internal construction of the nozzle or by deflecting the liquid stream from a deflector plate after nozzle's orifice (illustrated on

the right in **Figure 7**). The latter provides basically clog-free nozzle since the liquid is brought to the deflector plate with a solid liquid stream. [10]



**Figure 7. Possible constructions of flat spray nozzles.** [11]

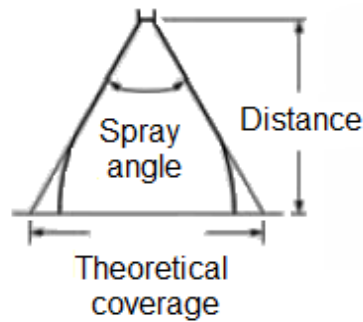
Other nozzles commonly used are solid stream nozzle, which creates a solid jet of liquid and is generally used in washing or cutting materials, two-fluid and air assisted nozzles, which both create small droplets with a combination of air and liquid streams. For spraying chemicals to pulp, perpendicular spraying can be used as seen in **Figure 8**. Spraying provides better mixing of chemicals to the pulp than mixing in storage tower would [12]. Perpendicular spray system can provide similar spray cone than the one provided by full cone nozzle but with very high pressure to ensure optimal mixing. [4]



**Figure 8. Typical construction of perpendicular chemical spraying system.** [12]

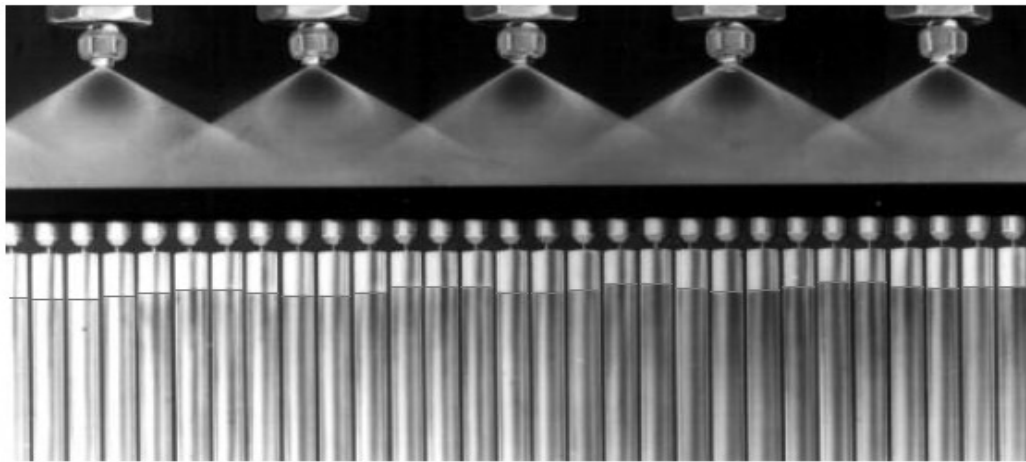
### 3.2.4. Spray angle

Spray angle varies according to the geometry of nozzle type and is also affected by liquid properties and pressure in the process. Manufacturers usually provide spray angles for at least few different pressures in the optimal pressure range of the nozzle. Due to air resistance and turbulence, further the nozzle is from the surface, more the coverage will be reduced from the theoretical coverage as illustrated in **Figure 9**. In coating applications, changing spray angle while keeping the liquid flow constant will alter the coat weight. [10, 11]

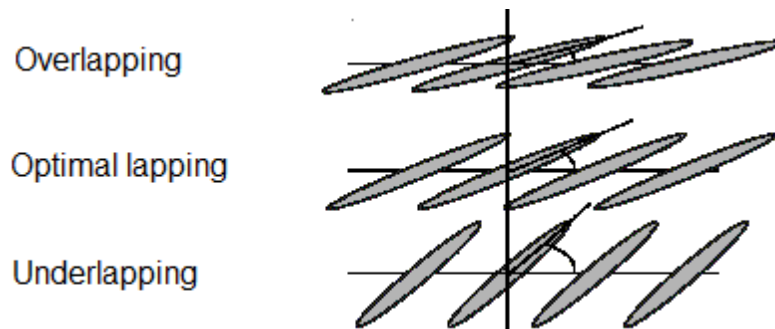


**Figure 9. Illustration of theoretical coverage.** [11]

Liquid's viscosity affects spray angle as follows: increasing viscosity will result in a decrease of spray angle. This can be negated by increasing the liquid temperature or spray pressure to an extent [11]. To achieve a uniform coverage for a wide surface there are usually multiple nozzles used. As seen in **Figure 10** the nozzles are typically aligned so that the individual sprays overlap with each others. The nozzles are also turned in an angle so that the sprays do not merge to prevent larger droplets from forming which is illustrated in **Figure 11**. The uniformity of a coating layer which would result from optimal nozzle set-up can be seen from the tubes below the nozzles in **Figure 10**. There is only minor variation in the liquid levels across the sprayed surface.



**Figure 10. Distribution of sprayed liquid with optimal lapping nozzles.** [9]



**Figure 11. Lapping principles of spray patterns.** With too much or too little of an overlap, liquid distribution will not be even. [2]

### 3.2.5. Liquid properties affecting spray characteristics

Flow rate of a liquid through a nozzle is dependant on the properties of the liquid. If the flow rate of water through a nozzle is announced by manufacturer in a given operating pressure then equation 4 can be used to calculate flow rate of liquid used.

$$Q = Q_w \frac{1}{\sqrt{d}}, \quad (4)$$

where  $Q_w$  is the flow rate of water,  $Q$  flow rate of liquid used and  $d$  is the density of the liquid. Adjusting flow rate can be used to achieve the desired coat weight and coverage.

When considering different operating pressures, the characteristics of sprayed liquid must be taken into account. If the sprayed liquid has long branched polymers for example, high pressure could possibly cause the polymers to disintegrate which can reduce the impact from the chemical. In typical spray coating applications raising pressure doesn't usually have the aforementioned effect since it is beneficial for the coating process to have as homogeneous consistency as possible in the colour and turbulence in nozzle chamber has a positive effect on this. [11]

It can be said that liquid temperature doesn't contribute to the spray properties on its own. Its role is secondary through affecting viscosity, surface tension and density which however do affect droplet size and other spray characteristics vastly.

Viscosity, as stated in previous chapters, does have a major role in forming of optimal droplets and spray shape. It is also considered to be the most common source of problems affecting spray performance and nozzle selection. Considering individual nozzle types it can be stated that increase in viscosity will

- in hollow and full cone nozzles increase flow capacity by decreasing turbulence and rotation of the liquid in the nozzle chamber but
- in flat spray nozzles it decreases capacity due to the increased friction.

Surface tension of the liquid has only a minor decreasing effect on spray angle with high values. Increase in operating pressure will increase spray angle up to a certain limit after which it starts to deteriorate. [11]

### 3.3. Applications

Currently spray technology can be used in variety of tasks in paper industry. In wood handling plant spray nozzles are used for debarking, dust control, washing and moistening logs [13]. Other major roles for spray technology in papermaking are:

Washing and bleaching pulp

- Cleaning wires and felts
- Moisturising pulp prior to grinding to improve performance.
- Spraying reinforcing agents on paperboard to increase strength.

- Coating kraft paper with polyethylene emulsion to reduce friction when fluting.
- Applying starches, lotions, brighteners, surfactants and other chemicals on paper or board.
- Coating paper.
- Adding adhesives for tissue lamination.
- Moisturising corrugated products to prevent curling.
- Controlling moisture profiles on papermachines.
- Environmental solutions in controlling of air and water pollution. [14]

Spray technology has been used in variety of applications within paper industry for several years. More complex uses have been applied only recently. Even though spray coating process has been well known and used by industries in general, its importance to papermaking and converting has been very low. [2]

In a study performed by Kuusisto-Rajala [15] spray technology was used to control oil absorption of paper. Spraying was performed on a laboratory scale to adjust the oil absorption by applying different chemicals on the substrates. Solids content of the sprayed liquid was found to be optimal at around 3 %. When solids content and viscosity of the sprayed liquid rose, it was found that the absorption properties deteriorated. Chemicals used in the study were primarily modified wax corn starch, carboxymethyl cellulose (CMC) and a mixture of CMC and poly(amido-amine)-epichlorohydrin (PAE).

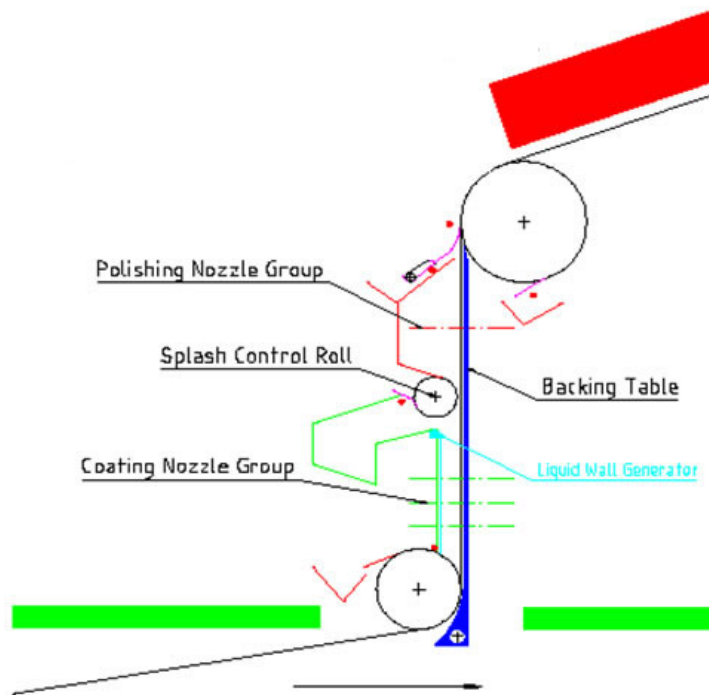
As an example of paperboard strength modification, a study performed by Ryu & Lee [16] showed that plybond strength of multiply boards was dependant on wet web dryness as well as on the amount of starch sprayed. Starch spraying has been adopted by industry because of its high efficiency in terms of starch retention and the control that spray technique gives over distribution of starch.

In the aforementioned study maximum strength values were observed at 10 - 11 % of dryness when using starch solutions. Highest strength values were observed when spraying 1.5 g/m<sup>2</sup> of unmodified corn starch on the two-ply handsheets. Increasing or decreasing starch amount resulted in reduction of Scott's internal bond strength. When using lower than 1.5 g/m<sup>2</sup> starch solutions the decrease in strength was interpreted to occur because of heavier starch migration with water towards the inner structure of the hand sheets. At higher solids contents the reason for lower strengths was thought to be on account of deficiency of moisture for starch gelatinization to occur.

Regarding spray technology most prominent research from paper industry's point of view relates to spray coating. Metso's OptiSpray for example have had factory scale applications for some time now. Studies in other areas are ongoing also; application of xyloglucan via spraying can be considered one of most recent ones. In a study performed by Ahrenstedt et al. [17] spraying was used to spread xyloglucan and borate on to hand made sheets which improved sheets' tensile and tear strengths.

Currently there are also other commercial applications in research in the field of spray sizing and coating. Already in pilot scale use is a solution for spray sizing

constructed by Dryad Technology Inc. (DTI) which uses a low pressurized system that atomizes the size with aid of gas pressurised at under two bars. DTI has a spray coater under development which is waiting for pilot scale tests. Schematic of the coater structure is illustrated in **Figure 12**.



**Figure 12. Illustration of DTI's spray coating technology.** [18]

DTI is also researching into a new technology of a spray former. This new former type, according to them, is in need of higher risk research and development effort, but when completed can achieve up to 90 % savings in water usage with sizeable reduction in energy consumption in the paper forming section. [16, 18, 19]

### 3.3.1. Benefits

When distributing chemicals on paper and board spray technology does excel. The high adjustability of spraying systems gives them an advantage over other techniques. As long as chemical is in liquid form, spray systems can usually transfer the chemical onto substrate with required parameters.

According to recent studies, spray coating can bring various benefits for coating newspaper grades, magazine papers, and boards over traditional coating technologies. As a contact-free technology it allows much weaker paper webs to be used as substrates with good runnability. Spray coating, and usually any spray application, does also save space on the paper machine. It can be fitted to coat both sides of the paper web simultaneously with very low space requirement. The benefits listed for spray coating apply to other chemical spraying also. [2]

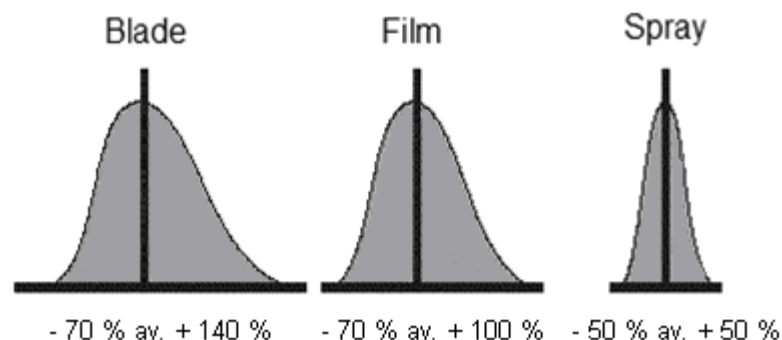
In coating applications spray technique can provide 5 - 6 % improvement in overall production efficiency when compared to blade coating with reduced broke and downtime. The difference with film coating is 2 % in favour of the spray technique. Spray technology doesn't have a speed limit in a way that blade coating has and it has been used in speeds up to 2500 m/min. As a contact free technology, spraying doesn't require as strong base paper as the other conventional techniques – hence less expensive fibres, fillers, and coatings can be used. In sizing applications energy consumption can be lowered using spray technology when solids content is increased from 6 - 15 % to 25 - 30 %. [18, 19]

For low pressurised coating and sizing systems advantages over conventional methods are:

- Speed – no speed limit in paper surface treatment
- Cost savings – as bleaching of the paper could be significantly reduced with controlled application of pigment layers on the paper surface.
- Sizing – reducing the need for after-dryer capacity when spraying starch at high solids contents

It is yet to see whether DTI's technology for example does achieve all the goals its designers have set for it. [19]

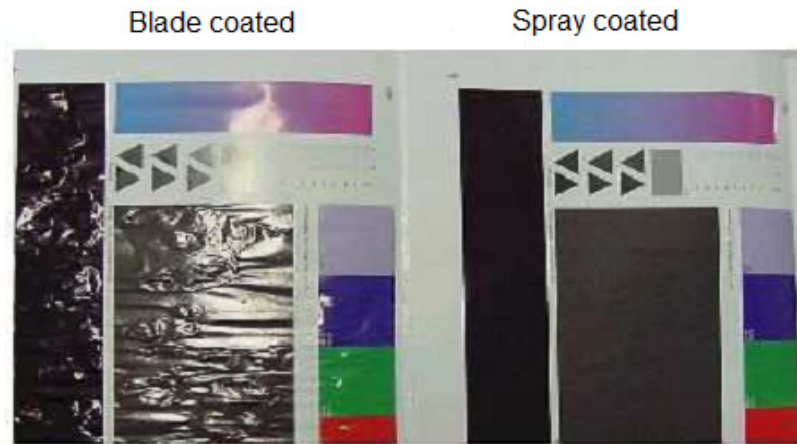
In general, as long as the mist control and nozzle maintenance is handled correctly spray coating can provide uniform quality. Spraying systems provide the ability to spray exactly the amount of coating colour, size, or chemical needed on substrate. The range can vary from 1 to 20 g/m<sup>2</sup> for example. In industry applications nozzles' lifetimes are usually in range of one week which is longer than that of rods and blades currently [20]. Coat weight distribution provided by spray coating is easily comparable to, and can be considered even better than, the ones provided with blade and film coating. Differences in coat weight profiles between the three techniques are presented in **Figure 13**. [2, 20, 21]



**Figure 13. Typical coat weight distributions in traditional and spray technologies. [2]**

Uniformity of thickness in the coating layer is advantageous for brightness and opacity of the coated substrate. Spray coating also minimizes mottling and fibre roughening. In **Figure 14** can be seen an example of blistering caused by bad moisture

profile in base paper with blade coated product. In the spray coated version the excess moisture doesn't cause such severe defects. [21]



**Figure 14. Example of worst case scenario regarding blistering in blade coated paper on the left. On the right is a sample from same base paper batch coated with spray technology. [21]**

In moisture control, automated spraying provides increased production and even moisture profiles. Well adjusted nozzles provide fewer brakes and less broke and also contributes to better gloss and smoothness when calendered. If the spraying system is well sealed it doesn't give out any excess humidity to the machine hall. [22]

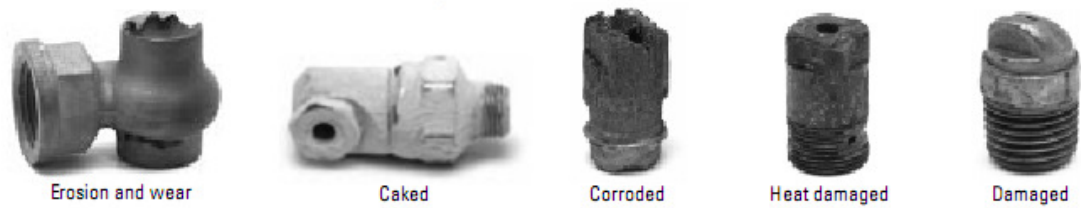
### 3.3.2. Problems

Spraying systems have also many challenges when trying to optimize their operation. Generally speaking highly pressurised systems can seem like an unattractive option due to occupation safety considerations as if breakage happens the system can cause fatalities in worst case scenarios. [19]

In coating applications mist control has to be taken care of since the substrate, running at high speeds, can transfer the mist easily further to the machine hall and cause depositions on machinery's surfaces for example. Furthermore if the coating colour mist isn't controlled it can clog nozzles which leads to defects in the end product. [2]

Clogged nozzles can result in warping when moisturising corrugated products for instance. Uneven spraying profile can't be easily seen by the line operators as the nozzles seem to be spraying correctly upon visual inspection. Key factor in preventing this is regular maintenance after the initial implementation of the system. Automated spraying systems can also have a built-in functionality in them to spot the minor variations in operating pressures and flow rates between the different nozzles which results from clogged orifices. This can be used to prevent excess reject from forming on the machine in advance. In **Figure 15** can be seen different types of nozzles in need of service. [23, 24]





**Figure 15. Different cases of nozzle malfunction. [25]**

In coating application gloss and smoothness of uncalendered product are worse than in blade and film coating. These can be negated by optimising base paper formation and coating colour formulas. When comparing blade and film coating to spray coating, it has been stated that eliminating coating colour binder migration caused by the low solids content is one of the main challenges in the spray coating process [6]. Downside of using spray technique for coating is the increased water consumption when comparing to film coating for example. In traditional coating techniques platy pigments, such as clay, higher viscosity and solids content can be used which contribute to better water retention and lesser degree of binder migration to the base paper.

### 3.3.3. Identifying problems

In any spraying application it is of utmost importance to be able to identify possible problems in advance to limit downtime and extra costs. In the following are listed general guidelines how to spot whether a spraying system is not working at its optimal capacity:

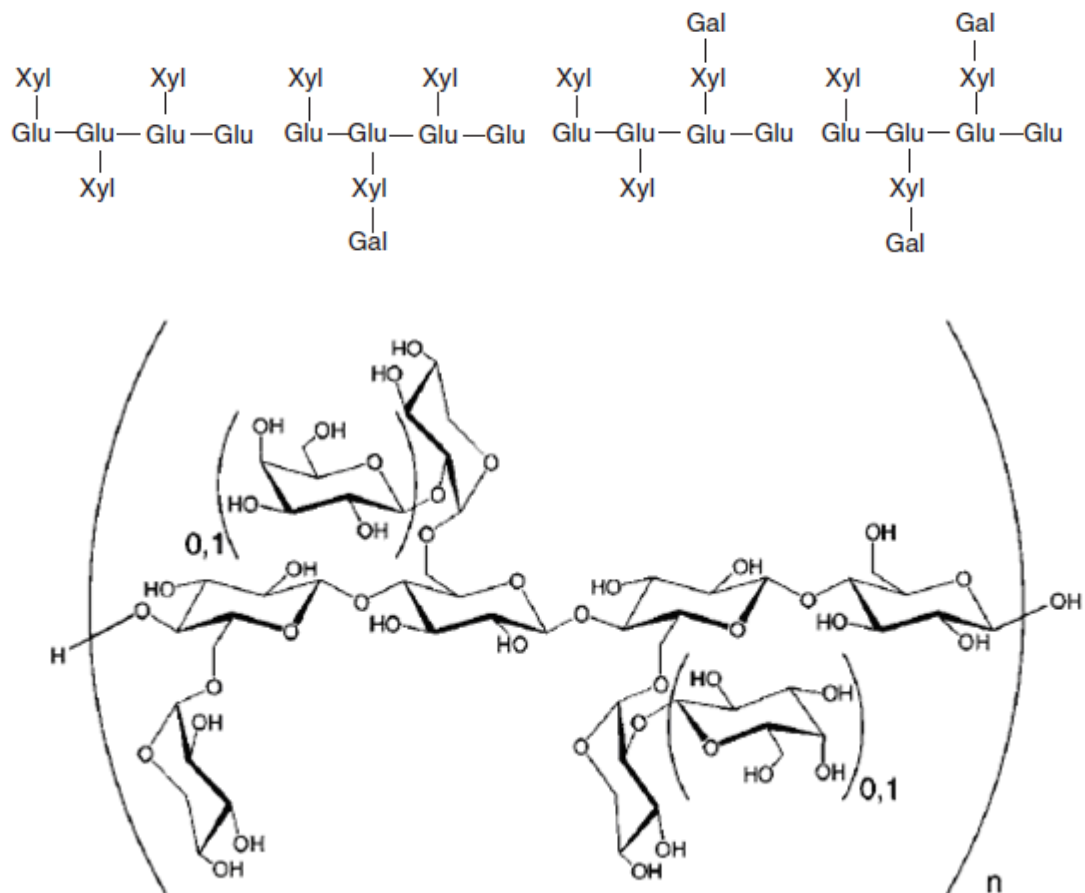
- Flow rate change:
  - If the surface of the orifice or internal core of the nozzle begins to deteriorate, there can be seen an increase in flow rate and in most cases decrease in operating pressure. This can result in increase in droplet sizes.
- Spray pattern changes:
  - Depending on nozzle type, spray pattern can have streaks or sections with heavier flows and effective spray angle can decrease.
- Lowered spray impact:
  - With clogged or worn out nozzles, the spray impact on substrate lowers or increases depending whether the system has centrifugal-type pumps installed. [25]

These problems are commonly caused by erosion or corrosion of the nozzle, also high temperatures used can cause nozzle material to soften. Bearding, accumulation of materials near the orifice, can cause sever problems especially to air assisted nozzles. [25]

To prevent unnecessary erosion and corrosion of nozzles, spraying pressure can be decreased when possible. Decreasing the amount of abrasive particles or the concentration of corrosive chemicals should also be considered.

## 4. XYLOGLUCAN

Xyloglucan is a water soluble structural polysaccharide which can be found in the primary cell walls of all higher land plants (dicotyledons and non-graminaceous monocotyledons). It associates tightly with cellulose microfibrils in the cell walls of plants by hydrogen bonding with them or accumulates as a storage polysaccharide in seeds. The structure of this neutral hemicellulose consists of a cellulose-like glucan backbone substituted by xylosyl and galactosyl residues, as illustrated in **Figure 16**, which are also sometimes substituted with R-fucosyl residues. [26–28]



**Figure 16. Basic structure of xyloglucan presented in two different forms. In the lower picture variable galactosylation is indicated,  $n \approx 800$  [17, 29]**

Cellulose is insoluble in water due to its crystal structure having many hydrogen bonds. Xyloglucan's side chains steric hindrance, however, prevents this by not

allowing the molecules to form similar crystallized structure and thus making it water soluble. [30]

Xyloglucans, apart from interlacing cellulose microfibrils, also controls the cell expansion and plays a role as a carbon reserve in the seeds [31]. When plant's cell walls grow an enzyme called xyloglucan endotransglycosylase (XET) temporarily loosens and reinforces the xyloglucan networks crosslinking the microfibrils. Recent studies have been made where XET is used to modify the structure of xyloglucan by adding new functional groups to it. These groups can be used to introduce new unique properties to the xyloglucan molecules and onwards to paper products for example. Most basic example is adding a functional group of fluorescent tracer to the xyloglucan. After adsorption of the modified xyloglucan, the paper will absorb light and emit it at higher frequency. [26]

#### **4.1. Usage and availability**

Xyloglucan's main source is the seed of tamarind tree (*Tamarindus indica*). Other sources of xyloglucan are seeds of *Copaifera langsdorffii*, *Hymenaea courbaril*, *Azelia Africana*, *Detarium senegalense*, *Mucuna Slonaei* and *Mucuna flagellipes* which aren't commercially used. The seed kernels of tamarind tree are grinded and the seed coat is removed to produce tamarind kernel powder (TKP) which contains approximately 60 % of xyloglucan by mass. Pure xyloglucan, which is usually supplied as a powder, is obtained from TKP by boiling it in water. In pulping process, the xyloglucan present in the wood chips is extracted by the highly alkaline conditions. [32–34]

Xyloglucan has been used especially in the eastern parts of the world for textile sizing of mainly cotton and jute. The usage has historically aimed to improve the processing of the textiles. Xyloglucan has also been used to coat fabrics prior to dyeing with the aid of xyloglucanase to partially remove the dye thus resulting in a worn look of the finished product. [34]

Xyloglucan has many beneficial properties for biomedical applications. It is non-toxic, biocompatible and –degradable with no apparent carcinogenic effects [35]. It is also used as a swelling agent and stabilizer in the food industry. Other applications of xyloglucan include pharmaceuticals, cosmetics, and explosives. Reports of its usage in wastewater treatment have been promising also. [32]

#### **4.2. Adsorption to fibres, principle behind strength increase and improvement of formation**

When introduced to the surface of a wood fibre xyloglucan binds to it irreversibly with high affinity improving the mechanical properties of the sheet. Addition of xyloglucan to the pulp prior to sheet forming has been examined in previous studies [33, 36] and it was shown to increase tensile strength of paper by approximately 25 % and to improve

formation. According to Brumer et al. [40] and Yan et al. [37] the effect is caused most likely by friction reduction of the fibres in the wet state, which improves the formation by reducing fibre flocculation, and is then followed by stronger inter-fibre crosslinking when water is removed from the sheet. The seemingly converse properties of xyloglucan are explained according to Brumer et al. [33] by the fact that the strong adhesion is only activated after the fibre surfaces are forced into contact by the aid of capillary forces during drying. Until that the friction reduction is explained by repulsive forces between xyloglucans in the suspension.

Adsorption of xyloglucan to a wood fibre depends on the purity of fibres' surfaces and molecular weight and sugar composition of xyloglucan. Mechanical pulps which still have relatively high amount of hemicellulose and lignin present on the surfaces of the fibres do not go through similar increase in strength and formation than chemical pulps. It has also been shown that addition of xyloglucan after refining – compared to prior – achieved better response due to higher hydrogen bond formation between celluloses. [34, 36, 38]

Xyloglucan exhibits Newtonian flow properties in aqueous solutions when its concentration is relatively low (under 0.5 %). When the concentration is increased the solution starts exhibiting shear-thinning behaviour [39]. At lower concentrations xyloglucan solutions are very stable against heat, pH and shear. Adhesion of xyloglucan to wood fibres is also unaffected by temperature and pH – apart from very high pH values. [31, 34]

### **4.3. Synergism with borax**

According to Brumer et al. [17] borax, sodium tetraborate decahydrate, cross-links plant originated polysaccharides. In aqueous solutions of xyloglucan borax forms complexes with xyloglucan and this leads to an increase in viscosity and furthermore an increase in strength properties of the final paper product.

The chemical does have some unique advantages; it is possible to increase the total dry weight of the solution without compromising viscosity too much. Due to borax having a saturation point at around 10 % it has its limits when raising the dry weight is considered.

## 5. PAPER STRENGTH

To understand how paper strength develops, the basics behind inter-fibre bonding have to be discussed. Due to the fibres being natural polymers, adhesion between them depends heavily on the number of molecular contacts available. As the fibre is a complex polymer it can adhere to another fibre in few different ways. Fibre bonding can occur due to nonpolar bonding of crystalline surfaces, hydrogen bonding or interdiffusion of protruding polymer chains. [40]

Strength of the fibre does not on its own reflect the strength of the fibre matrix even though the hydrogen bonds that exist inside the fibre are alike to the hydrogen bonds that keep the matrix together. As an example the tensile strength of a wood fibre can be around 100 - 200 mN which is originated from the internal structure of the fibre; bond strength has been estimated to be around 10 mN. [40]

The strength of the fibre matrix develops gradually when excess water is removed from the paper sheet. Surface tension forces pull fibres closer while external fibrillation and fines aid in the formation of inter-fibre bonds. The total strength of a fibre bond is the result of the hydrogen bonding layer between the two fibres as well as a covering layer formed by external fibrils and fines which strengthens the bond. Strength of the sheet arises from the multiple fibres bonding to each others in a complex three-dimensional fibre matrix where the strength of the single bonds are additive to the total strength of the sheet. In a wet paper web the strength of the paper web originates from van der Waals forces. These forces are much weaker than hydrogen bonds but unlike the hydrogen bonds their affect is not limited to a certain direction. [40]

### 5.1. *Strength additives*

Since hydrogen bonds require close contact and their effectiveness is hindered if water is present, various chemicals have been created to increase the wet paper web strength. Some of these resins are aimed to increase the strength of the wet paper web before drying section; some are aimed to increase the strength of the paper after rewetting. These wet-strength resins can retain 10 - 30 % of the tensile strength of dry paper. [41]

The resins aim to achieve at least one of the following:

- Strengthen the existing fibre to fibre bonds;
- Protect the existing fibre bonds from water;
- Create water-insensitive covalent chemical bonds;
- Create polymer network which entangles the fibres.

As an example, poly(amido-amine)-epichlorohydrin (PAE) has a cationic charge. When in close proximity with the anionic fibre material it attaches itself to them while making polymer bridges between the fibres which promotes wet strength of the paper web. It is important to note though that not all of the conventional wet-strength resins increase dry strength of the paper web due to the nature of their method in which they increase the wet strength. As an example of dry-strength additive, starch, improves especially the z-directional strength of the paper web once the paper web has been dried by forming chemical bonds between fibres. [41]

## 6. THEORETICAL DISCUSSION

By using spray technology in coating and sizing, similar paper attributes can be achieved as in conventional techniques with even smaller energy and raw material consumptions in ideal situation. Investment costs are considered low when modernizing old equipment as the space requirement of spraying system is minimal compared to other options. When distributing chemicals on paper and board spray technology does excel. The high adjustability of spraying systems gives them an advantage over other techniques.

Spraying being still considered a new technique in coating it does intimidate potential users as it doesn't have the same user base as film coating for example already has. With more and more companies researching spray technology it will without a doubt happen that spraying will come common in paper and board industry - spraying does offer some unique advantages over other techniques, most important being the seemingly limitless speed in all spray applications.

When considering the problems that spray systems bring up, most common are nozzle malfunction or lowered spray efficiency relating to other sprayed liquid originating issues. Selection of nozzles can be considered most important task, along with properly setting up the system of course, when taking spray systems in use. The sheer volume of different nozzle types does not make this task easy. To be able to understand the characteristics of the nozzle best suited for the task at hand, nozzle manufacturer should be consulted.

In current applications spray technology still suffers from using lower solids values than other techniques. This may lead to higher energy consumption in drying section when coating and sizing are considered. Research on nozzle technology capable of creating uniform sprays with high viscosity and solids content is ongoing to get past this handicap.

As the droplet formation due to atomization and droplet impacts on substrate have been well researched in other industries, viscosity modification of sprayed chemicals should also be considered to get under further research. If viscosities can be lowered enough even with high solids values, the energy efficiency of chemical spraying will get an edge over traditional techniques in paper and board manufacturing. Chemical penetration to substrate has to be well known in any application that needs migration of liquid to the paper web. This further emphasizes the need of knowledge on sprayed chemical's characteristics.

## **7. OBJECTIVES OF THE EXPERIMENTAL PART**

In the following section the characteristics of XG, TKP and few starches are examined. The main aim of the experiments was to study the attributes which contribute to sprayability of the solutions and the strengthening potential they provide. The former in layman's terms; the tests were carried out to figure out the highest level of consistency that XG or TKP solution had which still could be used for industrial purposes.

During the tests especially borax was found to be a good addition in terms of strengthening properties as well as when considering the total dry weight of the sprayed liquid. Other modifications XG such as sonication and enzymatic shortening of the chains were found problematic.



## 8. MATERIALS AND METHODS

### 8.1. *Materials*

Xyloglucan and Tamarind Kernel Powder were obtained from KTH Royal Institute of Technology, Sweden. Xyloglucan (XG) had a moisture content of 5.61 % and Tamarind Kernel Powder (TKP) of 6.9 %. The purity of XG was announced to be over 97 % and for TKP, the XG fraction was at 60 %. Molecular mass of XG was 202 000 g/mol. In sonication experiments a semi-purified sample of XG was also used. No other specifications were available from the chemical other than its purity was in between of the pure XG and TKP.

For spraying, there was also a batch of shorter chain length XG available. The chain lengths were 15 kDa and 50 kDa. The chains were cut by KTH Royal Institute of Technology enzymatically. Original XG was estimated to have a chain length of 150-200 kDa.

During the spray tests water was sprayed to act as a comparison tool to the other spray solutions; reference XG 0.5 w/w%, reference TKP 0.5 w/w%, and a sonicated sample of TKP at 0.5 w/w%. The sonicated sample was first diluted to a 2.0 w/w % concentration, then sonicated for 10 minutes and diluted further to spraying concentration of 0.5 w/w%. To clarify the effects of shorter chain length, XG was also sprayed with chain lengths of 15 000 Da and 50 000 Da at consistencies of 0.5 %. Borax was used in conjunction with all but the sonicated sample to allow especially the comparison of strength properties between borax and non-borax solutions.

After spraying the handsheets were compressed with 0.5 and 3.5 bar pressure for 2 minutes and stored overnight (the second batch of handsheets were left to dry in laboratory for 2 to 4 days and from these handsheets the strength properties were measured with Lloyd testing machine). XG's with shorter chain lengths were only compressed with 3.5 bar pressure as the amounts available of the chemicals were very limited and therefore a full set of handsheets could not be made.

Borax (di-Sodium tetraborate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ ) was used in solutions in conjunction with the aforementioned chemicals. It was commercially available and attained from VWR International. Borax had moisture content of 35.45 %. The three starches used in the experiments, Raisamyl's 01151, 23121 and 42151, were supplied by Ciba Specialty Chemicals, Raisio Finland. Moisture contents of the starches were 88 % for both 01151 and 42151, and 83 % for 23121.

The handsheets used in the spray tests were made from unrefined ECF birch pulp which was obtained from Metsä Botnia, Äänekoski Finland. Below in **Table 3** can be found the results of mass analysis done with FiberMaster.

**Table 3. Fibre analysis.**

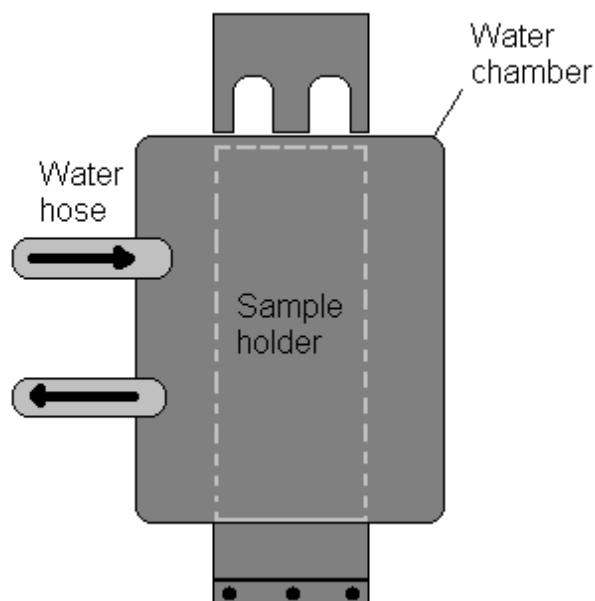
	CSF [ml]	WRV	Length [mm]	Width [μm]	Fines fraction [%]	Kinks [1/mm]
<b>Mean</b>	533	1.07	0.867	21.400	8.13	0.56
<b>SD</b>	0	0.02	0.001	0.141	0.18	0.02

## 8.2. Rheometer

Viscosity measurements were carried on a Haake VT 501 -rheometer with single-gap MV2 -geometry. With the used geometry, the rheometer was able to measure viscosities varying from 5 to 30 000 mPas as long as the torque affecting the geometry was under 1.1 Ncm and above 0.01 Ncm. Shear rate was varied from 0 to 520 1/s. Maximum shear rate used in a given measurement was dependent on the initial viscosity of the sample at room temperature.

The sample holder had a capacity of 55 ml. To counteract the evaporation of the samples during measurements at higher temperatures, a maximum of 1 ml of a given sample was added when the surface level was observed to decline. After addition of the sample, the solution was left to homogenize for 5 minutes while stirring. This evened the temperature gradients also.

Viscosity measurements were made with rheometer at temperatures varying from 25 °C to 85 °C to study the temperature dependency of chemicals' viscosities at different concentrations. Temperature was controlled by using a water bath, equipped with a pump which directed the warm water flow to the water chamber constructed around the sample holder as illustrated in **Figure 17**. The samples were stirred for 5 minutes after achieving the target temperature to even out the temperature gradient within the sample.



**Figure 17. Illustration of temperature controlling equipment around the sample holder.**

### **8.3. Sonicator**

Ultrasound device used in the experiments was a laboratory scale horn sonicator VCX 600, illustrated in **Figure 18** (Sonics & Materials Inc., CT, USA), which had a maximum output of 600 W. Sonicator probe was of model CV26. Exact data how much of the output energy was transferred to the horn was not available.

According to the sonicator manufacturer the fundamental principle behind the effect of ultrasound on the solutions is as follows: *“The ultrasonic power supply converts 50/60 Hz voltage to high frequency electrical energy. This alternating voltage is applied to disc-shaped ceramic piezoelectric crystals within the converter, causing them to expand and contract with each change of polarity. These longitudinal vibrations are amplified by the probe and transmitted into the liquid as alternating high and low pressure ultrasonic waves.*



**Figure 18. Laboratory scale sonicator.** [42]

*The pressure fluctuations pull the liquid molecules apart creating millions of micro-bubbles (cavities), which expand during the low pressure phases, and implode violently during the high pressure phases. As the bubbles collapse, millions of shock waves, micro streams, eddies and extremes in pressures and temperatures are generated at the implosion sites. Although this phenomenon, known as cavitation, lasts but a few microseconds, and the amount of energy released by each individual bubble is minimal, the cumulative amount of energy generated is extremely high. This process is self-stimulating because the imploding bubbles create new sites for bubbles to form.”* [43]

#### **8.4. Tensiometer**

Surface tensions were measured with Küss Digital Tensiometer at room temperature. Between each measurement the measuring ring and sample holder were cleaned with ion exchanged water and acetone. The platinum ring was also heated with a Bunsen burner until glowing to remove any remaining impurities from the surface of the ring.

Principle of surface tension measurement is based on du Noüy’s ring method. The method relies on weighing a platinum ring first when it is hanging free in the air. After this it is then sunk to the measured solution and raised steadily. The change in the measured force pulling the ring down at air-solution interface is then interpreted as surface tension. Principle is illustrated in **Figure 19**.

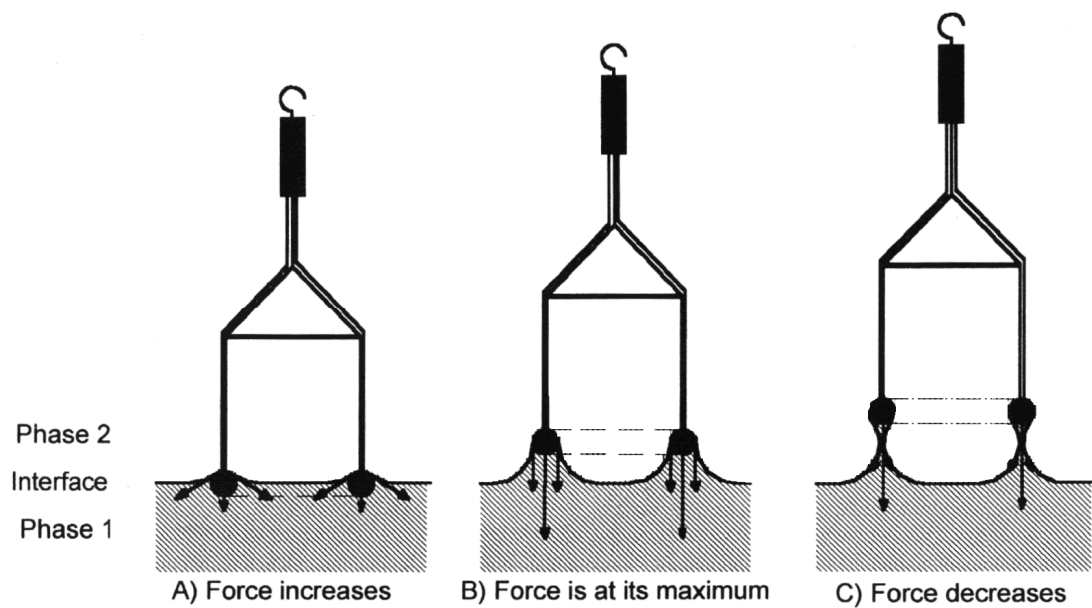


Figure 19. Surface tension measurement. Du Noüy's method.

### 8.5. Impact

An experimental measuring device, developed by VTT and Metso Paper Oy, was used to study the effects of sprayed solutions to paper strength properties. The device, named Impact (can be seen in **Figure 20**), offers more paper-machine-like paper strength testing than normal measuring devices.

Impact can achieve straining speed of 1 m/s compared to normal laboratory testers' 10 - 20 mm/min. This reflects more appropriately the forces affecting the paper web at paper machine; especially the ones present at open gaps where cylinders and alike aren't supporting the paper web.

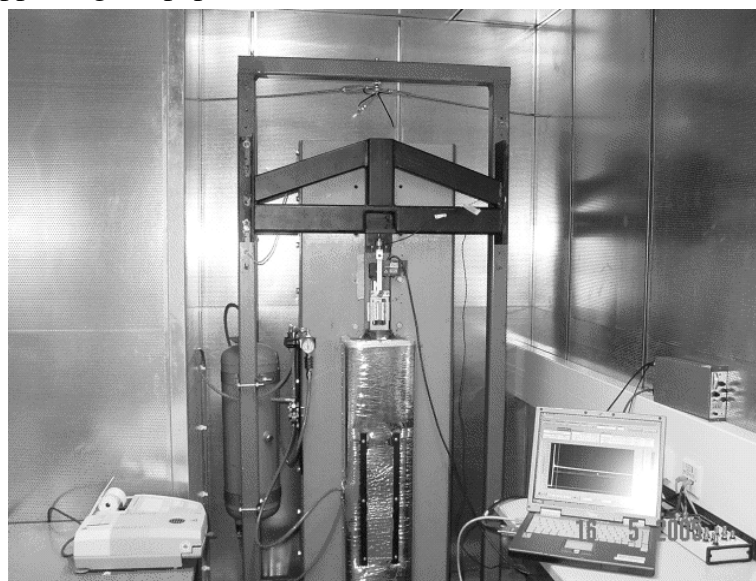
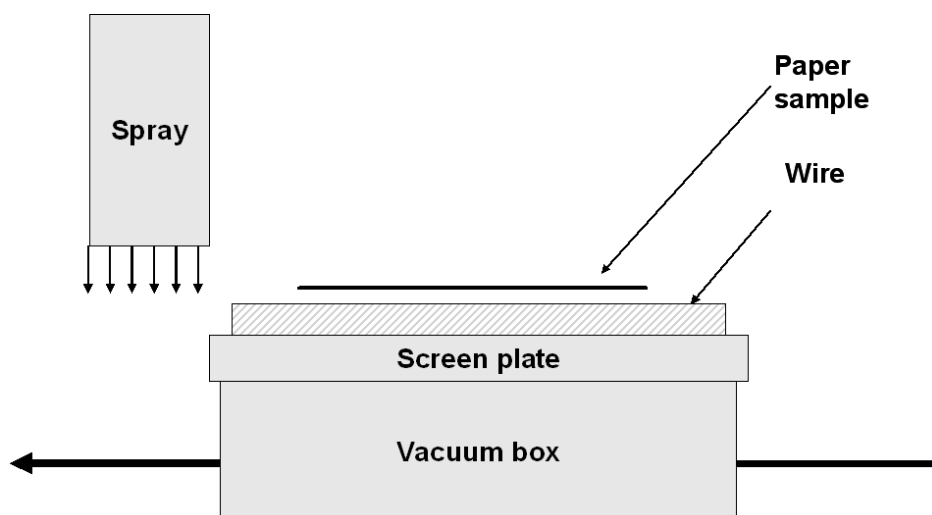


Figure 20. Impact.

## 8.6. *Spray applicator*

The device used for spray tests was a laboratory scale apparatus developed by VTT, Jyväskylä Finland. Basic concept of the device can be seen in **Figure 21**. The sprayed sheet is placed on a mobile sledge. A vacuum is generated under the sledge to keep the sheet firmly at place during spraying. Above the sledge is a flat spray nozzle to which a pump supplies the tested solution.



**Figure 21. Spray applicator.** [44]

The amount of sprayed solution is controlled by modifying the movement speed of the sledge while spraying volume was kept constant. When spraying, the sledge moves at a fixed movement speed. The spraying itself starts before the sledge is under the nozzle and stops briefly after the sledge has gone past the spraying line. Sledge moves on a fixed track and the movement is controlled by electrical motor and magnetic sensors.

The dosage was 0.5 w/w % of XG on the handsheets and was kept constant during all the spray tests. On solutions where XG was not present the target dosage was either to have equal amount of dry TKP than in the XG solutions or to have equal amount of borax as was present in XG solutions.

## 8.7. *Analyzing spray characteristics*

Variations in spray angles were studied by examining pictures taken by a high speed MotionPro Y3 -camera with a frame rate of 30 1/s. To further evaluate the changes in spray angles the pictures were analyzed manually with ImageJ -program. The angle was measured as a difference between the edge of the spray and a vertical line starting from the base of the spray as seen in **Figure 22**. The form of the spray was also described according to smoothness of the spray and how much striping occurred in it.

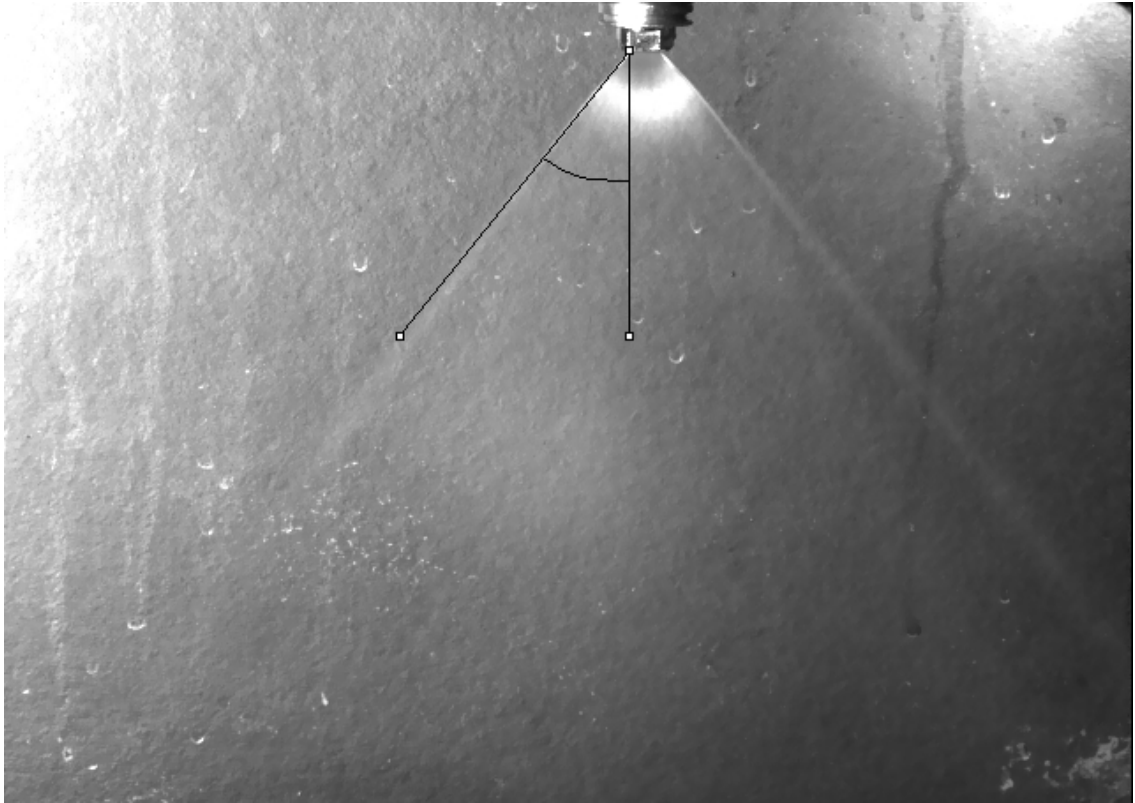


Figure 22. Principle of spray angle measurement.

## 8.8. Other measurements

The equipment and standards used to determine other measured parameters can be found in the following **Table 4**.

**Table 4.** Measuring standards.

Parameter	Standard	Equipment
<i>Optical properties</i>		
<i>ISO-brightness</i>	SCAN-P 3:93	Minolta CM-3610d spectrophotometer
<i>others</i>	SCAN-P 8:93	Minolta CM-3610d spectrophotometer
<i>Basis weight</i>	SCAN-P 6:75	
<i>Thickness</i>	SCAN-P 7:75	Lorentzen & Wettre thickness tester
<i>Tensile strength and strain at break</i>	SCAN-P 38:80	Lloyd testing machine
<i>Elastic modulus</i>	SCAN-P 67:93	Lloyd testing machine
<i>Scott bond</i>	TAPPI T 569	Scott Internal Bond Impact Tester
<i>Air permeance</i>	SCAN-P 26:78	L&W Air permeance tester SE 166

## 9. RESULTS AND DISCUSSION

In the following chapters the chemicals will be analyzed. Especially the effect of concentration in viscosity for TKP and XG are carefully examined. Due to the temperature dependant nature of TKP and XG solutions they were measured at variety of temperature levels.

Laboratory scale spraying was performed to determine the effect of sonication, borax addition, and shorter chain-lengths to the properties of handsheets. Especially strength properties were of great interest.

### 9.1. *Viscosity*

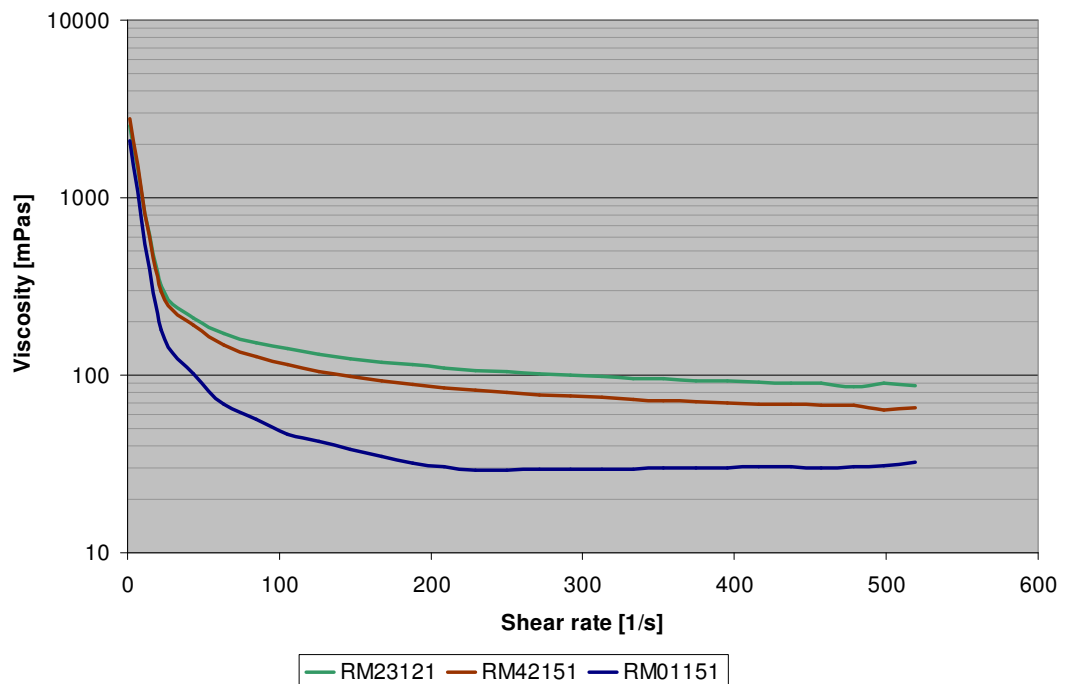
Solutions of different XG, TKP, borax and starch mass proportions were prepared for viscosity measurement. The samples were prepared by diluting the chemical into ion exchanged water at 65 °C (for XG and TKP) or 95 °C (for starches) for 2 to 6 hours depending on the chemical's concentration and composition.

Diluting was done by using a thermostat equipped laboratory stirrer. In some cases, when consistency got high enough, it was required to use a mounted drill with a blade bit.

#### 9.1.1. Starch

Viscosity measurements for starches were made at 10 % and at either 20 or 30 % depending on the starch used. It was shown that all measured starches can be sprayed with industrial equipment at 10 % dry weight fraction as their viscosities were under 100 mPas. The higher concentrations turned out to be too viscous, apart from RM 42151, which reached the minimum of 100 mPas at 85 °C with 20 % concentration.

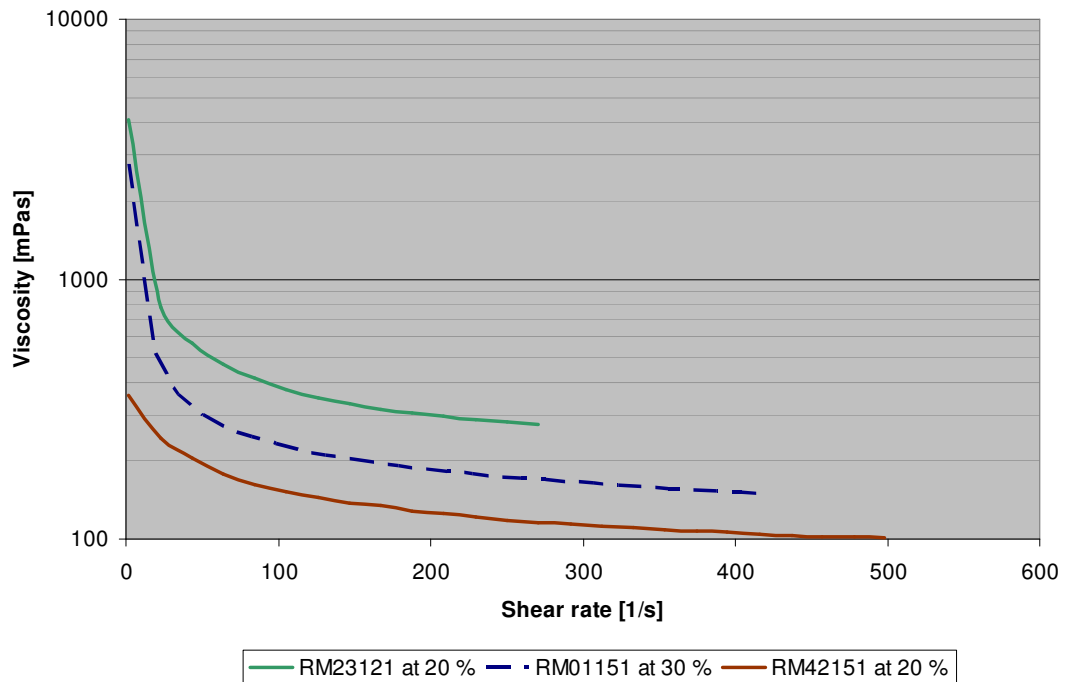




**Figure 23. Viscosity of starches at 25 °C and 10 % consistency.**

It can also be assumed that RM 01151, which was measured at 30 % concentration, to have a viscosity less than 200 mPas at temperature levels of 75 °C and higher, will be sprayable at a concentration of 20 w/w %. All the starches started to form gels at higher concentrations when the temperatures of the samples were lowered enough. RM 42151 experienced an increase of 100 % in viscosity when lowering temperature from 55 to 45 °C and formed a gel which couldn't be measured with the used viscometer geometry.

Due to the time delay to heat up from 25 °C all the way to 85 °C there were some losses due to evaporation and minor sedimentation at the sample-air interface near the edges of the sample holder. To counteract this a millilitre of the measured solution was added every 10 °C after the solution temperature rose above 45 °C. The surface of the solution in the sample holder was observed to remain constant with the aforementioned countermeasure.



**Figure 24. Starch viscosities at 85 °C and different consistencies.**

All starches can be characterized to have a pseudoplastic behaviour which can be seen from both **Figure 23** and **Figure 24**. All solutions became runnier and less viscous as they flowed in response to the applied force. Shear thinning reached its cap with lower concentrations approximately at the shear rate of 300 1/s. This can be assumed to be caused by the fact that after a certain force is applied most of the polymer chains are parallel to each others and the direction of the movement, thus reducing viscosity.

In response to increasing temperature, both RM23121 and RM42151 experienced a quite steady decrease in viscosity which can be seen from **Figure 25**. On the other hand RM01151 which was already at low viscosity level in room temperature showed practically no response when temperature of the sample was increased. Due to the nature of the starches, i.e. when the industrial applications of the starches are considered, these results were expected. RM01151 is characterized as surface sizing starch but RM23121 and RM42151 are aimed mainly to be added in the wet end - thus lowering the viscosity of the latter two is not of major importance.

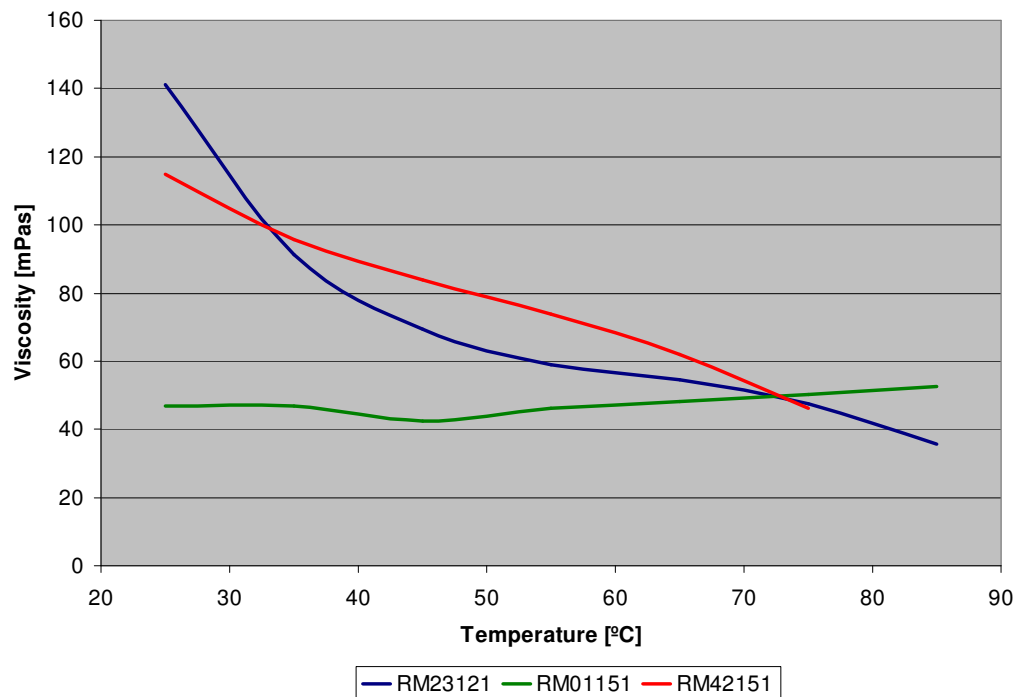


Figure 25. Temperature dependent starch viscosities at 10 w/w % with 100 1/s.

### 9.1.2. Tamarind kernel powder

Shear rate dependent viscosity of Tamarind kernel powder (TKP) was studied at five different consistencies varying from 1.0 % to 6.0 % to determine sprayability of the solutions. In previous studies [17] TKP has been sprayed onto substrates at relatively low dry weight fractions. Aim was to find out at which consistency TKP is still usable in industrial applications. From **Figure 26** can be seen that even at as high as 2.0 % dry weight fraction, the 100 mPas viscosity marker can be achieved at moderately low temperatures. The 2.0 % solution had viscosity under 100 mPas also at 45 °C with shear rate of 500 1/s.

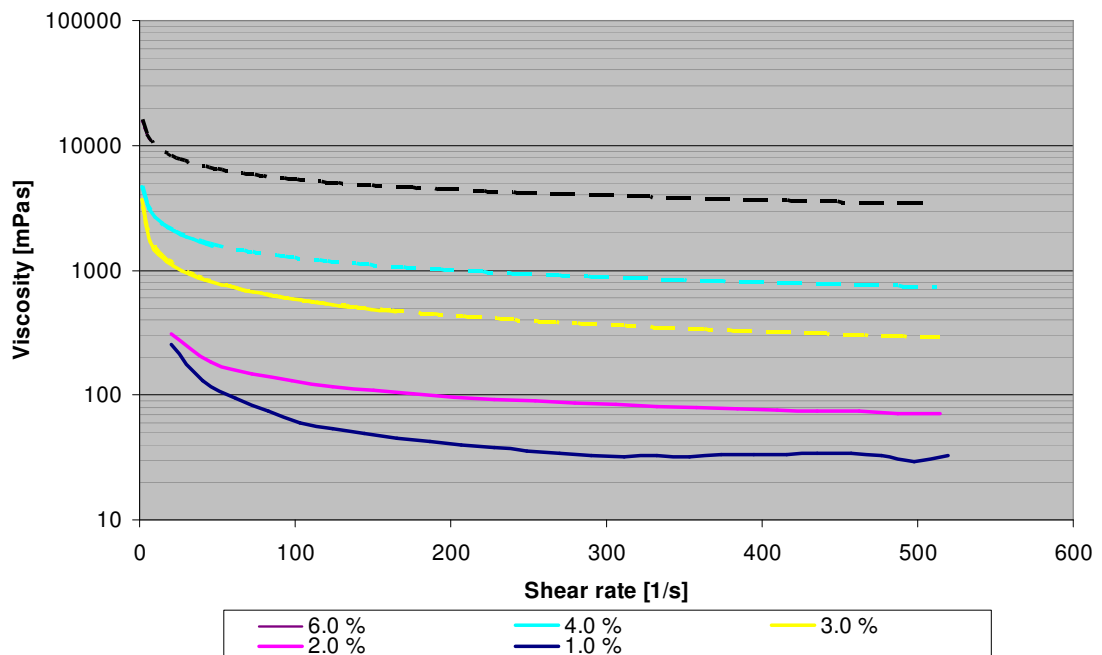


Figure 26. Viscosity of TKP at different consistencies at 65 °C.

### 9.1.3. Xyloglucan

As expected, XG expressed similar shear thinning behaviour as TKP and the starches. When compared to TKP, XG can be characterized as more viscous at same temperatures and consistencies. With 1.0 % consistency XG reached a minimum of 30 mPas at high temperature and shear rate. Shear rate dependant viscosity curves of the 1.0 % solution are represented in **Figure 27**.

At higher consistencies XG had much higher viscosity than TKP. For example with 4.0 % consistency and high shear rates TKP's viscosity was roughly extrapolated to be 800 mPas but XG's would have been above 2000. The measured data from low shear rates does confirm the vast gap between the two; at 15 1/s XG's viscosity was at 5300 mPas but TKP's only at 3200 mPas, as can be seen from **Figure 26** and **Figure 28**.

Viscosity measurements of pure XG show high temperature dependency with all but lowest levels of concentrations. The solutions started to form gels at higher concentrations at room temperature, thus accurate measurement of viscosity became problematic. The rheometer was not able to measure high shear rate viscosities from the most concentrated solutions at low temperatures but for spray applications viscosities notably above 100 mPas are not relevant. Viscosities were measured consistently from all concentrations to enable possible comparison with ultrasonically treated solutions.

Comparison of pure XG solutions' viscosities could be done at 65 °C as most of the solutions could be measured at that temperature – excluding 6.5 % which could be only measured at 85 °C. **Figure 28** shows the concentration dependent viscosity of XG at 65 °C.

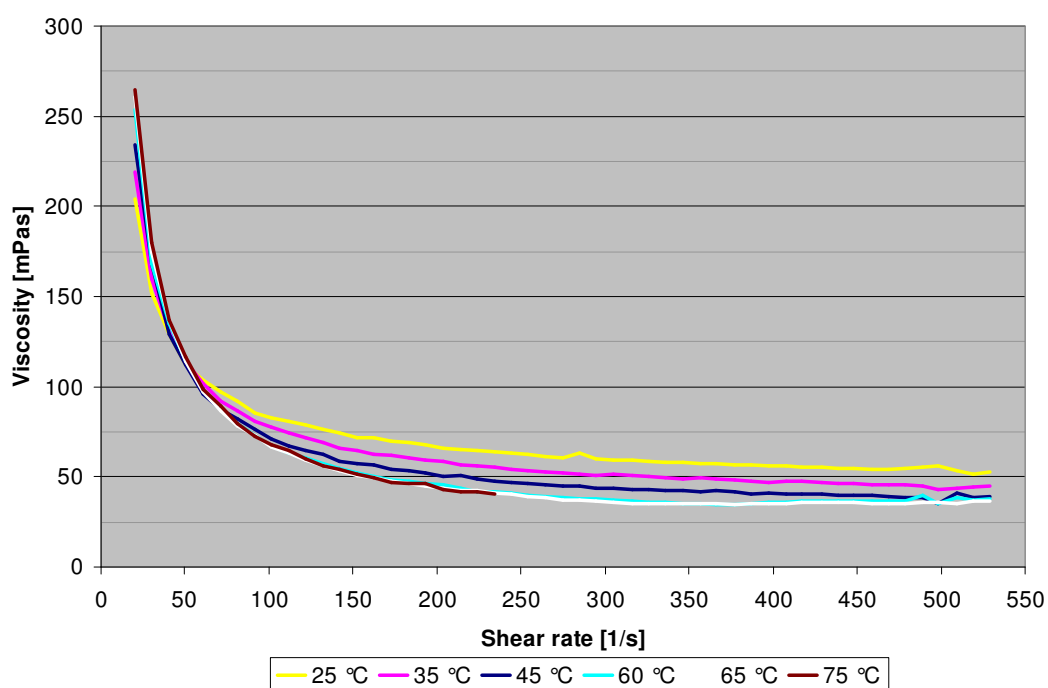


Figure 27. Viscosity of 1.0 w/w% XG at different temperatures.

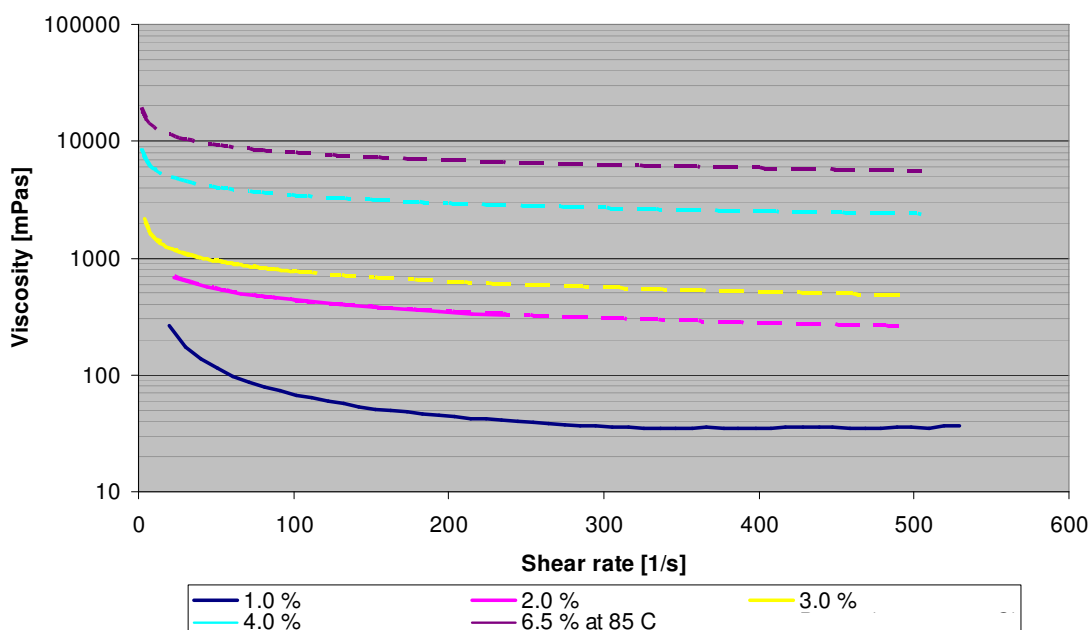


Figure 28. Viscosity of XG at different consistencies at 65 °C. Cut lines are rough estimates how viscosity would develop (measuring device was not able to record data at higher consistencies after certain shear rates).

#### 9.1.4. Borax

It has been shown [17] that with the addition of borax the strength properties of paper can be greatly increased when used in conjunction with XG or TKP. The effect of borax on the viscosity of XG solution was studied. When compared to the reference sample of 1.0 % XG solution the viscosities increased. A solution with 1.0 w/w % XG and 1.0 % of borax had a viscosity increase of over 100 % at higher shear rate values.

The addition of borax to the solution of 1.0 % XG / 1.0 % borax, however, lowered the minimum viscosity of the solution. From **Figure 30** can be seen that by adding 3 % more borax to the initial solution lowered the minimum viscosity from 125 to 100 mPas. This can be seen as highly beneficial for industrial spraying solutions as the increased dry weight fraction should reduce the need of drying energy. Excessive addition of borax to the solution, however, started to raise the viscosity again. At 10 % of borax, the viscosity had risen above 200 mPas and therefore is not sprayable with industrial equipment anymore in room temperature.

In **Figure 30** can be seen also that the solution of 0.5 % XG / 0.5 % borax had almost half of the viscosity of pure 1.0 % XG solution with the same total dry weight fraction. Effectiveness of the aforementioned solution in terms of paper strength improvement when comparing with 1.0 % XG solution is a matter of interest. The viscosity of 1.0 % borax solution was found to be under the viscosity of ion exchanged water. The rheometer, though, was not able to measure accurately the viscosities of the solution of water and borax as the viscosity levels were under the lower limit of the measuring range. Dynamic viscosity of water is reported to be less than 1 mPas which is substantially lower than the values presented in **Figure 29**.

The decrease in viscosity with addition of more borax should be more thoroughly studied. With the data available from this study it can be only assumed that the viscosity of borax becomes dominant when the amount of borax increases in relation to the amount of XG thus reducing the viscosity of the solution. Also the strengthening potential of solutions should be more closely studied; is there any benefit from adding borax in excess or is there a certain threshold after which any additional borax addition does nothing – or even worsens – the strength properties of the paper web.

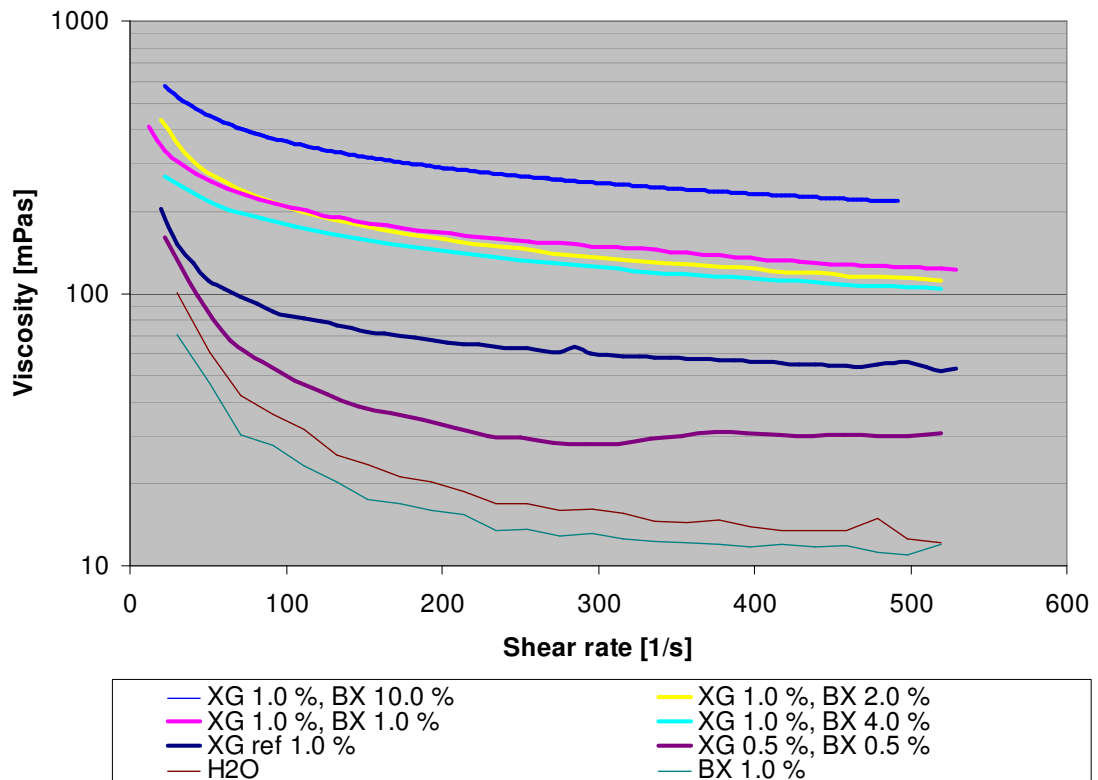


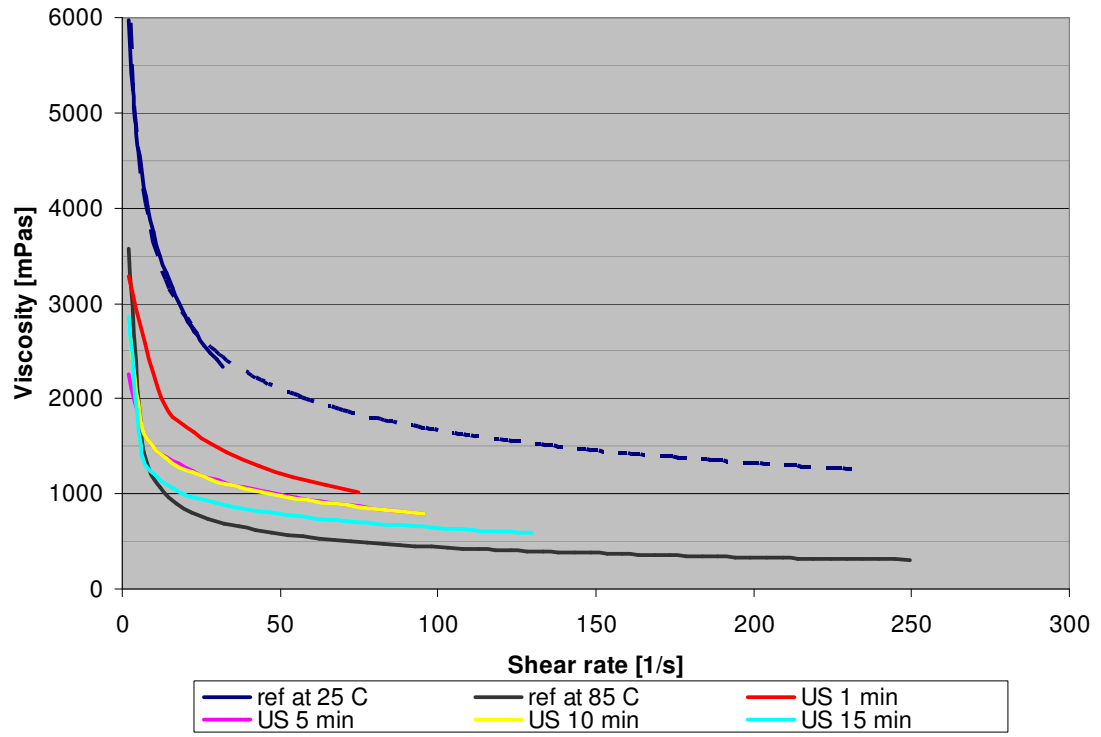
Figure 30. Viscosity of borax and XG solutions at different consistencies at 25 °C. Percents in the legend reflect the dry weight proportion of the given chemical.

### 9.1.5. Ultrasound

Based on the literary analysis ultrasound seemed a promising way to decrease the viscosity of the more concentrated solutions. The effect of ultrasound on viscosity was studied with TKP and a semi-purified XG with sonication times ranging from 1 to 15 minutes. With TKP a drastic decrease in viscosity was observed already with 1 minute of sonication. Viscosity decreased roughly 50 % when measured in room temperature. From **Figure 31** can be seen that with sonication time of 15 minutes the viscosity of the 3.0 w/w % solution in room temperature was close to what the reference sample of non-sonicated TKP had at 85 °C.

The less drastic decrease in viscosity, illustrated in **Figure 32**, of the semi-purified XG can be assumed to be accounted for the lower consistency. With high consistency the power of ultrasound gets into contact with more agglomerates thus with same treatment time, and energy, it will tear the polymer clusters apart more effectively. Some of the sonication energy also shortens the molecular chains; XG, TKP and sonicated TKP were sent to VTT Espoo to be measured for molecular chain length distribution. The results can be found in appendix III. From those results it clearly shows that with as long as 10 minutes sonication time at least some of the most

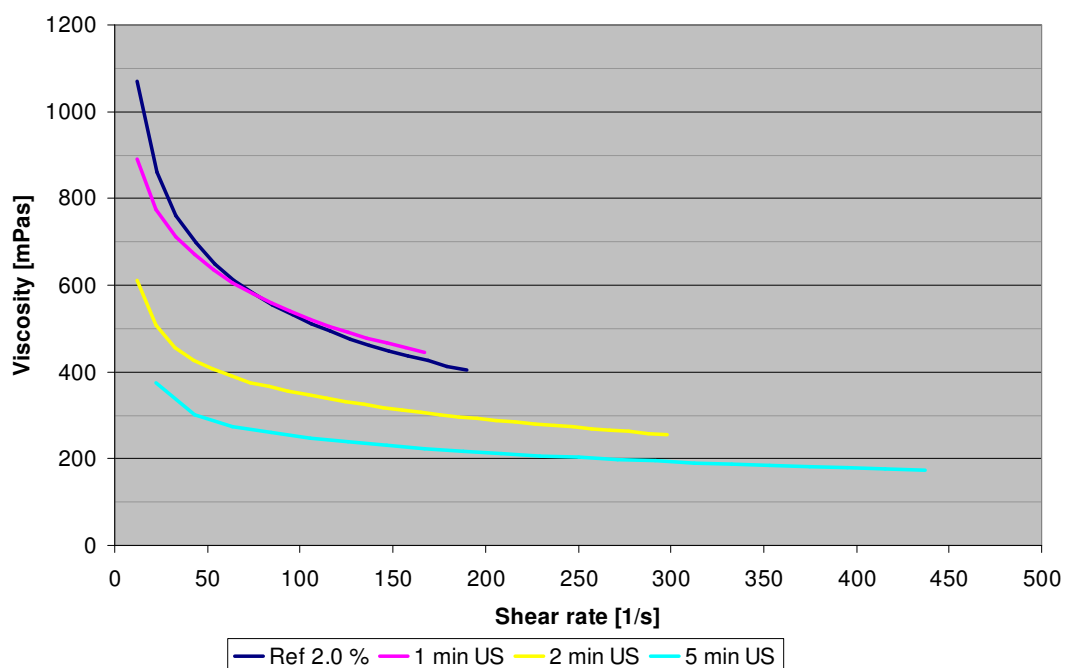
effective chains are cut down thus reducing their strengthening value but lowering the total viscosity of the solution.



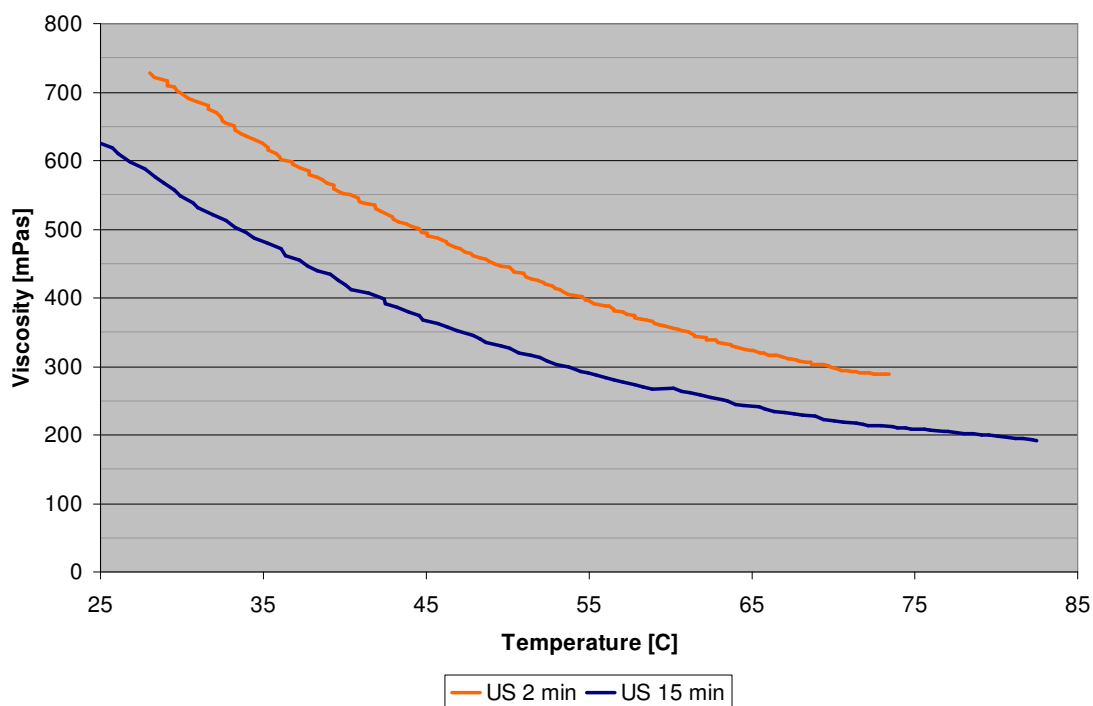
**Figure 31. Effect of ultrasound on viscosity of TKP at 3.0 %. The blue cut line represents rough viscosity estimation of the 25 °C sample based on the available measured data. Viscosities were measured 12 – 24 hours after sonication to even out the temperature of the sample.**

Increasing temperature reduces viscosity of sonicated samples in the same manner than before sonication. From **Figure 33** can be seen that there's only a minor variation in the form of viscosity plots between the two different samples (both at consistency of 3.0 %) when temperature is raised from room temperature all the way up to 85 °C. Due to sonication time being longer the values basically just drop to a lower level.





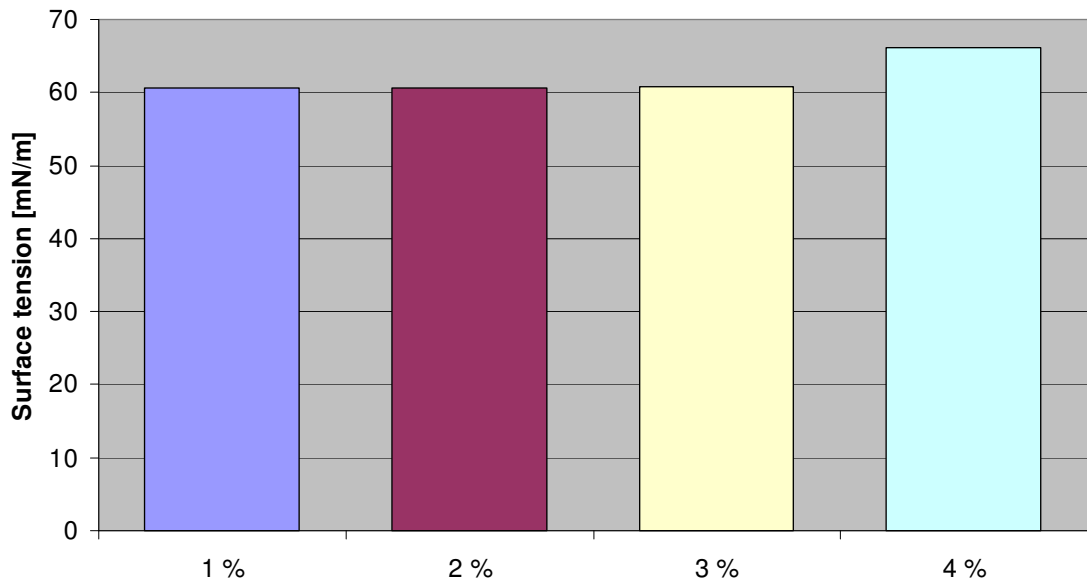
**Figure 32. Effect of ultrasound on viscosity of semi-purified XG at 2.0 %. Viscosities were measured 12 – 24 hours after sonication.**



**Figure 33. Temperature dependant viscosities of two sonicated 3.0 w/w % TKP samples.**

## 9.2. Surface tension

TKP was used to determine the effect of concentration on the surface tension of the solution. A series of 1 to 4 % solutions were measured and results can be seen from **Figure 34**. Surface tension is not affected by concentration until the solution becomes gelatinized. The 4 % solution of TKP was gelatinized at room temperature.



**Figure 34.** Surface tensions of TKP at different concentrations

Surface tensions were measured also from sonicated 3.0 % TKP and 2.0 % semi-purified XG solutions. Results were inconsistent. With TKP surface tension was reduced already with 1 minute sonication time; with longer sonication times, however, there was practically no notable fluctuation in surface tension values. All sonicated samples were slightly above 60 mN/m apart from the sample that was sonicated for 15 minutes, and was measured to have a surface tension of 56 mN/m.

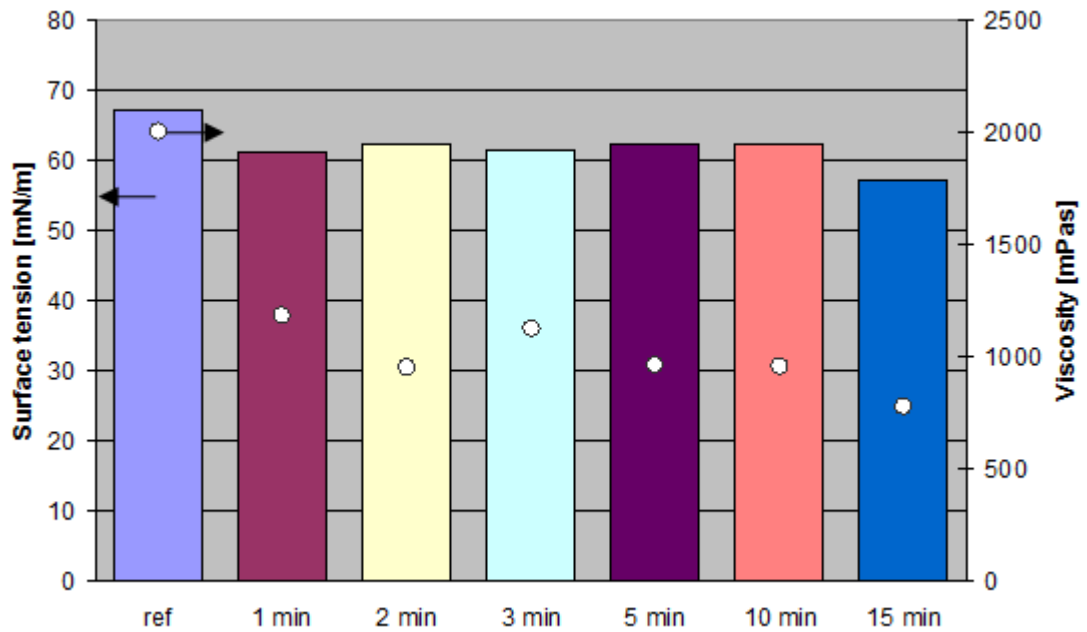


Figure 35. Surface tensions (bars) and viscosities (dots, 50 1/s) of sonicated TKP at 3.0 % consistency with a temperature of 25 °C. Reference point was TKP solution of 0 min sonication time.

Figure 35 shows that viscosity does go through more drastic changes after sonication than surface tension. There can be seen slight correlation between the two when TKP is considered. Both viscosity and surface tension of the 15 minutes sonication sample were lower than those of other sonicated samples. Figure 36 shows that with semi-purified XG surface tensions are practically unaffected by the sonication time but the viscosities show a vast decline after 1 minute processing time.

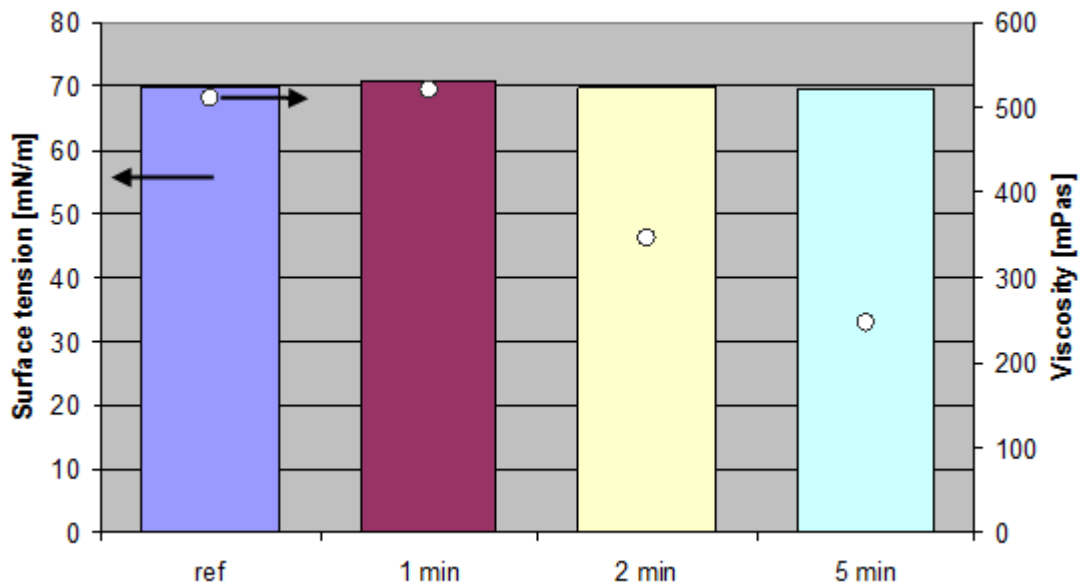
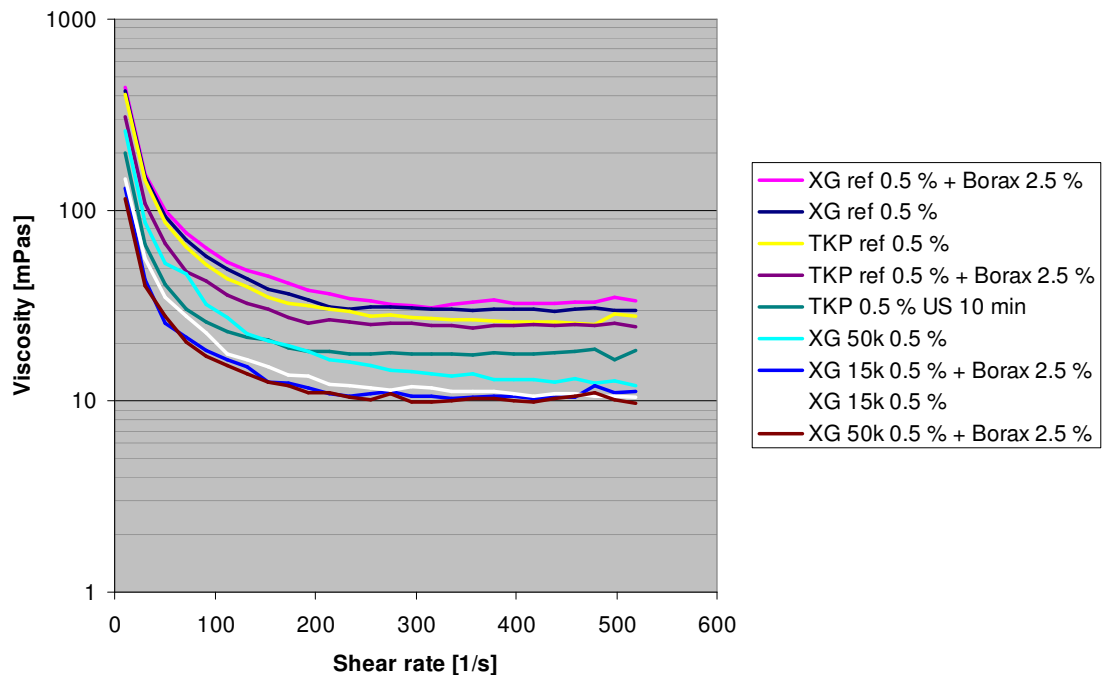


Figure 36. Surface tensions (bars) and viscosities (dots, 100 1/s) of sonicated semi-purified XG at 2.0 % consistency with a temperature of 25 °C.

### 9.3. *Effect of sprayed solutions on the properties of wet and dry paper*

First batch of spray tests were performed with a variety of solutions. In **Figure 37** are presented the measured viscosities of all the sprayed solutions.

It can be seen that chain length modifications reduced the viscosity of the samples. Both of the enzymatically modified XG's and sonicated TKP were notably under other solutions.



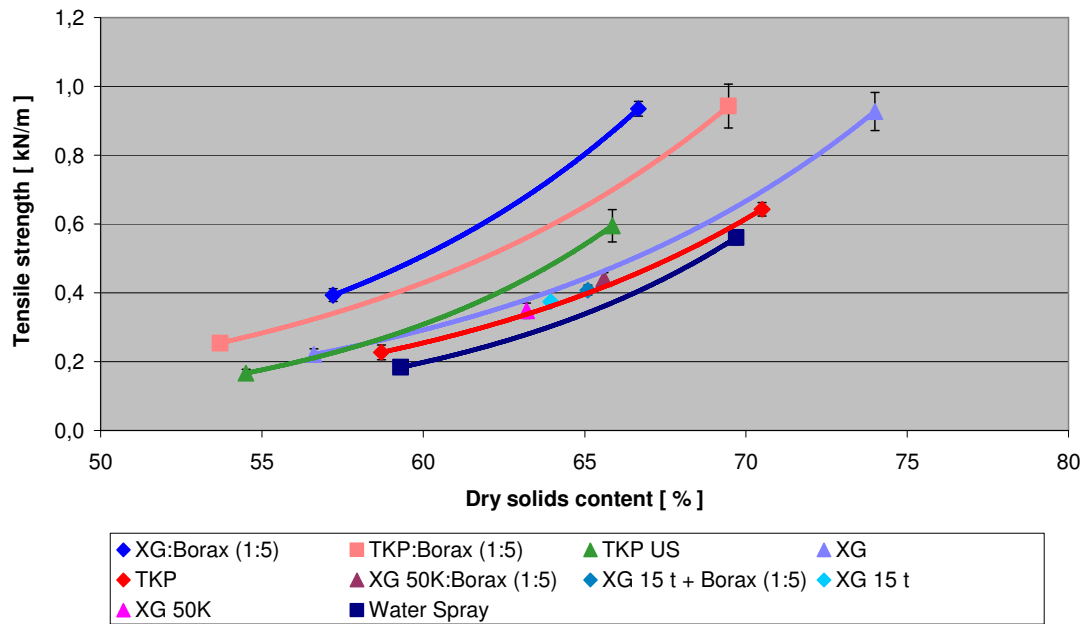
**Figure 37.** Viscosities of the sprayed solutions.

#### 9.3.1. Wet handsheets

After an overnight storing the sprayed handsheets were measured with Impact and standard measuring devices. In **Figure 38** are illustrated the measured tensile strengths. The data points are from 3.5 bar (upper dot) and 0.5 bar (lower dot) of a given spray solution.

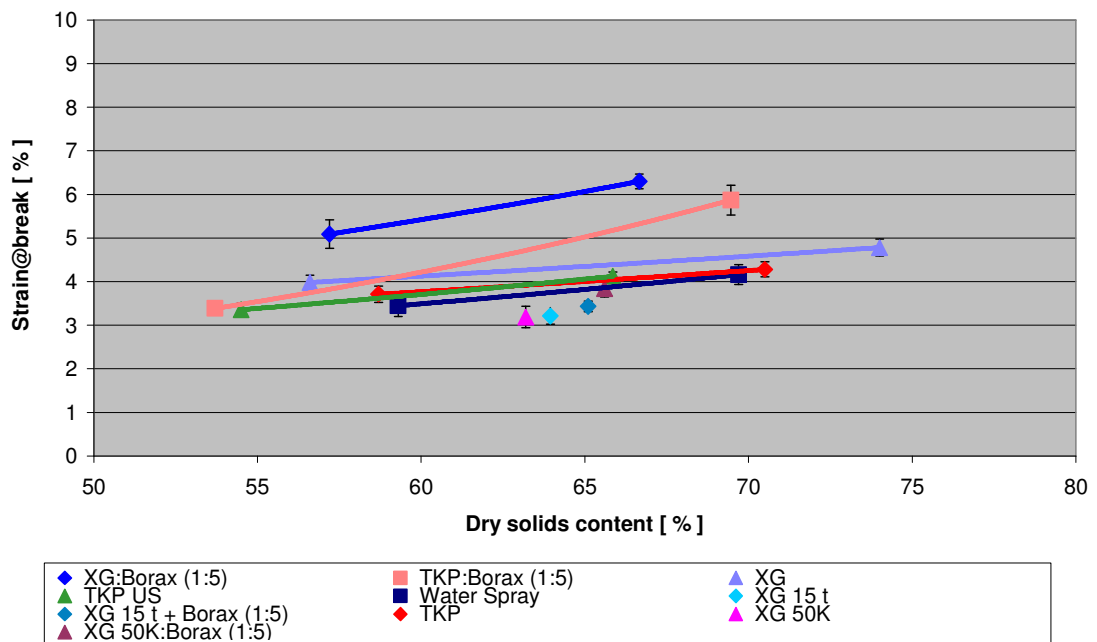
From the figure it can be seen that spraying of all the solutions improved tensile strengths of the handsheets at constant solids content when compared to water spray. Best performance had the XG/borax solution which was expected according to previous studies [17]. The solution of TKP and borax was just behind the XG/borax solution.

It can be said that the enzymatically cut short chained XG's didn't perform as well as the sonicated TKP solution. This can be concluded from the fact that pure XG performs better than TKP and similar behaviour should be expected from the short chained products.



**Figure 38. Wet tensile strengths of sprayed handsheets. Error bars reflect a 95 % confidence interval (95 % CI).**

**Figure 39** shows the measured strain at point of break. At higher wet pressing pressure the solutions containing borax excel. Addition of borax to XG solution increased the maximum strain by 1 % at lower solids content, but at 65 % dry solids content it can be assumed to be almost 2 % better. Rest of the solutions were on the same average maximum strain level, apart from the enzymatically cut XG's which were worse than the others – even with borax addition.



**Figure 39. Measured strain at break for sprayed handsheets (95 % CI).**

The tensile energy absorption of sprayed solutions, illustrated in **Figure 40**, shows that the runnability of a paper web sprayed with XG and borax is the best. Even with lower solids content the solution increased T.E.A. by almost 10 % when compared to the second best, solution of TKP and borax. Addition of borax to both XG and TKP improved T.E.A. especially at higher solids content. Sonication of TKP brought its T.E.A. to the level of normal XG. The XG's which had been enzymatically cut were again at lower level than the untreated XG.

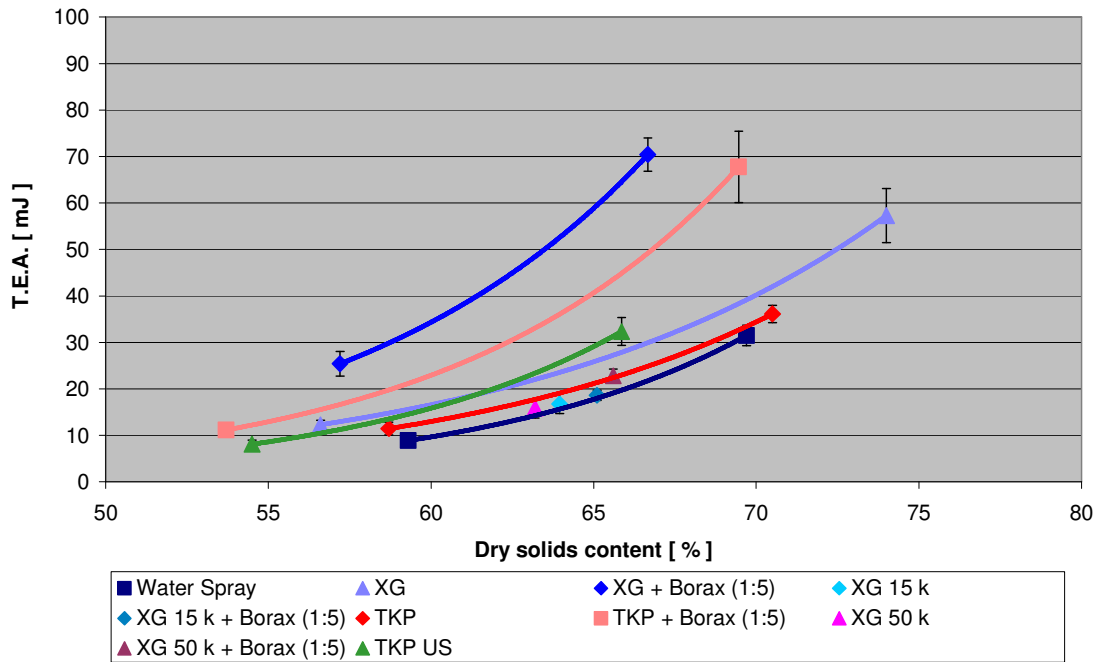
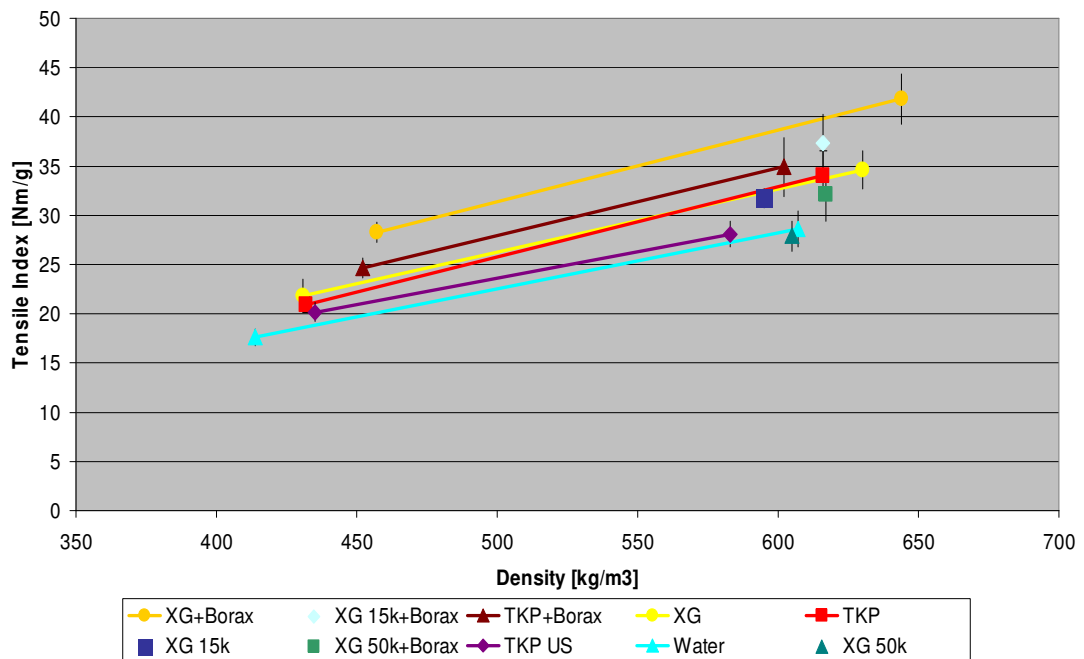


Figure 40. Tensile energy absorption of sprayed handsheets (95 % CI).

### 9.3.2. Dry handsheets

From **Figure 41** can be seen that the spraying of 0.5 % XG increases tensile index in comparison to plain water spraying by approximately 20 % (from 20 to 24 Nm/g at the lower end of the plot). Addition of 2.5 % borax to the spray solution of XG increased tensile index further by 17 % (from 24 to 28 Nm/g) when compared to spraying with XG.

With the modified XG's (Mw averages of 50 000 and 15 000) the results were inconsistent; XG with a Mw of 50 000 decreased tensile index by 15 % (from 33 to 28 Nm/g) but with a Mw of 15 000 the tensile index was virtually unchanged. When borax was added to these solutions, it can be estimated that the increase of tensile index was 12.5 % (from 28 to 31.5 Nm/g) for XG with a Mw of 50 000 and 16.6 % (from 32 to 37.3 Nm/g) for the lower molecular weight when compared to their respective values if sprayed without borax.

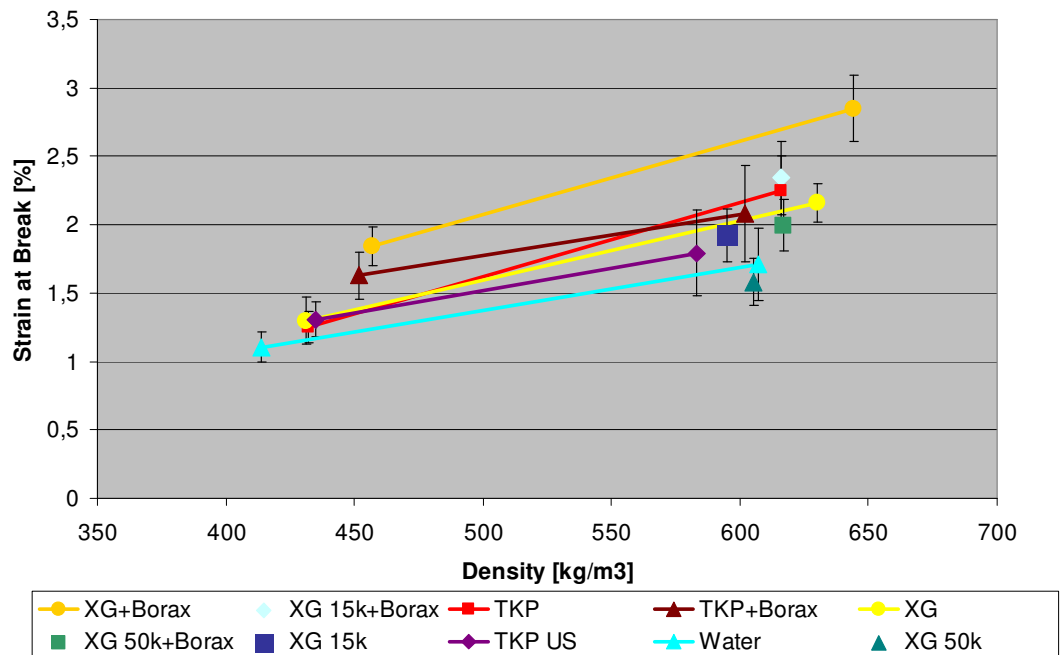


**Figure 41. Tensile index' of dry handsheets (95 % CI).**

Spraying with TKP increased tensile index by roughly the same amount as spraying with XG did. At lower density the tensile index of TKP was slightly below XG but when measuring errors are considered, the values can be estimated to be identical. Same applies to higher densities apart from the fact that the average tensile index of TKP went slightly above XG's. When borax was added to the spray solution of TKP the increase was not as massive as it was with XG. Tensile index increased by 11.8 % (from 22 to 24.6 Nm/g). The sonicated sample of TKP performed poorly; tensile index was at the level of sprayed water.

In **Figure 42** are presented the measured strains at break for dry handsheets. From the figure can be seen that the solution of XG and borax excels when compared to the other solutions. All plots are quite parallel apart from the solution of TKP and borax. When the error is taken into consideration it can be assumed that the solution in question does in fact follow the same guidelines as the other plots; so instead of decreasing the amount of strain the handsheet can take at higher densities it actually does increase it when compared to the data from TKP handsheets. It can be that there was an unknown error in the application of TKP and borax so that the amount of chemical present in the handsheet differed from the amounts present in other handsheets. Further measurements should be done to verify this.

If the inconsistent data from the solution of TKP and borax is disregarded the results are quite consistent with the results from tensile strength measurements; borax solutions are notably better than the plain solutions in terms of how much pulling the handsheets can take before break happens. Other solutions are all at the same range especially at lower densities. When errors are taken into account the maximum strains at higher densities are also quite similar.

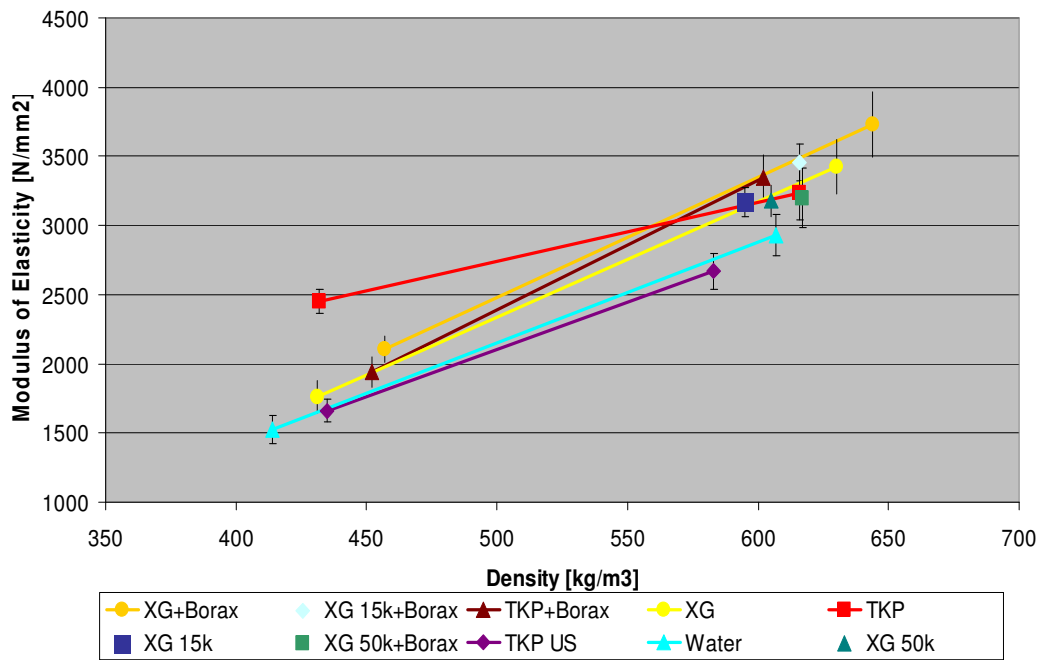


**Figure 42. Strain at break measurements from handsheets (95 % CI).**

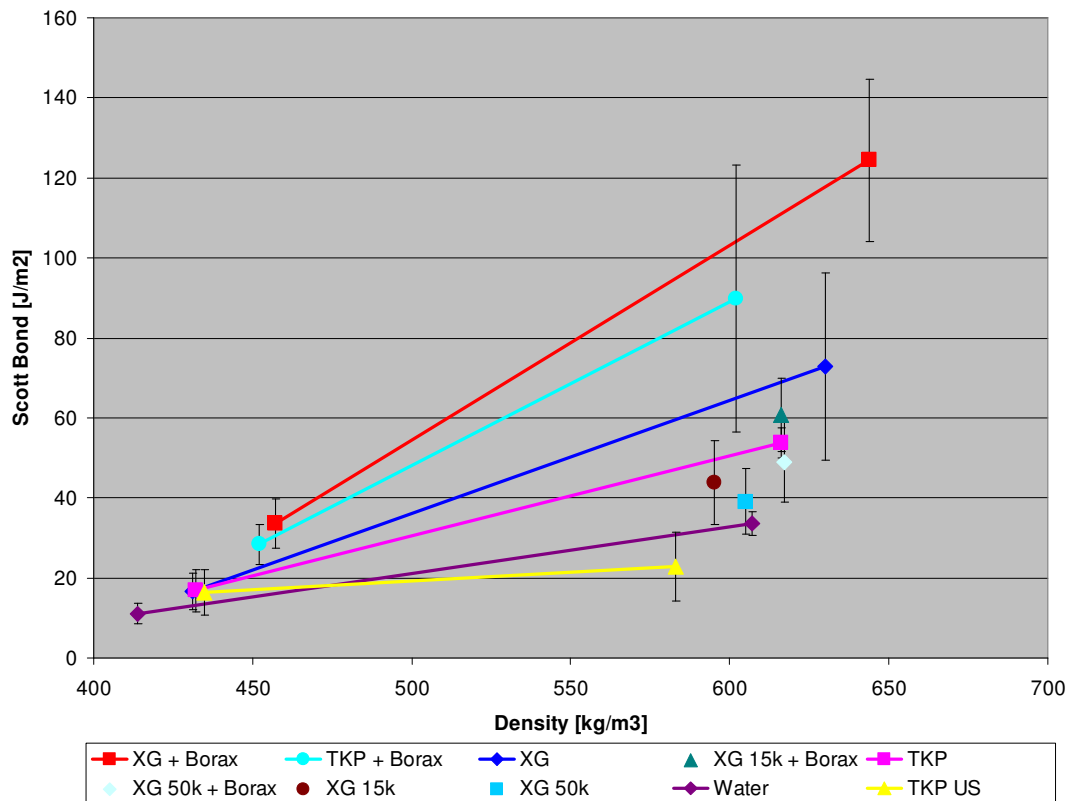
In general, the extensional stiffness of the handsheets can be described through elastic modulus. The higher the modulus, harder it is to cause a reversible deformation to the handsheet. As seen in **Figure 43** handsheets with borax solutions sprayed upon are at slightly higher level than others. The difference between borax and non-borax solutions is not as clear as it was in other measured parameters. What is notable is the placement of sonicated TKP; it averages lower than water and performs considerably worse than any other measured solution. The data from TKP measurements introduced some inconsistencies; at lower densities elastic modulus of TKP sprayed handsheets was double the value of any other measurement at the given density. It can be assumed that this was either caused by a measuring or dosing error because at higher densities TKP's modulus averaged to the same level with other samples.

Scott Bond was measured from the dry handsheets to determine chemicals' influence on the internal bonding within the handsheets. The results are presented in **Figure 44**. From the figure can be seen a similar pattern than from most of the other measurements; XG with an addition of borax does provide the best results followed closely by TKP with borax addition. Borax improved the Scott Bond value of the two short chained XG's as well. Noteworthy is also the poor performance of sonicated TKP which averaged even under the values of water.





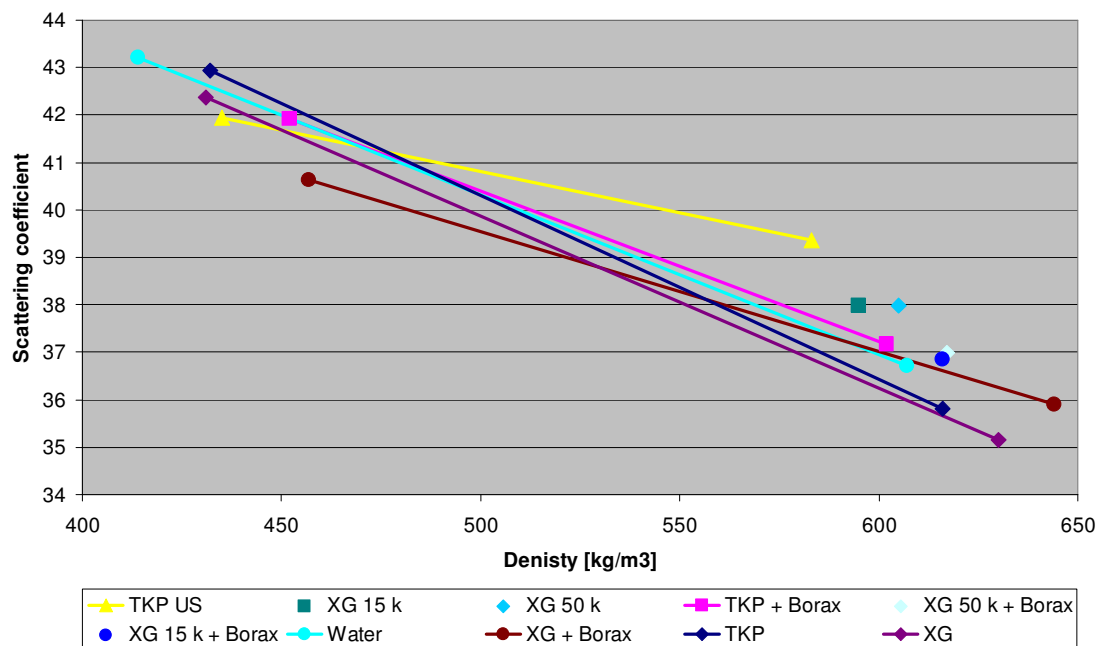
**Figure 43. Modulus of elasticity for dry handsheets (95 % CI).**



**Figure 44. Scott Bond results for dry handsheets (95 % CI).**

Optical measurements from the dry handsheets were carried out to determine whether there was any impact on the appearance of the handsheets caused by the sprayed chemicals. Results, which are presented in Appendix II, show that opacity,

absorption coefficient, and brightness remained practically unaffected by the chemicals. Light scattering coefficient (as seen in **Figure 45**) decreases as the density of the sheets increases, which is caused by the decreased porosity and availability of light scattering surfaces. When individual chemicals are observed it can be seen that they all perform in relatively similar manner; at lower densities the addition of borax to any of the sprayed chemicals did reduce scattering coefficient marginally, at higher densities, however, the results were inconsistent mainly due to the fact that addition of borax to XG seemed to increase light scattering coefficient when compared to pure XG addition. The differences were not significant enough to draw any certain conclusions from the data.



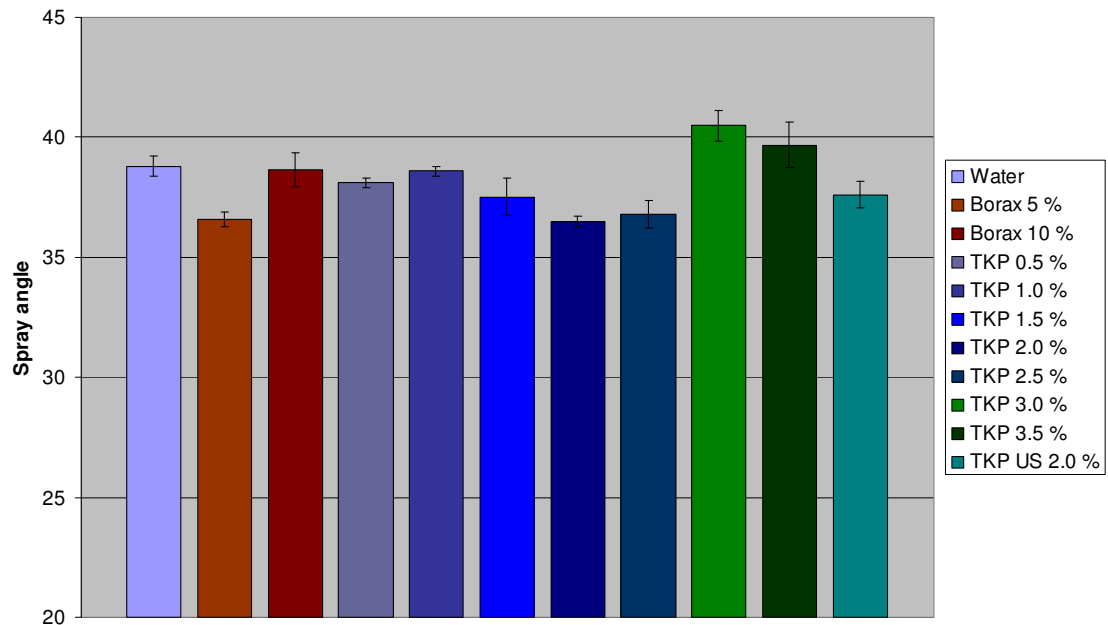
**Figure 45.** Light scattering coefficients from dry handsheets.

### 9.3.3. Spray characteristics

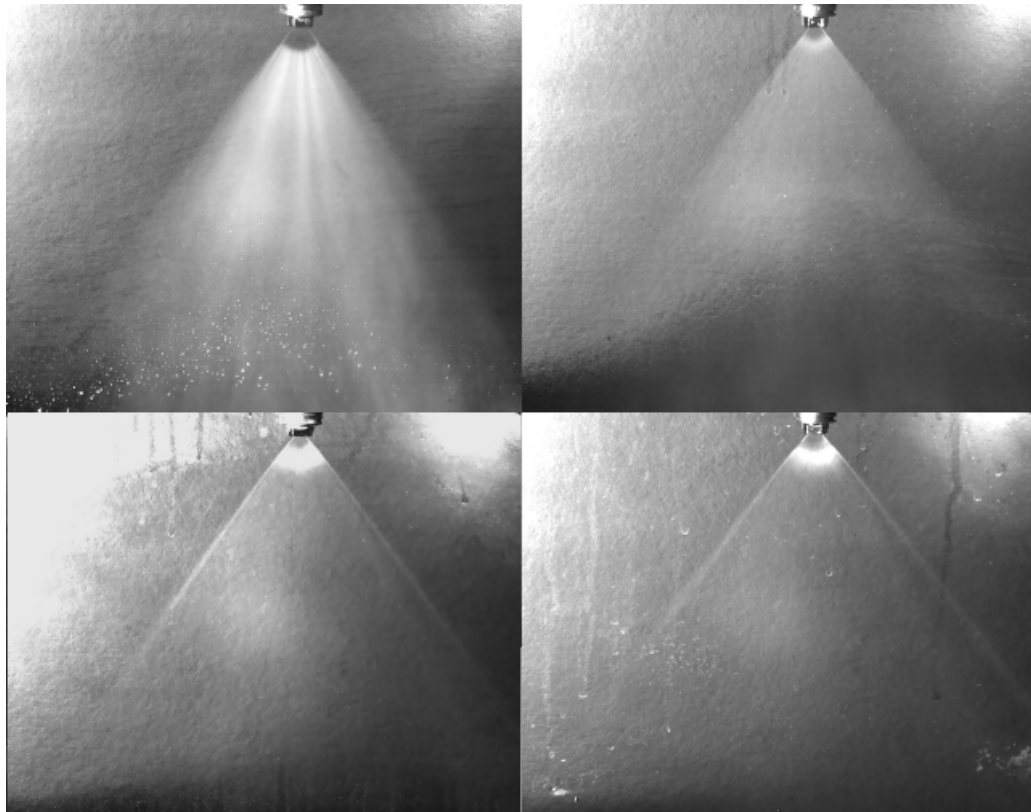
According to theory an increase in viscosity of the sprayed solution should reduce the coverage and thus spray angle. From **Figure 46** can be seen that in TKP's case theory does not concur with practice. A solution of TKP with 3.5 % dry weight fraction had practically identical spray angle in lateral direction with water even as the viscosity of the said TKP solution is tenfold when compared to water's.

Most significant change in spray characteristics when viscosity was increased were in the general shape of the spray. At lower viscosities the spray pattern was more of an oval shape compared to the line shaped pattern of higher viscosities. From side view this manifested as a clearer spray at higher viscosities as seen on top left, bottom left and bottom right in **Figure 47**. So rather than reducing the spray angle in lateral direction of the spray, the increase in viscosity reduced the depth of the spray.

The aforementioned also means that the lighter picture on the top right has more droplets present because the lighter colour is a result of increased light scattering. Decrease in viscosity also reduced the perceived striping in the spray as the spray become more film-like.



**Figure 46. Average spray angles (95 % CI).**



**Figure 47. Form of the spray. Top left: water; top right: TKP at 1.0 %; bottom left: TKP at 2.0 %; bottom right: TKP at 3.5 %.**

## 10. CONCLUSIONS

In Table 5 is compiled the factors affecting viscosity, surface tension and sprayability of the tested solutions. Generally it can be concluded that the factors which improve sprayability do unfortunately deteriorate paper web's runnability. When controlled properly, however, all of the negative effects which results from all of these can be overcome by addition of borax in conjunction with TKP or XG.

**Table 5. Summary of factors affecting viscosity, surface tension and sprayability.**

	<b>Viscosity</b>	<b>Surface Tension</b>	<b>Sprayability</b>	<b>Strength</b>
<b>Concentration increases</b>	Increases	Increases after a point	Deteriorates	Increases
<b>Surface tension increases</b>	Insignificant		Deteriorates	N/A
<b>Temperature increases</b>	Decreases to a point	N/A	Improves	N/A
<b>Shear rate increases</b>	Decreases to a point	N/A	Improves	N/A
<b>Borax content increases</b>	First decreases, then increases	Inconsistent	First improves, then deteriorates	Increases
<b>Sonication time increases</b>	Decreases	Insignificant	Improves	Deteriorates
<b>Chain length increases</b>	Increases	Increases	Deteriorates	Increases
<b>Viscosity increases</b>		Insignificant	Deteriorates	N/A

There were no significant differences between the solutions when surface tension is considered. Due to the inconsistent results – and the fact that there was no solution pair available which had other attributes exactly the same apart from surface tension – the modification of XG's surface tension should studied further.

Addition of borax to TKP and XG solutions was the most significant factor increasing strength – and thus runnability – properties of the handsheets. Borax addition lowered viscosity to a certain point at lower dosages and increased the dry weight proportion of the solutions which decreases energy consumption at paper machine due to the less amount of water to be evaporated

XG with an addition of borax had the highest percentage of strain at break by far. Addition of only TKP or XG to the handsheet did not improve the sustained strain notably thus the runnability improving properties of borax seem to be excellent with conjunction of XG. In conclusion the addition of borax is highly beneficial to spraying of both XG and TKP when paper making process as a whole is concerned.

Enzymatic shortening of XG's chains worsened all attributes of the measured handsheets when compared to untreated XG. It can be concluded that the length of the XG chain is of utmost importance to the strengthening ability when the chemical is applied to paper via spraying. Although the availability of the modified XG's was at

poor level and thus more tests on them should be done in the future to improve the reliability of the results.

Introducing ultrasound to higher concentrations of TKP showed a vast decline in viscosity already at short processing times. It can be assumed that sonication reduces viscosity via deflocculation to a certain point. This point seemed to be at 1 minute marker in TKP's case. Further sonication of the sample showed minor response until 15 minutes was exceeded. After 15 minutes it can be concluded that the power of ultrasound started to cut the chains of TKP more rapidly thus lowering the viscosity of the solution. The strength properties deteriorated even with 2 minute sonication time when compared to unmodified TKP. Further tests should be done to determine if there is an optimal processing time where viscosity is lowered but the strength properties do not get worse.

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Sprayed Chemicals	Target consistencies	H2O	Chem. dryness	Total chem	Dry chem	Chem proportion	BX dryness	Total BX	Dry BX	BX proportion	Total weight	Chem/Borax ratio
XG	0,50 %	990	94,53 %	5,30	5,01	0,50 %					995,30	
XG + Borax	0,5 % + 2,5 %	990	94,53 %	5,50	5,20	0,50 %	68,27 %	38,08	26,00	2,52 %	1033,58	1/5
XG 50k	0,50 %	900	90,00 %	5,00	4,50	0,50 %					905,00	
XG 50k + borax	0,5 % + 2,5 %	434	90,00 %	2,50	2,25	0,50 %	68,27 %	16,48	11,25	2,49 %	452,50	1/5
XG 15k	0,50 %	900	90,00 %	5,00	4,50	0,50 %					905,00	
XG 15k + borax	0,5 % + 2,5 %	430	90,00 %	2,50	2,25	0,50 %	68,27 %	16,48	11,25	2,51 %	448,98	1/5
TKP	0,50 %	1020	94,91 %	5,40	5,13	0,50 %					1025,40	
TKP + borax	0,5 % + 2,5 %	982	94,91 %	5,40	5,13	0,50 %	68,27 %	37,54	25,63	2,50 %	1025,40	1/5
TKP + US10min	2 %	200	94,53 %	4,35	4,11	2,01 %					204,35	
	dilution to 0,5 %	820	addition of 620 ml	4,35	4,11	0,50 %					824,35	
Borax ref	2,50 %	800		0,00	0,00	0,00 %	68,27 %	30,40	20,75	2,50 %	830,40	0/5

estimated not enough short chained XG to measure dryness

XG target	H2O	Dryness	Total XG	Dry XG	Consistency	TKP target	H2O	Dryness	Total TKP	Dry TKP	Consistency
1 %	186	94,39 %	2,0	1,888	1,00 %	1 %	186	93,10 %	2,0	1,862	0,99 %
2 %	186	94,39 %	4,0	3,776	1,99 %	2 %	186	93,10 %	4,0	3,724	1,96 %
3 %	400	94,39 %	13,0	12,271	2,97 %	3 %	400	93,10 %	12,7	11,824	2,86 %
4 %	186	94,39 %	8,2	7,740	3,99 %	4 %	186	93,10 %	8,0	7,448	3,84 %
6,5 %	247	94,39 %	18,4	17,368	6,54 %	6 %	247	93,10 %	16,0	14,896	5,66 %

Starch	Target consistency	H2O [ml]	Dryness	Total starch [g]	Consistency
RM 01151	10 %	200	88,81 %	22,82	10,00 %
	30 %	200	88,81 %	70,13	29,97 %
RM 23121	10 %	200	83,39 %	24,47	10,00 %
	20 %	200	83,39 %	49,92	19,98 %
RM 42151	10 %	200	88,54 %	22,88	10,00 %
	30 %	200	88,54 %	46,36	19,99 %

XG Borax ratio calc.	H2O [g]	XG dryness	Total XG [g]	Dry XG [g]	XG proportion	BX dryness	Total BX [g]	Dry BX [g]	BX proportion	Total weight [g]
0,5 / 0,5	370	94,53 %	2	1,8906	0,50 %	68,27 %	2,7692984	1,8906	0,50 %	374,7692984
1 / 1	185	94,53 %	2	1,8906	1,00 %	68,27 %	2,7692984	1,8906	1,00 %	189,7692984
1 / 2	182	94,53 %	2	1,8906	1,00 %	68,27 %	5,5385967	3,7812	1,99 %	189,5385967
1 / 4	176	94,53 %	2	1,8906	1,00 %	68,27 %	11,077193	7,5624	4,00 %	189,0771935
1 / 10	160	94,53 %	2	1,8906	1,00 %	68,27 %	27,692984	18,906	9,97 %	189,6929837

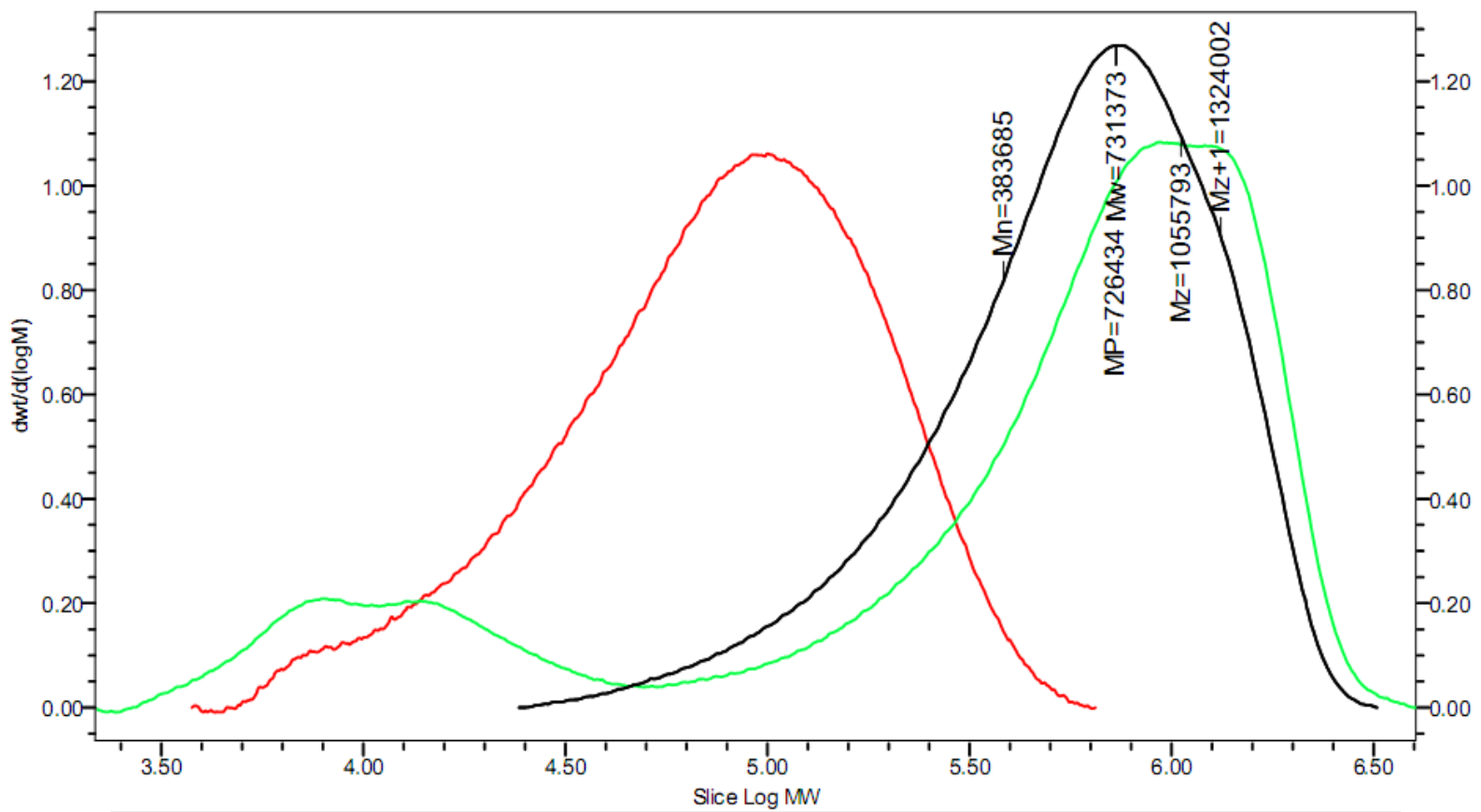
Opacity, brightness, scattering and absorption coefficients from sprayed handsheets. Top side measurements.

Chemicals	p	Opacity	Scatt. coefficient	Absorp. coefficient	L* C/2	a* C/2	b* C/2	R457 C/2 + UV	R457 C/2 - UV
TKP 0.5 bar	432	76,19	42,93	0,08	97,72	-0,93	3,38	89,70	89,37
TKP 3.5 bar	616	72,18	35,81	0,08	97,52	-0,95	3,54	88,99	88,69
TKP + Borax 0.5 bar	452	77,01	41,92	0,12	97,17	-0,76	4,00	87,54	87,22
TKP + Borax 3.5 bar	602	73,70	37,17	0,09	97,35	-0,93	3,94	88,06	87,77
TKP ultrasound 0.5 bar	435	75,98	41,94	0,07	97,76	-0,95	3,37	89,8	89,51
TKP ultrasound 3.5 bar	583	74,21	39,37	0,08	97,58	-0,93	3,39	89,35	89,05
Water 0.5 bar	414	76,07	43,21	0,08	97,67	-0,94	3,27	89,71	89,41
Water 3.5 bar	607	73,00	36,72	0,09	97,37	-0,9	3,68	88,46	88,15
XG 0.5 bar	431	75,72	42,38	0,08	97,63	-0,91	3,47	89,36	89,06
XG 3.5 bar	630	72,05	35,15	0,07	97,57	-1,02	3,66	88,97	88,63
XG + Borax 0.5 bar	457	75,48	40,64	0,09	97,46	-0,92	3,89	88,39	88,06
XG + Borax 3.5 bar	644	72,56	35,91	0,09	97,33	-0,99	4,09	87,82	87,52
XG 15 k 3.5 bar	595	73,41	37,99	0,08	97,58	-1,02	3,60	89,06	88,76
XG 15 k + Borax 3.5 bar	616	73,01	36,86	0,08	97,42	-0,96	3,69	88,58	88,28
XG 50 k 3.5 bar	605	73,53	37,98	0,08	97,51	-0,95	3,70	88,75	88,45
XG 50 k + Borax 3.5 bar	617	72,93	36,99	0,08	97,51	-0,99	3,89	88,51	88,21
Std.Dev.		Opacity	Scatt. coefficient	Absorp. coefficient	L* C/2	a* C/2	b* C/2	R457 C/2 + UV	R457 C/2 - UV
TKP 0.5 bar		0,17	0,35	0	0,02	0,01	0,01	0,04	0,05
TKP 3.5 bar		0,72	1,12	0	0,03	0,01	0,02	0,08	0,07
TKP + Borax 0.5 bar		0,10	0,21	0	0,08	0,08	0,37	0,66	0,64
TKP + Borax 3.5 bar		0,33	0,56	0	0,03	0,01	0,03	0,10	0,07
TKP ultrasound 0.5 bar		0,08	0,16	0	0,01	0,01	0,02	0,04	0,06
TKP ultrasound 3.5 bar		0,35	0,62	0	0,02	0,01	0,02	0,05	0,04
Water 0.5 bar		0,12	0,24	0	0,02	0,02	0,05	0,08	0,05
Water 3.5 bar		0,52	0,85	0	0,03	0,03	0,07	0,11	0,10
XG 0.5 bar		0,19	0,37	0	0,01	0,02	0,04	0,03	0,05
XG 3.5 bar		0,15	0,23	0	0,02	0,01	0,02	0,02	0,04
XG + Borax 0.5 bar		0,3	0,57	0	0,02	0,01	0,03	0,06	0,06
XG + Borax 3.5 bar		0,15	0,23	0	0,01	0,01	0,01	0,04	0,05
XG 15 k 3.5 bar		0,16	0,28	0	0,03	0,01	0,02	0,09	0,10
XG 15 k + Borax 3.5 bar		0,86	1,36	0	0,03	0,01	0,03	0,09	0,08
XG 50 k 3.5 bar		0,27	0,45	0	0,04	0,01	0,03	0,07	0,07
XG 50 k + Borax 3.5 bar		0,57	0,93	0	0,02	0,02	0,03	0,05	0,07

Opacity, brightness, scattering and absorption coefficients from sprayed handsheets. Bottom side measurements.

Chemicals	$\rho$	Opacity	Scatt. Coefficient	Absorp. Coefficient	L* C/2	a* C/2	b* C/2	R457 C/2 + UV	R457 C/2 - UV
TKP 0.5 bar	432	76,06	42,65	0,08	97,72	-0,94	3,43	89,63	89,32
TKP 3.5 bar	616	72,01	35,43	0,08	97,47	-0,96	3,59	88,83	88,53
TKP + Borax 0.5 bar	452	76,78	41,58	0,11	97,2	-0,74	3,92	87,71	87,4
TKP + Borax 3.5 bar	602	73,16	36,2	0,09	97,31	-0,93	4	87,89	87,61
TKP ultrasound 0.5 bar	435	75,96	41,98	0,07	97,78	-0,95	3,32	89,91	89,61
TKP ultrasound 3.5 bar	583	74,13	39,21	0,08	97,57	-0,94	3,41	89,3	88,98
Water 0.5 bar	414	75,95	42,97	0,08	97,67	-0,95	3,29	89,69	89,36
Water 3.5 bar	607	72,76	36,25	0,09	97,34	-0,9	3,69	88,37	88,05
XG 0.5 bar	431	75,59	42,21	0,08	97,66	-0,91	3,48	89,4	89,1
XG 3.5 bar	630	71,94	34,99	0,07	97,57	-1,03	3,68	88,93	88,65
XG + Borax 0.5 bar	457	75,4	40,57	0,09	97,48	-0,93	3,89	88,43	88,13
XG + Borax 3.5 bar	644	72,4	35,57	0,09	97,3	-1	4,09	87,74	87,45
XG 15 k 3.5 bar	595	73,33	37,86	0,08	97,58	-1,03	3,64	89,02	88,74
XG 15 k + Borax 3.5 bar	616	72,75	36,42	0,08	97,41	-0,96	3,71	88,53	88,21
XG 50 k 3.5 bar	605	73,3	37,43	0,08	97,45	-0,94	3,69	88,63	88,33
XG 50 k + Borax 3.5 bar	617	72,76	36,62	0,08	97,47	-1	3,89	88,43	88,14
Std. Dev.		Opacity	Scatt. Coefficient	Absorp. Coefficient	L* C/2	a* C/2	b* C/2	R457 C/2 + UV	R457 C/2 - UV
TKP 0.5 bar		0,22	0,45	0	0,01	0,01	0,01	0,04	0,01
TKP 3.5 bar		0,63	0,97	0	0,02	0,01	0,02	0,07	0,07
TKP + Borax 0.5 bar		0,1	0,19	0	0,07	0,06	0,3	0,55	0,55
TKP + Borax 3.5 bar		0,83	1,3	0	0,02	0,02	0,05	0,08	0,12
TKP ultrasound 0.5 bar		0,11	0,22	0	0,02	0,01	0,04	0,08	0,09
TKP ultrasound 3.5 bar		0,37	0,65	0	0,02	0,01	0,03	0,06	0,05
Water 0.5 bar		0,1	0,21	0	0,02	0,01	0,04	0,06	0,09
Water 3.5 bar		0,34	0,54	0	0,01	0,02	0,06	0,08	0,09
XG 0.5 bar		0,2	0,39	0	0,01	0,01	0,03	0,05	0,04
XG 3.5 bar		0,24	0,36	0	0,02	0,01	0,01	0,06	0,05
XG + Borax 0.5 bar		0,26	0,48	0	0,03	0	0,03	0,09	0,08
XG + Borax 3.5 bar		0,2	0,3	0	0,02	0,01	0,04	0,07	0,07
XG 15 k 3.5 bar		0,15	0,26	0	0,03	0,05	0,08	0,13	0,13
XG 15 k + Borax 3.5 bar		0,95	1,49	0	0,02	0,02	0,06	0,11	0,09
XG 50 k 3.5 bar		0,3	0,49	0	0,04	0,01	0,02	0,09	0,11
XG 50 k + Borax 3.5 bar		0,54	0,87	0	0,02	0,01	0,02	0,05	0,03

APPENDIX III: Molecular chain length distribution measurements of XG, TKP and sonicated TKP samples.



	SampleName	Mn (Daltons)	Mw (Daltons)	Mz (Daltons)	MP (Daltons)	Polydispersity	Area ( $\mu\text{V}\cdot\text{sec}$ )	Processing Method	Result Id
1	Xyloglucan	383685	731373	1055793	726434	1.906184	11065191	0_1 NaOH_Pull_RI_2	2395
2	TKP	56162	781876	1281258	930993	13.921823	8589495	0_1 NaOH_Pull_RI_2	2397
3	TKP, sonicated 10 min	47856	105180	173082	100202	2.197824	3278687	0_1 NaOH_Pull_RI_2	2399