Department of Bioproducts and Biosystems

Foam as a carrier phase – a multipurpose technology for industrial applications

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Karita Kinnunen-Raudaskoski

Aalto University

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Karita Kinnunen-Raudaskoski

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Abstract

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Abstract

The applicability of foam in paper/board manufacturing processes was studied. The pulp and paper production in Finland has been forecast to decrease by up to a third from 2007 to 2020. The declining trend is mainly due to the weakening of main export markets. (Hetemäki et al., 2009). For the renewal of paper industry new solutions for savings in energy and raw materials are needed. Newly developed materials like nano materials may also challenge the conventional processes. New technologies are needed and the interest towards foam technology is growing. The main focus in this thesis was on foam forming and coating and on nano/microfibrils. The suitability of foam in biosludge treatment was also studied. The work showed that the strength loss due to the bulky structure of the foam formed paper, can be regained by using cellulose microfibrils (CMF) as strength additives, instead of wet pressing or beating. The strength enhancement was received with a lower bulk lost. The studied CMF grades had different responses to the strength properties of the pulps used; bleached soft wood pulp and chemi-thermo mechanical spruce pulp. This indicates that CMF used has to be chosen depending of paper properties needed. Dewatering was more effective due to the porous structure of the foam formed sheets and the formation of the papers better than in water forming, even with 12 mm synthetic fibers. Foam coating applications were done both to dry and wet fiber webs. Two different coating methods were used in the dry web applications. The work showed that using foam it is possible to create thin functional surfaces on paper/board. Titanium dioxide and zinc oxide functionalized cellulose nanofibrils (CNF) created antimicrobial and photocatalytic properties on the paper and grease and water vapour barriers were achieved with polyvinyl or ethylene vinyl alcohol foam. In wet web application done at the former section polymers known to enhance the strength properties of paper were used. Due to foam destruction using vacuums, the whole web structure was treated with the chemical. The enhancement both on wet and dry web strength properties was detected with an increase in the dry matter content of the paper and without bulk lost. In addition to 'a carrier phase' function, the ability of foam to displace liquid water from a porous medium, was investigated. The foam enhanced dewatering in foam forming as well as in foam coating of the wet web. Based on these observations the foam assisted dewatering was studied on biosludge treatment. According to the results, the filtration time was shortened, the filtrate was cleaner and the sludge cake 10% drier. The change in dry solids content was quite small due to the insufficient vacuum level in filtration, 2 kPa. However, the result indicates that with a more efficient filtration vacuum it is possible to use foam to assist filtration. This thesis shows that foam technology offers several benefits for the paper/board industry, and combining it with nanomaterials enables the development of novel paper products.

Keywords foam technology, foam forming, foam coating, foam assisted, aqueous foam, wet strength, dry strength, formation, dewatering, dryness, thin layers, nanoparticle, cellulose nano fibrils, cellulose micro fibrils, surface properties, biosludge

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Tiivistelmä

Työssä tutkittiin vaahtoteknologian soveltuvuutta paperi- ja kartonkiteollisuuden eri prosessivaiheisiin. Suomen sellun ja paperin tuotannon ennustetaan vähenevän kolmanneksen vuodesta 2007 vuoteen 2020. Laskeva trendi aiheutuu pääsiassa päävientituotteiden heikentyneistä markkinoista (Hetemäki et al., 2009). Paperiteollisuuden rakennemuutoksessa etsitään uusia ratkaisuja tuotantokustannusten vähentämiseksi ja se on osaltaan kasvattanut kiinnostusta vaahtoteknologiaa kohtaan. Markkinoille on tullut myös uusia materiaaleja kuten nanomateriaalit, jotka haastavat nykyisiä tuotantoteknologioita. Työn pääpaino oli vaahtorainauksessa ja -päällystyksessä ja nano/mikroselluloosan yhdistämistä vaahtoteknologiaan. Työssä tutkittiin myös vaahdon soveltuvuutta biolietteen käsittelyyn. Tutkimuksen mukaan vaahtorainatun paperin huokoisesta rakenteesta aiheutuva lujuuden heikkeneminen voidaan kompensoida käyttämällä mikroselluloosaa (CMF) märkäpuristuksen tai jauhatuksen sijasta. Tällöin lujuus saadaan pienemmällä bulkkimenetyksellä. Työssä käytetyillä CMF-laaduilla oli erilainen vaste käytettyjen massojen, valkaistun havusellun ja kemi-mekaanisen kuusimassan lujuusominaisuuksiin. Tämä indikoi sitä, että CMF-laadun valinnalla voidaan vaikuttaa lopputuotteen ominaisuuksiin. Vaahtorainauksessa vedenpoisto oli tehokkaampaa rainan huokoisesta rakenteesta johtuen ja pohjapaperin formaatio parempi kuin vesirainauksessa, myös käytettäessä 12 mm synteettistä kuitua. Vaahtopäällystyksessä päällystettiin kuivaa ja märkää kuiturainaa. Kuivan kuiturainan päällystyksessä käytettiin kahta eri vaahtopäällystysmenetelmää. Työssä osoitettiin, että vaahtopäällystämällä saadaan ohut, toiminnallinen pinta paperille ja kartongille: titaanidioksidilla ja sinkkioksidilla funktionalisoidulla nanoselluloosalla mikrobiologisia ja fotokatalyyttisiä ominaisuuksia ja rasva- ja vesihöyryestokerros polyvinyyli- ja etyleenivinyylialkoholivaahdolla. Formeriosalla tapahtuvassa märän rainan vaahtopäällystyksessä vaahto poistetaan imun avulla, jolloin vaahdotettu kemikaali saadaan koko rakenteeseen. Työssä osoitettiin, että kemikaalit, jotka tunnetusti kasvattivat märkä- ja kuivalujuutta, toimivat myös vaahtopäällystyksessä. Samalla havaittiin myös rainan kuiva-aineen nousu ilman bulkin menetystä. Kantajaväliaineominaisuuden lisäksi työssä tutkittiin vaahdon kykyä syrjäyttää nestettä huokoisesta materiaalista. Vedenpoiston tehostuminen havaittiin niin vaahtorainauksessa kuin märän rainan vaahtopäällystyksessä. Näiden havaintojen perusteella vaahtoavusteista vedenpoistoa tutkittiin biolietteen käsittelyssä. Tulosten mukaan biolietteen suotautuminen nopeutui, suodos oli kirkkaampi ja lietekakku 10 % kuivempi. Kuiva-aineen muutos oli pieni, sillä käytetty alipaine oli vain 2 kPa. Tehokkaampi alipaine todennäköisesti tehostaisi suodatusta. Tutkimus osoitti, että vaahtoteknologia tarjoaa useita etuja paperi/kartonkiteollisuudelle, ja teknologia yhdessä nanomateriaalien kanssa tarjoaa mahdollisuuden kehittää uusia paperi- ja kartonkituotteita.

Avainsanat foam technology, foam forming, foam coating, foam assisted, aqueous foam, wet strength, dry strength, formation, dewatering, dryness, thin layers, nanoparticle, cellulose nano fibrils, cellulose micro fibrils, surface properties, biosludge

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Preface

This thesis work was carried out during 2009-2013 at the VTT Technical Research Centre of Finland. The work is based on the research at Oy Keskuslaboratorio-Centrallaboratorium Ab (KCL) during 2005-2009. KCL is acknowledged for the open-mindedness and the support in the early stage of the foam research as well as for providing excellent pilot facilities for the foam coating trials. VTT is acknowledged for providing the possibility to widen the foam research area and for the excellent working facilities. It has been a privilege to carry out this work at KCL and VTT. The work has also been funded by Tekes – the Finnish Funding Agency for Technology and Innovation in the “Intelligent and Resource-Efficient Production Technologies” (EffTec, 2007-2010) and in “Efficient Networking towards Novel Products and Processes” (EffNet, 2010-2013) research programs of Forestcluster Ltd, as well as, from the European Community’s Seventh Framework Programme under Grant Agreement No 228802 in the EU-project ‘Scale-up Nanoparticle Production in Modern Paper Making’ (SUNPAP, 2009-2012).

When I was a kid, my dream was to become a veterinarian. I spent a lot of time in a cow shed and read tens of books dealing with the diseases of pigs and cows. But after high school the target changed: I would like to become a brain surgeon. When the doors did not open on the first time to medical school, I decided in the meantime study organic chemistry at Jyväskylä University. Somehow, I felt a weird attraction to log tracks passing me on their way to Varkaus Paper Mill. The attraction was so strong that during my university studies at Jyväskylä I spent more time in the mill’s labs than in the lecture rooms. Finally, I was lucky enough to get the possibility to do my M.Sc. thesis at the mill. My companions in the starting phase of this great adventure to papermaking, and the people to whom I owe gratitude, are my first bosses at Varkaus Mill: Raija Mattelmäki, Anneli Monto, Lyyli Marttinen, Juhani Vase and especially Reino Panula, whose encouraging advice I will always remember: “Papermaking you can learn in practice, but organic chemistry, which will help you to understand papermaking, not.” Also I own gratitude to my colleagues in the mill and to my team, whose leader I had the honour to be. I will never forget our 180’s anniversary! I own also deep gratitude to Enso Gutzeit and Reino Panula for offering me a ‘once in a life time’ job, Manager of the laboratory project at Sachsen Paper Eilenburg green field project. That project changed my

life in many ways: without it KCL, VTT, foam technology research, my family and this thesis would not be in my life.

I would like to thank Martin Holmberg, professor Kaarlo Niskanen and professor Thad Maloney for inspiring research projects at KCL. You with persons mentioned above confirmed that it was a right choice to follow my instincts! During the years, I found a second ‘once in the lifetime’ job, a combination of papermaking and foam. I would like to thank Kay Rökman for his help in the early stage of my foam research and Horst Ross from Zimmer for giving me a chance to run the first foam coating trials. I would like to gratefully acknowledge KCL. I wish to express my warmest gratitude to Timo Lehto, Raimo Pollari and to the great staff of KCL’s pilot plant: Hemppa, Kari R, Jykä, Ville, Jarmo, Helge, Martti, Heikki, Esa, Kari J, Kari S, Marko and Matti. Your input was already extremely important in the early stage of my foam coating research and became crucial to the start-up company Paptic Ltd, where I nowadays continue the work with foam technologies. In this context, I own warm gratitude to my husband Vesa. Your deep experience in machine engineering and processes and innovativeness were crucial in the starting phase of our pilot line. It also enabled and inspired me to fulfill my wish of many years: the finalizing of my dissertation.

I am deeply grateful to VTT and my ex-colleagues there: Jani Lehmonen, Petri Jetsu, Harri Kiiskinen, Eija Kenttä, Marja Juvonen, Ulla Forsström, Annaleena Kokko, Hanna Koskela, Timo Kaljunen and Erkki Saharinen. It was so rewarding and fun to work with you, some of you were already at KCL my colleagues! Tuomo, I did not forget you! My special thank goes to Dr. Tuomo Hjelt, my supervisor and work mate at KCL and VTT. A foam course held in the Alps gave me a buttress to foam research! Working with you was fun: ‘Laugh (orig. Whistle) While You Work’! Also, I am grateful to all my great colleagues and laboratory personnel at KCL and VTT with whom I have been so lucky to work during these years.

I would like to thank all the co-authors of the original publications.

I would like to warmly thank professor Jouni Paltakari and my thesis’ examiners professors Tetsu Uesaka and Markku Kataja for the valuable advices on my thesis.

Finally, I wish to express my warmest thanks to my family, especially to my mom – I have no words to thank you enough. And kids, Iiro and Kiira, and Hertta the cat, you are my power supplies!

Espoo, April 14th, 2017

Karita Kinnunen-Raudaskoski

List of publications

This thesis is based on the following original publications, which are referred to in the text as I - VI. The publications are reproduced with the kind permission of the publishers.

I **Kinnunen-Raudaskoski, Karita**; Hjelt, Tuomo; Kenttä, Eija; Forsström, Ulla. (2014) Thin coatings for paper by foam coating, TAPPI Journal Vol. 13 No. 7 July 2014, pp 9-19.

II **Kinnunen-Raudaskoski, Karita**; Hjelt, Tuomo; Sadocco, Patrizia; Forsstöm, Ulla; Paltakari, Jouni. (2017) Novel thin functional coatings for paper by foam coating, TAPPI Journal Vol. 16 No. 4 April 2017, pp. 179-186.

III **Kinnunen-Raudaskoski, Karita**; Salminen, Kristian; Lehmonen, Jani; Hjelt, Tuomo. (2016) Increasing dryness after pressing and wet web strength by utilizing foam application technology. TAPPI Journal Vol. 15 No. 11 November 2016, pp. 731-738.

IV **Kinnunen, Karita**; Lehmonen, Jani; Beletski, Nikolai; Jetsu, Petri; Hjelt, Tuomo. (2013) Benefits of foam forming technology and its applicability in high NFC addition structures, 15th Fundamental Research Symposium, Oxford, UK. Proceedings of the 15th Pulp and Paper Fundamental Research Symposium, Cambridge, Sept 8-13.

V Lehmonen, Jani; Jetsu, Petri; **Kinnunen, Karita**; Hjelt, Tuomo (2013). Potential of foam-laid forming technology for paper applications. Nord. Pulp Pap. Res. J. 28:3, 392-398.

VI **Kinnunen-Raudaskoski, Karita**; Pirkonen, Pentti; Lehmonen, Jani; Hjelt, Tuomo. (2014) Foam-aided sludge treatment, Filtration Journal, vol 14 number 3 August, pp 174-180.

Author's contributions

The author's role in each of the publications has been the following:

I The author had the main responsibility for the technology development and the practical work and the author planned and wrote the manuscript as a principal author taking into account the comments of the co-authors. The author researched the relevant literature. The author was responsible for the research idea.

II The author had the main responsibility for the technology development and the practical work and planned and wrote the manuscript as a principal author taking into account the comments of the co-authors.

III The author had the main responsibility for the technology development and its application and planned and wrote the manuscript of the paper taking into account the comments of the co-authors. The author was responsible for the research idea.

IV The author planned and performed the experimental work in co-operation with the co-authors and wrote the manuscript of the paper taking into account the comments of the co-authors. The material characterizations were carried out by experts.

V The author participated to the planning and performing of the experimental work and was a co-author of the manuscript.

VI The author planned and performed the experiments in co-operation with the co-authors and had a main responsibility for writing the manuscript of the paper. The author was responsible for the research idea.

Supporting publications

I Al-Qararah, A.M., Hjelt, T., **Kinnunen, K**., Beletski, J., Ketoja, J.A. (2012). Exceptional pore size distribution in foam-formed fibre networks, Nordic Pulp Paper Res. J. 27(2012) 226–230Kenttä E, Kinnunen, K., Hjelt, T. (2012). Characterization of thin pigment coating layers produced by foam coating. 12th TAPPI Advanced Coating Fundamentals Symposium, September 10-12, Atlanta, Georgia.

II Heiskanen, I., **Kinnunen, K.,** Hjelt, T. (2013). Hydrophobically sized web and a method for the preparation of the sized web layer. Pat. WO2013160564 A, publication date 31 October 2013, application number FI2013050471, application date 25 April 2013, priority FI20125463 (25 April 2013).

III Hjelt, T., **Kinnunen, K**. (2011). Surfactants. VTT report of Efficient Networking towards Novel Products and Processes-project, Forestcluster Ldt, Finland.

IV Hjelt, T., **Kinnunen, K**., Lehmonen, J., Beletski, N., Hellén, E., Liljeström, V., Serimaa, R., Miettinen, A., Kataja, M. (2011). Intriguing structural and strength behaviour in foam forming. Progress in Paper Physics Seminar, Graz, 2011, p. 135.

V Immonen, K., **Kinnunen, K**., Lehmonen, J., Hjelt, T., Erkkilä, A. (2012). Peat moss structures. Pat. WO2013144449 A, publication date 3 October 2013, application number FI2013050342, application date 27 March 2013, priority FI20125353 (27 March 2012).

VI Juvonen, M, Hiltunen, J., Jetsu, P., Gestranius, M., Harlin, M., Kunnari, V., Lattu, J., **Kinnunen, K.**, Hjelt, T., Nurminen, I., Saharainen, E., Lampinen, H. (2012). Mouldable fibrous product and method of producing the same. Pat. WO2014080084 A, publication date 30 April 2014, application number FI2013051097, application date 22 November 2013, priority FI20126227 (22 November 2012).

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X **Kinnunen, K**., Hjelt, T. (2012). Fibrous web of paper or board and method of making the same. Pat. WO2013160553 A, publication date 31 October 2013, application number FI2013050460, application date 24 April 2013, priority FI20125462 (26 April 2012).

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XVI Torniainen, E., Mustonen, T., **Kinnunen, K**., Hjelt, T. (2014). Fiber sheets and structures comprising fiber sheets. Pat. WO2016083667 A, publication date 2 June 2016, application number FI2015050811, application date 20 November 2015, priority FI20146033 (24 November 2014).

Contents

List of symbols and abbreviations

CFU	the number of living cells in the extracted suspension, was evaluated by the count plate agar method
CNF	cellulose nanofibrils
CNF-TE	TEMPO oxidized CNF
CMC	carboxymethyl cellulose
CMC	critical micelle concentration
CMF	cellulose microfibrils
CTMP	chemi thermo mechanical pulp
CTP	Centre Technique du Papier, France
DS	dry solids
EVOH	ethylene vinyl alcohol
FAD	foam-assisted dewatering
HW	hardwood kraft pulp
IR	infra red
KCL	Oy Keskuslaboratorio-Centrallaboratorium Ab, Finland
NO	nitric oxide
NO_2	nitrogen dioxide
NO_x	The generic term NO_x includes NO and NO_2
NTU	Nephelometric Turbidity Unit
PP	polypropene fiber
PTS	Papiertechnische Stiftung, Germany
PVA	polyvinyl alcohol
RH	relative humidity
RoR	roll-to-roll
rpm	revolutions per minute
SEM	scanning electron microscope
SDS	sodium dodecyl sulphate
SFC	soap-film coating

^{o}SR	Schopper-Riegler value (drainability of a pulp suspension)
SW	softwood kraft pulp
TiO_2	titanium dioxide
TMP	thermo mechanical pulp
tDS/a	tons dry solids/year
VTT	Technical Research Centre of Finland
WVTR	water vapour transfer rate
WWTP	waste water treatment process
ZnO	zinc oxide

1. Introduction

1.1 Background

Foam can be defined as a collection of small bubbles formed in or on a liquid by, e.g. agitation or by a chemical reaction, such as fermentation. A foam may appear as a thick frothy fluid made of large number of small bubbles (e.g. shaving cream). On the other hand, foam can also be defined to be a dispersion of gas bubbles in a solid, a soft material that is used to make many products like foam rubber, foamed metal, or polyfoam. Common to all foams is that they are substances that consist of bubbles filled by a gas. Figure 1 shows examples of unstable and stable foams, and materials that have a foamy structure.

Figure 1. Examples of foams and foamy structures.

Applications involving foams are found in the food, petroleum, mining (Riegel's, 2003) and gas industries, oil recovery (Fainerman et al., 2001, Hahn et al., 1985), and in waste-water treatment. In addition, foams are used in fire fighting applications (Kruglyakov, 1999). In the early twentieth century, a series of patents were issued in the textile industry for the use of soap lather in a batch process for silk treatment (Schmid, 1905, 1911). In 1957 Kumins et al. disclosed an early example of continuous foam application for textiles, where foam from an aqueous mixture of colorant, thickener, emulsifier and foam stabilizer was applied using an engraved printing roll. According to them, the foam method reduced thickener requirements and gave a better colour yield. The Sancowad process, developed in the early 1970s, was the earliest foam process that received widespread attention (Albrecht, 1971; Lister, 1970). The process was a low-liquor-ratio batch method for in-situ foam generation to distribute dyes or finishing chemicals. A wide variety of foam application techniques, in which foam is used as a carrier phase for treatment chemicals, have been developed in the textile industry (Eltz et al., 1972, 1976; Faber and Carrol, 1930, 1931; Stritzko, 1969; Abrahams and Graham, 1971; Maier 1978; Schwemmer et al., 1975; Childers and Fesperman, 1972). The composition, the structure and the properties of the foams used vary widely, as does the manner by which the foams are applied on the substrate. Dying, printing, warp sizing, fabric preparation and chemical finishing are mentioned as application areas. The main benefit of using foams instead of conventional liquids in these applications arose due to the lower net amount of liquid needed (Gregorian and Namboodri, 1977). The interest in foam-based technologies seems to be increasing in the textile industry (Abhishek and Nitin). The reasons for this include the potential for optimizing the use of costly chemicals and reducing the considerable amount of energy used in drying (Faber and Carrol, 1930; Abrahams and Graham, 1973; Eltz et.al., 1976, Abhishek and Nitin).

Foam, instead of water, can also be used to produce fiber webs. In the non-woven material industry, aqueous foams are used as one method of forming long fiber based webs (Hanson, 1977). In papermaking, the technology has concentrated on the wet web forming process based on water. In this environment, a foam unintentionally appearing in the process can induce a harmful aggregation of soluble chemicals. Much attention has thus been devoted to developing and using foam control agents. Currently, the only common foam process within the paper industry is the flotation process used for de-inking recycled newsprint.

Although water as the carrier fluid has dominated papermaking technology, foam does have a role in its history. In the 1970s foam was explored for the first time as a replacement for water in papermaking (Smith et al., 1974; Kidner, 1974; Radvan, Gatward, 1972; Punton, 1975a, 1975b); a pilot paper machine was operated at speeds of up to 900 m/min (Punton, 1975). The foam technique, known as Radfoam process, was found to enhance product properties and especially formation (Radvan, Gatward, 1972; Punton, 1975; Kidner, 1974; Smith, Punton, 1975; Smith et al., 1974). Despite the successful research work carried out in this field and promising technological innovations and the highlighting of the benefits (Attwood, 1984), the foam technique was not able to break through in the field of paper and board production. New interest towards the utilization of foam has appeared after several decades of low activity. This is also reflected by the number of recent articles related to using foams in papermaking. Pure foams have been studied intensively by, e.g. Weaire et al. (1997, 1999, 2003, 2012) and Hutzler (1999). Single foam films have been the object of extensive studies (e.g. Exerova et al., 1998 and 2003, Sedev et al., 1999, Langevin, D., 2001, Karraker et al., 2002), because they are convenient model systems to investigate interaction forces in dispersed systems of various kind (foams, emulsions). The properties of single films are of crucial importance for the formation and stability of foams. The majority of the studies have been carried out under static conditions and special measures were applied to avoid any external disturbance. Malysa and Lukenheimer (2008) in their review focusing on the importance of dynamic effects in foam formation and stability summarized that such situation is rather hard to meet during foam formation and therefore forces stabilizing thin liquid films under dynamic conditions should be taken into consideration, e.g. under static conditions surface elasticity is not important, but it may become of a great importance under dynamic conditions (Stubenrauch and Miller, 2004). Stubenrauch and Khristov showed that the foam properties can depend on the conditions of the foam generation and existence. Therefore, for a proper comparison of the properties of films and foams, the conditions of their existence should be similar during the measurements. Malysa and Lukenheimer (2008) also reviewed methods of. foam measurements.

Madani et al. (2014) and Jahangiri et al. (2014) have performed studies showing that foam structure and rheology can be varied to tune the density. The report of Hjelt and Kinnunen (2011) gives an overview of the wide area of surface active agents, and their functionality in foam. An article comparing different surfactants in foam forming of CTMP or kraft pulp fibers was published by Mira et al. (2014). They concluded that the effect of wood fiber type on the foaming performance of the suspensions was smaller than the effect of the surfactants used, their type and concentration. Surfactants with an anionic character were found to reach the target foam volumes with the minimum surfactant concentrations. Recently, Lappalainen and Lehmonen (2012) and Al-Qararah et al. (2012, 2013, 2015) have published studies concerning fiber foams. Lappalainen and Lehmonen developed a method for quantitative determination of the bubble size distribution of foam containing cellulose fibers. Al-Qararah studied the link between fiber network structure and foam properties by comparing a pore structure with a measured bubble size distribution (2015b). The conclusions were that foam formed sheets have larger pores compared to the water formed sheets and the pore size distribution is more strongly affected by the fiber type than by small changes in bubble size distribution. In addition, he studied fiber foams generated with axial mixing (Al-Qararah et al., 2015a, 2016). The bubble size and its distribution in his studies were affected by several factors such as rotational speed, air content and surface tension. He concluded that natural fibers containing foam had a smaller mean bubble size than foam with regenerated fibers. Also the bubble size distribution became narrower for natural fibers. According to Al-Qararah's studies the reason for the behaviour was likely to be the rough surfaces of the natural fibers and their fine particle fraction, which are absent with regenerated fibers. Alimadadi and Uesaka (2016) created a 3D-oriented fiber network at laboratory scale by using foam forming and by modifying consolidation and drying procedures. They found that a 3D-oriented network with amazingly good structural integrity requires much less fiber-fiber contacts to create a connected network than a 2D oriented one. The created sheets have also unique compression behaviour in the thickness direction due to the extreme bulk, and a long initial rise of compression load and high strain recovery after compression, because of their fiber-reorientation during compression. Koponen et al. (2016) showed formation improvement with degreasing foam density in pulp fiber and 6 mm long lyocell fiber studies and presented a new formulation for formation. Matula (2014) introduced a method, where he combines the formation of fibrous foam with the simultaneous production of precipitated calcium carbonate (PCC), i.e. in-line (Imppola et al., 2011). The fibrous foam is produced using an injection mixing station. In addition to the aforementioned papers, conference papers and presentations and patents from foam forming and foam coating can be found, e.g. Hjelt, 2014; Hjelt et al., 2011; Kinnunen et al., 2006, 2011, 2012a, 2013a, 2013b, 2015; Heiskanen et al., 2013; Kinnunen and Hjelt 2012, 2014; Lappalainen et al., 2014. Metsä Board Oyj published a press release about starting mill scale testing of foam forming technology at Kyro Mill (27.5.2015).

The driving forces behind 'foam new coming' is the ever-increasing need for more cost-efficient and versatile production methods capable of handling a variety of raw materials for the manufacture of sustainable and value-added fiber products. According to Radvan and Gatward (1972) the foam forming technique enables high uniformity and bulk even at low base weight, but the strength loss due to the bulky structure is the main disadvantage. They also stated that wet-pressing and beating have an effect on the strength properties. The problem with wet-pressing is that the strength increases with an apparent decrease in bulk, which leads to poorer mechanical properties of the final product, such as bending resistance. Another way of increasing both wet and dry strength is to use strengthening additives, typically dosed in the process at the wet end or applied on the web with a spray.

Material development has brought to market new materials, which enable future paper products with more intelligent and functional properties. These materials could be very expensive, but the amount needed can be very small. The new materials can also possess intricate properties such as already high viscosity at low solids content. This may pose a challenge to conventional coating methods. Zhang et al. (2013) introduce a simple wet-chemical method for depositing nanometre thin films at a speed comparable to the one employed in the roll-to-roll (RoR) techniques. They called it soap-film coating (SFC) or bubble soap-film coating (bSFC), which is based on forcing a substrate through a soap film/bubbles containing nanomaterials. The method is similar with foam coating technology, because both techniques utilize foam as a carrier phase for molecules or particles. The difference between the techniques is that in foam coating the entire foam is applied on to the substrate and allowed to dry, where as in SFC the soap film or bubbles are penetrated by the substrate.

Wiggings Teape, known for the 'Radfoam' foam forming technology, also used foam in coating applications (Robertson, 1974) applying dispersions containing microcapsules. Another known application was at Wolvercote Paper Mill, Oxford, England. In the textile and nonwoven industries foam coating is an established technology (Capponi at al., 1982) and is primarily used in the efficient application of dyestuffs or finishing agents while minimizing the amount of required water. Previous efforts in the paper industry (Isaacson, 1965; Wallsten, 1977) to utilize foam for coatings have been reported, but in spite of these examples the technology has yet to gain ground in paper applications, and no present applications in the paper industry can be found.

In addition to 'a carrier phase' function there is another interesting effect of foam, which is its ability to displace liquid water from a porous medium. The known phenomenon enhances dewatering by the use of agents that lower the surface tension of the saturating liquid, and forms the basis for the commercial cleaning processes in the coal industry (Keller et al., 1979). The static experiments done by Lauchenauer and later dynamic processes described by him by a patent of the 1980s (Lauchenauer, 1982, 1985) showed, that foam spread over the sheet, immediately before the sheet was exposed to vacuum, enhanced dewatering. Skelton (1987) reported about the foam assisted dewatering trials done at the former and at the pilot paper machine. The results showed enhancement in dewatering, thus a drier web – especially when the surface-active agent was used in a foamed state, and the effectiveness of the foam appears to be the same whether it is sucked through the sheet by vacuum or forced into the sheet by external pressure.

Our foam research in the year 2005 was started by efforts to find companies using foam technology in a coating application or companies manufacturing foam coating equipment, i.e. foam generators and foam applicators. Benchmarking of existing technologies in practice was found to be impossible and thus the focus was set towards manufacturing companies. A laboratory scale foam coating was found to be challenging due to the difficulty of controlling the foam density and foam layer thickness in static experiments, and therefore pilot scale trials, a dynamic research, were a crucial requirement. We contacted several manufacturers and performed pilot scale trials using different applicator designs, e.g. open chambers and devices based on gear systems. The first successful trials were run at the supplier's textile coating line using an uncoated and uncalendered fine base paper. The trial results of the application of Masuko ground TMP fines to fine paper (Saharinen and Kinnunen, 2005), showed the potential of the foam coating technology in the paper application. The applicator from a store shelf, a prototype #1, basically designed for glue applications, was modified for our purposes after the testing trials. With rental equipment, the prototype #2, we started foam coating trials at the KCL paper machine in the Tekes funded, Silsurf-project targeting to production and application of silica nanoparticles. The applicator was installed between the first and second drying sections of the pilot paper machine. The challenges in the trials were, first, to keep the web tension constant at the manually controlled machine, because even a low amount of water applied in foam was enough to stretch the web causing the tension to be lost. Second, the applied silica nanoparticles attached to the drying cylinder surface in contact drying. For these reasons in the EU-project 'SUNPAP' we continued the development of the foam coating method at the KCL pilot coater. The application materials were native and functionalized cellulose nanofibrils. The functionalization was done using titanium and zinc oxide nanoparticles.

As a side stream of 'Silsurf' the foam forming research started, when a suitable method and a design for a foam hand sheet mould was found from the glass fiber industry. The results from the experiments performed in foam forming enabled the research continuation in the Tekes' funded Forest Cluster projects 'Re-Engineering paper' (REP), 'Efficient Production Technologies' (EffTec), and 'Efficient Networking towards Novel Products and Processes' (EffNet) (Kinnunen and Hjelt, 2013). Outside conventional fibers (pulp, synthetic) we have shown the foam forming potential in applications of materials from nature: peat and moss (Immonen et al., 2012, Erkkilä et al., 2013) and lignin (Ojala et.al, 2013, 2014). Also, the potential to form mouldable or structural webs has been demonstrated (Juvonen et al., 2012, Kiiskinen et al., 2013) as well as the production of paper with plastic like properties (Torniainen et al., 2014). Kenttä et al. (2012, 2014, 2016) have published articles concerning characterization of foam coated surfaces.

1.2 Thesis objectives and scope

The main objective of this thesis is to determine the applicability of foam as a carrier phase in various industrial applications in paper and board making. The scope of this thesis is to study, how aqueous foam can be utilized in the conventional forming, coating and dewatering processes of paper and board manufacturing. The targets and the focus were the following:

1) To determine the applicability of foam in the paper and board surface treatment process.
    - In the coating application, the main focus was on dry paper/board surface treatment using a curtain-like foam coating process, where foam destruction is induced by absorption of the substrate followed by drying using IR-dryers or by using a nip pressure. Other foam application techniques like application on the paper surface or on the roll surface and foam is destructed mechanically, e.g. using air knifes or blades, have been left out of the focus. The wet web application was in the focus in two aspects: dewatering enhancement and chemical application based on foam technology.
2) To determine the applicability of foam in the paper and board forming process.
    - In the forming process the focus was on planar structures made from natural fibers like cellulose fibers. Moulded structures and synthetic fibers have been left out of the focus. Also technical issues in the water or foam forming process, like pipelines and pumps, have been left out. The forming studies have been made in fixed forming environments, laboratory and semi-pilot scale environments, and comparison with other technical solutions has been left out of the focus.
3) To determine the applicability of foam in the dewatering process of biosludge from a paper mill.
    - In the dewatering processes the focus was to show how foam could enhance the dewatering process of paper and board and how the procedure was also applicable in other fields like dewatering of bio based sludge from a paper mill.

Pure foams and one/two bubble layer systems have been studied intensively, and for example Madani et al. (2014) and Jahangiri et al. (2014) have performed studies showing that foam structure and rheology can be varied to tune the density. One factor that influences to the foam stability is the foam density. Thermodynamic of stable foam systems is not valid in systems studied in the thesis. In foam coating the foam produced using foam generators based on rotor-stator mixing heads or an oscillation, the foam is under dynamic conditions. Inside the generators the foam is under shear forces and in the pipe line, the foam flows under pressure. In foam forming the foams are also in dynamic conditions. On the other hand, chemical compositions of foams are not simple systems. In addition to surface active agents, the foams contain particles, fibers and molecules of the applied chemicals. For these reasons the intensive discussion and review of foam physics, foam creation, foam stability and foam rheology have been left out on purpose from the thesis.

In the area of foam coating the use of nanomaterials (nanoparticle or native or functionalized cellulose nanofibrils) has not been studied before. Also no articles have been published about barrier applications using foam coating. **Papers I** and **II** evaluate the foam coating technology in cellulose nanofibrils applications of dry paper. The research in to foam coating in the barrier application is reported by a conference paper (Kinnunen-Raudaskoski et al., 2015).

In the area of foam forming technology, this thesis shows the uniform formation enabled by foam forming by using wood fibers, but also using six and twelve millimeter long synthetic fibers. In addition, this thesis shows the influence of the foam forming technology on the sheet structure (porosity), and shows that by using cellulose nano/microfibrils (CNF, CMF) it is possible to compensate for the strength loss of the bulky structure formed by foam forming. (**Papers IV, V**) Articles from these research issues have not been published earlier.

Publications related to the foam applications to wet web, which simultaneously enhances the dewatering and strength properties of dry and wet paper **(Paper III)**, have not been published earlier. **Paper VI** evaluates the foam-assisted-dewatering method in the treatment of sludge from a paper mill. The method has also been studied in mineral sludge treatments (Kinnunen et al., 2012b).

The research questions of this thesis are shown in Table 1 and the interfaces of the thesis's research areas in Figure 2.

Table 1. Structure of this thesis.

Research questions	Surface treatment	Forming	Dewatering of sludge
The interest towards foam technology is growing, why now?	Papers I-III	Paper IV	Paper VI
What are the main foam properties as a carrier phase, which ensure the proper functioning of foam processes?	Paper I	Paper IV	Paper VI
What are the main benefits of foam forming technology to paper and board processes? How to maintain the strength properties in bulky structures?		Papers IV, V	
Is foam coating technology used in the textile and non-woven industries also applicable for paper and board? Can new materials like nanomaterials – cellulose nanofibers and nanoparticles – be applied to paper by foam coating?	Papers I-III		
How foam affects the dewatering of paper, board and sludge?	Paper III	Paper V	Paper VI

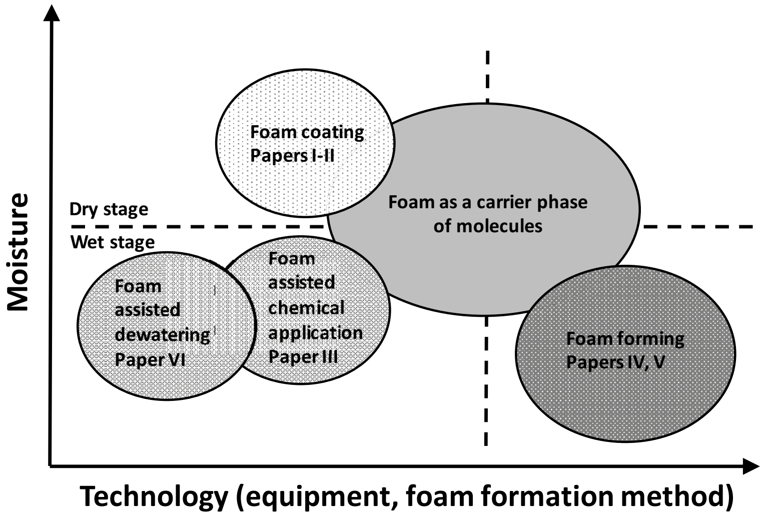


Figure 2. A visualization of the thesis describing the interfaces of the thesis's papers in the technology and a moisture content level of process stages in applications. The grey shade indicates the air content of the foam used in applications; the darker the shade, the lower the air content of the foam, i.e. the wetter the foam.

2. Foam properties and foam technologies

2.1 Foam as a material

The term foam describes many kinds of systems. Foams can be described as a collection of small bubbles formed in or on a liquid by agitation or as a dispersion of gas bubbles in a solid material. In this thesis, the technologies used in web forming, coating and in dewatering are based on aqueous foams. In the aforementioned applications foams were used as a carrier fluid of materials and the end products produced in the processes did not have any foamy structure. The foam destruction was done by means of suction or by absorption combined with heating or a pressure pulse in the processes.

2.1.1 Aqueous foam

Most of the foams are defined as gas emulsions, where the dispersed phase is gas (most commonly air) and the continuous phase is liquid (water in aqueous foams) (Chistyakov, 2001). Aqueous foam is a metastable system consisting of water and air bubbles. The structure of the foam is described either by the density of foam or by the blow ratio combined with the bubble size distribution and the average bubble diameter. Aqueous foams share common mechanical properties with emulsions, which are dispersions of liquid droplets in another liquid phase.

To get a liquid to foam it is necessary to introduce gas into the liquid. This can be done by a cavitation mechanism, e.g. shaking or beating the liquid, when gas is in solution, or by injecting gas into the liquid. The presence of some contamination leading to surface tension gradients is necessary, because chemically pure liquids do not foam. Making foam is easy, but in most cases, it is unstable. Mechanical mixing with high shear forces is a common method of foam generation. Mechanical mixing introduces air/gas in to liquid causing bubble formation through the entrapment of gas pockets in the liquid. When mixing continues with high shear forces, larger bubbles break up into smaller ones.

When a liquid does foam, it may be described coarsely by its foaminess (ease of foaming) and stability (measured by the time of collapse of foams). Surface active agents, surfactants, decrease the surface tension of liquids and so play a very important role in foam generation and in foam stability, e.g. they make the foam bubble surface elastic and so that the bubbles can be squeezed, bumped and deformed. The more elastic the surface is the more stable the foam is.

Surfactants are amphiphilic molecules containing a hydrophobic tail and a hydrophilic head. The surfactant tail is a linear hydrocarbon chain in the surfactants considered in this thesis. This structure means that the surfactant molecule has a water soluble and a water insoluble (or oil soluble) component. When surfactant molecules are dissolved in water at low surfactant concentration the surfactant molecules arrange on the interphase between gas and liquid; the hydrophobic part is in air phase and the hydrophilic part is in water phase (Figure 3), and the foam film is stabilized by van der Waals interaction in the presence of adsorption layers (Kralchevsky, 2009). But when the interphase becomes saturated above the critical micelle concentration (CMC), the separate surfactant molecules start to form aggregates known as micelles (Figure 3). In a micelle, the hydrophobic tails flock to the interior in order to minimize their contact with water, and the hydrophilic heads remain on the outer surface in order to maximize their contact with water (Chevalier and Zemb, 1990; Tanford, 1980). The micellization process (Figure 3) in water results from a balance of intermolecular forces, including van der Waals interactions, hydrogen bonding, electrostatic, steric and hydrophobic forces.

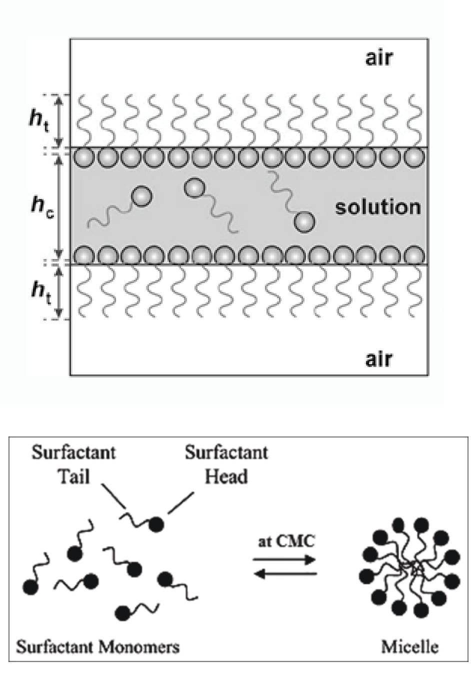


Figure 3. At low surfactant concentration, the surfactant molecules arrange on the interphase between gas and liquid (left; Kralchevsky, 2009), but when the interphase becomes saturated (after adding more surfactant), formation of micelles start (right, a schematic illustration of the reversible monomer-micelle thermodynamic equilibrium (Liu et al., 1996)).

Foams can also be stabilized by nanoparticles, without surfactants (Pugh et al., 2016). Sun et al. (2016) for example studied the effect of nanoparticle stabilized foam in oil recovery. The foam stabilization was done using silica nanoparticles combined with hexylamine. The structure of foams is described in terms of bubbles, films, Plateau borders and junctions. Figure 4 shows an image taken by the photographer-artist Michael Boran, showing the structure of foam.

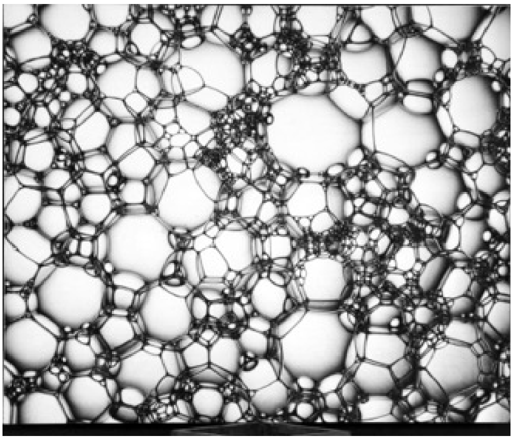


Figure 4. An example of 3D aqueous foam consisting of bubbles of many different sizes as seen by the photographer-artist Michael Boran.

The bubbles, separated by thin films, are pressed together to form a foam. Between the bubbles are liquid-filled interstitial channels, where the films meet along a line or curve, called Plateau borders. At a junction, several Plateau borders meet to form an interconnected network (Figure 5).

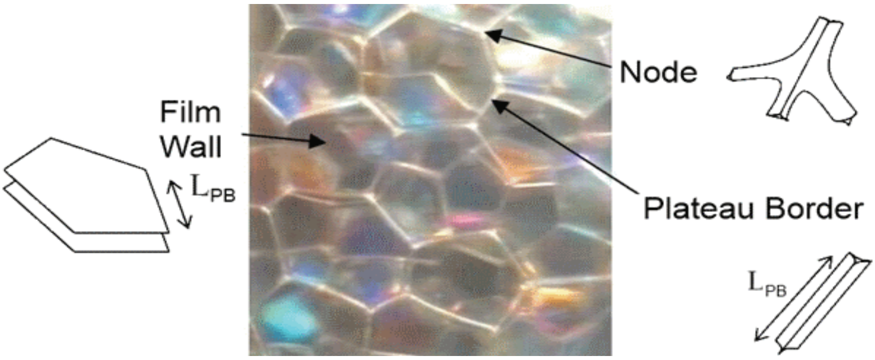


Figure 5. An image from Prof Stubenrauch's group in Stuttgart captures the three key components of a foam: Film (or wall), Plateau border (PB) and node. (The image taken from the Internet).

Foams can be classified as dry or wet according to their liquid content. There is no exact definition for the transition from wet foam to dry foam, however, there are some guidelines describing when the transition happens. By eye the difference between wet and dry foams is easily noticeable; wet foam's surface smoothens when the foam is poured into a container. One definition is that when foam follows Plateau's laws, it is a dry foam. According to the Plateau laws, three faces (films) meet symmetrically in a line at angles of 120 degrees. Four such lines meet in a vertex at the tetrahedral angle of ≈109.43 degree. This is called the Maraldi angle, where six cells meet symmetrically at every corner (Weaire et al., 2012).

Another definition of wet/dry limit is to put the limit in the same foam density as the jamming transition. Foams, as well as amorphous materials like emulsions, colloidal suspensions and granular media, can jam and undergo a transition from a flowing to a rigid state (Liu and Nagel, 2010; Siemens and van Hecke, 2010). In jamming a system has a disordered internal structure, and in this way jamming differs from crystallization (Liu and Nagel, 2010). The (un)jamming point corresponds to the dry-wet limit, where the bubbles become spherical and just form contacts (Katgert et al., 2013). Below the jamming transition, the foam is wet and above it, the foam is called dry (Katgert et al., 2013).

The gas fraction ϕ plays a crucial role in determining foam's structure and rigidity. When the gas fraction is lowered, the foam becomes wetter, and the gas bubbles become increasingly spherical. For some critical gas fraction ϕ_c the bubbles lose contact with each other, and the foam loses its rigidity (Figure 6).

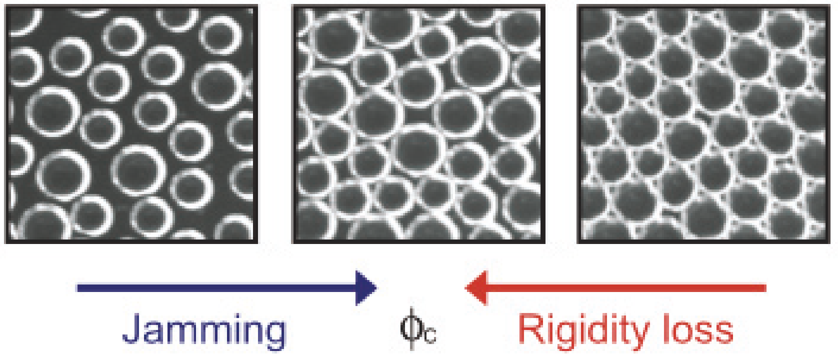


Figure 6. Top views of 2D foams. Foams consist of 2 and 3 mm bubbles, which are trapped below a top plate. On the left bubbles are low packed, and the spherical gas bubbles do not form contacts. On the right the bubbles are tightly packed. The bubbles are squeezed together and they form a jammed, rigid state. The bubbles start to form a honeycomb structure. In the middle, for some critical gas fraction ϕ_c the bubbles lose contact and just touch each other. (Figure Katgert et al., 2013).

In practice the measurement of the jamming transition is rather difficult, because of drainage and coarsening, and thus it is not done to real foams. Foam drainage is a flow of liquid through Plateau borders and nodes between the bubbles and is driven by gravity and capillarity (Weaire and Hutzler, 1999). Gas diffusion through the thin films from bubble to bubble due to a pressure difference causes coarsening (Weaire and Hutzler, 1999). The process is known as Ostwald ripening. In coarsening the volume of certain bubbles increases at the expense of others, and thus the average bubble size grows with time; these effects can be minimized by studying 2D foams and using inert gases (Weaire and Hutzler, 1999). Jamming is also studied by using models. In most models, frictionless soft spheres are used. The interactions between bubbles are viscous and repulsive and, therefore, static foams are similar in behavior to those spheres (Katgert et al., 2013).

One property, which is reasonably easy to measure, is shear modulus. Shear modulus can be used as an indicator of jamming transition. When foam has a shear modulus it is dry and when it is wet, it does not have one. This method gives rather low-density values for dry foam. Foam has a shear modulus when its behaviour is elastic; the foam deforms reversibly under stress. The bigger the shear modulus the more rigid the foam is, i.e. the drier the foam.

Figure 7 shows shear modulus G as a function of ϕ. G becomes zero when $\phi \sim 0.63$. The vertical line in this point shows the jamming point. The same figure also shows the behaviour of a non-linear shear modulus Gnl and the fitting of two theoretical curves. They are not of interest in this study, but more details of them can be found from the article written by A. Saint-James and D.J. Durian (1999). They used homemade aqueous foams made via the turbulent mixing of gas with a narrow jet of a surfactant solution inside a delivery tube (Saint-Jalmes et al., 1999). About 60% of the used foams had radii between 40 and 70 μm, with none larger than 100 μm or smaller than 10 μm. The average radius R was 55 μm. The slowly drained foams were produced from aqueous solution based on surfactant mixtures; olefin sulfonate (AOS) from Witco Corp., polyacrylic acid polymer (CARBOPOL 941) from BF Goodrich, cosurfactants (dodecanol), solvent (butanol) and water (Rand, 1984).

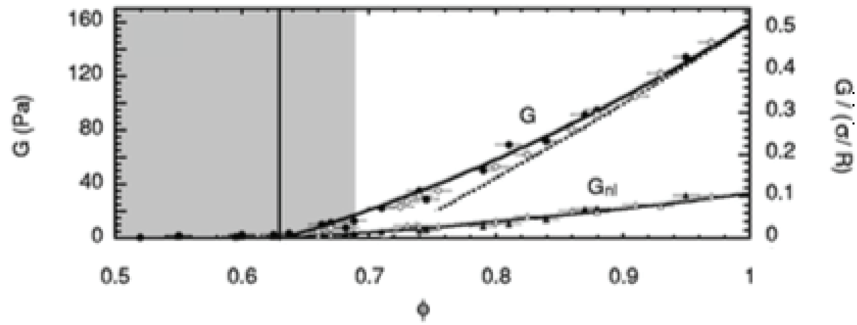
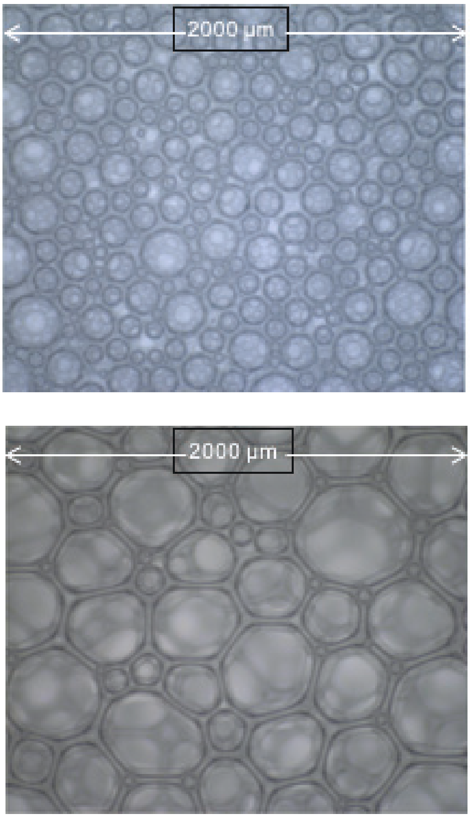


Figure 7. Dependence of foam rheology on gas volume fraction, ϕ. The shear modulus *G* (circles) and the non-linear modulus *G*nl (triangles) are shown as a function of ϕ. The continuous lines represent the Mason's ϕ dependence formula, while the dashed line is Princen's formula. More details on Gnl and Mason's and Princen's formulas can be found in Saint-James and Durian (1999).

Generally, most of the foam research deals with dry foams with an air content above 80% (Exerowa et al., 1998) and the properties of wet foams are much more poorly understood. These wet foams are free-flowing and shear-thinning liquids, and these properties are beneficial when foam is used as a carrier phase to produce particle or fiber structures (e.g. Radvan and Gatward, 1972; Smith et al., 1974; Skelton, 1987).

In dry foam the bubbles have the form of polyhedral cells (like a honeycomb structure, Figure 5) and it can have any liquid fraction in a range from zero to about 35%. Above that, at the wet limit, the bubbles can move around each other and have the form of spheres. Figure 8 shows the difference between a wet and a dry foam. The figures are from the foams used in the thesis's research, wet in foam forming and dry in foam coating. In the wet foam example with a density of 340 g/l (air content of 66%), the foam bubbles are round, the average bubble radius is below 100 µm and the foam is liquid-like in behaviour. In contrast, the structure of dry foam with a density below 200 g/l (air content above 80%) resembles a honeycomb with an average bubble radius around 100 µm and the foam is like a stable shaving cream.



F**igure 8**. Foam with air content of 66% and round bubbles is called wet foam (left) and the dry foam with air content of 94% has honeycomb structure (right) (Kinnunen et al., 2013a).

2.1.2 Pseudoplastic nature of foam

Aqueous foams are pseudoplastic, i.e. shear thinning (Figure 9), having very high viscosity at low shear conditions, but at high shears strongly shear-thinning and therefore reasonable easy to pump. Due to its pseudoplastic and viscoelastic properties foam is an excellent material for transporting particles and fibers in a dispersed state, leading to excellent formation of the paper (Punton, 1975a, 1975b; Riddell and Jenkins 1976). Punton (1975a, 1975b) has suggested that for most fibers the optimum dispersion is achieved when the foam air content is approximately 65%. If the foam air content drops below 55% the pseudoplastic behaviour of the foam disappears. In addition, these foams allow the use of a wide variety of different raw materials, from nanoparticles up to 200 mm long fibers and also low density materials.

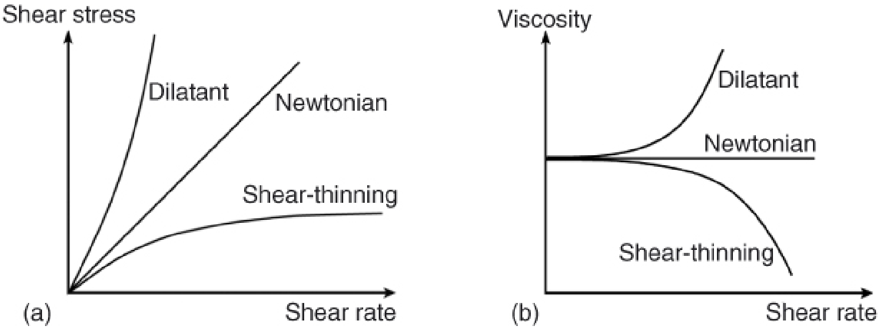


Figure 9. Typical flow curves for Newtonian, shear thinning and shear thickening (dilatant) fluids: (a) shear stress as a function of shear rate; (b) viscosity as a function of shear rate. (Willenbacher and Georgieva, 2013).

2.1.3 Particles in foam

The flow of liquid through a foam occurs mainly in its Plateau borders (Figure 10, left), i.e. flow in the films is neglected (Weaire et al., 1997; Koehler et al., 2000; Cox et al., 2000). When particles are clearly smaller than foam bubbles they are located in the bubble pockets (vertices) and in Plateau borders. Particles are not able to move through Plateau borders connecting vortices thus preventing aggregation. If the 'particles' (e.g. fibers) are bigger than bubbles the surface of the particles is covered by bubbles (Figure 10, right). Bubbles behave as a mechanical barrier between particles again preventing flocculation. Particles can also be used as foam stabilizers, for example Gonzenbach et al. (2007) used inorganic colloidal particles as foam stabilizers and tailored the microstructure of the stabilized foams; foam air content, average bubble size, and bubble size distribution by changing the composition of the initial colloidal suspension.

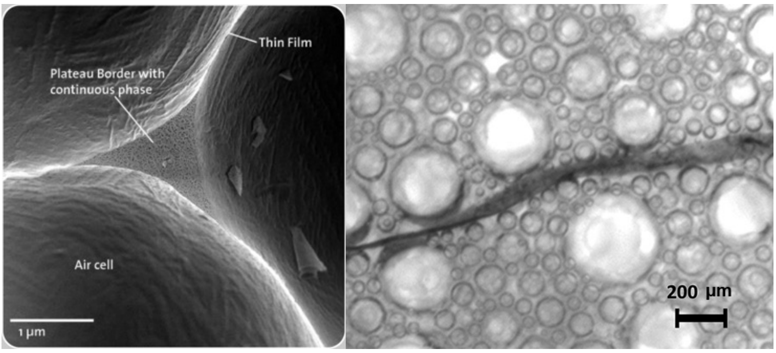


Figure 10. Left: Nanometric details of the Plateau Border visible in a picture obtained by a Cryo-Scanning Electron Microscope (image credit N. Duerr-Auster/ETH/2008). Right: Example of bubble images from foam with long fibers (Al-Qararah et al., 2012). The fiber surface is covered by foam bubbles.

When foam is generated using mechanical mixing one of the advantages is that it ensures high homogeneity of the solution. Therefore, bubbles, fibers, fillers and papermaking chemicals are uniformly distributed in the vessel. It is known that mechanical mixing produces a wide distribution of bubble sizes (Weaire and Hutzler, 1999). However, the average bubble size decreases and the bubble size distribution narrows as the mixing speed increases (Isarin et al., 1995; Engelsen et al., 2002; Al-Qararah et al., 2012). A plug flow behaviour is typical for foams in straight tube flow induced by a pump or by gravity.

Most of the research on aqueous foams has concentrated on the so-called “dry” foams with air content above 80% (Cantat et al., 2013). Recently Al-Qararah et al. has studied the properties of pure wet foams and wet fiber foams (Al-Qararah et al., 2012, 2013). They reported that rotation speed, air content and surface tension dominate the average bubble size, and the fibers (unrefined bleached kraft pulp, Scots pine, SR 7.6, consistency 1.4%, freeness 607 ml) did not change the main trends, but they reduced the bubble size. In addition, Al-Qararah et al. (2012) have found that pore size distribution of hand sheets made with foam forming depends on the properties of the foam. The largest pores in foam-formed paper samples have a similar size to the largest bubbles in the corresponding foam. Smith et al. (1974) suggested that the increased bulk and porosity could be traced to the presence of bubbles in the sheet. These bubbles may survive into the early stages of drying.

2.2 Foam technologies

In foam technology, foam is used as a carrier phase of a material, e.g. fibers, particles or chemicals. Roughly, it can be said that the foam forming of webs utilizes wet foam, and dry foam is used in coating applications. However, wet foam is also applicable in coating applications and the usage of wet or dry foam depends on mechanical breaking methods of foam and coating performance targets.

2.2.1 Foam coating

Foam coating technology is one of the technologies used in the textile and nonwoven industries. The manner of application to the substrate varies widely, as well as the properties of the recommended foams. Application areas include dying and printing, warp sizing, fabric preparation and chemical finishing, e.g. Faber and Carrol, 1930; Abrahams and Graham, 1971; Gregorian and Namboodri, 1977. When it comes to paper, only a few applications can be found in the European paper industry, e.g. coatings with dispersions containing microcapsules with natural foaming agents such as gelatin, casein, and soybean extract have been applied as foam to the paper web by the Wiggins Teape company, known for the Radfoam foam forming technology (Robertson, 1974). The method has also been used to correct an inherent curl in one-side coated papers and for the controlled addition of materials such as starch, wet strength resin, poly vinyl alcohol, wet-end sizing agents, and direct dyes (Riddell and Jenkins, 1976, 1977, 1978).

Another known application was at Wolvercote Paper Mill, Oxford, England. Low-density starch foam was applied directly on to the wet web immediately before it entered the wet press. At the press nip, the foam was mechanically broken, and the starch was dispersed through the sheet. By controlling the foam density, bubble size, and starch concentration, a wide variety of results were achieved (Riddell and Jenkins, 1977, 1978). The benefit was the possibility to use low-cost unmodified starch and high starch concentrations. The technology called a 'Foamcote' system is described in patents issued to Jenkins (1975a, 1975b). The speed limit of the system due to turbulence was 65 m/min. Eklund and Hobbs (1986) presented a foamed starch application system at high speeds. At a pilot size press, they conducted studies at speed up to 610 m/min, for two-side application, and higher speeds of 1160 m/min, and one-side applications were conducted using the roll applicator position of the blade coater.

In foam coating, the main requirement is the foamability of the coating material and the focus is on the compatibility between the foaming chemistry, the coating material and the substrate surface. The coating material can be a commercial product as is or a diluted one. It can also be cooked like starch, PVA and EVOH or dispersed material. Foaming agents are needed if the material is low-foaming or not self-foaming. For foam production from the coating material equipment based on, e.g. rotor-stator mixing heads, or an oscillating process are used. The foamed coating material is then pumped forward to the coating unit, and the application on to the moving web is done using a narrow slot type applicator. After the foam application, the foam is destructed by the means of pressure, heat or vacuum.

The technology can offer savings in investment costs since there is no need for massive coating kitchens or circulation systems of coating material, and also a saving in raw materials. The foam normally contains 90–95% air and in order to achieve the desired coat weight, instead of a 1 µm layer of liquid, a 10 µm layer of foam is spread on the moving web. This makes it possible to spread a small amount of nanomaterial evenly over the substrate. The applied coat-weights are from 0.1 up to a few g/m^2.

In the textile and nonwoven industries foam coating is an established technology (Capponi at al., 1982) but in the paper and board industries the technology has yet to gain ground and no present applications can be found.

2.2.2 Foam forming

The aqueous foam used in foam forming, instead of water as a process fluid and flowing medium, is known to be excellent at transporting particles in a dispersed state (Smith and Punton, 1975). Foam forming technology typically utilizes surface active agents in the production of process foam. Using surface active agents or non-surfactant foaming agents, the surface tension of the flowing medium can be lowered, which enhances air dispersion into the medium (Nicolaysen and Borgia, 1954; Riddell and Jenkins, 1976; Touchette and Jennes, 1960). The Radfoam process, descried by patents (Gatward and Radvan, 1966; Gatward et al., 1972; Robertson, 1972; Radvan and Green, 1973; Wallace and Willis, 1987; Wiggings Teape, 1973) is the only process, which has been published in articles (e.g. Smith and Punton, 1975) and conference papers. Based on those some details are known from the process: drainage capacity needs to be higher than for conventional papermaking, the production machine was run at a speed of 1300 m/min, the main focus was in long fiber forming, i.e. non-woven applications; fibers up to 12 mm were commonly used, also fibers up to 25 mm. However, printing papers with improved formation and bulk were produced with a favourable balance between bulk and surface smoothness.

In the process the pulp slurry was added to a foamed liquid comprising water, surfactant and air. The foamed liquid made by a tank generation method had 55 to 80 percent air by volume. The foamed fiber furnishes had a consistency in the range of from about 0.1 to about 3 weight percent fiber. On the paper machine wire, foam was broken down by physical means to form a foamy-water medium; this could be done by vacuum or by pressure in the nip of any configuration (Riddell and Jenkins, 1977). Under the influence of suction, these foam-fiber mixtures drained rapidly producing sheets of a higher uniformity than that of a water slurry of the same weight consistency (Punton, 1975a, 1975b). Figure 11 shows the flow chart of the Radfoam process (Wiggings Teape, 1971). After drainage they had a normal papermaking process system. Tringham (1974) reported further development of the process.

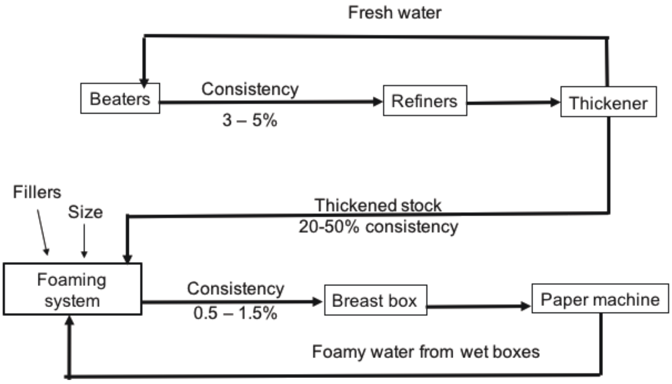


Figure 11. The flow chart of the Radfoam process.

The foam forming method, which utilizes foam with 55 to 80 percent air by volume produced by tank generation, requires changes to a conventional paper machine to some extent (e.g. higher vacuum levels at forming section), and so the latest studies at VTT, Technical Research Centre of Finland and at Valmet, have focused on foam generation in-line/on-site near the headbox and higher density foams (approx. 400-700 g/l). However, trials and applications have been run at VTT utilizing low density foams (Koponen et al., 2016; Torvinen et al., 2015).

3. Materials

3.1 Fibrillated cellulose

Fibrillated celluloses are novel bio-based materials, which have potential for numerous applications. Two types of fibrillated celluloses manufactured by mechanical treatments, or with combination of enzymatic or chemical and mechanical treatment, are generally recognized, namely cellulose microfibrils (CMF, or microfibrillated cellulose, MFC) and cellulose nanofibrils (CNF, or nanofibrillated cellulose, NFC) (Kangas et al., 2014). A proposal by the European Commission for definitions of CNF/CMF states that nanomaterial is “a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the size distribution, one or more external dimension is in the size range 1 nm – 100 nm” (European Commission 2011). This thesis combines novel foam based forming and coating methods in the paper industry with CNF/CMF applications.

3.2 Materials in foam coating

Functionalized paper and board were prepared by bringing additional features to the paper/board surfaces. Antimicrobial and photoactive surfaces were performed by applying CNF-TiO_2 and CNF-ZnO&TiO_2 composites on the paper surface. In the barrier targeting trials polyvinyl alcohol and ethylene vinyl alcohol were used. In the wet web coating trials three different polyvinyl alcohol grades, guar gum, starch and CMF were applied to water formed paper of pine fibers. Table 2 summarizes the materials used in the foam coating and Table 3 shows the characteristics of the base paper used in the foam coating trials. The base board used in the PVA foam trial in barrier application was 200 g/m^2 uncoated and uncalendered paperboard produced from recycled fibers with slightly slower absorption properties. Foam coating was done on the grey side of the board. Table 4 shows the characteristics of the native CNFs used in the trials. The data of the functionalized CNFs is reported in Table 5 and in Table 6.

Table 2. The materials used in the foam coating trials.

Web	Materials	Solids %	Applied amount, g/m^2	Foaming agent
dry	Native CNF (Table 4)			SDS
	CNF with TiO_2/ZnO (Table 5 and Table 6)			SDS
	Mowiol 40-88 (PVA1)$^{1)}$)	6.8	Up to 8	
	Exceval AQ-4104 (EVOH$^{1)}$)$^{6)}$	16.0	Up to 8	-
	Base paper and board$^{4)}$			
wet	PVA1$^{1)}$) (degree of hydrolysis 88%, viscosity 30-42 mPa·s$^{2)}$)	7.0	1.8	-
	PVA2$^{1)}$) (degree of hydrolysis 99%, viscosity 26-30 mPa·s$^{2)}$)	10.8	2.7	-
	EVOH$^{1)}$) (degree of hydrolysis 98-99%, viscosity 3.8-4.5 mPa·s$^{3)}$)	10.8	2.7	-
	Guar gum, non-ionic, commercial	0.9	0.2	SDS$^{5)}$
	Starch, cationic, cooked	2.1	0.5	SDS$^{5)}$
	CMF by Masuko collider device at VTT	2.8	0.7	SDS$^{5)}$
	Pre-refined softwood pulp from a Finnish pulp mill, SR° 19			-

1) dispersed with water and cooked below 100 ˚C until they were clear viscous solutions

2) of a 4% aqueous solution at 20 ˚C determined by Höppler-viscometer (DIN 53015)

3) of a 4% aqueous solution at 20 ˚C determined by Brookfield synchronized motor rotary type viscometer

4) CNF trials: The base paper was 80 g/m^2 uncoated and uncalendered fine paper produced from hardwood and softwood fibers without hydrophobic sizing agents with fast absorption properties. See Table 5. PVA trials: The base paperboard was 200 g/m^2 uncoated and uncalendered paperboard produced from recycled fibers with slightly slower absorption properties. Foam coating was done onto the grey side of the board.

5) The amount of added sodium dodecyl sulphate (SDS) was 0.2 vol-%. The chemical supplied by Sigma-Aldrich.

6) In the foam coating trials of dry web, it was named as PVA2.

Table 3. Characteristics of the base paper used in the foam coating trials.

Grammage g/m^2	Bulk cm^3/g	Gloss 75^o md	Roughness PPS, µm	Air permeance µm/Pas
80	1.2	5.8	4.9	5.8

Table 4. Native cellulose nanofibers used in the foam coating trials.

	CNF-CTP	**CNF-TE/CTP**	**CNF-TE/PTS**
Pre-treatment	Enzymatic	TEMPO oxidized	TEMPO oxidized
Homogenization	micro fluidizer by CTP	micro fluidizer by CTP	Cavitron by PTS
Solids content	2%	2%	9%
			
Gel type	opaque, viscous	transparent, solid	white, fluent
Zeta potentials	-25.0 mV	-69.5 mV	-55.5 mV

CNF, for the functionalized CNF trials, was produced by the Centre Technique du Papier, France (CTP). The enzymatic pre-treatment of cellulose fibers, followed by low consistency refining was first carried out. Then the pre-treated and refined fibers were disintegrated to nanoscale particles by running them through a homogenizer several times. The produced CNF, with a solids content of 2.3%, was then functionalized by INNOVHUB, Italy. For functionalization of the CNF, inorganic nanoparticles TiO_2 and ZnO were produced by Colorobbia, Italy.

Table 5. Physico-chemical characteristics of inorganic nanoparticles delivered by INNOHUB, Italy.

	±	TiO_2	ZnO
Concentration (%w/w)	0.5	6.0	1.0
Density (g/cm^3)	0.05	1.20	1.12
Viscosity (25°C) (mPa/sec)	0.1	2.00	ND
Particles Dimension (nm) (DLS Malvern Instruments)		40.0	45.0
Polydispersity Index	0.05	0.25	0.20
pH	0.5	1.0	ND
Cationic surfactant (%w/w)	0.05	0.1	-

The CNF functionalization was based on a direct physical adsorption of inorganic nanoparticles to CNF. The nanocomposites were prepared by mixing CNF (2.3% in water) with TiO_2 (6% in water) and/or ZnO (1% in ethylene glycol) for 15 minutes. The mixtures were washed three times with water after mixing, followed by centrifugation to eliminate not-adsorbed inorganic fillers. The mixing and washing were carried out as follows: CNF and inorganic nanoparticles suspensions were mixed together as supplied by an immersion mechanical blade stirrer for a few minutes. Centrifugations were performed and washings were carried out three times with water to eliminate excess TiO_2 or ZnO. After each washing a homogenization by stirring was carried out. The centrifuge took around two minutes to reach 7,000 rpm, which was then maintained for five minutes. After centrifugation, the water supernatant was discarded. The pellet was suspended in the same volume of fresh water that had been removed by ultracentrifugation and then mixed with the mechanical stirrer. For the trials 25 kg of CNF-TiO_2 (2.8% dry weight) and 15 kg of CNF-ZnO-TiO_2 (4.8% dry weight) were produced. The concentrations of TiO_2 and ZnO in the final nanocomposites were determined by ICP analysis. Table 6 shows the mixing ratios and the TiO_2 and ZnO contents of the prepared CNF composites.

Table 6. Analysis of CNF/inorganic nanoparticles suspensions (TiO_2 and ZnO determined by ICP analysis by INNOHUB, Italy).

Nano-composite	Solids content, %	Initial mixing ratio of the preparations (as dry weight)	TiO_2 content (% dry weight)	ZnO content (% dry weight)
CNF-TiO_2	2,8	1 : 1	24	-
CNF-ZnO&TiO_2	4,8	10 : 1 : 10	42	2

The foams were produced by mixing the foaming agent and CNF containing nanoparticles with pressurized air in the mixing head of the foam generator. The air content of the foams was adjusted to 80-90%, for a foam density of 100-200 g/l. The anionic foaming agent used was sodium dodecyl sulphate, SDS, in a ratio of 0.2% of CNF composite volume (The addition of a surface active agent is based on the liquid volume; due to the low solids of CNF, the liquid volume can be considered to be practically the same as the CNF composite volume).

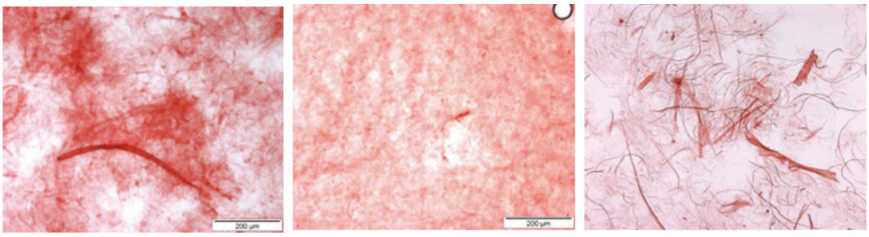
3.3 Materials in foam forming and foam assisted dewatering

The raw materials used in laboratory scale studies for the foam forming and foam assisted dewatering trials are shown in Table 7.

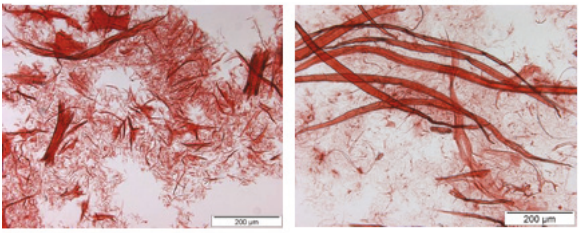
Table 7. The materials used in the foam forming and foam assisted dewatering trials and the characteristics of the pulps used in the foam forming trials**.**

Materials	Average fiber length, mm	Coarseness, µg/m	Shopper-Riegler, °SR/ Canadian Standard Freeness value, ml	Foaming agent
Foam forming				
Chemical pine	2.19	141.7	26 °SR	SDS
Chemical birch	0.91	101.9	26 °SR	SDS
Spruce-CTMP	1.60	220.3	566 ml	SDS
CMFs, see Figure 11.				SDS
Foam assisted dewatering				
Biosludge (pulp&paper mill)	Solids content 1.2%			SDS
Fennopol K1390				

Five different fibrillated celluloses with different degrees of fibrillation were used as strength additives in the foam forming studies. Commercial CNF Daicel Celish KY-100G was purchased from Daicel Fine Chemicals, Tokyo, Japan. The dry matter content of Daicel was around 10%. The VTT grades, fine and coarse, were manufactured by an ultra-fine friction grinder (Masuko Supermasscolloider) from bleached hardwood kraft pulp. They were ground to different coarseness levels by varying the number of passes of the material through the grinder. The coarse grade passed through the grinder three times and the fine grade eight times. The dry matter content of both fine and coarse grades was 3%. Two pre-commercial CNF samples manufactured on a pilot scale were obtained from the manufacturers. The samples are denoted by P1 and P2. Both samples had a dry matter content of 2%. Figure 12 shows the optical microscopy images of the samples.



VTT coarse VTT fine Daicel



P1 P2

Figure 12. Optical microscopy images of the fibrillated cellulose samples.

The characteristics available from the different CMFs are shown in Table 8. Kangas et al. (2014) have published an article describing the characterization methods and the characteristics (morphology, rheological properties, average size, size distribution, and the amount of the true nano-sized material) of these five mechanically manufactured fibrillated celluloses. They reported that the samples have very different properties and the phenomena behind their behaviour proved to be complex, and in their characterization, a combination of methods must be applied.

Table 8. The characteristics available from the nanofibrillated celluloses used in the studies.

Sample	Shear viscosity, mPas·s 10 rpm 1.5% conc.	Transmittance, % (800 nm, 0.1% conc).	Content of smallest fraction (FR4), %	Content of nanosized fraction, %	Visual appearance (optical microscopy)
VTT coarse	23176	34	3.5	5.6	Coarse/fine, few large fragments, slightly heterogeneous, film-like fibril network
VTT fine	22502	60	4.8	6.9	Fine, homogeneous, film-like fibril network
Daicel	15777	8	1.3	2.6	Coarse, long slender fibrils, heterogeneous, film-like fibril network
P1	3654	26	4.7	20	Coarse, large fragments, heterogeneous, porous and bulky fibril network
P2	2784	25	0	50.7	Coarse, unfibrillated fibers, heterogeneous, porous and bulky network

4. Methods

4.1 Foam coating

The foam coating trials were performed on a pilot scale to dry and wet paper.

4.1.1 Measuring of foam stability

The prerequisites set for the coating foam depend on several things like the methods used in foam destruction, coating speed and substrates to be coated. The foam quality must fulfil the requirements of the coating process and the coating target. These aforementioned issues set the requirements for the foam: its average bubble size, size distribution and stability. The basic requirement is that the distance between particles correlates with the size of the bubbles, meaning the smaller the bubbles, the closer the particles and after foam destruction the more uniform the coating. In our foam coating trials at the KCL pilot coater, foam was produced by a foam generator at floor level and was fed via a several meter long plastic hose to the foam applicator, five meters above, and applied on to the substrate. On its way to the applicator, the foam faced temperatures ranging from 15°C (the hose on the cold floor) to tens of degrees higher (influenced by the drying section). The controlling factors in foam productions are the back pressure (measured by the generator), foam chemistry, pumping speed and foam density. As we used a foam generator with a rotor-stator-mixing head, the rotation speed of the mixing head was also one of the factors. The length and the diameter of the hose affect the pressure inside the hose; therefore, different hose lengths of 3, 5, 7 and 10 meters were tested. The inner diameter of hoses was kept constant at 12 mm. The experimental set-up (Figure 13) was built to study the quality of the foam produced. Under the applicator a steel plate with a steep slope was placed so that the foam slid along a smooth surface after coming out of the applicator. The effect of foam temperature was tested by placing a part of the hose in a water tub containing cold (16.5°C) or warm (55°C) water, with the reference being the pilot plant ambient temperature of about 25°C. At some test points, the air content of the foam was also varied, from 90% to 94%. The foam stability tests were run using diluted 1% CMF dispersion and sodium dodecyl sulphate (SDS) as a foaming agent. The addition amount of SDS was 0.2% of the diluted CMF volume.

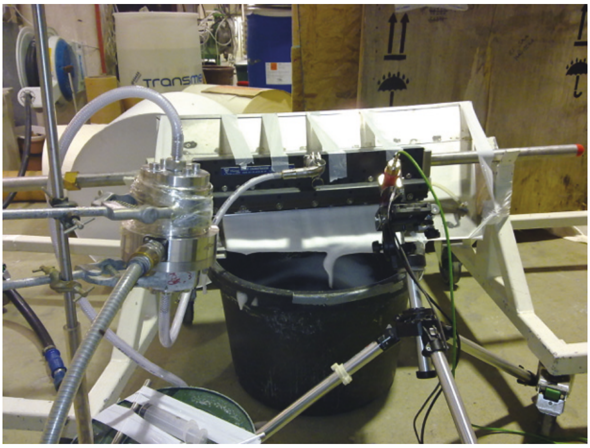


Figure 13. Experimental set-up for the measurement of the foam quality with analysing devices: Turbiscan online (left) and a high speed camera (right).

4.1.2 Foam coating trials to the dry web

The main components in a foam coating line are a foam generator and a foam applicator. Our trials used a Top-Mix type 60 foam generator manufactured by Hansa Industrie-Mixer GmbH & Co. KG, Germany (Figure 14). The unit has a chemical feeding capacity of 6–60 kg/h, and it can produce foam with density range of 50 to 400 g/l. The generator is connected to the compressed-air pipeline of the pilot plant. The coating material and foaming agents are mixed with pressurized air in a mixing head having a rotor-stator unit.

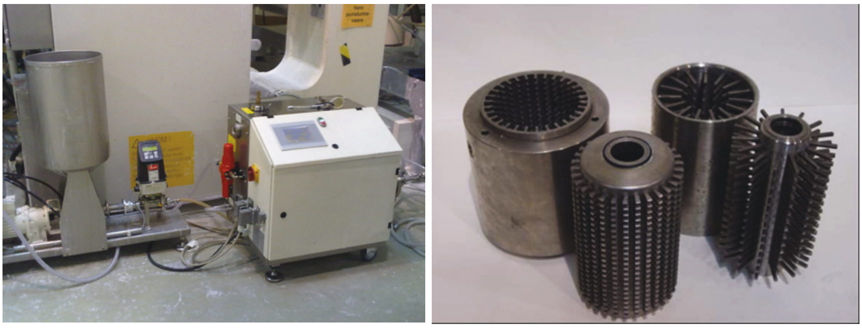


Figure 14. The foam generator (left) and examples of the mixing head's rotor-stator sets (right).

For the application of the foam to the paper web, a narrow slot type applicator, the Magnojet – MJ-Do manufactured by J. Zimmer Maschinenbau GmbH Klagenfurt, Austria, was employed and is shown in Figure 15. The applicator (left), originally designed for glue and paste applications, was modified for our purposes by the manufacturer. The application width is adjustable, the maximum being 600 mm. The foam enters the applicator chamber in the middle of the unit and the channels inside the applicator divide the foam flow enabling a uniform outflow of foam. The smaller applicator (right), with an adjustable application width of 160-250 mm, has chambers inside and foam enters in to both ends of the applicator.

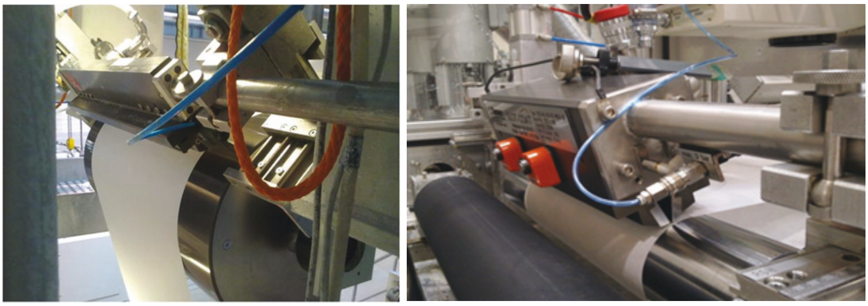


Figure 15. On the left the channel type applicator at KCL coater and the chamber type applicator at the VTT's SutCo line on the right.

The foam coating trials were conducted at the KCL pilot coater (Espoo, Finland). The maximum web width of the coater is 550 mm and the maximum speed is 3000 m/min (180 km/h) (Figure 16).

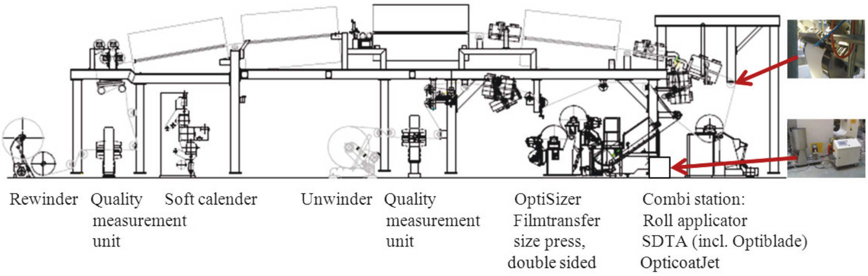


Figure 16. Schematic picture of the KCL pilot coating machine and the location of the foam generator and the foam applicator.

The drying capacity of the pilot coater is extensive with one electric IR preheater with a counter radiator, three electric IR dryers (two with a counter radiator and one with a reflector), and four gas-heated air floatation dryers. The coater fits well with the non-contact drying requirement of foam coating in nanomaterial applications. To ensure the foam curtain stability and stable foam application, the applicator was installed before the IR dryers. The existing web guiding roll was replaced by a precise backing roll with a 320 mm diameter in order to improve coating quality. The bigger diameter enabling longer contact area with the web would have been better, but the available space limited the roll size. We also tried a foam application position between the 2nd and 3rd air floats, but the air flow from the air floatation dryers disturbed the foam curtain by oscillating the paper web. In the trials the main drying of the web was performed using the IR dryers and the end moisture content of paper was controlled using gas-heated air floatation dryers. The line also has an on-line soft calendar with two nips. The maximum pressure available is 300 kN/m and maximum temperature 250 ^{o}C.

The coating speed used in the foam coating trials was typically 100 m/min. The lower speed was essential, due to the low consistencies of cellulose nanofibers, in order to obtain high enough coat weights. However, the maximum speed we have obtained so far with the KCL pilot coater is 400 m/min. In order to increase the speed and to improve the evenness of the coating layer, technical improvements are needed to remove the air coming with the paper web. In some applications we double coated the paper in order to increase the coat weight. This was done by returning the single foam-coated paper to the unwind position and the second coating layer was applied on top of the first layer. The pumping speeds of coating materials were 30–60 l/h, foam densities 100–200 g/l and paper web speed 100 m/min. The open cap between the applicator and the moving web was 300 µm. The coated paper was on-line calendered using a nip load of 100 kN/m, two nips and temperature of 55 ^{o}C. Base paper for the reference was calendered under the same conditions.

The trials of CNF functionalized with nanoparticles (ZnO and TiO_2) were performed at the Zimmer coating line in Austria. The chamber-type applicator was used in the trials. A 400 µm open gap between the slot and the moving web was used. The IR-drying with the dryers on both sides of the web was followed by drying with hot air ovens at a temperature of 150 ˚C. The maximum speed of the line is around 180 m/min, but the coatings were applied at 100 m/min. This coating speed allowed for the low consistency of the cellulose nanofibrils coating to achieve the desired coat weights, while at the same time providing enough speed to obtain a good quality coating layer. The applied coat weights in trials at Zimmer were 0.4 - 1.8 g/m^2.

The trials of paperboard, targeted to create a barrier layer with polyvinyl alcohol (named in the trial points PVA1) and ethylene vinyl alcohol (named in the trial points PVA2) foams were performed at a semi-pilot scale surface treatment line of the Technical Research Centre of Finland, VTT, Espoo. The line was manufactured by Coatema Coating Machinery GmbH, Germany. The trials were very preliminary trials testing the applicability of contact foam destruction. The target of the trials was to form a dense and pinhole-free PVA or EVOH coating layer on the board, which can be utilized as a pre-barrier layer of a multi-layer barrier structure or as a grease barrier packing material in short-term packaging solutions. In order to form a dense coating foam destruction needs to be done using nip pressure, which causes the foam to collapse and the formed liquid phase is forced into the structure by a pressure pulse. At the same time the applied surface layer will be densified. The foam was applied with the narrow Magnojet foam applicator to the paperboard, as in the non-contact method. The open cap between the slot and the moving web was 300 µm. After a short time delay between the application and the nip, the foam was destructed with the nip pressure formed by running the paperboard through a nip of two rolls, hard and soft. The coated paperboard web was then dried using the IR-driers and the air floatation dryers. Figure 17 shows the basic idea behind the method. The left figure is from our line with a short delay time between the application and the nip and the other figure is from our customer trial carried out earlier with a slightly longer distance between the application and the nip and with bigger rolls forming the pressure pulse.

Figure 17. In the contact foam coating method, the foam is applied as a foam curtain, but the foam destruction is accomplished with nip pressure. The left nip arrangement with small rolls is from the VTT line used in the thesis' trials. The right picture is an example from the customer trials.

The idea was to form a 'rolling foam band' in front of the nip and by controlling its size control the foam application. The controlling parameters were web speed, coating material pumping speed, foam density and nip pressure. As seen from the shape of the foam band, in our first trials, the coating profile was not even and technical improvements to our line are needed. Also the nip pressure should be known, in these trials it was controlled manually without any measuring device. The trial conditions were the following:

- Coating line running speed 20-40 m/min (maximum 90 m/min)
- material pumping speed 15-20 l/h to the foam generator
- foam density 100-150 g/l

In order to increase the coat weight in some trial points we double-coated the paperboard in the same way as in CNF applications done at the KCL pilot coater. The total applied coat weights of PVA and EVOH were 1.4-8.2 g/m^2.

4.1.3 Foam coating trials to the wet web

The wet web trials were performed at VTT’s pilot papermaking research environment at Jyväskylä. The narrow Magnojet applicator, with an adjustable application width of 160-250 mm, and the Hansa foam generator were used in the trials. The foam application was done above the high vacuum suction boxes (HiVac) (Figure 18), where the dryness level of the web was around 22.8% ± 0.4%.

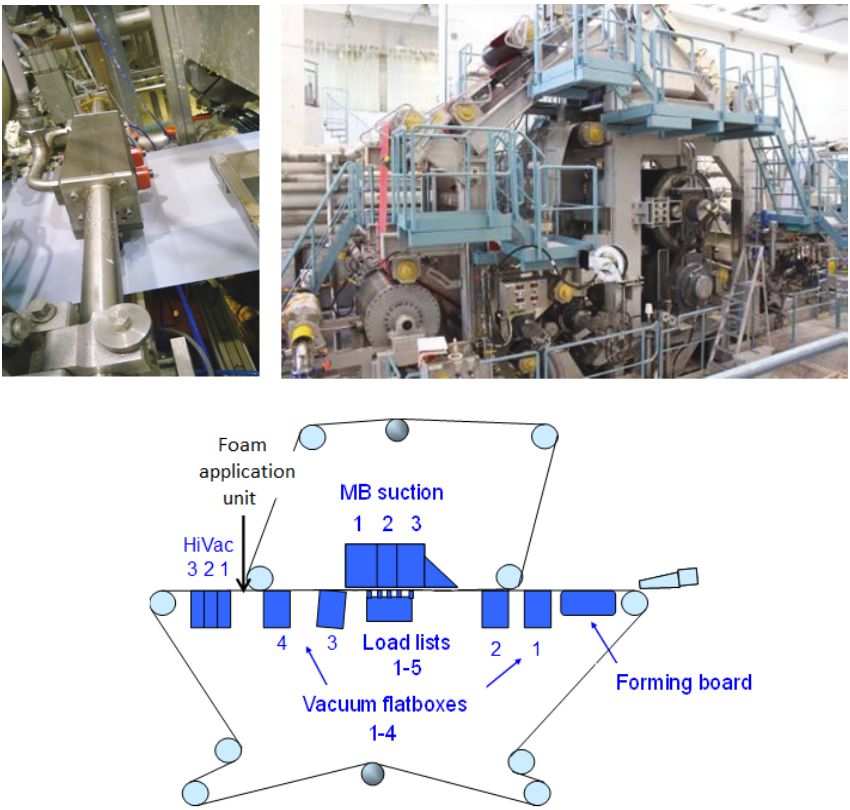


Figure 18. The foam applicator (top left), VTT’s papermaking research environment (top right) and a schematic picture of the addition point in the line (bottom).

The following process set-up was used in the trials:

- Headbox: Optiflow
- Former: Hybrid former
- Wet press: 1 shoe press: 400 and 1200 kN/m
- PM speed: 300 m/min
- Grammage**:** 80 g/m^2
- Material feeding speed to the foam generator: 55 l/h
- Foam density: 200 g/l, with PVA 300 g/l

The VTT research equipment can be run either as a loop returning the formed web back to the process, or taking wet web samples after the press section by reeling the wet web. The latter method was used in our trials. The experiments were performed using a ‘one after another’ procedure: the studied additive was poured in to the feeding tank of the foam generator, foamed, and after checking the foam quality the foam was applied to the wet web. The wet web sample was taken after the press section. The sampling lasted as long as the chemical foam was applied to the paper web. After sampling the web was led back to the pulper. A new chemical was changed into the feeding tank of the foam generator. In order to see the impact of the polymers on the wet web properties, taking into account the limits defined by the polymers (e.g. solids content), reasonably high amounts of the polymers were applied to the web. The addition amounts differed between the polymers, as well as the retention of the polymers, when the polymer foam was sucked through the web by high vacuum suction boxes. The addition amounts were calculated from the trial parameters: material solids content, material density, pumping speed of the foam generator, application width and web speed and the amounts are not the amounts retained in the web structure.

4.2 Foam forming

Laboratory and pilot scale trials were performed in the foam forming experiments.

4.2.1 Laboratory scale studies

In the laboratory scale studies foam laid handsheets measuring 38.5 cm x 26.5 cm (area 0.1 m^2) were made by the following procedure: foam was produced by stirring water and sodium dodecyl sulphate (SDS) as a surface active agent in a ratio of 0.15-0.2 g/l of water at 3500 rpm, as far as the air content of foam was 60-70%. The target air content of foam was determined by the foaming set-up; when the foam reached the target air content, the level of the foam surface did not rise anymore and the mixing started to decrease the bubble size of the foam. When the foam was ready a fiber suspension comprising refined chemical pine pulp, or chemi thermo mechanical (CTMP) spruce pulp was mixed with the prefabricated foam. The amount of added dry fiber content was 10 fold smaller than the target sheet grammage, e.g. addition of 6 grams’ dry pulp to the foam for 60 g/m^2 paper. Stirring continued until the target air content was reached again. In stable conditions the distances between fibrous particles in the foam remained constant and no flocculation happened. In CNF studies CNF amounts of 5% and 15% as dry of the dry pulp fiber content was mixed in to the pulp fiber foam. The fiber foam was decanted into a handsheet mold (a special design, adopted from the glass fiber industry) and filtrated through a wire using a vacuum (Figure 19). The wire was of the type conventionally used for water based forming. Then the wire and the handsheet formed thereon were removed from the mold and pre-dried on a suction table by use of an exhauster. The suction table has a suction slit, of width 5 mm, which sucks air through the sheet with 0.2 bar vacuum.

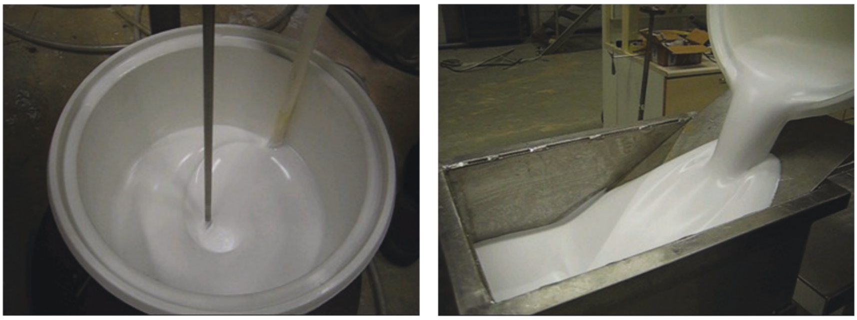


Figure 19. The procedure of the foam laid handsheet making. (1) An aqueous fiber suspension is mixed with a prefabricated foam produced from water and sodium dodecyl sulphate (SDS) in ratio 0.15-0.20g/L. (2) The fiber foam is decanted into the handsheet mould and filtrated through a wire using a vacuum chamber. The sheet is pre-dried on a suction table (0.2 bar vacuum).

The water formed handsheets were made and wet pressed according to ISO 5269-1 (2005-02-01) using a pressure of 400 kPa +/- 10 kPa as stated in the standard. The sheet size was 16.5 cm x 16.5 cm. The foam formed sheets were wet pressed using a couch roll either 1 or 10 times. The method is rather crude, but enables sheets with different bulk values. Part of the water and foam formed sheets was left unpressed in order to see the bulk potential. The couch roll used in wet pressing had a mass of 13.0 kg, length of 178 mm, and diameter of 102 mm as stated in the standard ISO 5269-1 (2005-02-01).

4.2.2 Dynamic semi-pilot scale studies

The dynamic water forming studies were carried out with a Short Circulation Device, and foam forming studies with the same device modified for foam forming (Figure 20).

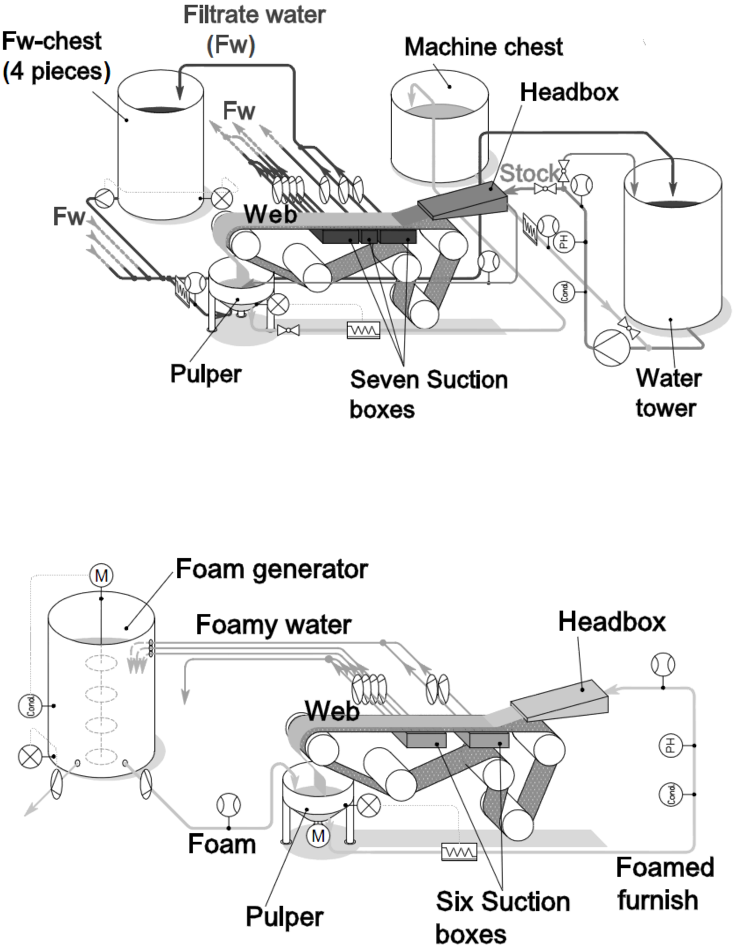


Figure 20. Schematic diagram of the water and foam forming process research environments. The foam forming environment was modified from the water forming environment.

The water forming environment consisted of one-sided dewatering with seven adjustable vacuum box elements. The width of the suction slot was 160 mm and the length of the suction slot was 10 mm. The volume of the machine chest was 0.5 m^3 and the water tower volume 1.0 m^3. The volumes in the white water chest varied between 0.1 and 0.8 m^3. A retention agent and filler feed systems were also included in the research environment. The monitoring of the chemical state of the process was done using online pH, conductivity, turbidity and temperature measurements. Dewatering velocities and vacuum levels were also measured in the forming section. The trials were run with an average forming speed of 210 m/min. The orientation level of web samples could be controlled by using a jet-to-wire ratio. In the current experiments the wire speed was constant and the speed of slice jet varied from 190 m/min to 263 m/min corresponding to jet-to-wire ratio values from 0.90 to 1.25. The surface velocity of the slice jet was characterized using a laser and a camera. The volume flow rate in the case of water-laid forming studies was measured by using an electromagnetic flow sensor. The average flow rate was 4.95 l/s for water-laid forming studies.

The foam forming process used in the trials was based on the tank generation of the process foam and recirculation of its flow. When upgrading the former into foam forming, a closed flow loop was built for the recovery, recirculation and refoaming of the process foam and foamy waters coming from the forming section (Paper VI). Dosing systems were also implemented for the surface active agent used in foam generation. The same suction boxes in the forming section were used for the drainage of process foam and foamy water as in the water process. The intensity of the process foam drainage level was adjusted using vacuums. A vacuum-assisted water separator and foam generator (a tank having a height of 1.28 m and a diameter of 0.59 m) were included in the flow loop. The average forming speed was changed from 36 m/min to 125 m/min corresponding to jet-to-wire ratio values from 3.0 to 0.9. The average speed of the slice jet was 110 m/min. The limited feeding capacity of the headbox feeding pump (not designed for air containing suspensions) and the headbox geometry used in the first version of the environment limited the usage of higher forming speeds.

The average flow rate was 2.5 l/s for foam-laid forming studies. It was measured using a scale and by defining the amount of foam suspension as a function of time, because electromagnetic flow sensors could not be used due to the high amount of dispersed air.

The raw materials were mixed with the process foam in a pulper. Sodium dodecyl sulphate was used as a foaming agent. The average surfactant dosage in the trials was 3 – 3.5 kg/tn. The average density of the process foam was 330 kg/m^3 ± 20 kg/m^3. The average mixer energy consumption per foam volume was estimated to be -7.4 kW/m^3, and per fiber weight was approximately 154 kWs/kg as estimated by average consistency. The characterized Sauter mean radius r[3,2] bubble size of the process foam was 58 µm (Lappalainen and Lehmonen, 2012). The quality of new and recovered process foam was controlled with conductivity measurements and mixing conditions in the foam generator were adjusted on the basis of these measurements. The process water amount and the conductivity of process foam were measured within the foam generator. According to earlier studies the air content of the foam correlates with conductivity measurements (Kruglyakov 1999; Weaire, Hutzler 1999). The average mixing speed of the foam generators' mixer was around 2000 rpm. In order to maintain the process stability, extra process water originating, e.g. from sealing waters used for the pumps and cleaning waters used for forming fabrics, was removed.

4.3 Foam assisted dewatering

Laboratory and pilot scale trials were performed in sludge treatment studies.

4.3.1 Static setup

Based on the dewatering results from the semi-pilot Short Circulation Device, we tested if the method is also applicable to dewatering other materials, for example biosludge from a paper mill. The first experiments were run using a static vacuum filtration set-up. The measurement arrangement is presented in Figure 21. It consisted of a funnel-based filtrate device, a scale and a filtrate bowl. The average vacuum level in the funnel was 0.5 bars. The effectiveness of dewatering was characterized by measuring the amount of filtrate as a function of time. The tested sludge was biosludge from a mill producing both pulp and paper. The test procedure was as follows: sludge, dry solid content of 1.2% was pre-treated with a flocculant, Fennopol K1390, addition amount of 5 kg/tDS. 200 g of flocculated sludge was poured into the funnel; on the top of the sludge 36 g foam (density 100 g/l) was dosed, which was made separately from water, surface active agent and pressurized air using a mixer; the surface-active agent was sodium dodecyl sulphate (SDS) the addition amount was 2.5 g/l; the sludge was drained through a filter. An example of the filtrate cake is shown in Figure 21. In the static studies, the filtrate was only analysed visually, without verifying the observations with analytical methods.

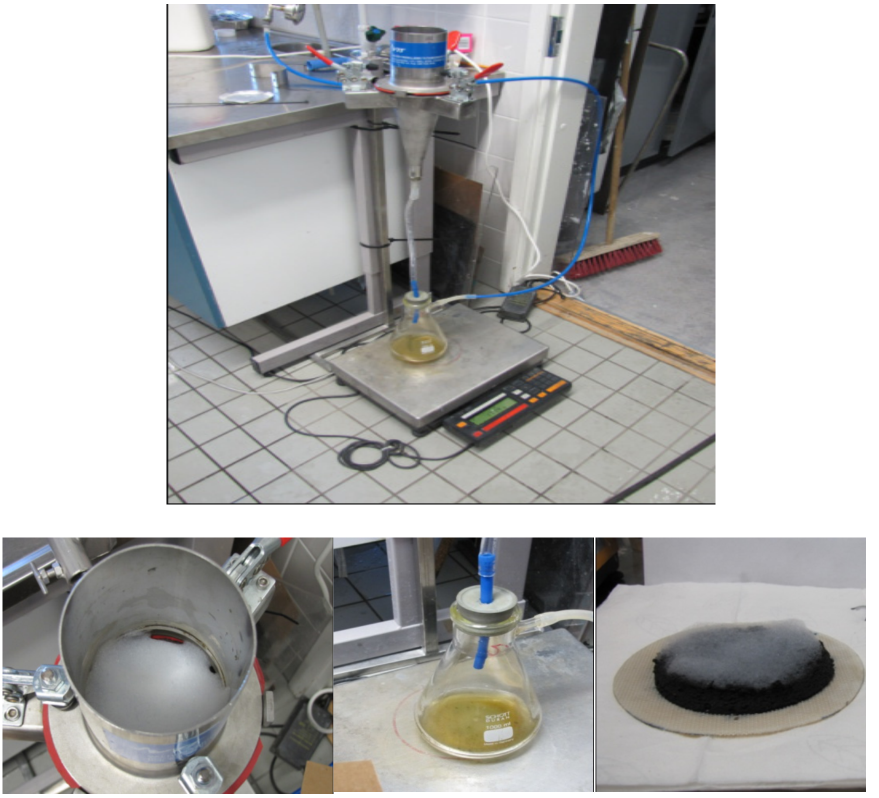


Figure 21. Foam-assisted dewatering (FAD) arrangement in the sludge dewatering studies: a funnel-based filtrate device, a scale and a filtrate bowl (top); foam layer on the top of the sludge (bottom, left) a filtrate bowl on the scale (bottom, middle), and an example of the filtrate cake produced by using a foam-assisted thickening method in the treatment of biosludge from a paper mill (bottom, right).

4.3.2 Dynamic setup

The results obtained in the static experiments were confirmed in dynamic conditions using a dynamic filter unit. The dynamic set-up is presented in Figure 22. The filter unit consists of a feeding chest, a feeding line with a feed pump, free and vacuum-assisted dewatering sections, an adjustable wire device and a unit for the filtrate collection. The lengths of the dewatering sections of different type were; free 90 mm, and vacuum-assisted 410 mm. The width of the sludge web was 95 mm. A low average vacuum level, of around 2kPa, was used in the sludge dewatering. Thus, in these conditions dynamic filtration was actually thickening due to insignificant vacuum pressure. For foam generation, the same foaming unit as in the foam coating trials was used. For foam application, an old headbox from a Short Circulation Device was used.

Figure 22. The dynamic set-up consists of a dynamic thickening unit and a foam generator.

In the first dynamic experiments, the focus was on finding the optimum foam application point and the application direction. Due to the high organic material and microbe content, biosludge is very perishable material and therefore a new batch was obtained from the mill. The sludge quality depends on the paper/board mill production, and that was also noticed; a little bit lower dosage of Fennopol K1390, 4 kg/tDS, was needed to produce proper flocculation. The polymer was dosed online before a headbox feed pump. Foam with an average density of 100 g/l was produced online from water, surface active agent and pressurized air by a foam generator based on a stator-rotor mixing system. SDS was used as a foaming agent, the dosage used was 2.5 g/l, as in the static studies. The flocculated sludge from the feeding chest was pumped to the filter cloth, and a foam layer was applied to the surface of the sludge web. The old headbox functioned as a foam applicator. As it was easily transferable, several application possibilities of applying foam on to the sludge web were tested during the thickening process in order to find the optimum foam application point. Due to the high foam pumping capacity of the foam generator (the material input to the foam generator is 6-60 l/h), the optimum foam amount was not possible to test. Therefore, a by-pass flow was constructed without any measuring devices in order to decrease the foam amount. This set-up enabled only a 'less – more' estimation of applied foam. In addition, the different application directions, downstream and upstream, were tested (Figure 23). For reference, the flocculated sludge was thickened without using the foam. The turbidity and dry solids content of the filtrates were measured for evaluation of the filtering results.

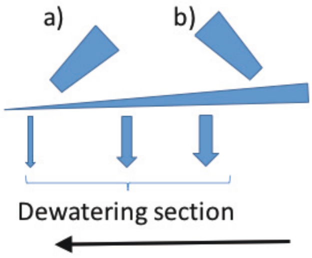


Figure 23. A schematic picture of the foam application methods. Applications were done before and at the dewatering section using methods 'downstream' (a) and 'upstream' (b) i.e. opposite direction applications.

Another test series was run with a new batch of biosludge based on the earlier results. The focus was on optimization of the flocculant dosage. The experiments were performed at two different levels, namely 0.95 kg/tDS and 1.9 kg/tDS. The polymer dosing, foam generation and sludge application were carried out as in the earlier tests. The position of the foam application was just before the dewatering section. For reference, the flocculated sludge was thickened without foam. The thickening results were evaluated by measuring the dry solids content of the filter cakes and the turbidity of the filtrates.

4.4 Characterization methods

4.4.1 Foam coating

4.4.1.1 Foam stability tests

Bubble sizes and bubble amounts were measured by means of photographs taken with a magnifying high-speed camera as the foam was coming out and sliding along a smooth surface. Photographs from only four test points were analysed, because of the laborious work. A Turbiscan Online (Formulaction; L'Union, France) measurement device was also installed between the foam generator and the foam applicator (Figure 13). The equipment uses multiple light scattering to measure average bubble size.

4.4.1.2 Foam coating of dry and wet web

Table 9 summarizes the characterized properties, equipment used and standards or methods from the raw materials and samples from foam coating trials.

4.4.2 Foam forming and foam assisted dewatering

Table 10 summarizes the characterized properties, equipment used and standards or methods from the raw materials and samples from foam forming and foam assisted dewatering experiments.

Table 9. The characterized properties of the foam coated substrates, used equipment and standards/methods, Papers I, II, III and IV.

	Property	Equipment	Standard/Method	Note
Coating of dry web, coated with				
CNF	Surface layer	Hitachi S-3400N scanning electron microscope (SEM)*)		
	Surface layer	Thermo Scientific’s Noran System Six EDX spectrometer.		
	Gloss (75°)	Elrepho2000	ISO 8254-1:2009	
	Air permeance	Parker-Print Surf (20 kPa pressure)	ISO 5636/1: 0-14 μm Pas	
	Roughness	PPS S10	ISO 8791-4:2007	
	Hydrophobicity	CAM 200 (Contac angle of water, 2 µl drop size)		
Func. CNF	TiO_2/ZnO element map	SEM/EDS *) **)		
	Antimicrobial activity			App. A
	Photocatalytic activity			App. A
PVA, EVOH	Pinhole			App. A
	KIT-test		Tappi T559 cm-12	App. A
	Grease barrier		Mod. TAPPI 507 T cm-09	App. A
	Grease barrier		Scanning method	App. A
	Water Vapour Transfer rate (WVTR)		Mod. ASTM E-96	App. A
Coating of wet web				
	Tensile strength, relaxation	IMPACT-fast tensile test rig		See 1)
	Internal bonding strength,	Huygen Internal Bond Tester	TAPPI T569 om-09	
	Moisture	Moisture analyser		

*) an S-3400N scanning electron microscope (SEM) (Hitachi; Tokyo, Japan) and Noran System Six EDX spectrometer (Thermo Scientific; Watham, MA, USA).

**) Data type: Counts, Image resolution 1024 by 1024, Image Pixel Size1.06 μm, Map Resolution 256 by 256, Map Pixel Size 4.24 μm, AC Voltage 12.0 kV, Magnification 100.

Table 10. The characterized properties of the samples from foam forming and foam assisted dewatering trials, used equipment and standards/methods, Papers V, VI and VII.

	Property	Equipment	Standard/Method	Note
Web forming				
Pulps	Average fiber length	Fiber Quality Analyser (Fiber-Master)		
	Coarseness, [µg/m]	Fiber Quality Analyser (Fiber-Master)		
	Schopper-Riegler value		ISO 5267-1:1998	
	Canadian Standard Freeness value		ISO 5267-2:2001	
Paper	Grammage		ISO 536:1995	
	Thickness		ISO 534:1998	
	Density, bulk		Calculated from grammage and sheet thickness	
	Tensile strength	Lloyd tensile tester	ISO 5270:1998	
	z-strength		ISO 15754:2009	
	Internal bonding strength, modified Scott bond	Huygen Internal Bond Tester	TAPPI T569 om-09	
Foam assisted dewatering				
Biosludge	Dry solids content [%]			
	Weight, cake [g]			
	Weight, filtrate [g/s]			
	Turbidity [NTU]	Hach 2100AN IS Turbidimeter	ISO 7027	

In addition to the above-mentioned analyses, the following analyses were used:

- The IMPACT-fast tensile test rig (Figure 24) was used for paper tensile strength and relaxation tests. The strain rate used was 1 m/s. The relaxation tendency of wet paper was estimated by straining the paper to 2% elongation followed by 0.475 seconds of relaxation. In addition to the tensile- and relaxation test instrument, an essential instrument in the test procedure was a moisture analyser, with which the dryness of wet paper samples was measured after tests. Z-direction strength (Scott-bond Internal bonding strength, modified Scott, J/m², Huygen Internal Bond Tester) was measured according to TAPPI T569 om-09.

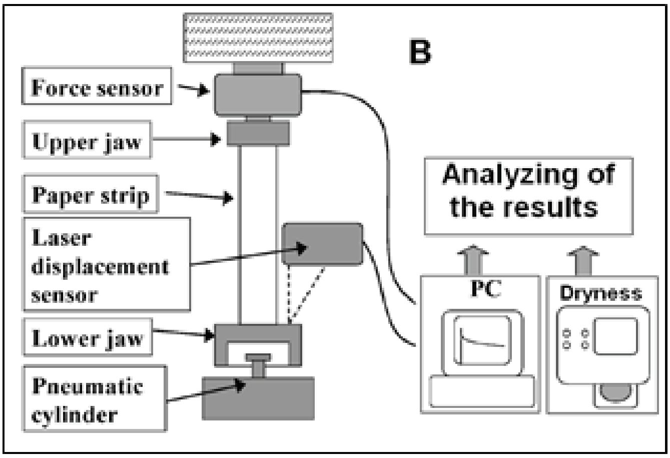


Figure 24. Schematic illustration of IMPACT -fast tensile- and relaxation test rig (Salminen, 2010).

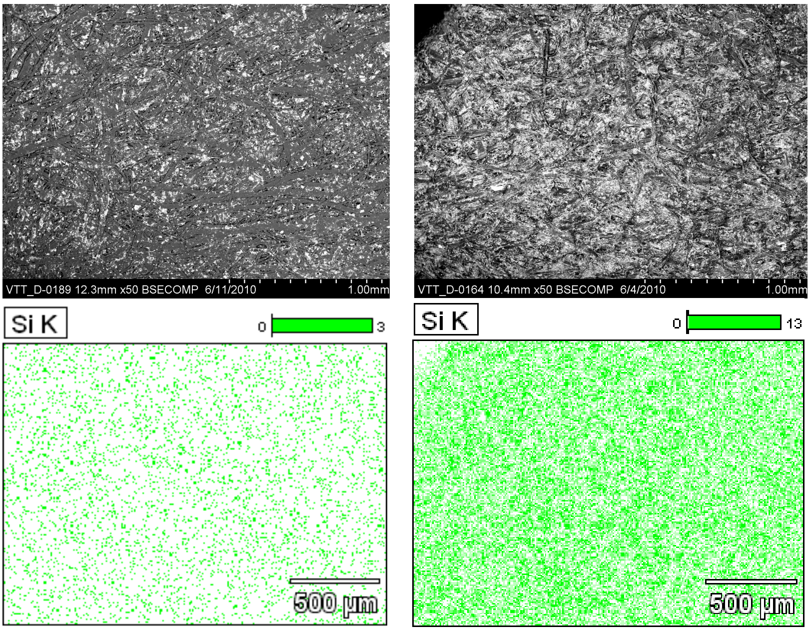
- **Formation**: Based on the β-formation measurement for the current study, a storage phosphor screen (SPS) was exposed to β-radiation through the paper sample, with Carbon-14 as the radiation force. This was done in order to evaluate the radiation absorption map. Thereafter, the screen was scanned with a Fuji BAS-1800 II SPS reader. Then, the measured values were converted into a grammage map. The size of the scanned area was 100 mm x 100 mm and the scanning resolution was 100 µm. Following this, the resolution was transformed to the Ambertech resolution (Ø 1 mm). The characteristics of the nanofibrillated celluloses were delivered with the samples.
- **Pore network**: The x-ray microtomography images of water and foam formed CTMP samples were done and analysed in the Department of Physics University of Helsinki, Helsinki, Finland (Prof. R. Serimaa, V. Liljeström).

5. Results and discussion

5.1 Foam coating

In dry web applications, typically performed at coating machines or at the drying section of paper machines, dry foam with an air content greater than 80% (foam density < 200 g/l) and preferably 90–95% (foam densities 50–100 g/l) is used. The trials of this thesis were done using a method resembling a curtain method; foam performs as a foam curtain, with a height of a few hundred microns, between the foam applicator and the fiber web. After the foam application foam destruction, the mechanical breaking down of the foam on the paper sheet or board can be achieved in several ways. In the non-contact method, the foam collapses through absorption of the paper web and through infrared (IR) drying. This method is especially suitable for small application amounts with hydrophilic substrates with fast absorption properties. In a contact method foam collapses due to a pressure pulse. This can be done by means of e.g. a blade or rolls. The pressure pulse, which causes the foam to collapse, forces the formed liquid phase to flow into the sheet structure. At the same time the applied surface layer will be densified.

The main requirement for successful foam coating is a proper foam. The foam stability across the process (from the foam generator via the foam applicator to the substrate surface) is the most important property, besides the bubble size and bubble size distribution, in order to get an even, thin coating layer. What a proper foam for the process depends on many things, e.g. technology solutions used in the process and its dynamics like velocity, foam chemistry and materials to be applied to a web. SEM-EDX element maps of coated and uncoated paper surfaces from our earlier foam coating studies show the silica nanoparticle layer covers the paper surface uniformly (Figure 25). Silica pigments in the foam coating trials were commercial Bindzil (Eka Chemicals AB; Bohus, Sweden) water-based colloidal solutions in which the main component is silicon dioxide (Kenttä et al., 2014).



Fine paper (Si-element map) Foam coated (Si-element map)

Figure 25. SEM-back scattered electron (BSE) image of 50 x magnification and silicon (Si)-element map of base fine paper (left) and silica-foam-coated paper (right). The images show that the silica nanoparticle layer covers the paper surface uniformly.

5.1.1 Foam quality

In the foam coating process the most important prerequisite is foam stability. The back pressure measured by the generator and the visual appearance of the foam, in the transparent plastic hose feeding the foam from the generator to the foam applicator and in the gap between the applicator and the substrate, are practical indicators of the stability of the foam. However, in development phases more sophisticated methods are needed, and for that an experimental set-up for stability measurement was built. Our measurements showed that when the foam quality fulfills the process demands, the foam is rather insensitive to changes in process conditions, such as foam temperature and pressure. The required foam, especially in dry web coating, has to be stable and have a narrow bubble size distribution with average bubble diameter around 100 µm. In our study we used SDS as a foaming agent. Figure 26 shows the results obtained from high speed camera photos; the values were calculated as average values of temperature test points. As the method was quite laborious, only four test points were analysed: 3m90%, 5m90%, 10m94% and 10m90%. The first number is the length of the hose and the second the air content in the foam. The temperature was the ambient temperature.

According to the results, the smallest bubbles and the narrowest bubble size distribution were obtained using a three-meter long hose and 90% air content.

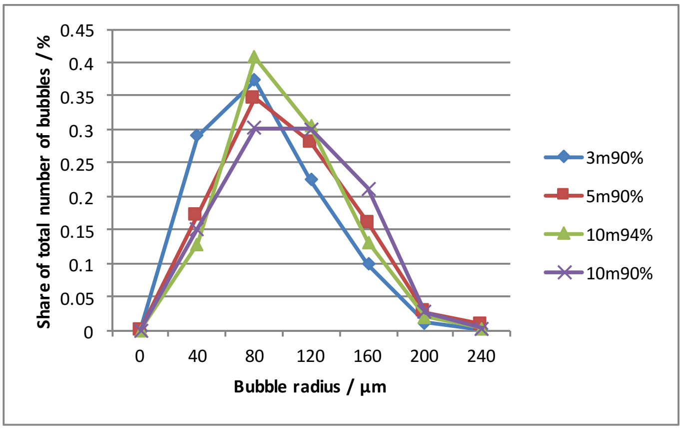


Figure 26. The measured bubble size distributions. The first number appearing in the legends is the length (m) of the used hose and the second number the foam air content (%). The vertical axis shows the share of total number of bubbles (%) as a function of bubble radius (µm).

The values were compared to the data obtained using Turbiscan on-line equipment (Table 11). The increase in hose length and temperature increased average bubble size. However, it was difficult to conclude if the differences were real or only due to the scattering of the data. In any case, the differences in bubble sizes were rather small. The results also showed that the stability of the foam could be measured using devices based on light scattering.

Table 11. Average bubbles sizes measured with Turbiscan Online and image analysis.

Test points (length of the hose, air content, temperature)	Bubble size, µm Turbiscan	Bubble size, µm from images
3m, 90%	75	68
3m, 90%, 16.5 ˚C	75	
3m, 90%, 55 ˚C	80	
5m, 90%	81	84
7m, 90%	86	
10m, 90%	88	88
10m, 94%	80	81
10m, 90%, 16.5 ˚C	78	

Besides bubble size and bubble size distribution, a critical foam property is the stability of the foam. In general, the stability of aqueous foams can be characterized by determining the time elapsed after cessation of mixing to when the liquid volume reaches half of its initial height (Lappalainen et al., 2014). However, when the air content is high, 80-95%, the half-life time can be hours or days, especially if the foam contains stabilizing particles. Based on our work, the best indicator of foam stability is the back pressure value measured by the foam generator. The more stable the foam, the higher the back pressure value, because the process resists movement of the foam. A liquid like foam is easier to pump forward, which can be seen with lower back pressure values. The variables that result in an increase in back pressure are: increasing hose length between the foam generator and the applicator, decreasing diameter of the hose, higher surfactant amount, and higher air content in the foam.

5.1.2 Improvements of surface using native cellulose nanofibrils

The possibility of using high viscosity materials in foam coating is a remarkable advantage. For example, CNF is already a very viscous, gel-like material in low solids contents like 2%. The nano sized cellulose fibrils have a high aspect ratio (length to width ratio), typically the width of fibrils is 5–20 nanometres and the length ranges widely from 10's of nanometres to several microns. The more nanoscale particles present in the CNF material, the more viscous and transparent the material. CNF is applicable as such in foam technology. However, due to the high viscosity of CNF even at low solids content, the use of CNF in spray technology requires significant dilution. This demonstrates a significant difference between spray and foam technologies in the amounts of water applied to the paper. In Figure 27 CNF of 2.9% solids content (left) did not flow by itself into the screw pump, but the generated foamed CNF with an air content of 90% (right) was a suitable material for the coating process.

Figure 27. CNF with solid content 2.9% (left), foamed CNF containing 90% air (right).

A native CNF layer was applied to the uncalendered fine base paper surface. The coat weights were rather low, 0.1 to 1.0 g/m2, due to the low solids content of unmodified CNFs. Since a higher amount of CNF coating was applied, it was possible to determine the coat weight by measuring the weight difference between the base paper and the coated paper; otherwise the coat weight was calculated from the trial parameters: pumping speed, application width, starting concentration and web speed. The coat weight obtained with a single layer coat was 1 g/m2 or less and for double coating from 1.0 g/m2 to 2.6 g/m2 (Figure 28).

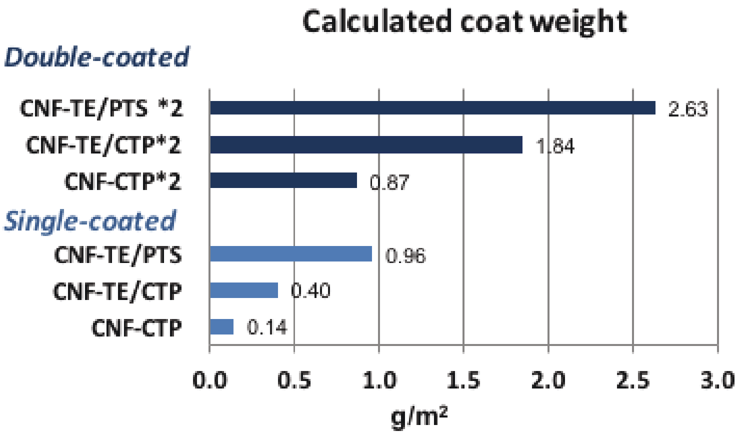
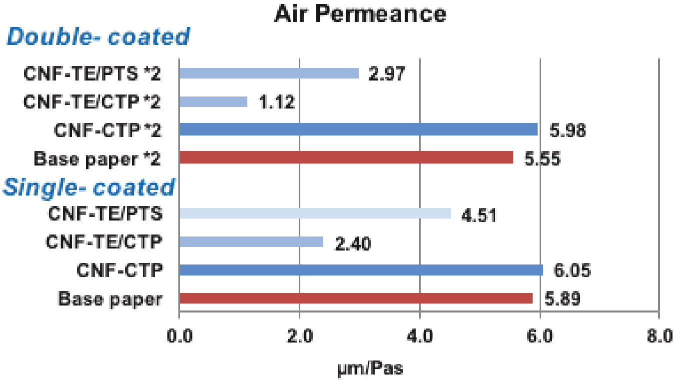


Figure 28. Coat weight of CNF coating in single- and double-coated samples (*2).

The test results show (Figure 29) that the surface properties of fine base paper were changed with a very thin layer of unmodified CNF having a coat weight of approximately 0.5 g/m^2. Air permeability was decreased with TEMPO CNFs (2,2,6,6-tetramethylpiperidine-1-oxyl CNFs) and in the case of micro fluidizer CNFs the coated paper surface was smoother compared to the base paper. The smoothing influence was obtained in small scale roughness (PPS S10), the values of which show that the smoothest surface is obtained with a CNF-TE/CTP coating. Smoothing is already obtained with a coat weight of below 1 g/m^2. The CNF-TE/PTS coating did not smooth the surface, probably due to a bigger particle size in the CNF-TE/PTS. Air permeance values show that CNF-TE coatings, especially CNF-TE/CTP, make the paper surface more closed.



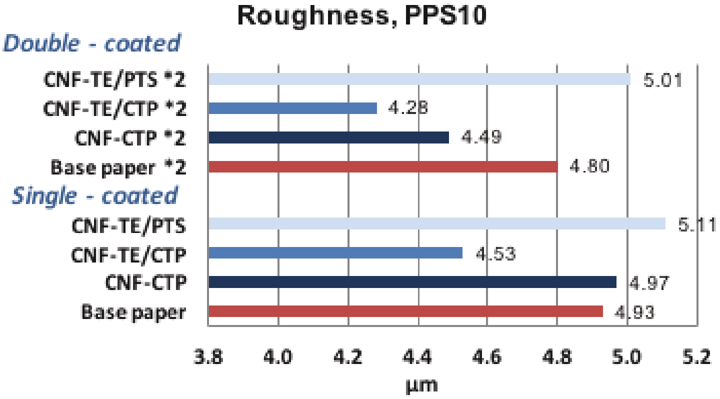


Figure 29. Air permeance and PPS-S10 Roughness values of base paper and CNF coated samples.

The unmodified CNFs also increased paper surface hydrophilicity. Figure 30 shows the contact angle values of base paper and foam coated samples using water as the fluid. The paper surface was more hydrophilic after CNF coating; an exception was the enzymatic pre-treated CNF-CTP sample. As might be expected after double coating, the effect of CNF coating was stronger than after single coating. CNF with TEMPO oxidized pre-treatment had a stronger influence than CNF with enzymatic pre-treatment.

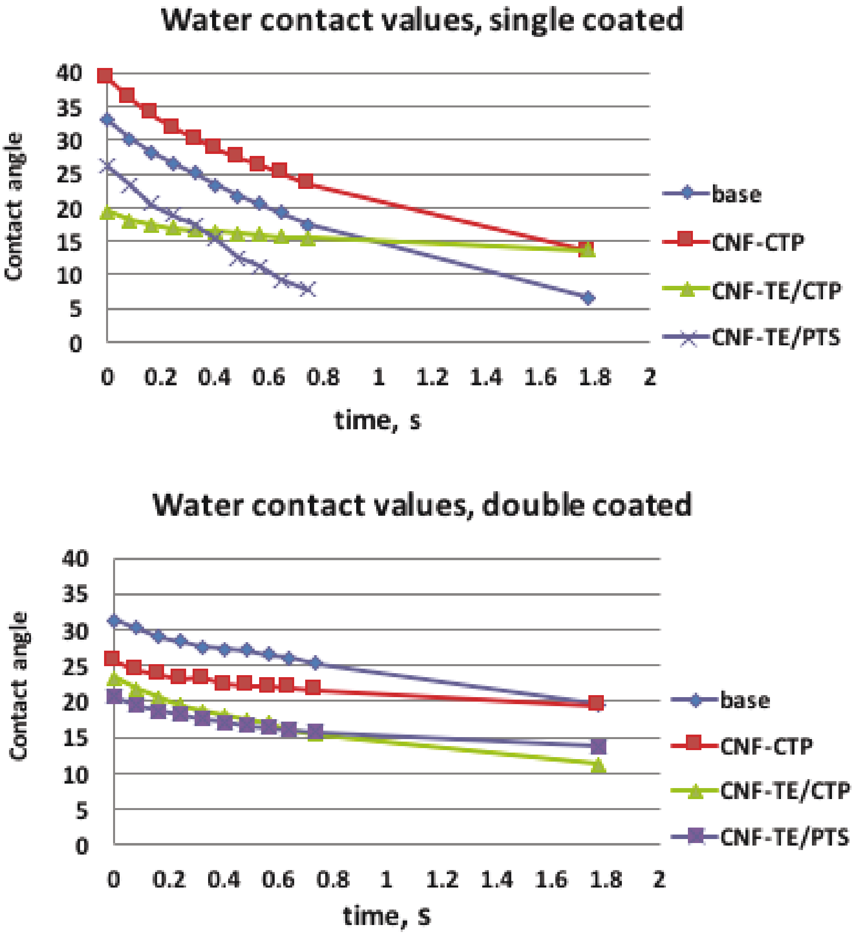


Figure 30. Water contact angle values of single- and double-coated papers show that unmodified CNFs increased paper surface hydrophilicity.

The paper surface structure of double CNF foam coated paper after on-line calendering was analysed with scanning electron microscope (SEM) imaging using a secondary electron (SE) detector. Surface images were compared to the base paper (Figure 33). The nanocellulose coating of CNF-TE/CTP did not clearly stand out in the SEM images of 100 x magnification, but the CNF-coated surface looks more opaque than the base paper surface. According to the SEM image the CNF coating has evened out the paper surface and reduced the surface porosity.

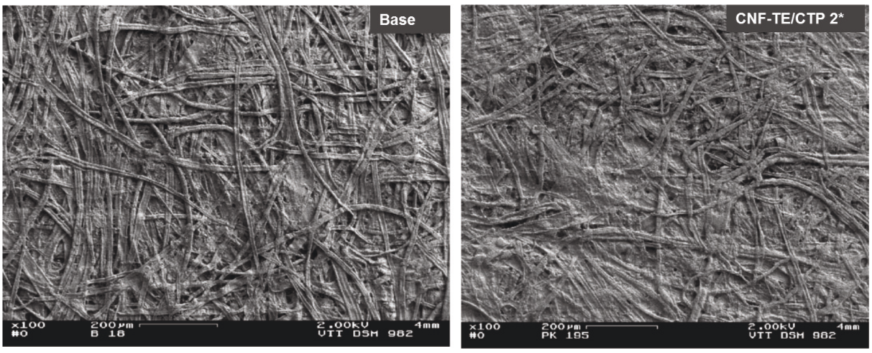


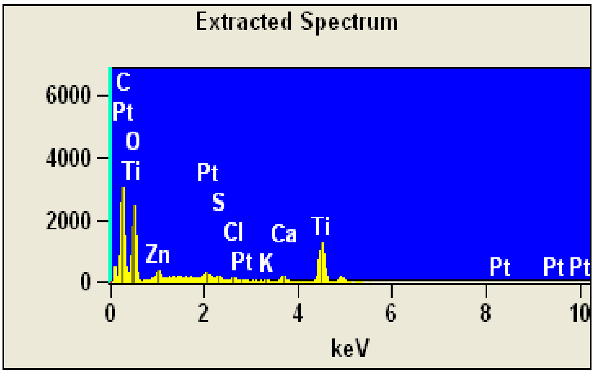
Figure 31. Topographic image (SE-SEM) of base paper (left) and CNF-TE/CTP double-coated paper (right). Magnification 100x.

5.1.3 Functionalization of paper surface

Materials used to functionalize paper surface are usually very expensive. For that reason, foam coating offers an excellent opportunity by providing a method of applying a small amount of material uniformly to the paper surface. The aim in the study was to obtain an antibacterial and photocatalytic surface on the paper. The photocatalytic properties of TiO_2 were first discovered forty years ago (Fujishima, 1972). TiO_2 is also a photoactive material with the ability to promote oxidation of organic adsorbates at the surface due to photogenerated electron-hole pairs after UV irradiation (Schiavello, 1997; Beydoun et al., 1999). The optical activity of TiO_2 has also been intensively exploited in the field of heterogeneous photocatalysis and solar energy conversion. Moreover, extended studies have been carried out on the photodegradation of volatile organic compounds. More recently, there has been great interest in TiO_2 as a photoactive antimicrobial agent. In addition, the antimicrobial properties of zinc oxide were considered to be of interest (Jehad and Enas, 2012). In this study the photocatalytic and antimicrobial properties of TiO_2 and ZnO were exploited for the first time in CNF-based products by the foam coating of paper.

5.1.3.1 TiO2 in foam coated paper

The TiO_2 was analyzed from functionalized CNF containing papers SEM imaging using BSE-detector and titanium element mapping. Titanium element maps show that the material on the paper surface is attached on the fiber surfaces to form a structure that resembles a honeycomb structure (Figure 32). This structure is an example from an unsuccessful foam coating trial where the used foam has not been stable enough and had time to form bigger bubbles.



4ZnO(12)

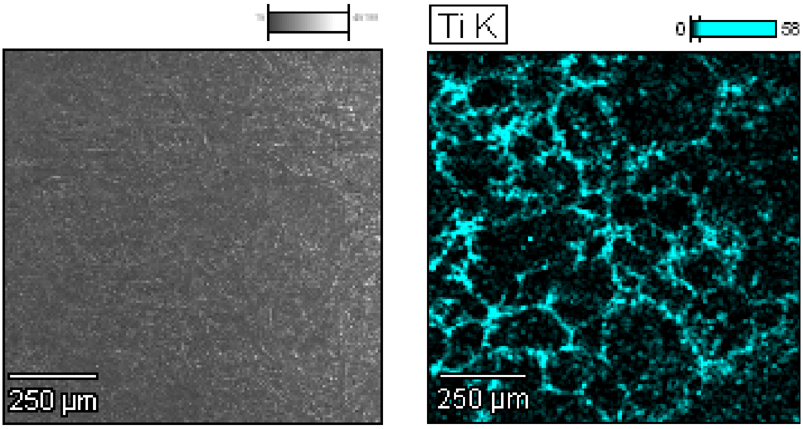


Figure 32. Titanium element SEM/EDS maps (magnification 100x) from calendered TiO_2/ZnO modified CNF containing paper.

5.1.3.2 Antibacterial Activity of the Foam-Coated Papers

The antibacterial activity was tested under both light exposure and dark conditions. *Staphylococcus aureus* and *Klebsiella pneumoniae* were used as test bacteria. Table 12 reports the results obtained with the different paper samples (logarithmic reduction of the number of living cells) for tests run under light exposure conditions. CFU, the number of living cells in the extracted suspension, was evaluated by the count plate agar method. Bacteria grown on untreated reference was 10^6 – 10^7 CFU (6-7 log).

Table 12. Antibacterial activity of foam-coated paper samples under conditions of light exposure.

Paper samples (coat weight)	ZnO ppm	TiO_2 ppm	*Staphylococcus aureus*		*Klebsiella pneumoniae*	
			Bacteriostatic activity (log reduction)	Bactericidal activity (log reduction)	Bacteriostatic activity (log reduction)	Bactericidal activity (log reduction)
Untreated paper	-	-	0	0	0	0
CNF-TiO_2 (0.4 g/m^2)	-	340	0	0	0	0
CNF-TiO_2 (0.9 g/m^2)	-	1670	1.3	0	0	0
CNF-TiO_2 (1.8 g/m^2)	-	2910	Total bacteriostatic	1.0	1.8	0
CNF-ZnO&TiO_2 (0.6 g/m^2)	38.4	1150	0.7	0	0	0
CNF-ZnO&TiO_2 (1.3 g/m^2)	104.6	3070	Total bacteriostatic	0.1	0.2	0
CNF/ZnO (0.8 g/m^2)	180	-	Total bacteriostatic	0.3	2.1	0

Significant antibacterial activity was obtained for paper samples treated by CNF-TiO_2 for TiO2 contents around 2910 ppm (0,3%), while for paper treated by CNF-ZnO a much lower 180 ppm (0,018%) inorganic filler content was needed to obtain similar effects. In general, bacteriostatic activity was obtained (inhibition to bacteria proliferation), while bactericidal activity (bacteria killing-reduction of initial inoculated cells) was not detected with these amounts of inorganic particles. For CNF-TiO_2 foam-coated papers bacteriostatic activity was also demonstrated under dark conditions with respect to *Staphylococcus aureus*, as reported in Table 13. The results show that under dark conditions TiO_2 or ZnO modified CNF coated papers had only a slight effect on bacterial growth, i.e. they need light exposure in order to show antibacterial activity.

Table 13. Antibacterial activity of foam-coated paper samples under dark conditions. Bacteria grown on untreated reference was $10^6 – 10^7$ (6-7 log).

Paper samples	ZnO ppm	TiO_2 ppm	*Staphylococcus aureus*	
			Bacteriostatic activity (log reduction)	Bactericidal activity (log reduction)
Untreated paper (control)	-	-	0	0
CNF-TiO_2 (1.8 g/m^2)	-	2910	1.7	0
CNF-ZnO (0.8 g/m^2)	180	-	1.2	0

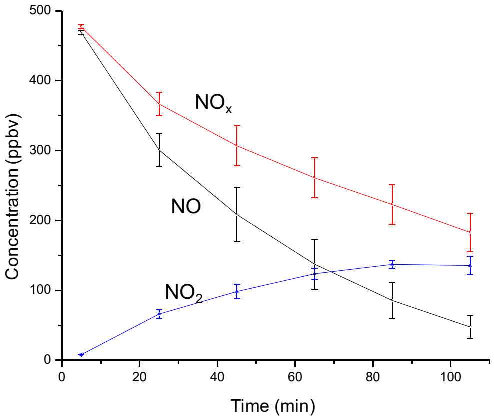
5.1.3.3 Photocatalytic Activity of the Foam-Coated Papers

Photocatalytic efficiency of the paper samples foam-coated by nanocomposites: CNF-TiO_2, CNF-ZnO, CNF-ZnO&TiO_2 are reported in Table 14.

Table 14. NO and NOx degradation by foam-coated papers.

Sample (coat weight)	ppm ZnO dry weight on paper (ICP analysis)	ppm TiO_2 dry weight on paper (ICP analysis)	% NO degradation after 105 min	% NO_x degradation after 105 min
Untreated paper	-	-	0	0
CNF-TiO_2 (0.4 g/m^2)	-	80	16.8	12.6
CNF-TiO_2 (0.9 g/m^2)	-	1670	72.6	46.0
CNF-TiO_2 (1.8 g/m^2)	-	2910	79.9	61.6
CNF-ZnO&TiO_2 (0.6 g/m^2)	38.4	1150	81.7	64.9
CNF-ZnO&TiO_2 (1.3 g/m^2)	104.6	3070	90.9	78.5
CNF/ZnO (0.8 g/m^2)	180	-	0	0

The results show that paper samples foam-coated by nanocomposites containing TiO_2 display photo activity for the degradation of volatile compounds at a TiO_2 content higher than 1150 ppm (0.1%). On the contrary, ZnO presence seems to have little influence on the photo activity of the paper. Photo-oxidation of volatile substances depends only on the TiO_2 content of the paper. The NOx photo degradation in gaseous phase by CNF-TiO_2 foam-coated paper is shown in Figure 33. Within 100 minutes, around 70% NOx oxidation occurred, this shows that foam-coated paper with CNF-TiO_2 had a significant effect on the oxidation of NO and NOx. In a coat weight of 0.9 g/m^2, the corresponding TiO_2 dry weight on paper was 0.162% (1620 ppm), this was enough to have an influence of 72.6% NO degradation after 105 min.



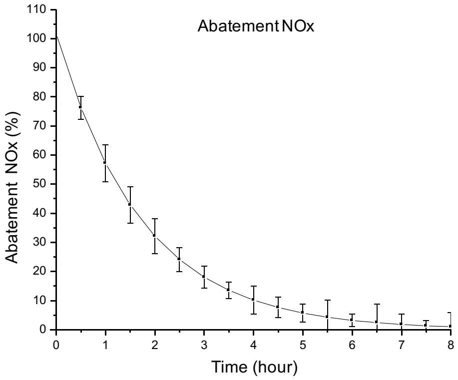


Figure 33. The NOx photo degradation in gaseous phase by CNF-TiO2 foam-coated paper. Note: coat weight below 1 g/m^2.

Photo-oxidation of NOx has important applications for the control of air pollution. In the case of active paper, it could be used for wallpaper, for example, for the control of indoor pollution. However, the photo-oxidation by TiO_2 can also work to oxidize/breakdown volatile organic compounds (not only for inorganic materials such as NOx), for example formaldehyde or other air pollution organic compounds (acetaldehydes, etc.) or it could be used in packaging systems to breakdown ethylene produced by fruits, which is responsible of ripening and fast spoilage of fruits and vegetables.

No related articles for the evaluation of the antimicrobial and photocatalytic results of foam-coated paper with CNF-TiO_2 and/or ZnO were found. The antimicrobial properties of paper have been created using different materials, like chlorhexidine or polyhexamethylene biguanide (BHMB) in the range of about 0.25% to about 3% by total weight of the antimicrobial currency paper web impregnating paper (Krupnick, 1998). The mentioned application methods varied, e.g. BHMB impregnation or the use of nanosized TiO_2-impregnated zeolite in a microparticle retention system in a wet end application (Ko, 2008). In the latter case the photo catalysis of sheets was evaluated with toluene used as a representative example of one VOC among indoor pollutants.

5.1.4 Barrier properties with foam coating

The target was to form a dense and pinhole-free coating layer on the board, which can be utilised as a pre-barrier layer of a multi-layer barrier structure or as a grease barrier packing material in short life-time packaging solutions. We applied polyvinyl alcohol (PVA) and ethylene vinyl alcohol (EVOH), which are commonly used to give grease barrier properties, to the paperboard. The cooked PVA and EVOH had solid contents of 6,8% and 16,0% respectively.

Compared to spray and film transfer, which are examples of other methods used in barrier applications, foam has several benefits, e.g. it is possible to use higher concentrations than in the spray method and it is more flexible and simple than film transfer as mentioned in Chapter 2.2.1.

5.1.4.1 Trials

The trials of paperboard with PVA and EVOH foam were performed at the semi-pilot scale surface treatment line (SutCo) of the Technical Research Centre of Finland, VTT, Espoo. The foam mechanical breakdown was done using a contact method, where foam collapses due to a pressure pulse formed by roll nips. The applied coat weights were a few grams, in single coatings below 4 g/m^2 and in double coatings up to 8.2 g/m^2.

5.1.4.2 Pinhole test (Appendix A)

In order to select proper samples for the barrier tests, the pinhole test was performed. The best results in the pinhole test were obtained with the double-coated trial points, which had either 3.0 g/m^2 of PVA1 or 8.2 g/m^2 of PVA2. No (or very few) pinholes were seen and thus those trial points were selected for further testing.

5.1.4.3 KIT-test

The KIT-test is not intended to determine the permeability of grease through the paper or board, but it gives some information about surface changes. The results from the foam coated samples were clearly improved and at the dewatering section using methods ‘downstream’ (a) and ‘upstream’ (b) i.e. opposite direction applications.

Another test series was run with a new batch of biosludge based on the earlier results. The focus when the board was coated with polyvinyl alcohol (maximum KIT value 12):

- Base paper/board: KIT-value 0
- PVA1 coated, coat weight 3 g/m^2: KIT-value = 7
- PVA2 coated, coat weight 8 g/m^2: KIT-value = 8.

5.1.4.4 Grease barrier tests

The grease barrier was tested first according to the standard (4h at 60ºC). The untreated base had no barrier and thus grease easily penetrated through, but with the coated samples that received good pinhole test results and KIT-values much better grease barrier properties were gained (Figure 34, top).

The promising results from the standard grease barrier test were verified with the modified grease barrier method. A grease barrier test with a scanning method was performed in order to see how quickly the grease penetrates into the untreated base material. Also the target was to find out how long the foam-coated samples can resist the grease. The test lasted 98 hours (= 4 days+ 2 hours). It was seen that the grease penetrated into the untreated base very quickly (Figure 34, bottom). After 30 minutes 30% of the sample area was covered with grease, and 50% after 3 hours, whereas the PVA-coated samples resisted the grease penetration throughout the test period of 98 hours.

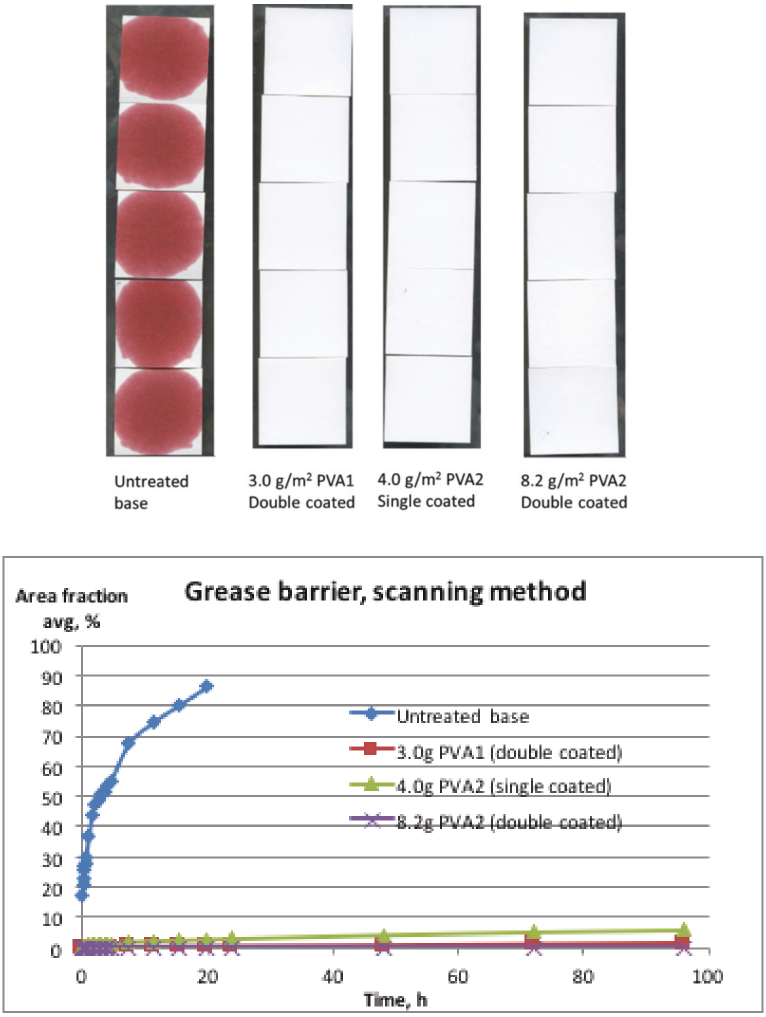


Figure 34. Results from the grease barrier test (4h at 60ºC). Tip: KIT test, bottom: Grease barrier test carried out with a scanning method. Untreated base and three foam-coated samples.

Figure 35 shows the more specific grease barrier data of the foam-coated samples. During four days there was practically no grease penetration in the double-coated sample, which had 8.2 g/m^2 of PVA2. Also 3 g/m^2 of PVA1 gave a very good result.

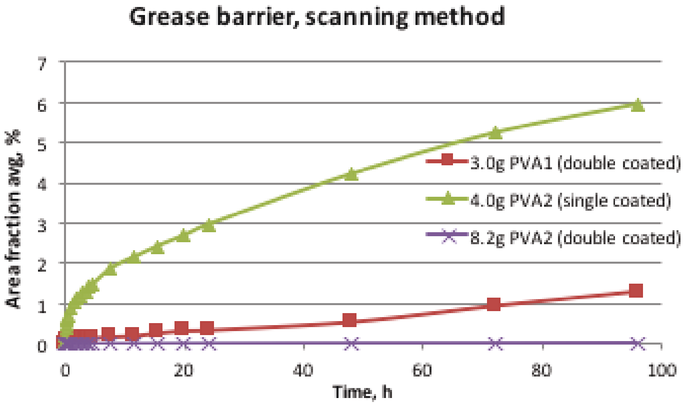


Figure 35. Grease barrier test carried out with a scanning method. Three foam-coated samples.

5.1.4.5 Water Vapour Transfer Rate (WVTR).

Similarly to the grease barrier results, water vapour transfer rate (WVTR) results were also greatly improved after the foam coating (Figure 36). The best results were obtained with PVA2. The Water Vapour Transfer rate decreased from the value 486 for untreated base paperboard to 13 for the single-coated PVA2 sample (4.0 g/m^2) and to 121 for the double-coated PVA1 sample (3.0 g/m^2).

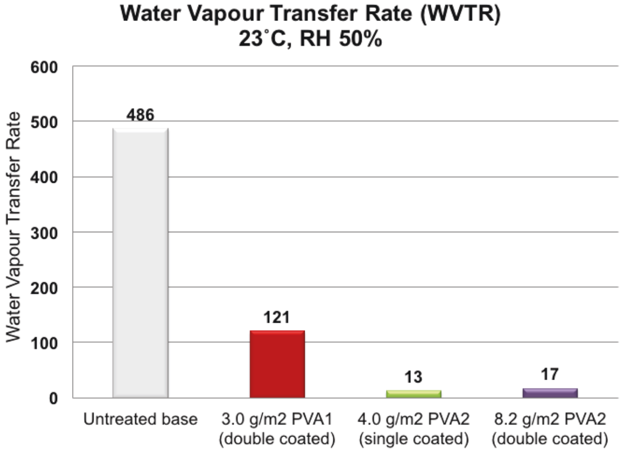


Figure 36. Water vapour transfer rate (WVTR), 23ºC, RH 50%.

5.1.5 Foam coating of wet web

In the paper and board industry energy efficient dewatering is of great importance and the capabilities of the press section have progressed significantly in the last several decades, allowing ever higher dryness levels to be achieved. In this study we examined the applicability of foam technology to simultaneously improve dewatering and strength properties of dry and wet paper/board in wet web treatment at paper and board machines. The results of the trials showed that foam application technology could be used in the wet section of a paper or a board machine to simultaneously improve the strength of the end product and enhance dewatering.

5.1.5.1 Dryness after Wet Pressing

The foam coating trials to the wet web were performed at VVT's papermaking research environment. The 80 g/m^2 samples from 100% bleached SW kraft pulp were produced using 300 m/min speed. The dryness level at the former section at the foam application point was 22.8% ± 0.4%. The results are shown in Figure 37. According to Bauman (2011) approximately 2/3 of the total energy consumed on the machine line is consumed in drying paper and board. Paper/board entering the dryer section contains approximately 50% water. At these dryness levels, a 1%-unit increase in dryness after wet pressing reduces roughly 4% of the drying energy required for a fixed basis weight product (Bauman, 2011). Foam-based chemical application in our trials increased dryness of wet pressed samples on average by 2.3%-units (Figure 37), 5.2%-units in the best case (CMF, pressing load 1200kN/m). Based on the given assumption, on the whole line, an average of approximately 10% (up to 21% with CMF application) savings in energy consumption could be reach with a foam based application compared to the situation when foam is not applied.

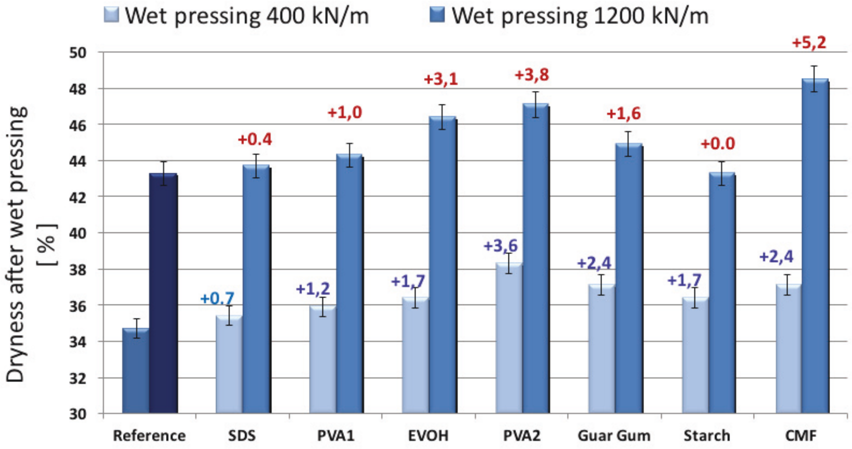


Figure 37. Foam-based chemical application increased dryness of wet pressed samples on average by 2.3%-units, 5.2%-units in the best case (CMF, pressing load 1200kN/m). The applied amounts of additives were between 0.2 (Guar Gum) and 2.7 g/m^2 (PVA2 and EVOH).

The effect of SDS spray was not studied. The SDS foam slightly enhanced dewatering. The effect of SDS foam on dewatering was lower than the effect of the other studied foams, which were more viscous than the SDS foam. The foams were more viscous due to the higher viscosity of the liquids used to make the foams. The result is similar to the findings made by Lindqvist et al. (2013). They showed that the addition of surfactants to pulp suspensions reduces surface tension forces and thus enhances dewatering in forming and wet pressing. According to Skelton (1987) there is also an additional effect attributable to the properties of foam, which enhances dewatering during forming. He claims that small air bubbles remove liquid water from the porous paper structure more efficiently than a stream of free air. According to Lindsay (1990, 1991) the analogy to oil recovery would appear to provide at least part of the explanation. Due to the high viscous foam, the viscous fingers become “self-sealing” to some extent, making the interface more stable. As a consequence of this, the stability of the displacement process in suction is increased and water removal becomes more efficient. One proposed means of achieving this objective, namely through displacement dewatering in which a pressurized gas phase is used to drive liquid water out of a mechanically compressed sheet, is described by Lindsay (1990, 1991). The theory of displacement dewatering is presented as follows according to him:

The key issue in displacement dewatering is the length of time the gas pressure must be applied. The motion of a stable gas-liquid interface driven by constant gas pressure is considered as a one-dimensional motion through a uniform porous medium of thickness L and permeability K. The gas liquid interface is at position x, with x = 0 at the flow exiting side of the sheet. ΔP is the pressure drop across the sheet. If the inertial effects and the viscosity of the gas phase are neglected, Darcy's law can be applied to determine the interface velocity:

$$V = -\frac{dx}{dt} = \frac{K\Delta P}{\varepsilon\mu x} \qquad (1)$$

where V is the interface velocity, ε is the sheet porosity, and μ is the liquid viscosity. The time required for the interface to move across the entire porous medium beginning at the upper surface (x=L) is given by integration:

$$\int_L^0 -x dx = \int_0^t \frac{K\Delta P}{\varepsilon\mu} dt' \qquad (2)$$

resulting in

$$t = \frac{\varepsilon\mu L^2}{2K\Delta P} \qquad (3)$$

where t is the required time for the movement of the interface through the porous medium.

As shown in equation (3), a thin and porous web requires less time than a thick or less permeable web. However, in practice the displacement process faces some inherent instability that reduces its efficiency. In a porous medium, when a liquid is displaced by another fluid of lower viscosity, the interface between the phases is often unstable. Disturbances on a smooth interface create ‘fingers’ that penetrate into the phase being displaced; see Figure 38. This phenomenon is called ‘viscous fingering’ (Lindsay 1990, 1991; Lenormand et al. 1988).

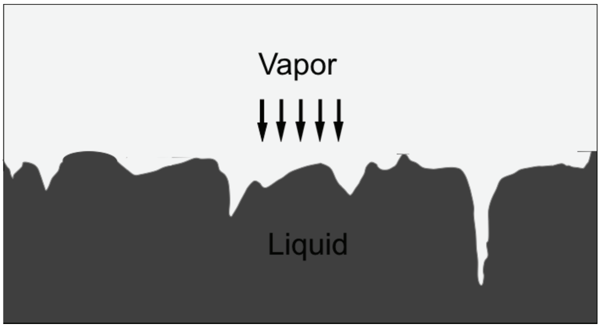


Figure 38. Viscous fingering in a porous medium as a gas displaces a liquid (Homsy, 1987).

This phenomenon means that a gas phase will tend to simply blow through certain paths, leaving much of the water behind. Lenormand et al. (1988) numerically examined the displacement process for a wide variety of conditions. The conditions typical to air-water displacement in paper clearly fall in to a regime, where significant viscous fingering likely happens.

In our trials the foam applications were done to the web above the high vacuum suction boxes (HiVac). The web dryness level at the application point was 22.8% ± 0.4%. The self-sealing phenomenon of foam can be seen from the vacuum levels -69,6 - -70,8 kPa, which were all higher compared to the reference -69,45 kPa, Figure 39. The vacuum levels are directive and thus comparison of vacuum level between the test points and applied foams will need more extensive studies.

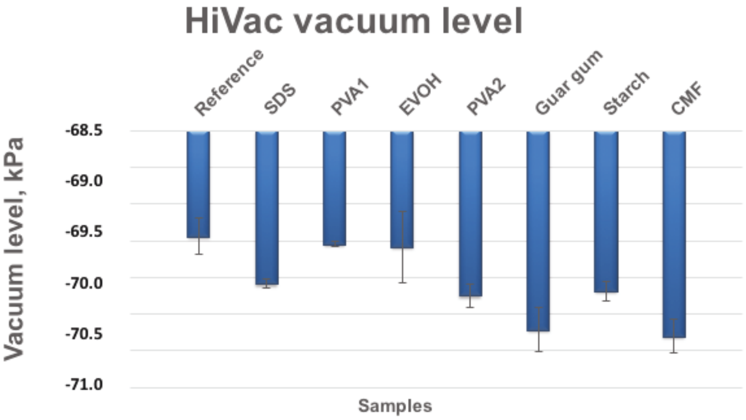
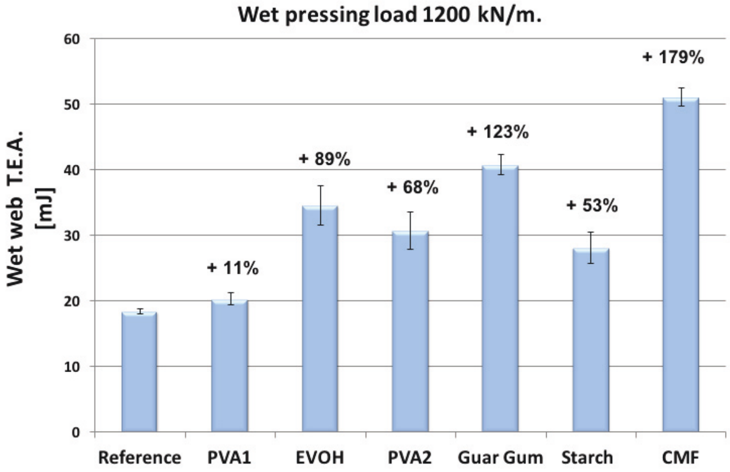


Figure 39. The vacuum levels of the high vacuum suction boxes (HiVac) in foam applications.

5.1.5.2 Mechanical Properties of Wet Web

According to Seth et al. (1982, 1984) a simultaneous increase on wet web strength and stretch reduces web breaks on a paper machine. The results of the trials performed showed (Figure 40, top) that wet web tensile energy adsorption T.E.A. (which also combines the stretch and strength of paper) was significantly increased at a given wet pressing level, but also at a given dryness level (Figure 40, bottom). According to these results the application of additives increased wet web T.E.A. significantly (11 to 179%) after the constant wet pressing line load of 1200 kN/m. Figure 40 (bottom) reveals that the development of wet web T.E.A. as a function of dryness was greatly dependent on the applied additive. Application of starch and polyvinyl alcohols had only a minor effect on T.E.A at dryness levels below 40%, but the effect increased strongly with increasing dryness. The addition of polyvinyl alcohol increased wet paper strength and also dry paper strength (Figure 41), which is in line with the earlier studies (Fatehi et al., 2009; Zunker and Breazeate, 1983; Salminen et al., 2012). It is likely that polyvinyl alcohol, as a high-molar-mass polymer having high affinity to fibers, may increase molecular-level interaction between fibers in a wet state. Polyvinyl alcohol is a hydrophilic polymer carrying a hydroxyl group on each of its repeating units, which permits the development of hydrogen bonds with hydroxyl and carboxylic groups of cellulose fibers, thus enhancing the tensile strength of dry paper (Fatehi and Xiao, 2008). Guar gum and CMF had a clear effect on wet web T.E.A also at lower dryness levels. In the case of CMF, an increase of surface fibrous area is believed to increase the surface tension forces in the network (Luukko, 1999), which could explain the increase of T.E.A. also at low dryness levels.



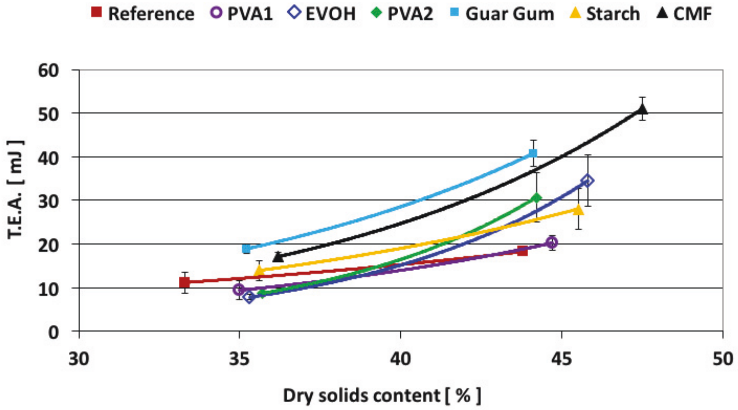
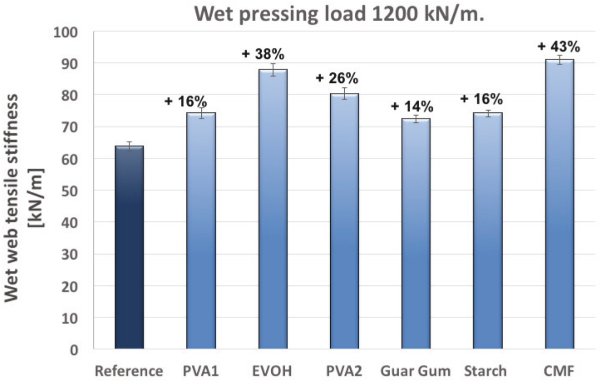


Figure 40. Foam-based chemical application significantly increased wet web tensile energy adsorption T.E.A. (which also combines the stretch and strength of paper) at a given wet pressing level, but also at a given dryness level.

Wet web tensile stiffness and residual tension after constant wet pressing conditions are given in Figure 41. Wet web tensile stiffness describes the tension response when paper is strained. For a paper having high stiffness, a lower amount of straining is needed to create a certain tension on open draws. Residual tension describes tension existing in the wet web at a certain time after straining. The effect of applied additives on wet web tensile stiffness and residual tension was quite similar and the effect of additives was lower than in the case of the wet web T.E.A. Earlier studies have given clear indications that the addition of chemicals increases the strength of fiber-fiber joints, which augments wet web strength and strain but has no effect on fiber network activation, and thus does not significantly influence wet web elastic tensile stiffness or residual tension at low strain levels. The results obtained in this study are in agreement with those earlier findings. The main improvements in tensile stiffness and residual tension were obtained through increased dryness after wet pressing.



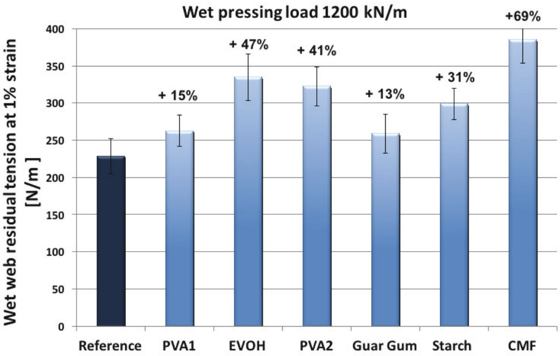
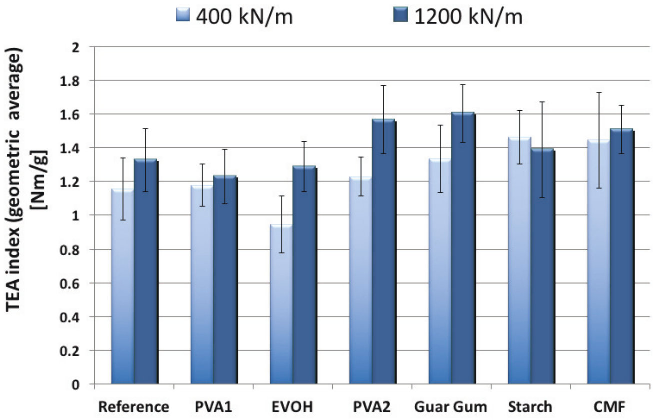


Figure 41. The effect of applied additives on wet web tensile stiffness and residual tension was quite similar and the effect of additives was lower than in the case of the wet web T.E.A.

5.1.5.3 Mechanical Properties of Dry Paper

The effect of the studied additives on dry paper T.E.A was not as clear as in the case of wet web. Figure 42 shows dry paper T.E.A and Scott bond delamination energy.



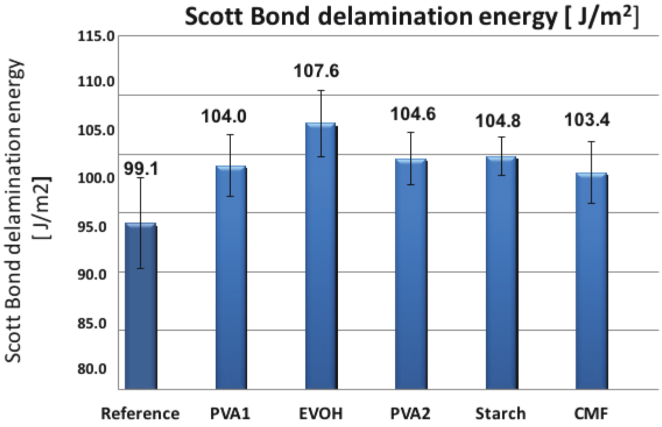


Figure 42. The hydrophilic polymers starch, guar gum and PVA increased the dry paper T.E.A. Application of additives increased 4 to 9% of Scott bond delamination energy.

The results show that with the application of CMF, starch, guar gum or PVA having a high hydrolysis level, there is a minor effect on the in-plane tensile properties of dry paper, but a stronger effect on out-plane strength properties. The application of additives increased Scott bond delamination energy from 4 to 9%. An increase of Scott bond delamination energy indicated that polymer have also penetrated the web structure in the z-direction. However, this does not indicate how even the distribution of each additive in the web structure has been. The applied amounts of the additives must be taken into account in a comparison of Scott bond improvement. Based on that, CMF and starch with applied amounts of 0.7 and 0.5 g/m^2 respectively, enhanced out-plane strength significantly more than poly and ethylene vinyl alcohols, which the applied amounts of were 1.8 and 2.7 g/m^2.

5.1.5.4 Increased bulk with higher dryness

The applied poly and ethylene vinyl alcohols enhanced dewatering, but densified the web structure compared to the reference sample. The strongest influence on dewatering was reached with CMF, which has a minor positive effect on bulk. Also starch and guar gum enhanced dewatering with a positive effect on bulk (Figure 43).

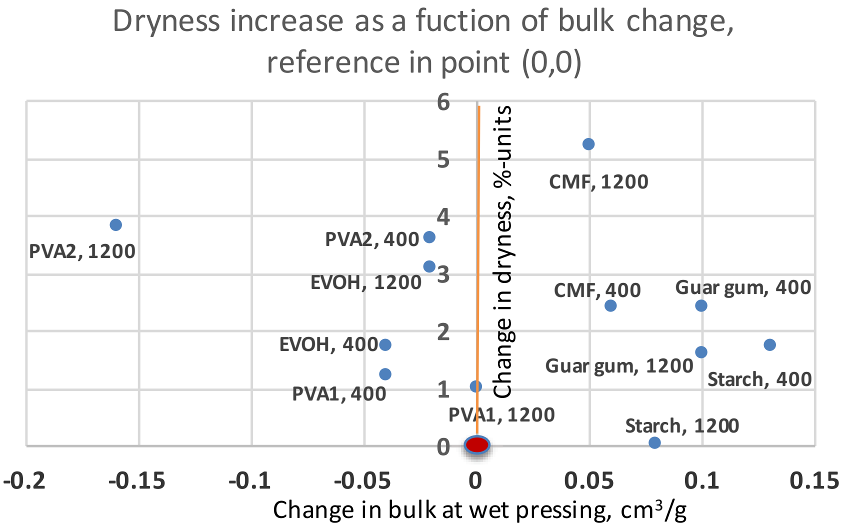


Figure 43.The dryness increase as a function of bulk change. The wet pressing load is marked after the applied additive. The reference is marked as a red oval in the point (0,0) and the results of the applied additives are compared as a change to the reference. 80 g/m^2 samples from 100% bleached HW kraft pulp were produced at a pilot paper machine using 300 m/min speed. The dryness level at the former section at the foam application point was 22.8% ± 0.4%. The applied amounts of additives were between 0.2 (Guar Gum) and 2.7 g/m^2 (PVA2 and EVOH).

5.2 Foam forming

In foam forming, a mixture of stock and foam is transported through a headbox to a wire, where foam is removed using vacuum. This forming method offers many positive effects. First, foam forming enables improved formation (Kinnunen et al., 2013c; Lehmonen et al., 2013), especially in the case of longer fibers (Koponen et al, 2016), because fibers are locked between the bubbles. Thus, they do not flock during the transportation to the wire. This gives better formation and allows one to use higher consistency stock. Combining foam forming with air drying leads to very bulky structures (Punton, 1975; Smith et al., 1974). It offers a potential solution to the increased need for more versatile, cost-efficient and environmentally sustainable solutions enabling the manufacture of totally new products. Some reduction in the strength properties of the foam formed paper samples was reported compared to the water formed samples. Based on the published results, the strength loss could be compensated for successfully through more intensive wet pressing of the web or by increased refining level of furnish (Radvan and Gatward, 1972).

In order to verify that the results obtained in the 1970s are still valid with modern furnishes and paper making technologies, we ran dynamic experiments using a semi-pilot scale research environment. The potential of CMFs as strength additives was studied in laboratory scale experiments. Below is the experimental evidence for some benefits of foam forming technology.

5.2.1 Improvement of formation

The excellent formation of the products formed is one of the major benefits of using foam forming technology claimed in the 1970s papers. A useful definition of formation is the standard deviation of grammage distribution in the plane of the paper sheet. Figure 44 shows the standard deviation values of papers from different pulps formed by water and foam forming. Formation was measured using Ambertech. For every pulp type, the formation of foam formed paper was significantly better than in the case of water formed paper. The greatest difference was in the case of spruce-CTMP, due to relatively stiff fibers compared to chemical pine and birch pulps. In the water forming method the formation is dependent on fiber length; good formation can be achieved with short fibers like birch. When the fiber length increases, the formation start to deteriorate. Also stiff fibers are challenging to form, since their coarseness affects the specific β-formation of water formed papers (Niskanen, 1999). In foam forming the formation is independent of fiber properties. When fibers are mixed with the foam, the foam bubbles attach to the fiber surface thus forming a bubble layer. This layer prevents fibers touching each other before the dewatering phase, thus preventing flocculation.

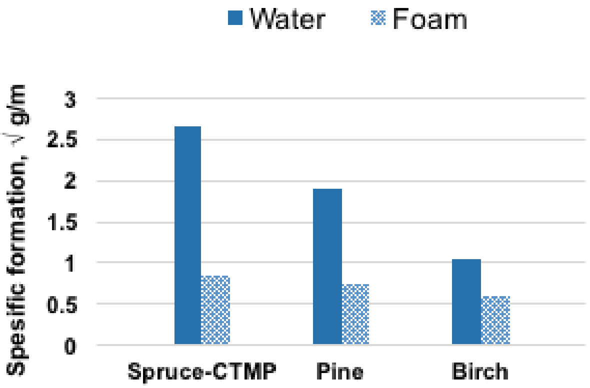


Figure 44. Formation of foam formed papers was significantly better compared with water formed paper, regardless of the fiber type.

Given that the headbox consistencies in the foam forming trials were higher compared to the water forming trials, the formation results are even better. The consistencies are shown in Table 15. In all cases there was a significant increase in the headbox consistencies.

Table 15. Headbox consistency, sheet grammage and dryness of the water and the foam formed samples using spruce-CTMP, and chemical pine and birch pulps.

Pulp	Foam forming			Water forming		
	Consistency, %	Grammage, g/m^2	Dryness, %	Consistency, %	Grammage, g/m^2	Dryness, %
Spruce-CTMP	1.45	108	19,5	1.15	107	13,2
Pine	1.30	82	24,6	0.67	84	18,8
Birch	1.38	84	32,0	0.72	83	22,6

In the Wiggins Teape Radfoam process even higher headbox consistencies were used. They managed to raise it 3 – 5% (Punton, 1975). In the Short Circulation Device, the dynamic former used in this thesis' research, the limitations to the consistencies in the foam forming come from the procedure of mixing fibers in to the foam.

According to Kerekes et al. (1985) and Martinez et al. (2001) the tendency to form flocs resulting in non-uniformity of the web increases significantly with increasing fiber length and furnishes consistency. Koponen et al. (2016) reported foam forming trials with bleached hardwood and softwood kraft pulps and long fibers (6 mm TENCEL® lyocel fibers). The highest mass fraction of lyocell fibers was 20%. According to them, formation was always very good, and for longer fibers formation improved with decreasing foam density. Specific formation with foam density 480 kg/m^3, 80% BSK and 20% lyocell was 0.54 √ g/m. We verified the uniform sheet structure by foam forming trials with unrefined softwood pulp and long polypropene fibers (PP) at the KCL pilot paper machine. The paper machine is a Fourdrinier machine built in 1968, which is now modified to foam forming. The foam generation is based on tank generation. Figure 45 shows the formation of the foam formed paper consisting of unrefined soft wood pulp and PP fibers with a length of 6 and 12 mm. The foam density was 370 kg/m^3. The reference water formed sample is from the trials done at the KCL pilot paper machine some years ago. The target of the water forming trials was formation improvement (Jakkula, 2012). Table 16 shows the information of the trials.

Table 16. The information from the water and foam formed samples run at the KCL pilot paper machine.

Method	Furnish	Ratio	Refining	Retention chemicals	Head box consistency, %
Water (Jakkula, 2012)	SW/HW	30/70	refined	yes	0.26
Foam	SW/synthetic PP fibers, 6 and 12 mm	70/30 50/50	Unrefined SW (SR^o 13)	no	0.61

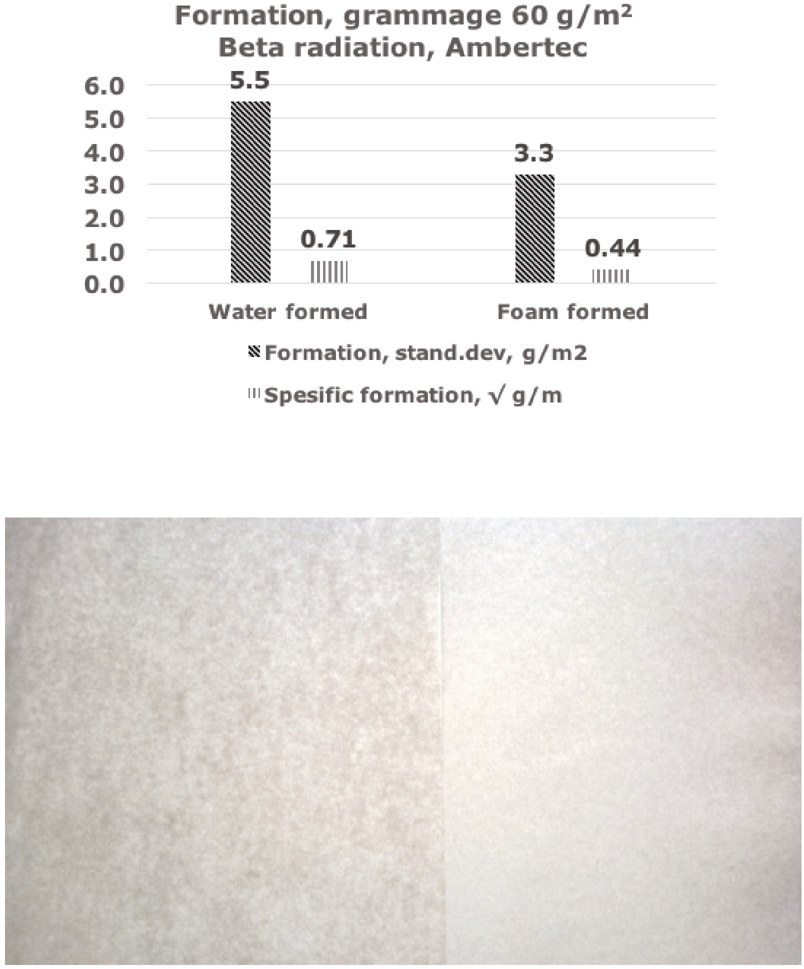


Figure 45. Comparison of formation from the samples run at the KCL pilot paper machine using water and foam forming techniques, the Ambertec beta radiation values and the images correspond to the values. Top: The specific formation, bottom: A picture from the sheets; water formed (left) and foam formed (right). The water formed sample consist of refined SW and HW pulps (30/70), and the foam formed sample unrefined SW and PP fibers (70/30). PP fiber fraction was a mixture of 6 and 12 mm fibers (50/50).

5.2.2 Improved dewatering

The dryness of the web before wet pressing for each pulp is shown in Table 15. In all cases the dryness was increased. In foam forming, the dewatering in a wire section is more effective than in the case of water forming. However, this is partly due to the fact that in foam forming the drainage capacity of the machine needs to be higher than for conventional papermaking (Punton, 1975), therefore higher vacuum levels are needed than in water forming. The vacuum levels used are presented in Figure 46.

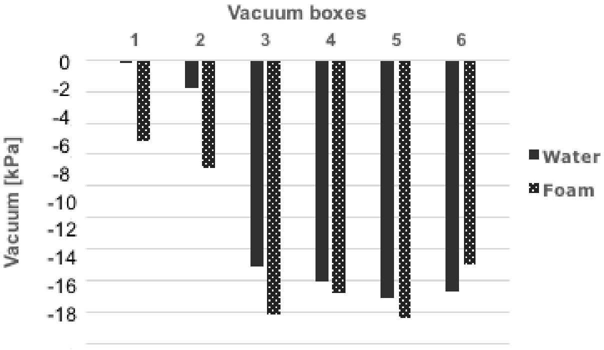


Figure 46. Vacuum levels in the forming section in the water and foam forming trials.

Another reason for the improved dewatering properties is due to the difference in pore size distribution in the paper structures. Al-Qararah et al. (2012) have found that pore size distribution of hand sheets made with foam forming depends on the properties of foam. The largest pores in foam-formed paper samples have a similar size to the largest bubbles in the corresponding foam. Smith (1974) suggested that the increased bulk and porosity could be traced to the presence of bubbles in the sheet. These bubbles may survive into the early stages of drying. The structure remains bulky partly due to smaller hydrostatic pressure in foam forming compared to water forming and partly due to foam bubbles that act as a ‘ghost’ particles (Figure 47).

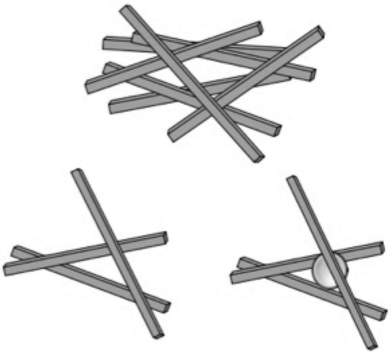


Figure 47. Foam bubbles act as “a ghost” particles increasing porosity (Hjelt, 2014).

According to Figure 48 the foam formed paper has bigger pores compared to the water formed paper. The biggest pores have a diameter up to 400 μm.

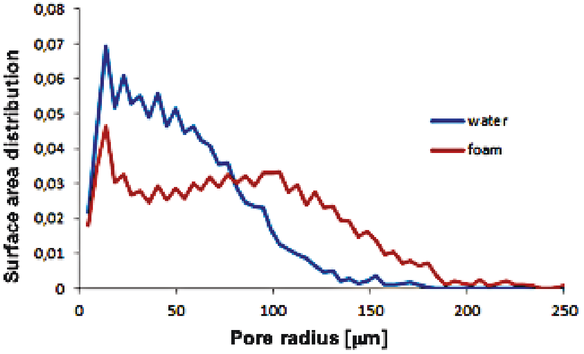


Figure 48. The pore size distribution of water and foam formed samples.

Figure 49 shows the analysis of the x-ray microtomography images of water and foam formed CTMP samples (Hjelt et al., 2011). A distance transform to a binary sample image was applied to characterize the pore network of the samples. Each local maximum in the distance transform is represented as a sphere of corresponding radius. In Figure 49, all spheres of a radius larger than 52 μm are plotted. The sphere colour indicates the z-directional position of the sphere in the structure, with red being top and blue bottom. In the foam-formed sample, big pores construct channels through the structure in the z-direction, whereas in the water-formed sample, large pores are almost isolated. The channels in the foam-formed samples are very beneficial for drainage properties.

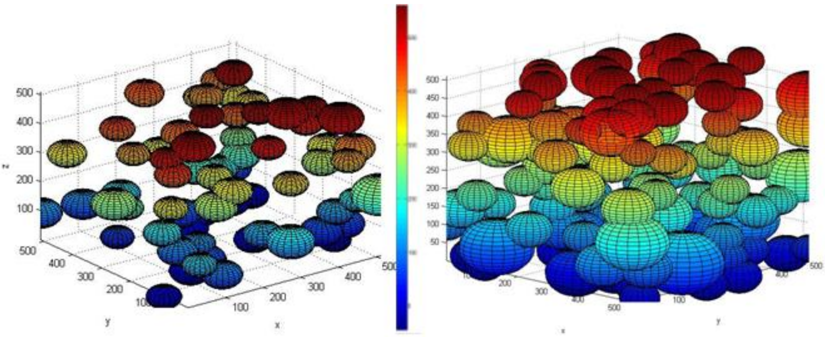


Figure 49. Characterization of the pore network by balls of radius larger than 52 µm. The figure on the left-hand side is a water-formed CTMP sample and on the right-hand side a foam-formed CTMP sample. The red colour indicates that pores are at the top of the paper and blue that pores are at the bottom (Hjelt et al., 2011).

5.2.3 Slower decrease of strength, when grammage is reduced

Refined chemical SW pulp (20 ^{o}SR) was used as a fiber raw material when studying the effect of grammage on strength. In the performed semi-pilot scale trials, water and foam, the grammage range of paper alternated between 25 g/m^2 – 135 g/m^2. Grammage was adjusted by changing the forming consistency, which varied from 0.26% – 1.24% by weight for water formed paper and 0.48% – 1.77% by weight in foam forming. The results, presented as a geometric mean value of the machine and cross-sectional direction (Figure 50), confirm the earlier results reported by Seth et al (1989) that the tensile index of water formed paper weakens if the grammage falls sufficiently. At higher grammage levels, the tensile index was reported to be almost constant, but our research shows that the tensile index of water formed paper began to fall notably at a grammage level of ~50 g/ m^2 instead. In the case of foam formed paper, the tensile index remained almost constant throughout the studied grammage range. The behaviour is due to good formation of foam formed paper. The formation results are presented in Figure 44.

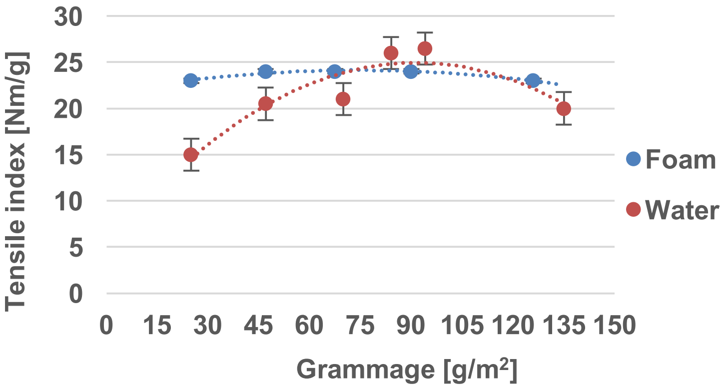


Figure 50. Tensile index of refined chemical SW pulp (20 ^{o}SR) sheets as a function of grammage. The results are presented as a geometric mean value of the machine and cross-sectional directions.

5.2.4 Better bulk strength ratio using CMF

Foam formed papers have high bulk and low strength characteristics in an unpressed state compared to a comparable water formed paper (Radvan and Gatward, 1972). The mechanical properties, tensile index and z-directional tensile strength, from our trials are presented as a function of bulk in Figure 52. These results are presented as a geometric mean value of the machine and cross-sectional direction. They indicate that the average tensile strength was somewhat higher for water-laid paper at the same bulk level. The water and foam formed samples were wet pressed and dried using the same methods.

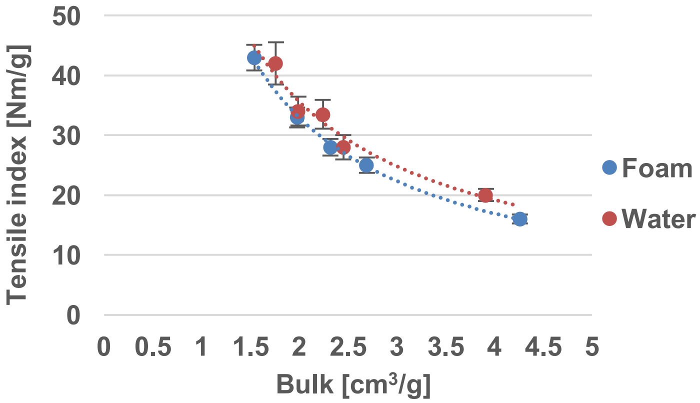


Figure 51. Tensile index in the case of water-laid and foam-laid paper as a function of bulk.

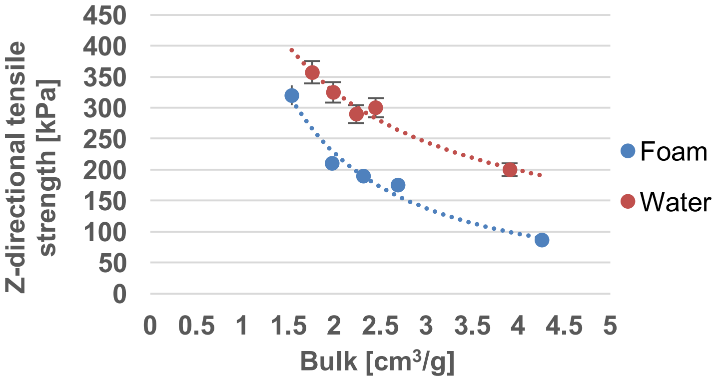


Figure 52. Z-directional tensile strength in the case of water-laid and foam-laid paper, as a function of bulk.

Z-directional strength was weaker in the case of foam formed paper (Figure 52). The reason for this difference could be in the difference of the pore size distribution of the paper samples. In foam formed samples there are a significantly large amount of big pores compared to the water formed samples (Figure 49). These big pores can act as weak points in the structure thus lowering the z-directional strength.

It is possible to regain the lost strength by beating or by pressing (Smith et al., 1974), in the latter case at the expense of the bulk. In paper physics, it is well known fact that there is a strong correlation between the porosity of a structure and the strength of a structure (Niskanen, 1999). In conventional water forming the strength required is attained using wet pressing. The green triangles in Figure 53 are the typical values for the CTMP paper produced at the KCL pilot paper machine trials. In the same figure are the laboratory scale formed samples; the blue squares are from water formed sheets and the brown diamonds are from the foam formed sheets.

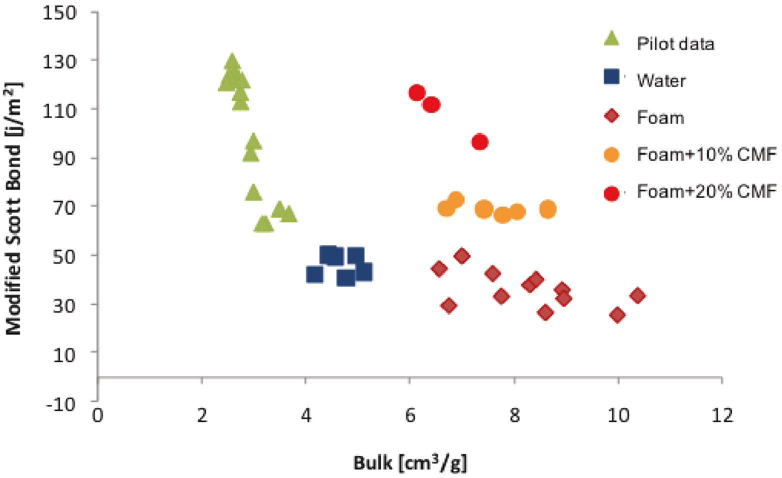


Figure 53. Scott bond values CTMP sheets as a function of bulk. The green triangles are the typical values for the sheets made from typical CTMP pulp obtained from the KCL pilot plant tests. The blue squares and red diamonds are values from water-formed and foam-formed laboratory handsheets, respectively. The circles show the values of the foam formed samples with different nano fibrillar cellulose contents (Kinnunen and Hjelt, 2013).

In the first experiments, we used the same CTMP as in the dynamic trials. After the forming the sheets were wet pressed as described in the Methods (Chapter 4). The results clearly show that foam forming enables much higher bulk values compared to water forming. The Scott bond values of water and foam formed samples go into the same curve as the pilot scale results. This shows that by reducing the bulk in the foam formed sheets by wet pressing to the level of 2-3 cm3/g, the rapid increase in the Scott bond is obtained leading to the required level in z-directional strength.

In order to maintain bulk and to increase the Scott bond values to the required level suitable for normal packaging applications, the potential of cellulose microfibrils as a strength additive was tested. The CMF used was Daicel, described in Figure 12 and Table 8. The addition amounts of CMF were 10% and 20%, which did not effect drainage times on a static foam former. Figure 53 shows the bulk and Scott bond values of the samples containing 10% (yellow circles) or 20% of CMF (red circles). These results show that it is possible to produce structures with extremely high bulk and the required strength properties by foam forming.

In the next test series, we used five different grades of cellulose microfibrils (described in Figure 12 and Table 10) in order to see their effect on both z-directional and plane strength properties. The pulps used were pine kraft pulp and mechanical spruce CTMP pulp. The addition amounts of CMFs were 0% (a reference), 5% and 15%. The sheets prepared were dried after forming without any wet pressing. The results from the CTMP series are shown in Figure 54.

Z-strength and modified Scott bond values were measured, because the latter is dependent on the formation. The tests gave similar results, which indicates good formation. The general trend of different CMFs' effects on strength properties is rather similar. The results show that CMF made the CTMP sheet structure denser leading to bulk loss to values of 6.5-9 cm^3/g. The reference (no CMF added) has the bulk value of 10 cm^3/g. However, the acquired z-directional strengths were reached in unpressed samples with CMF addition in high bulk levels of ca. 6 cm^3/g, by wet pressing the target was possible to reach in bulk levels of 2-3 cm^3/g. Remarkable in these results compared with the results showed in Figure 54, is that in bulk values above 6 cm^3/g the samples have Scott bond values above 50 J/m^2, whereas in the wet pressing case all Scott bond values were below 50 J/m^2.

Another interesting result is to compare VTT coarse and VTT fine. Especially in the case of the z-directional strength comparison, VTT coarse gives the highest Scott bond, even though it is coarser (and cheaper) than VTT fine. The addition of CMF also increases the plane strength of CTMP sheets significantly. However, in this comparison VTT fine gave the highest tensile index value showing that the selection of CMF depends on the property required.

The same study was done using pine kraft pulp. The results are shown in Figure 55. The general trend of effects of different CMFs on z-directional strength properties is rather similar to that in the CTMP series, except the behaviour of P1. With chemical pulp the influence of P1 is extremely interesting; the z- directional strengths were doubled without any bulk lost, likewise the stretch. The mechanism behind this behaviour is unclear to us and needs more investigation.

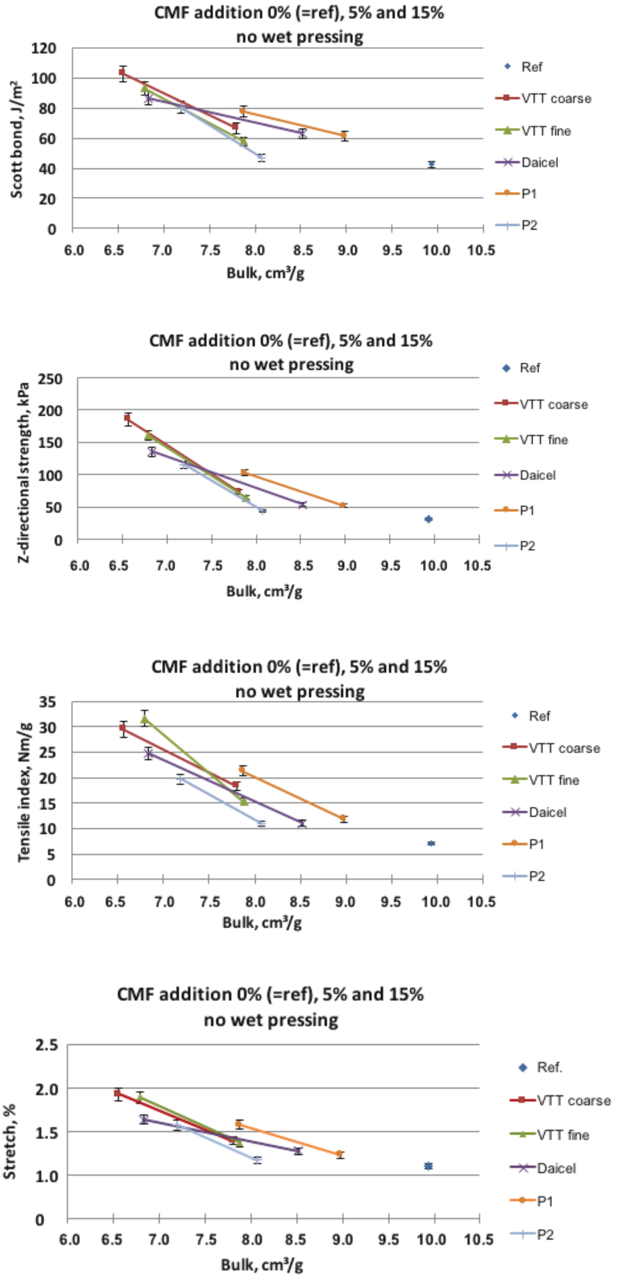


Figure 54. Effects of the addition of six different CMFs grades to the spruce-CTMP pulp. Figures from top to bottom: Modified Scott bond, Z-strength, Tensile index and stretch as a function of bulk. The right edge of the line equates the 5% addition amount and the left edge 15% addition amount.

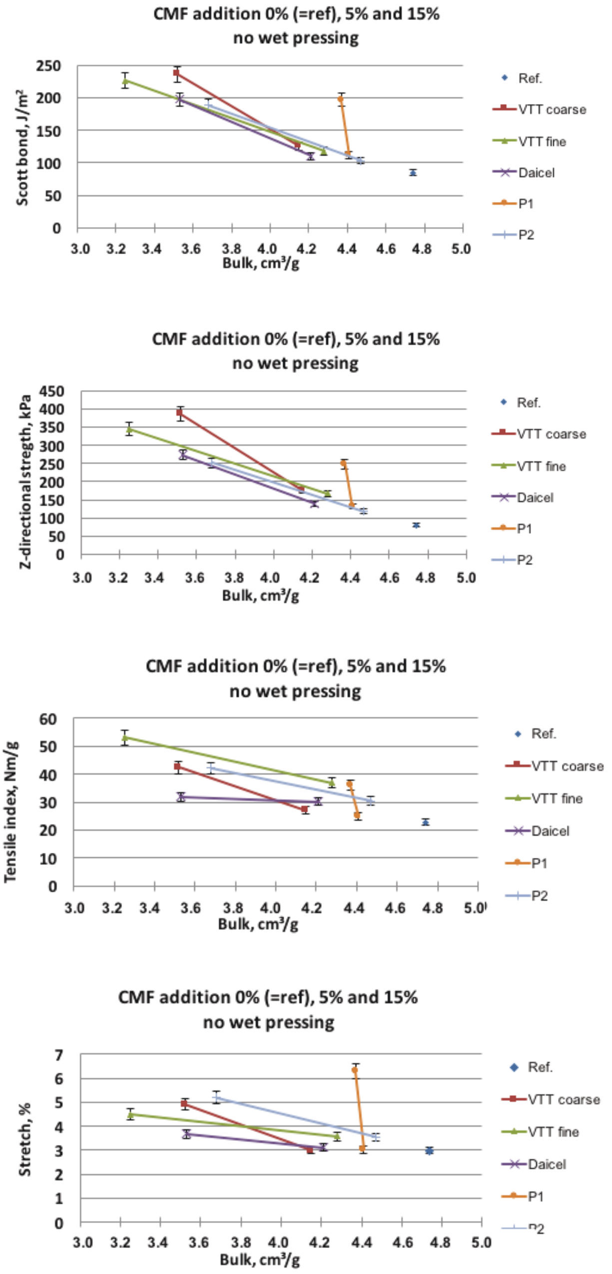


Figure 55. Effect of the addition of six different grades of CMFs to the kraft pine pulp. Figures from top to bottom: Modified Scott bond, Z-strength, Tensile index and stretch as a function of bulk. The right edge of the line equates the 5% addition amount and the left edge 15% addition amount.

5.2.5 Drawbacks

The main drawbacks of the foam forming technology are related to the use of surface active agents. They may react with the chemicals used in the web end, and cause extra load to the waste water treatment process.

5.3 Foam assisted dewatering

Municipal waste water plants produce 11 million tDS/a of sludge even in the EU. Increased industrial productions and the tightened legislation have led to increased quantities of sludge, high treatment costs and high landfill costs. Soon in the EU, organic matter such as waste water sludge will not be allowed in landfill at all (Kyllönen et al., 2010). Thus, there is a high demand for sludge minimisation.

In addition to the improved dewatering explained earlier (Chapters 5.15. and 5.2.), the focus of this research was to study if foam could be used as “filter aid” in sludge treatment. When foam bubbles are present during a filter cake formation, they may make the cake structure more porous. This would enhance water drainage. This increases the DS content in the sludge cake, which was shown in our laboratory tests. Also, the filtration time was decreased. As an additional effect the turbidity of the filtrate was greatly decreased. This implies that the filtration of micro scale particles was enhanced effectively. The property of foam to enhance dewatering was tested in filtering bio-based sludge from a paper mill and mineral slurry from the mining industry.

5.3.1 Improved dewatering in filtration, better holdout of small particles

The target in the static filtration was to demonstrate that the reported ability of the foam to displace liquid water from a porous medium (Skelton, 1987) is also applicable to sludge treatment. The foam layer worked as a lid on the cake surface enhancing water removal, when it was applied to the top of the sludge before dewatering. The viscous foam increased the interface stability and no ‘viscous fingers’ from the surface were observed. The applied foam prevented the gas phase from blowing through the cake, because of the missing paths, and water was removed evenly from the cake (Figure 56). Whether the lid effect or the viscous fingering effect is more dominant is not currently known.

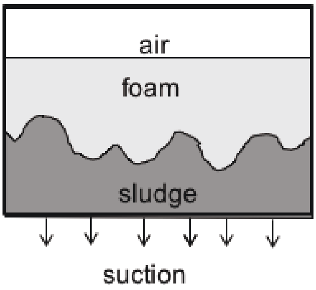


Figure 56. Foam layer "seals" the surface, which increases the pressure difference. The phenomenon is same as in oil recovery.

Comparing the foam-assisted filtration with the conventional filtration, the dry solid content of the cake clearly increases. The reason behind this was the large pores that foam had formed in the filter cake, which enhanced filtration. The average difference in dry solid content of the cake was around 10%. Figure 57 shows an enhancement in a dewatering process was obtained with a drier sludge cake.

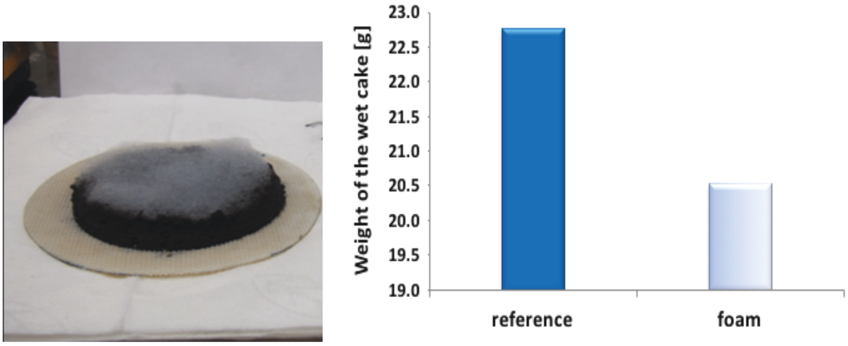
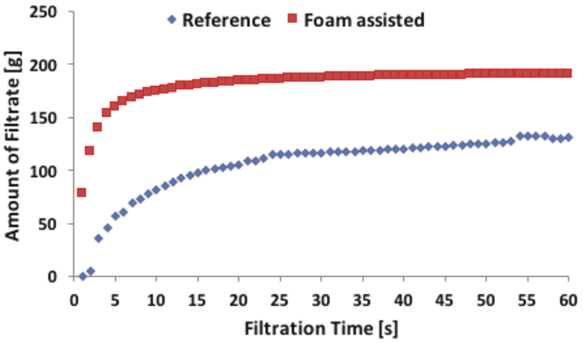


Figure 57. An example of the filtrate cake in FAD (left). The dry solid content of the cake was 10% higher in FAD experiments (right). The foam was applied to the top of the sludge before filtering.

The influence of the stable displacement process could also be seen in the dewatering time. The stable displacement process, where no paths leading through the cake exist, removed water effectively and faster from the cake compared to the reference (Figure 58). The sample treated with foam was dewatered very fast; in 20 seconds 95% of the total filtrate amount was removed from the sludge sample. Correspondingly only 60% of the total filtrate amount was removed from the reference sample in 20 seconds (Figure 58, top). Figure 58, bottom, shows the overall picture of the filtration process. In the foam case the process was very fast, happening in less than one minute. In the reference case, the filtration process was notably slower, taking six times longer. In spite of the longer filtration time, the total filtrate amount was 10% smaller in the reference case than in the foam assisted case.



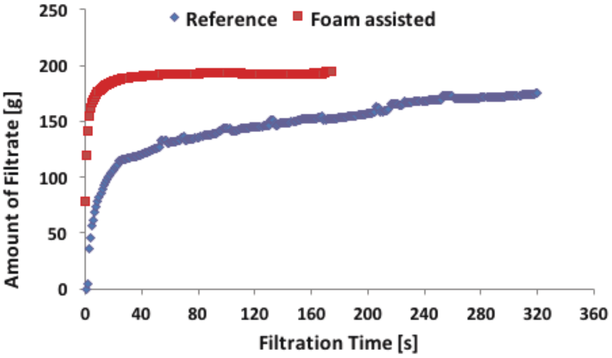


Figure 58. Foam increased 50% of the filtrate rate in 60 seconds of vacuum filtration compared to the reference (left). The overall filtration process happened very fast, in less than one minute, in the foam aided process.

One very interesting result was observed when examining the filtrates; visually the filtrates from foam-assisted filtration were much cleaner, containing fewer large particles, and also more transparent (Figure 59). According to these visual observations, it looks as if improvement in the retention of solids and enhanced dewatering are possible at the same time. The amount of sludge used in the filtration tests was the same in both cases.

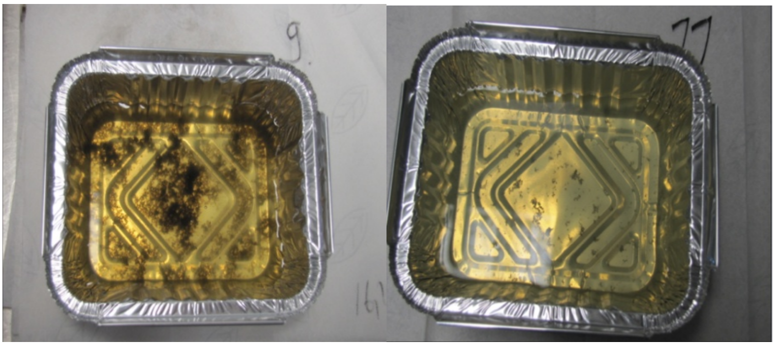


Figure 59. The effect of foam on the filtrate's properties. The right picture shows the cleaner filtrate from the foam-assisted sludge vacuum filtration. The reference is on the left.

5.3.2 Dynamic Thickening

The basic idea of the foam-assisted thickening process in dynamic conditions is shown in Figure 60. An example of the reference, where the flocculated sludge was thickened without using the foam, is in the left-hand picture. The right-hand picture is an example of the corresponding sludge web after applying a 3-6 mm layer of foam with an air content of 90% on the sludge surface.

Figure 60. An example of the sludge web before (left) and after applying foam (right) in the dynamic filtering process.

The influence of the application point, amount and the way foam was applied to the sludge surface was tested in the first experiment. The optimum position for the foam application was found to be just before the dewatering section, where foam aid was strongest, producing the highest dry solids content of the sludge cake. The foam amount needed at that application point was only tested roughly by increasing the by-pass flow of the foam. The results of these experiments show that neither foam amount nor the application direction (downstream/upstream, e.g.

opposite direction, Figure 23) have any influence on the dry solids content of the sludge web (Figure 61, top). However, the foam treatment had a significant effect on the turbidity of filtrates in all foam cases (Figure 61, bottom).

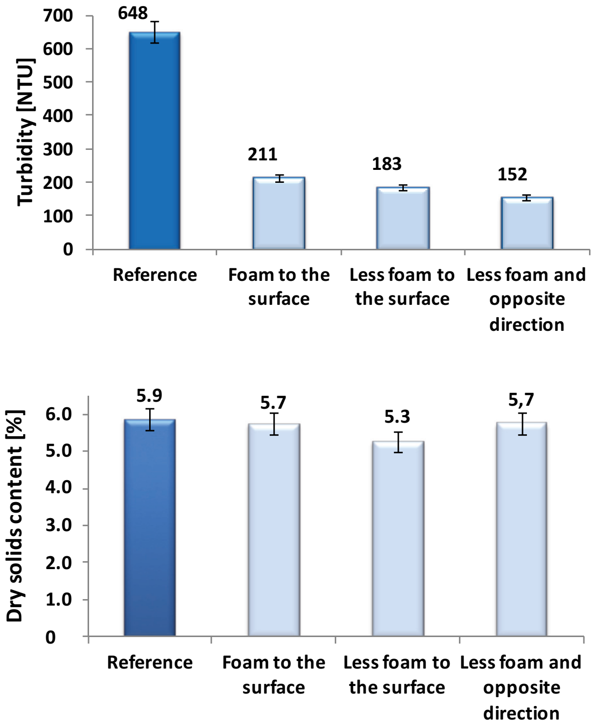


Figure 61. Foam had a positive effect on the turbidity of the filtrate, but no effect on dry solids content of the sludge dewatering in the dynamic condition in the first experiments.

In order to clarify whether the dry solids content results from the first experiments were caused by disturbances in the flocculation stage, experiments with two different flocculant dosage levels, namely 1.9 kg/tDS and 0.95 kg/tDS, were performed. The results showed that dry solid content without foam usage was 5.4% and 5.1% respectively. When the foam was used, the dryness was increased to the level of 5.6% and 5.7% (Figure 62). The increase in the lower polymer addition level was around 10%, the same as in the case of static filtration.

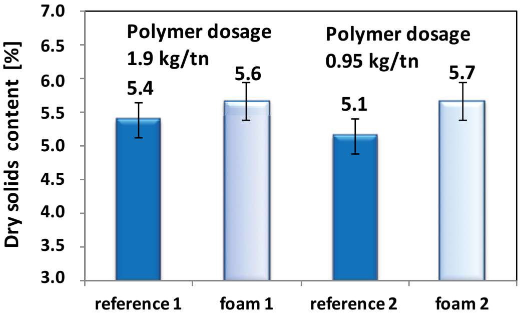


Figure 62. The increased in dry solids content at the lower polymer addition level was around 10%, the same as in the case of static vacuum filtration.

The results from the turbidity measurements of the filtrates were congruent with the results from the first experiments, showing a great decrease in turbidity when foam was used (Figure 63). This indicates that the retention of microscale particles was enhanced effectively. With the higher polymer dose of 1.9 kg/tDS, the decrease was almost 50%, from 80 NTU to 43 NTU and with the lower polymer dose of 0.95 kg/tDS the decrease was over 59%, from 215 NTU to 89 NTU. The latter result indicates the possibility of chemical optimization in the sludge foam-assisted thickening. The layer thickness of applied foam having an air content of 90% was 5–10 mm, corresponding to a 0.1–1 mm water layer, so there was no dilution effect caused by extra water.

The turbidity results were confirmed by measuring the dry solids content of the filtrates (Figure 63). With the higher polymer dose of 1.9 kg/tDS, the decrease in turbidity was almost 46%, and with the lower polymer dose of 0.95 kg/tDS the decrease was over 59%. The results show that when using foam-assisted thickening an enhancement of the retention of micro-sized particles was achieved.

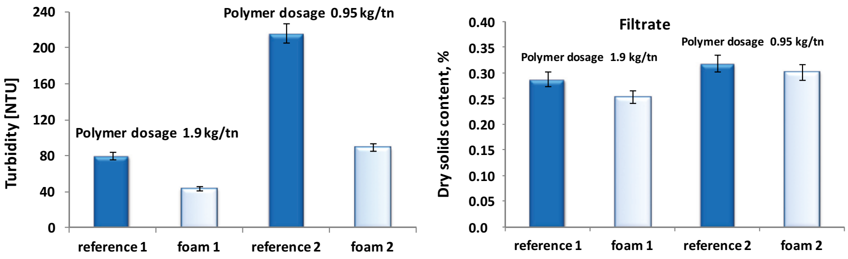


Figure 63. Effect of foam on filtrate turbidity in dynamic thickening of sludge and the dry solids content of filtrates (right).

Due to the very low average vacuum level, around 2kPa, which was used in the sludge dewatering the dynamic filtration of sludge was actually more thickening than filtration. However, the influence of foam-assisted filtration was seen from the slightly higher dry solids contents and from the turbidity measurements of the filtrates, which were cleaner compared to the reference. The results indicate that using more efficient equipment and higher vacuum levels it is possible to decrease the moisture content of sludge. Biosludge is landfilled or burned in mill's boilers. As seen from Figure 64 the influence of moisture content on boiler efficiency is remarkable.

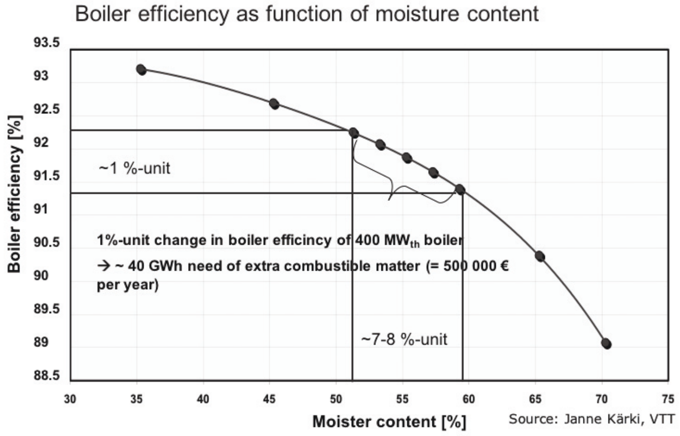


Figure 64. 7-8%-unit decrease in moisture content of burning materials, sludge, will have an 1%-unit change in boiler efficiency of 400 MWth boiler. This means around 40 GWh lower need of extra combustible matter meaning of half a million savings per year (Source: VTT)

6. Conclusions and future perspectives

The aim of this thesis was to study the applicability of foam as a carrier phase in several applications in paper/board manufacturing processes: in web forming, in chemical addition at wet web stage, in the coating of dry paper/board and in biosludge treatment.

The work presented in this thesis is both a study on the implementation of foam technology in the aforementioned areas as well as experiments combining foam technology with newly developed materials like cellulose nanofibrils. The main conclusions answering the research questions listed in Chapter 1.2 Table 1, are summarized as follows:

Throughout papermaking's history water has been used as a carrier fluid of furnishes, and a lot of effort has been put in to the development and use of defoamers in order to eliminate foam formation. However, the foam utilization started in the 70s in papermaking (Radvan, Gatward 1972; Smith et al. 1974; Smith, Punton 1975), but it has yet to gain ground in the paper industry. One reason for this was a lack of driving forces. After a long silent period, the interest towards foam technology is growing and there are several answers, as to why now? The pulp and paper industry production in Finland has been forecast to decrease by up to a third from 2007 to 2020. The declining trend is mainly due to the weakening of Finland's main export markets. Another reason is the weakening competitiveness of Finnish production relative to major competing countries, e.g. in Western Europe, Asia and Sweden (Hetemäki and Hänninen, 2009). Driving forces such as savings in energy and raw material consumption, lead the paper and board industry to search for solutions to regenerate. Newly developed materials like nano cellulose fibrils could enable new product development. However, the new materials may have properties that challenge the conventional processes. New technologies are needed.

Foam usage offers several benefits due to the specific properties of aqueous foams. The pseudoplastic and viscoelastic properties of foams enable the use of highly viscous materials like cellulose nanofibrils in foam form. In addition, the foam bubbles prevent aggregations and flocculation of particles and fibers. When particles are clearly smaller than foam bubbles they are located in the bubble pockets (vertices) and on the bubbles' surfaces, and not able to move through

Plateau borders connecting vertices. If the ‘particles’ (e.g. fibers) are bigger than bubbles the surface of the particles is covered by bubbles, and the bubbles behave as a mechanical barrier between particles and fibers again preventing flocculation. Proper foam is the prerequisite for successful foam usage and for the achievement of the target properties of the end product. The foam is characterized by its properties: an average bubble size, size distribution, stability and air content (i.e. density). What a proper foam is for the process depends on many things, e.g. the technology used in the process and its dynamics like velocity, foam chemistry and materials to be applied to a wire or to a web. The material base for foam technology is very wide; aqueous foams allow the use of a wide variety of different raw materials, from dispersion and nanoparticles up to 200 mm long fibers and also low density materials.

Foam forming

The work done in this thesis in foam forming of paper web showed that foam forming enhances dewatering and enables bulky structure and excellent formation even with long fibers. The work presented in Papers V and VI shows that foam forming provides several benefits to paper and board manufacturing. In many paper and board applications good formation is needed. The pilot scale foam forming trials were run with three different pulps: chemical softwood and hardwood pulps and spruce-CTMP. Improvement in beta formation was obtained even with a higher headbox consistency compared to water forming. Average forming consistency increased by 63%, while the average improvement in specific β- formation was 69%, in comparison to water-laid technology. In addition, good formation from pilot scale trials using 6 and 12 mm long synthetic fibers was obtained. According to the information from fiber suppliers the maximum length of synthetic fibers used in special paper production, e.g. in the wallpaper industry, is 5 mm. The application is also done using a very diluted fiber suspension. Foam forming also gave higher dryness levels before wet pressing. The structure of foam formed sheets is more porous, which is beneficial in the water removal process. The bulky structure means a low level of hydrogen bonds between fibers and thus low strength level. The average tensile strength and the z-directional strength were lower in the case of foam formed paper. However, the results also showed that foam formed paper enables a stronger lightweight web structure compared to the corresponding water formed web structure due to good formation. This is advantageous in the case of very thin paper products.

On the other hand, the work showed that the strength loss due to the bulky structure of the foam formed paper can be regained by using CMFs as strength additives instead of wet pressing or beating. The bulky structure combined with the good water drainage properties allows the high addition levels of strengthening agents such as CMF. This can be used to make savings on raw material especially in packaging applications. Also the ability to use a higher amount of cellulose microfibrils (CMF) compared to water forming opens up a wide window of different kinds of optimization of the end properties. A lot of different kinds of CMF grades are available to choose from. The performance of five different CNF grades was compared in forming of SW and CTMP papers. The results showed that the different grades seem to behave rather similarly in bulk vs. strength comparisons. However, in the case of the modified Scott bond the coarser and cheaper CNF gave a slightly higher value compared to more refined and expensive CNF. On the other hand, more refined CNF gave a higher tensile index value. This example illustrates that the CNF used have to be chosen depending on the paper properties needed.

Foam coating

Foam coating technology is a versatile technology. In this work the foam application was done using a slot type applicator and foam destructions were performed with non-contact and contact methods in dry web application and using vacuum in wet web application. The non-contact application method, where foam destruction is done with a pressure pulse in a nip formed by a rolls or roll and paper, is very applicable when coating with highly adhesive nanoparticles. Our research has also shown that silica nanoparticles (Kinnunen et al., 2011) and cellulose nanofibrils (CNF) (Kinnunen et al., 2012a, 2013b) do not need any binders. Nanoscale particles and nanofibers such as cellulose nanofibrils have sufficient bonding to the paper, because they attach to the substrate surface with short distance forces. When the coating material contains microscale, particles binders are needed, either by mixing the binder with the starting material or using a foaming agent, which also acts like a binder, e.g. polyvinyl alcohol.

Foam coating of dry web

The work done in this thesis in foam coating application to dry paper/board (Papers I-III) showed that using foam it is possible to create thin functional surfaces on paper/board. The technology offers a unique method for applying very light coat weights to the web surface with exceptional uniformity and absence of coating strike-in. The results obtained showed that even a small amount of nanomaterial could change the surface properties of the paper. A thin layer of unmodified cellulose nanofibrils (CNF) increased the hydrophilicity of the paper and closed the paper surface making it smoother and less permeable. The results obtained from the foam coating trials with TiO_2 and ZnO functionalized CNF showed that it is possible to create antimicrobial and photocatalytic properties on the paper and paperboard. CNF was used as a carrier of TiO2 and ZnO nanoparticles in the work, but other nanomaterials like silica can also be used. The results obtained from the foam coating trials with poly vinyl alcohol (PVA) and ethylene vinyl alcohol (EVOH) applications show that it is possible to create barrier properties (grease and WVTR) on the paper and paperboard.

Good runnability of paper machines, often evaluated by the number of web breaks in proportion to the production speed, is a crucial requirement in papermaking. Minimizing web breaks, broke amount and downtime in general and maximizing the production speed enable increased paper/board production (Kurki 2005, Kurki et al., 2000). The bottleneck in many cases is the runnability of the wet web in the press-to-dryer transfer and at the beginning of the dryer section (Kurki et al., 2004; Kouko et al., 2006; Retulainen et al., 2009; Hokkanen, 1996). Wet web transferred from one surface to another without any support of fabrics in an open draw of those points, and the stability of the running web depends mainly on web tension. After the press section wet web dryness varies typically between 40 and 50%.

Savings in raw materials, by using less and cheaper raw materials, have led to the use of a greater quantity of strength additives in order to compensate for the deterioration of mechanical properties of the wet and dry web. These traditional wet strength additives do not enhance wet web strength, i.e. the strength of never dried wet webs. This is because wet strength additives require usually heating and curing time (Salminen, 2010). Wet web strength can be improved by increased dryness. Chemicals such as retention aids increase the water removal of pulp, and thus the mechanical properties of the wet web are improved. Another way to improve wet web mechanical properties is the use of chemical additives that increase interactions between fibers in the wet state. These strength additives are, typically, either dosed at the wet end or applied to the wet web by spray. Wet end application is not a very effective way to apply additives and in many cases the chemicals have an effect on formation.

The results of the foam application of polymers to the wet web (Paper IV) showed that the technology provides a possibility to simultaneously improve dewatering and strength properties of dry and wet paper/board. Increased solids content of the web after pressing was obtained. CMF, starch and guar gum enhanced dewatering and had a positive impact on bulk. This implies direct energy savings during drying or possible material saving through improved bulk. Poly and ethylene vinyl alcohols enhanced dewatering, but had a negative impact on bulk.

Foam application could enable higher retention of different polymers through high mechanical retention, and thus, through lower additions, amount to savings in chemical usage. Foam could also make it possible to use polymers having no cationic charge. The polymers used (two PVA grades with different hydrolysis levels, EVOH, CMF, guar gum, starch) significantly improved tensile strength, TEA, tensile stiffness and residual tension of wet paper. The highest increase in wet web mechanical properties was obtained when the CMF, guar gum and polyvinyl alcohol had a high hydrolysis level. The effects on dry paper mechanical properties were smaller compared to those on wet web. There was a minor effect on the in-plane tensile properties of dry paper, but a stronger effect on out-plane strength properties. The application of additives resulted in increased Scott bond delamination energy from 4 to 9%.

Foam assisted dewatering

The work presented in Paper VI shows that the foam-assisted dewatering technology is applicable to sludge thickening and the vacuum filtration processes. Dewatering enhancement is due to the foam's viscosity. High viscous foam makes the interface more stable and the viscous fingers become, to some extent, "self-sealing". The stability of the displacement process in suction is increased and water removal becomes more efficient. In static filtering, the dry solid content of the filter cake using foam as a filtering aid was increased by 10% compared to filtration without foam. In addition, the rate of the dewatering was significantly increased, indicating savings in the dewatering energy or an increase in the capacity of the filter. In the dynamic thickening conditions, the same 10% difference in cake dry solid content was obtained as in the static experiments. Turbidity of the filtrate was clearly decreased indicating an enhancement of the retention of micro-sized particles. The results obtained may be valuable in the dewatering of wastewater treatment process (WWTP) sludge and industrial slurry. The expected benefits could be a higher dry solid content of filter cake, cleaner filtrates, a faster dewatering rate and lower flocculent consumption. In addition, the foam's property to enhance dewatering can be seen in web forming and biosludge treatment, which enables savings in energy consumption in the next process stage.

6.1 Future research recommendations

The foam technology research already has a continuation and for example the present project, VTT's Foam forming program, is targeted at mill scale installations.

In foam coating, further work with more focused targets for different end-applications including both product and process development at high speeds is needed.

In sludge treatment, more experiments should be performed using industrial slurries and different dynamic belt filtering techniques. Also the metal precipitate challenging to filtrate would be an area for interest for foam assisted filtration.

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Appendix A: Test methods of foam coated paper

Antimicrobial Activity of the Foam-Coated Papers

Photoactivation

In the presence of TiO_2 and ZnO nanocomposites the antibacterial tests were carried out on photoactivated samples as follows. The samples were sterilized before testing and the antibacterial tests were conducted by spreading a known number of living cells on the paper surface to yield a population of 10^5 CFU (Colony Forming Units). The paper samples were subjected to light exposure (4 hours by standard solar lamp 6.000 lux) to induce photoactivation of inorganic nanoparticles (TiO_2 and/or ZnO). The samples were then incubated by adopting testing conditions (temperature and nutrients) that promote bacterial growth. In addition, some tests were run in complete dark conditions (in absence of light). The inoculated paper samples were maintained for 20 hours under optimal nutrient and temperature conditions for bacterial growth. At the end of the test, the paper samples were extracted and the number of living cells determined by plating serial dilution on nutrient agar.

Testing conditions

The tests were performed according to AATCC 100 standard method under static conditions (AATCC Test Method 100, Quantitative assessment of antibacterial activity). The foam-coated paper samples were tested for antibacterial activity towards gram+ *Staphylococcus aureus* and gram- *Klebsiella pneumoniae*. The inoculated samples were subjected to overnight incubation (about 18 h) at 30 or 37°C, depending on the optimal temperature for microbial growth. After incubation, the bacteria were extracted from the samples under investigation by using a neutralizing solution. The number of living cells (CFU= colony forming units) in the extracted suspension was evaluated by the count plate agar method. The antibacterial activity of the sample, as bacteria log reduction, was calculated as follows:

log reduction = log CFU T_{18} blank (control) – log CFU T_{18} sample

where CFU T_{18} is the colony forming number corresponding to the bacteria living cells at time 18 hours. In general, two antibacterial effects can be distinguished:

- bactericidal: reduction (killing) of the number of bacteria initially inoculated (CFU at time 0),
- bacteriostatic: inhibition of bacteria growth under testing conditions favourable to bacteria proliferation, evaluated with respect to growth in the blank sample (CFU at time 18 h).

Untreated CNF was used as a blank untreated control (CNF control).

Photocatalytic Activity of the Foam-Coated Papers

The catalytic activity of the treated paper samples was tested using a device developed by Colorobbia, Italy, consisting of a glass chamber, with a quartz window, in which the treated samples were exposed. In the chamber, a NO_x-polluted atmosphere was created and the NO_x concentration, the humidity and the temperature were measured at fixed sampling time intervals. The measurements of NO_x concentrations were carried out by a chemiluminescence apparatus (Thermo, model 42i) (Figure1). The samples are continuously irradiated by a Hg vapours lamp (Osram, Ultravitalux 300W) to induce photoactivation. The measurements were made by passing the polluted air passed through a closed circuit including the reaction glass chamber, a bag in which the polluted air was stored and a pump. During the whole experiment the lamp remained on for activation of the samples. The data collected was used to assess the kinetics of the photocatalytic process.

Figure 1. The photodegradation kinetics of NO_x in gaseous phase by foam-coated papers were tested using a photo-reactor equipped with chemiluminescence and GC/MS by Colorobbia (Italy).

Pinhole Test

Pinhole tests (Figure 2) of the PVA-coated board samples were performed by applying coloured oil on to the coated surface and then wiping the excess off. If the oil penetrated through the pinholes, the product cannot act as a barrier material and continuation tests are useless

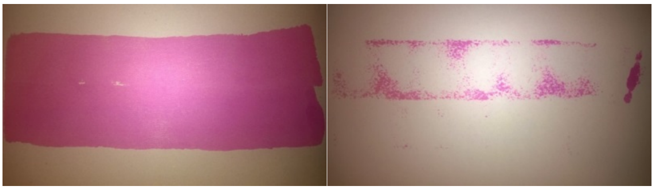

Figure 2. Pinhole test. A coloured oil is applied onto the surface (left). The penetration is observed from the opposite side (right).

KIT-Test (Tappi T559 cm-12)

Primarily, this method is intended to establish an approximate level of grease resistance, by testing the degree of surface repellency and/or anti-wicking characteristics of paper and board, internally or surface sized with organophopic materials such as fluorocarbons. This test is not intended to determine the permeability of grease through the paper or board. A range of numbered solutions referred to as KIT ratings are prepared, consisting of a mixture of castor oil and two solvents (n-heptane and toluene). Differing degrees of dilution of the oil with the solvents provides varying degrees of aggressiveness, and therefore different KIT ratings for the solution to be applied. A drop of one such solution is applied to the paper or board surface. The test continues until the highest numbered test solution does not cause a wetting interaction by darkening the paper or board surface. This number of solution is the KIT rate of the tested sample. A higher number implies a higher surface repellency.

Grease Barrier Test (4h, 60ºC) (Mod. TAPPI 507 T cm-09)

The grease barrier test is based on the TAPPI method 507 T cm-09. Test conditions are 60±3 ºC, 50% RH and 4 hours. Rapeseed oil is used as the test oil. Five parallel samples are measured.

Figure 3. Principle of the grease barrier test.

5 ml of the dyed grease is applied onto the absorbent paper and the grease transfers through that to the sample. The test sample is placed under the absorbent paper so that the barrier side is upwards. The absorbent paper is applied under the test sample. Both the non-barrier side of the test sample and the absorbent paper below the sample are scanned.

Figure 4. The upper photo series is taken from the non-barrier side of the test sample and the bottom photo series from the absorbent paper under the sample.

Grease Barrier Test with Scanning Method

Tested board samples of the size 5 x 5 cm were set on a glass plate. Dyed oil was pipetted automatically on to an absorbent paper placed on top of the board samples. A weight was placed on each individual sample. The test setup was transferred as such to the scanner and covered with a lid. These different phases are shown in Figure 5.

Figure 5. Test procedure of the scanning method.

Scanning is performed according to pre-selected times. A picture of the penetrated grease area is taken with a scanner and presented as a visual result (Figure6). In addition, numerical results are expressed as area fractions of penetrated grease, and they are automatically calculated with image analysis.

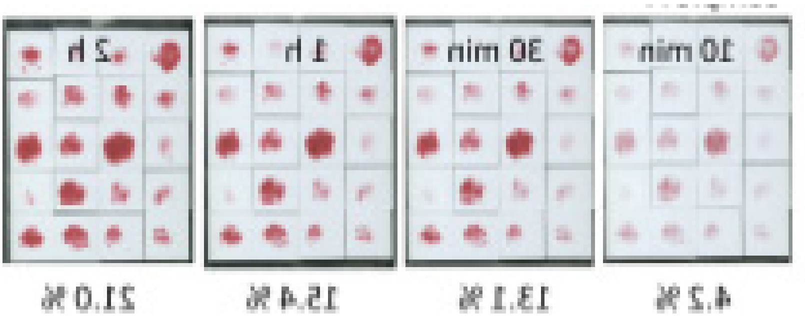

Figure 6. Visual and numerical results (area fraction %) of penetrated grease as a function of time.

Water Vapour Transfer Rate (WVTR) (Mod. ASTM E-96)

Water vapour transmission rates (WVTR) were determined gravimetrically using a modified ASTM E-96 procedure. Anhydrous calcium chloride was used as a desiccant and placed on the bottom of a circular aluminium dish. Coated board samples were cut and mounted on the mouth area of the dish. The uncoated surface faced the low RH environment, i.e. calcium chloride. Wax (beeswax 50% and paraffin wax 50%) was used to seal the samples tightly against the dish surface. Briefly, the wax was heated to 80ºC and applied as molten around the sample using a metallic template and placed concentrically on the sample. After cooling, the template was carefully removed and the dish was covered with a lid made from the same material as the dish and finally, weighed for the first time with an electronic scale and placed without its lid in test conditions. Weighing was repeated until a constant rate of weight increase was attained. WVTR was determined in 23ºC and at 50% RH.

Appendix B: Publications I-VI

I **Kinnunen-Raudaskoski, Karita**; Hjelt, Tuomo; Kenttä, Eija; Forsström, Ulla. (2014) Thin coatings for paper by foam coating, TAPPI Journal Vol. 13 No. 7 July 2014, pp 9-19.

II **Kinnunen-Raudaskoski, Karita**; Hjelt, Tuomo; Sadocco, Patrizia; Forsstöm, Ulla; Paltakari, Jouni. (2017) Novel thin functional coatings for paper by foam coating, TAPPI Journal Vol. 16 No. 4 April 2017, pp. 179-186.

III **Kinnunen-Raudaskoski, Karita**; Salminen, Kristian; Lehmonen, Jani; Hjelt, Tuomo. (2016) Increasing dryness after pressing and wet web strength by utilizing foam application technology. TAPPI Journal Vol. 15 No. 11 November 2016, pp. 731-738.

IV **Kinnunen, Karita**; Lehmonen, Jani; Beletski, Nikolai; Jetsu, Petri; Hjelt, Tuomo. (2013) Benefits of foam forming technology and its applicability in high NFC addition structures, 15th Fundamental Research Symposium, Oxford, UK. Proceedings of the 15th Pulp and Paper Fundamental Research Symposium, Cambridge, Sept 8-13.

V Lehmonen, Jani; Jetsu, Petri; **Kinnunen, Karita**; Hjelt, Tuomo (2013). Potential of foam-laid forming technology for paper applications. Nord. Pulp Pap. Res. J. 28:3, 392-398.

VI **Kinnunen-Raudaskoski, Karita**; Pirkonen, Pentti; Lehmonen, Jani; Hjelt, Tuomo. (2014) Foam-aided sludge treatment, Filtration Journal, vol 14 number 3 August, pp 174-180.

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Kinnunen-Raudaskoski, Karita; Hjelt, Tuomo; Kenttä, Eija; Forsström, Ulla. (2014) Thin coatings for paper by foam coating, Tappi Journal Vol. 13 No. 7 July 2014, pp 9-19.

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Thin coatings for paper by foam coating

KARITA KINNUNEN-RAUDASKOSKI, TUOMO HJELT, EIJA KENTTÄ,
AND ULLA FORSSTRÖM

ABSTRACT: The future of paper products is predicted to lie in intelligent and functional paper properties. These properties are achieved by using coating materials, which are usually very expensive, but the amount needed is also very small. The application of these small amounts requires a new type of coating method; conventional coating methods used in the industry today are not capable of providing ultrathin layers. In this study we introduce foam coating, a technology widely used in the textile and nonwovens industries. Foam coating technology offers a unique opportunity to apply coating on the web surface thinly enough to be economically viable. Our pilot-scale studies show that a thin coating of nanomaterial at a thickness of 1 μm or less and coat weight of 0.3-2.0 g/m^2 is enough to change paper surface properties and enable the functionalization of the paper surface. This report describes the applicability of the curtain-like foam coating technology in unmodified cellulose nanofiber (CNF) applications.

Application: Foam coating technology offers a unique opportunity to apply coating on the web surface thinly enough to be economically viable. The method is suitable for nanomaterial applications (e.g., cellulose nanofibers) onto fiber-based substrates.

Historically, much more attention has been given to the development and use of foam control agents to eliminate foam in the textile, nonwovens, and paper industries than to the science of foam generation. A number of publications and books deal with foam problems in processes and foam control [1]. In the textile industry, a purposeful use of foam is seen in a series of patents in the early 1900s, where “soap lather” was used in a batch process for silk treatment [2,3]. The earliest foam process to receive widespread attention was the Sancowad process, developed in the early 1970s [4,5]. The process was a low-liquor-ratio batch method for in situ foam generation to distribute dyes or finishing chemicals. In 1957, Kumins and coworkers [6] disclosed an early example of continuous foam application for textiles. Foam from an aqueous mixture of colorant, thickener, emulsifier, and foam stabilizer was applied using an engraved printing roll. The principal benefits were reduced thickener requirements and better color yield. Another benefit, reduced drying energy, was a secondary consideration at that time.

In the textile industry, a wide variety of foam application techniques have been developed in which foam is a carrier phase for treatment chemicals [7-15]. The composition, structure, and properties of the recommended foams and the manner of application to the substrate vary widely. Application areas include dying and printing, warp sizing, fabric preparation, and chemical finishing. The foam application method reduces the problems caused by the large amounts of liquid medium used in the more conventional treatments [16].

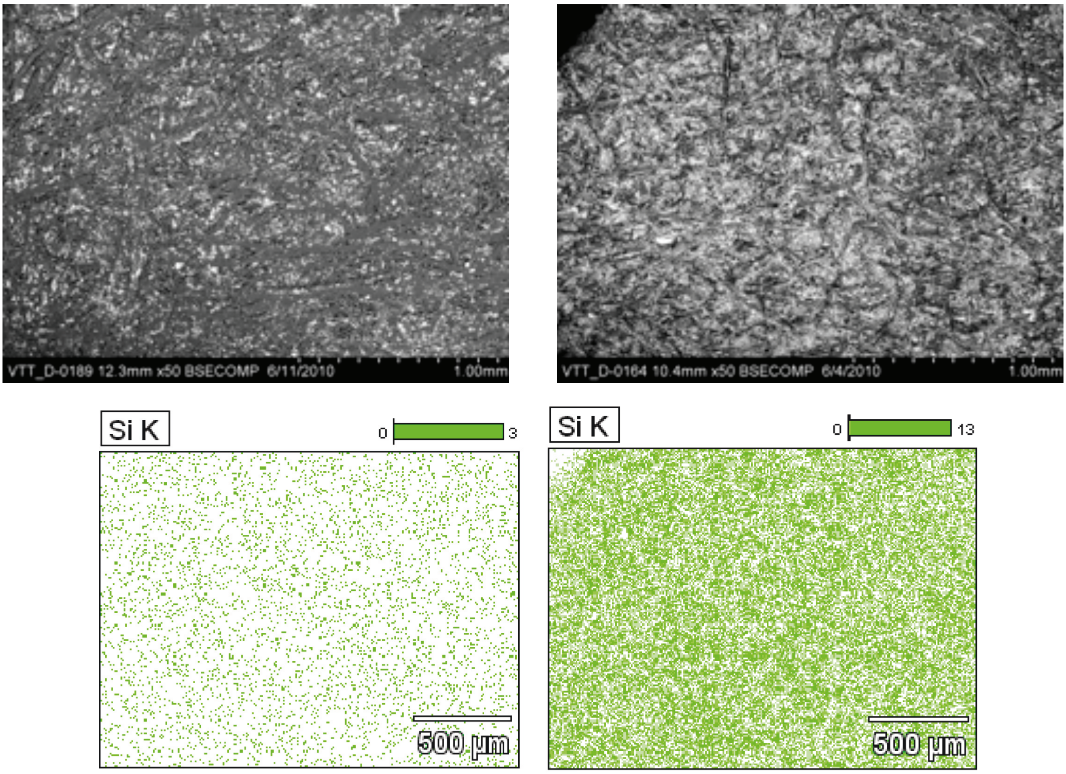
Although the technique is just one among many used by the textile industry over the past 10 years, its importance is growing as a means to optimize the use of costly chemicals and to reduce drying demands to generate energy savings [8,11,17]. Industry experts estimate that wet processes use approximately 60% of the energy consumed in the textile industry [18]. The textile industry is now going a step beyond the low-wet-pickup systems (i.e., foam and film applications), which still require water or solvent, by using totally waterless solid-on-solid (SOS) technology [18].

In paper applications, the first patents of foam technology date back to the beginning of the 20th century, but the technology has yet to gain ground, and only a few applications can be found in the European paper industry. Coatings with dispersions containing microcapsules with natural foaming agents such as gelatin, casein, and soybean extract have been applied as foam to the paper web [19] by the Wiggins Teape company, known for the Radfoam foam forming technology. The method has also been used to correct an inherent curl in one-side coated (C1S) papers and for the controlled addition of materials such as starch, wet strength resin, poly vinyl alcohol, wet-end sizing agents, and direct dyes [20-22]. This Foamcote system used at Wolvercote Paper Mill, Oxford, England, and described in patents issued to Jenkins [23,24] had a speed limit of 65 m/min because of turbulence. Eklund and Hobbs presented a Foamcoat application system for applying foamed starch to a paper web at high speeds [25]. Their studies were conducted on a pilot size press at speeds of up to 610 m/min for two-side foam application. Higher speeds, 1160 m/min, and one-side applications were conducted using the roll applicator position of the blade coater.

Foam enables thin film application, but so do spray and film transfer technologies. Spray technology is widely used in applications such as coating, cooling, fire protection, gas cooling, humidification, marking, misting, spray drying, and spray painting [26]. In papermaking, sprays are mainly used for web moisturizing before calendering, sizing between board layers, and washing. Spray applicators use nozzles that facilitate the formation of spray by producing a stream of droplets. The viscosity of a liquid influences droplet size and size distribution in the spray; the higher the viscosity, the bigger the droplets. In pigment coating, typically 90% of the droplets are in the range of 20–60 μm [27]. The surface energy of the paper and the surface tension of the liquid influence on the spreading of droplets.

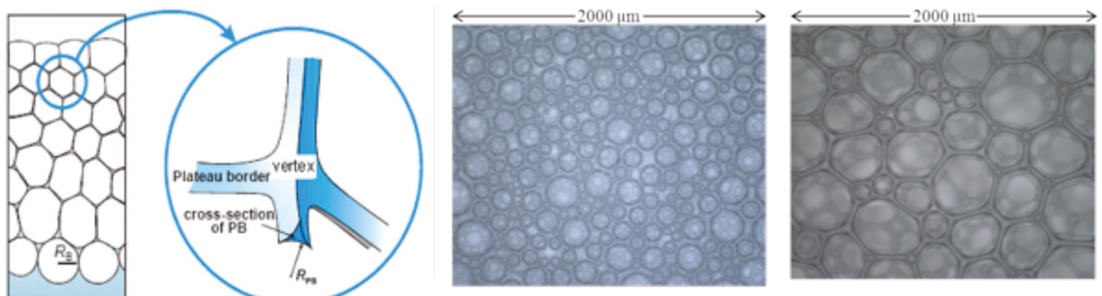
The spray method has a number of benefits. First, it is a noncontact coating method enabling coating of lower basis weights or weaker webs. Second, it has a higher web moisture tolerance, meaning greater flexibility for placing the coating station within the machine. Third, coat weight variation is better than in blade or film coating, with a usual peak-to-peak profile of ±5% of the coat weight. In addition, spray technology is suitable for low-speed and high-speed machines [27]. There are, however, several technical challenges to be faced, including nozzle blockage, coating evenness, and over-spray handling. As a result, the technology has not gained wider acceptance in the paper coating industry. The mist handling aspect becomes a serious issue when coating with substances (e.g., nanoparticles) that have unknown health effects. To avoid this, spray coaters that use a liquid other than water normally have an enclosed design.

Film transfer technology does not present such occupational safety and hygiene issues. A thin film of sizing agent or coating color is applied with a short-dwell type applicator to the surface of a transfer roll. The premetering of the film with a metered size press is adjusted partly volumetrically with grooved rods or with smooth large-diameter rods that create a hydrodynamic force in the premetering nip. This film can then be transferred to both sides of the paper sheet in a nip formed between two transfer rolls, allowing coat weights on both sides at the same time [28]. The coat weight can be applied in a range from small amounts of surface sizing agents to medium amounts of coatings. The challenges in film trans-



Fine paper (Si-element map) Foam coated (Si-element map)

1. Scanning electron microscopy-backscattered electrons (SEM-BSE) image of 50× magnification and silicon-element map of base paper (left) and silica foam-coated paper (right). The images show that the silica nanoparticle layer covers the paper surface uniformly.



Air Content 66%

Air Content 94%

2. Coating material is located in bubble pockets (left). Foam with air content of 66% and round bubbles is called wet foam (center) and the dry foam with air content of 94% has a honeycomb structure (right).

fer technology lie in the interactions between coating liquids and transfer rolls that may influence the flexibility of the process and coating results, e.g., film transfer and film release. Especially in thin film coating, the surface material of the transfer rolls plays an essential role in highlighting differences between a coating fluid, a roll, and a substrate. In nanoparticle applications, the viscosity of the coating fluid versus the stability of the nanoparticle solution is also a challenge.

Foam coating enables layering of paper structure in wet or dry web applications [29]. Foam coating can be accomplished using different methods, but in this paper we focus on a curtain-like foam coating method with foam destruction through liquid absorption by the absorbent web and through infrared drying. In this method there is an open gap between the slot and the moving web. Depending on the application, we used a gap of 200-800 μm.

In dry web application, we have proven its applicability to paper on a pilot scale using the KCL pilot coating machine. In this study, we show its applicability to paper in cellulose nanofiber applications. Our earlier studies [30,31] showed that the foam coating technique is able to create a thin pigment layer on paper. The characterization of thin coating layers is challenging and requires a combination of different microscopic and spectroscopic analyses. Our results from nanosilica application show that the nanoparticle layer uniformly covers the surfaces of of coated and uncoated papers, based on surface SEM-EDX element maps (**Fig. 1**) [32].

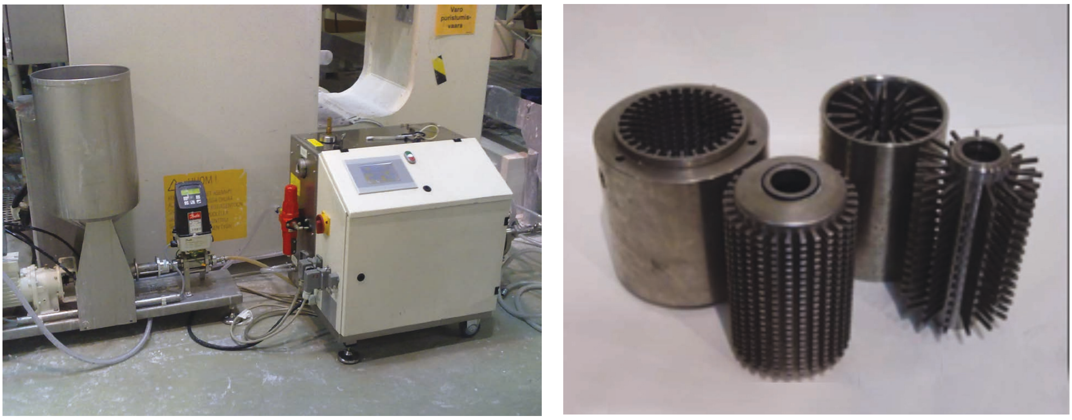
EXPERIMENTAL

Foam coating technology

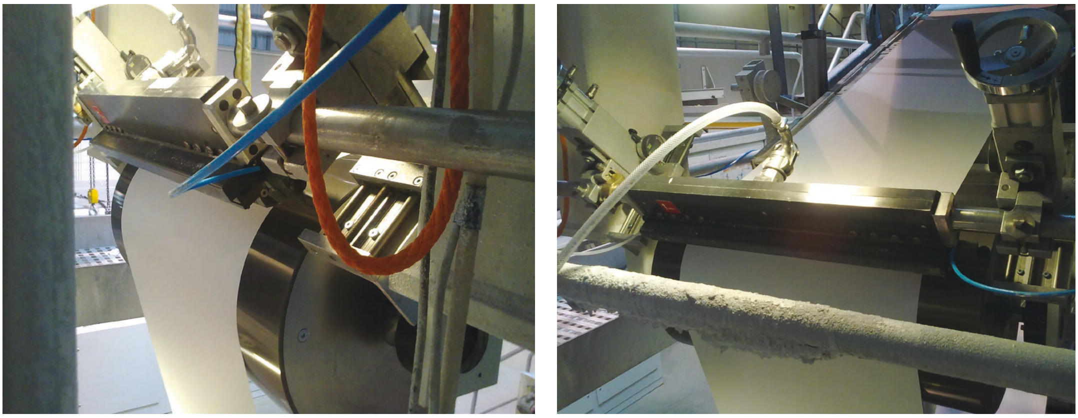
In the foam coating process, dry foam with an air content greater than 80%, and preferably 90%–95% (corresponding to foam densities of 50–200 g/L), is used as a carrier phase for the coating material. **Figure 2** shows the difference between a wet and a dry foam. In the wet foam example, having air content of 66%, the foam bubbles are round, the average bubble radius is less than 100 μm, and the foam is liquid-like in behavior. In contrast, the structure of dry foam, with air content greater than 80%, resembles a honey comb, has an average bubble radius of about 100 μm, and the foam is like a stable shaving cream. The coating material is located in the bubble pockets (vertices) for both processes.

In the foam coating process, the starting material containing foaming agents is mixed with pressurized air using a foam generator. The coating material foam is then pumped forward to the coating unit via a narrow hose. The hose is one of the factors that influences foam stability, along with proper foaming chemistry. The stability of the foam in the foam coating process is the most important property, in addition to bubble size and bubble size distribution, to achieve an even, thin coating layer. The best indicator for stability is the back pressure value measured by the foam generator. By choosing a hose with the right length and diameter, we can control the foam stability. Application on to the moving web is done using a narrow slot-type applicator. After foam application to the web, the bubbles collapse because of absorption, leaving the collapsed foam coating material on the web surface. Because the foam normally contains 90%-95% air, to achieve the desired coat weight, instead of a 1 μm layer of liquid, a 10 μm layer of foam is spread on the moving web. This makes it possible to spread a small amount of nanomaterial evenly over the substrate. The applied coat weights are as thin as 0.1 g/m^2.

Foam coating technology has several benefits. It can offer savings in raw materials and in investment costs, because there is no need for massive coating kitchens or circulation systems of coating material. The method is versatile, allowing the use of a large variety of materials because of the viscoelastic nature of the foam, whereas in film transfer and spray technologies the material base is more limited. In nanomaterial applications, the benefits that foam coating offers are very important. When foam coating nanoparticles and nanofibers, the materials are located between the air bubbles, preventing flocculation of the nanomaterials. Foam coating is also a noncontact application method, which is important when coating with highly adhesive nanoparticles. This is a beneficial property of nanomaterials in foam coating recipes, which has



3. The foam generator (left) and examples of the mixing head's rotor-stator sets (right).



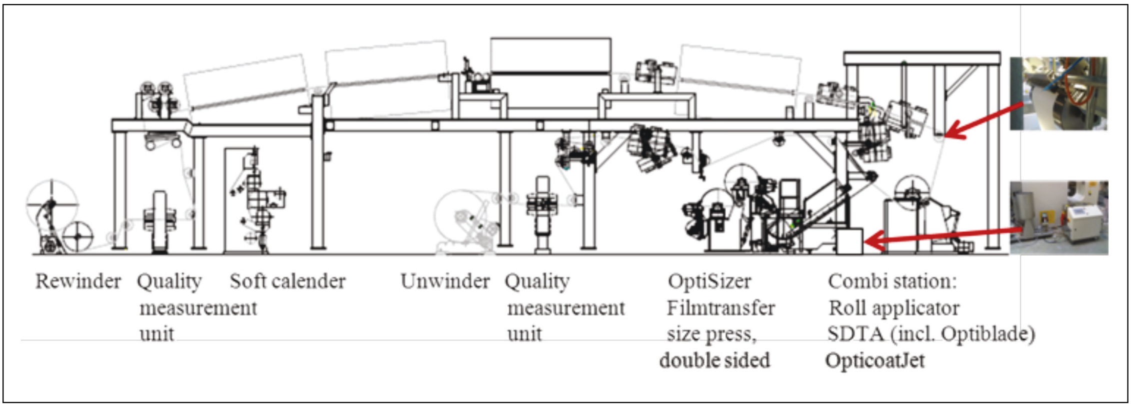
4. The narrow slot-type foam applicator.

shown some nanomaterials do not need any binders [30,31]. Nanoscale particles and nanofibers such as cellulose nanofibers have sufficient bonding to the paper because they attach to the substrate surface with short distance forces. Binders are needed when coating material contains micro-scale particles. The starting material can be mixed with a binder formulated to enable foam formation or it is possible to use a foaming agent that also acts as a binder. Simple coating recipes make foam coating an attractive surface method for functionalized nanomaterial applications [30,31].

Compared with spray technology, foam has two significant advantages. First, higher concentrations and viscosities of the starting material can be used. The key requirement of foam coating is that the material needs to be able to be pumped and to hold a stable foam. The ability to use high viscosity materials is a remarkable advantage in cellulose nanofiber (CNF) applications. CNF is a very viscous, gel-like material already in low consistencies (e.g., 2%). It is therefore impossible to use CNF in spray technology without significant dilution, whereas CNF is applicable as such in foam technology. This demonstrates a significant difference between spray and foam technologies in the amounts of water applied to the paper. Second, the foam coating method is an occupationally safe method, because there are no airborne particles.

In comparison with film transfer, the main benefits of the foam coating operation are flexibility and simplicity and a lower space demand. In film transfer applications, a compatibility of surface material of transfer rolls, coating material, and substrate surface is crucial. In nanoparticle applications, a further challenge is the viscosity of the coating fluid versus the stability of the nanoparticle solution. In foam coating, the focus is on compatibility between foaming chemistry and substrate surface.

The main components in a foam coating line are a foam generator and a foam applicator. In our trials, we used a Top-Mix type 60 foam generator (Hansa Industrie-Mixer GmbH & Co.; Heiligenrode, Germany). The capacity of the generator is 6–60 kg/h, which can produce foam with densities of



5. Schematic picture of the KCL pilot coating machine and the location of the foam generator and the foam applicator.

50–400 g/L. The generator is connected to the compressed-air pipeline of the pilot plant. The coating material and foaming agents are mixed with pressurized air in a mixing head having a rotor-stator unit. **Figure 3** shows two examples of rotor-stator setups.

For the application of the foam to the paper web, we used a narrow slot type applicator, the Magnojet – MJ-Do (J. Zimmer Maschinenbau GmbH; Klagenfurt, Austria) (**Fig. 4**). The applicator, originally designed for other applications, was modified for our purposes by the manufacturer. The application width is adjustable to a maximum of 600 mm. The foam enters the applicator chamber in the middle of the unit and the channels inside the applicator divide the foam flow, enabling a uniform outflow of foam.

We have demonstrated the applicability of the foam coating method to paper on a pilot scale using the KCL pilot coater (Espoo, Finland). The pilot coater is equipped with many of the coating units used in the paper industry (**Fig. 5**), and the only difference from a mill-scale coater is its maximum web width of 550 mm. The maximum speed of the coater is 3000 m/min (180 km/h).

The drying capacity of the pilot coater is extensive and includes one electric IR preheater with a counter radiator, three electric IR dryers (two with a counter radiator and one with a reflector), and four gas-heated air floatation dryers. The equipment fits well with the non-contact drying requirement of foam coating in nanomaterial applications. To ensure the foam curtain stability, the applicator was installed before the IR dryers, and the existing roll was replaced by a precise, 320 mm diameter backing roll to improve coating quality. The size of the roll was the maximum for the space available. We also tried a foam application position between the second and third air floats, but the air flow from the air floats disturbed the foam curtain by oscillating the paper web. The web was primarily dried using the IR dryers, and the end moisture content of paper was controlled using gas-heated air floatation dryers. The line also has an on-line soft calendar with two nips. The maximum pressure available is 300 kN/m and maximum temperature is 250°C.

The coating speed used in the foam coating trials was typically 100 m/min. The maximum speed we have obtained so far with the KCL pilot coater while applying foam is 400 m/min. To increase the speed and to improve the evenness of the coating layer, technical improvements are needed to remove the air coming with the paper web. Lower speed was essential to obtain high enough coat weights because of the low consistencies of cellulose nanofibers. To increase the coat weight in some applications, we double coated the paper. After the first coating with foam, the paper was returned to the unwinder and the second coating layer was applied. The coated paper was on-line calendered using a nip load of 100 kN and temperature of 55°C.

MATERIALS

Cellulose nanofibers applications

CNF is a material composed of nanosized cellulose fibrils with a high aspect ratio (length-to-width ratio). The width of fibrils is typically 5-20 nm and the length can range from 10 nm to several microns. The more nanoscale the CNF material is, the more viscous and transparent it appears. We used three different types of cellulose nanofibers isolated from the wood-based fibers in our trials. The unmodified, native CNFs were produced in the European Union's Scale-up of Nanoparticles in Modern Papermaking (SUNPAP) project. **Table I** shows the pretreatment methods of the starting wood pulp and the homogenization methods in isolation of fibrils [33]. **Figure 6** shows the benefit of foam coating compared with a spray application method in the cellulose nanofibers application, namely that higher solids content can be used in foam coating. The starting CNF has solids content of 2.9% and does not flow by itself into the screw pump, but the resulting foamed CNF from the generator with air content of 90% is a suitable material for the coating process. The CNF was pushed to the pump because of the neck (10 cm length and 4 cm diameter) combining the feeding tank and the screw pump. In the other generator, the tank opens straight to the pump and

	CNF-CTP	CNF-TE/CTP*	CNF-TE/PTS**
Pre-treatment **Homogenization**	Enzymatic micro-fluidizer by CTP	TEMPO oxidized micro fluidizer by CTP	TEMPO oxidized cavitron by PTS
Solids content	2%	2%	9%
Gel type	 opaque, viscous	 transparent, solid	 white, fluid
Zeta potentials	-25.0 mV	-69.5 mV	-55.5 mV
* CTP – Centre Technique du Papier; Saint-Martin-d'Hères, France. * PTS – Papiertechnische Stiftung; Munich, Germany.			

I. Unmodified cellulose nanofibers used in our foam coating trials.

6. Carbon nanofiber (CNF) with solid content 2.9% (left) and foamed CNF containing 90% air (right).

it does not face this kind of problem, but it was not used in these trials.

Unmodified, negatively charged CNFs with zeta potentials of -25.0 mV, -69.5 mV, and -55.5 mV were foamed using an anionic surfactant (sodium dodecyl sulfate) as a foaming agent. Foam stabilizers were not needed because the nanofibrils and particles stabilized the foam. The base paper used in the trials was 80 g/m^2 uncoated and uncalendered fine paper. **Table II** lists the base paper characteristics.

CHARACTERIZATION

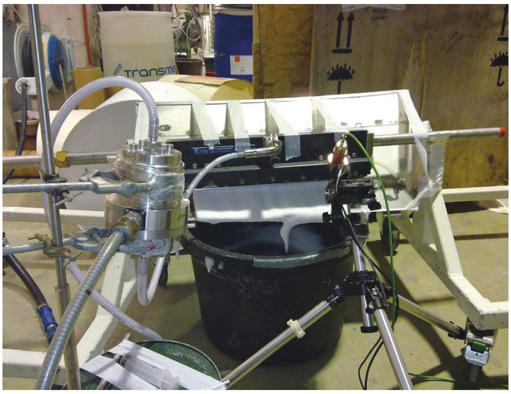
Characterization of foam

For successful foam coating, one of the most important prerequisites is proper foam generation, with an average bubble size and stability suitable for the process. Inside the foam, nanosized particles are located in the vertices between bubbles (Fig. 2); thus, the size of the bubble is directly related to the distance between applied particles. The smaller the bubbles, the more uniform the coating.

In our process, foam is produced by a foam generator at floor level and is fed via a plastic hose several meters long to the foam applicator 5 m above, and applied on to the substrate. On its way to the applicator, the foam faces temperatures ranging from 15°C (the hose on the cold floor) to dozens of degrees higher (influenced by the drying section) as it travels to the slot for application. The back pressure, measured by the generator, is one of the controlling factors in foam production. Other important factors are foam chemistry, pumping speed, foam density, and rotation speed of the mixing head. The length of the hose affects the pressure inside the hose; therefore, different hose lengths were tested. The experimental setup (**Fig. 7**) was built to study the quality of the foam

Grammage (g/m^2)	Bulk (cm^3/g)	Opacity	Gloss (75° md)	Roughness (PPS, µm)	Roughness (Bentsen, mL/min)	Air Permeance (µm/Pas)
80	0.0012	94	5.8	4.9	150	5.8

II. Base paper characteristics.



7. Experimental setup for the measurement of the foam quality with analyzing devices: Turbiscan Online (left) and a high speed camera (right).

produced. A steel plate with a steep slope was placed under the applicator so that the foam slid along a smooth surface after coming out of the applicator. Hose lengths of 3 m, 5 m, 7 m, and 10 m were studied. The effect of foam temperature was tested by placing a part of the hose in a water tub containing cold (16.5°C) or hot (55°C) water, with the reference being the pilot plant ambient temperature of about 25°C. At some test points, the air content of the foam was also varied, from 90% to 94%. The foam was produced from diluted 1% CNF dispersion and analyzed for bubble sizes and bubble amounts by means of photographs taken with a magnifying high-speed camera as the foam was coming out and sliding along a smooth surface. Because of the laborious work, photographs from only four test points were analyzed. A Turbiscan Online (Formulaction; L'Union, France) measurement device installed between the foam generator and the foam applicator was also used.

Characterization of foam coated paper

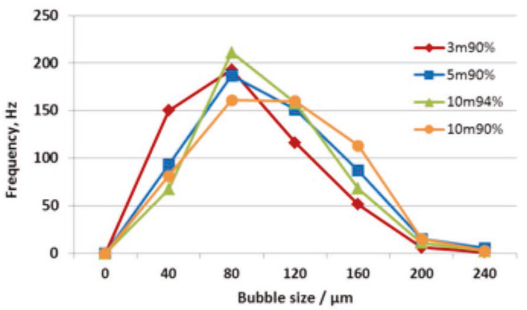
The surface layer and paper characterization of foam-coated paper samples was done with the combination of two different methods [27], e.g., an S-3400N scanning electron microscope (SEM) (Hitachi; Tokyo, Japan) and Noran System Six EDX spectrometer (Thermo Scientific; Watham, MA, USA). Measurement was carried out after laboratory calendering of the foam-coated papers. Paper gloss (75°), air permeability, and PPS S10 roughness were also measured from laboratory calendered samples. The contact angle of water was measured with a CAM 200 device (KSV Instruments; Monroe, CT, USA) to measure the wetting of foam-coated paper.

RESULTS

Foam stability

Our measurements showed that an acceptable foam was rather insensitive to changes in process conditions such as foam temperature and pressure. A good foam is stable and has a narrow bubble size distribution, with an average bubble size around 100 µm. This means that foam chemistry was suitable for the coating material and for the coating process. **Figure 8** shows the the high-speed camera results; the values were calculated as averages of the temperature test points. According to the results, the smallest bubbles and the narrowest bubble size distribution were obtained using 3 m length hose and 90% air content.

The values were compared with the data obtained using Turbiscan Online equipment (**Table III**). Increases in hose length and temperature increased average bubble size. Although it was difficult to conclude if the differences were real or the result of data scattering, the differences in bubble sizes were rather small. The results also showed that the stability of the foam could be measured using devices based on light scattering. Besides bubble size and bubble size distribution, a critical foam property is the stability of the foam. Based on our work, the best indicator of foam stability is the back pressure value measured by the foam generator. The variables that increase back pressure are: longer hose length between the foam generator and the applicator, smaller diameter of the hose, higher surfactant amounts, and higher air content in the foam.



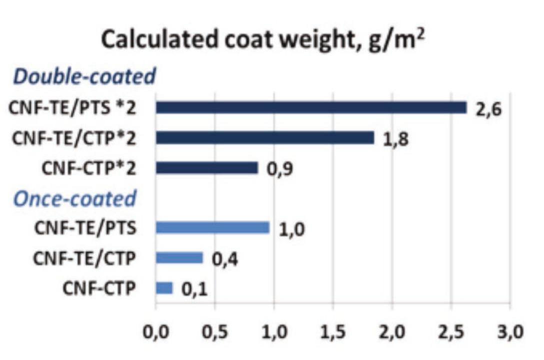
8. The measured bubble size distributions. The first number is the length of the used hose, and the second number is the foam air content (%).

Test Points (length of the hose, air content, temperature)	Bubble Size Turbiscan (μm)	Bubble Size from Images (μm)
3 m, 90%	75	68
3 m, 90%, 16.5°C	75	
3 m, 90%, 55°C	80	
5 m, 90%	81	84
7 m, 90%	86	
10 m, 90%	88	88
10 m, 94%	80	81
10 m, 90%, 16.5°C	78	

III. Average bubble sizes measured with Turbiscan Online and image analysis.

Native cellulose nanofibers layer

Because of the low solids content of unmodified CNFs, the once-coated paper had coat weights of 0.1-1.0 g/m². To maximize the amount of CNF coating on the paper surface, the coated paper reel was returned to the unwind position and coated again using the same CNF coating and conditions. The pumping speeds of coating materials were 30-60 L/h, foam densities 100-200 g/L and paper web speed 100 m/min. After foam coating, the paper was on-line calendered using 55°C temperature and nip load of 100 kN. Base paper was calendered under the same conditions. Because a higher amount of CNF coating was applied, it was possible to determine the coat weight by measuring the weight difference between base paper and coated paper; otherwise the coat weight was calculated from the trial parameters. The coat weight obtained with single layer coat weight was 1.0 g/m² or less and 1.0-2.6 g/m² for double coating (**Fig. 9**). The test results show (**Fig. 10**) that a very thin layer of unmodified CNF having a coat weight of approximately 0.5 g/m² changed the surface properties of fine base paper. Air permeability was decreased with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) CNFs and coated paper surface was smoother in the case of micro-fluidizer CNFs compared with the base paper. The smoothing influence was obtained in small-scale roughness (Parker Print Surf [PSS]). Paper roughness (PPS-S10) values show that the smoothest surface is obtained with coating that uses CNFs with TEMPO oxidized pre-treatment and micro fluidizer homogenization made by Centre Technique du Papier (CNF-TE/CTP). Smoothing is already obtained with coat weights less than 1 g/m². The coating made using CNFs with TEMPO oxidized pre-treatment and Cavitron homogenization made by Papiertechnische Stiftung (CNF-TE/PTS) of Munich, Germany, did not smooth the surface, probably because of a larger particle size in the CNF-TE/PTS. Air permeance values show that CNF-TE coatings, especially CNF-TE/CTP, make the paper surface more closed (Fig. 10).



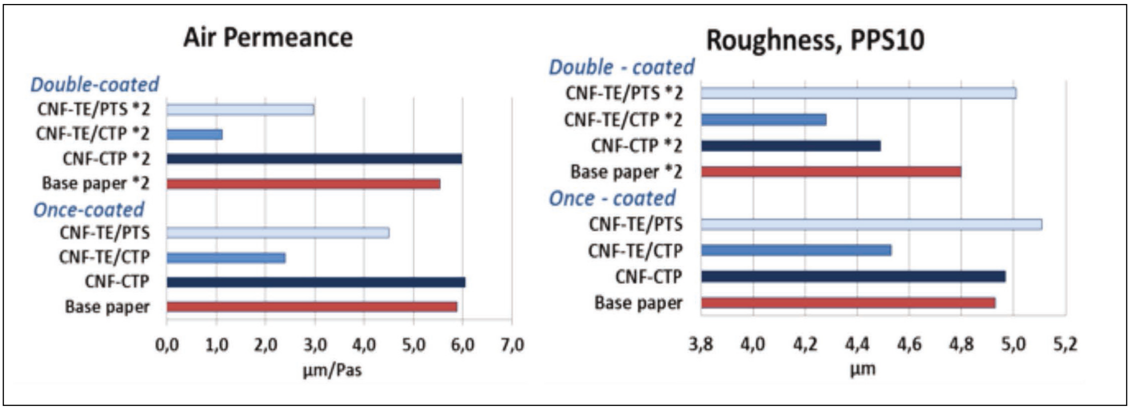
9. Coat weight of carbon nanofiber coating, once- and double-coated samples (*2). The coat weight obtained with double-coating was from 1.0 g/m² to 2.6 g/m², and single-layer coat weight was 1.0 g/m² or less.

The results also show that unmodified CNFs increase paper surface hydrophilicity. **Figure 11** shows the contact angle values of base paper and foam-coated samples using water as the fluid. The paper surface is more hydrophilic after CNF coating, except for the once-coated CNF-CTP sample that had very low coat weight. CNF with TEMPO oxidized pre-treatment has a stronger influence than CNF with enzymatic pretreatment. As might be expected in single-coated samples, the effect of CNF coating is not as strong as after double-coating.

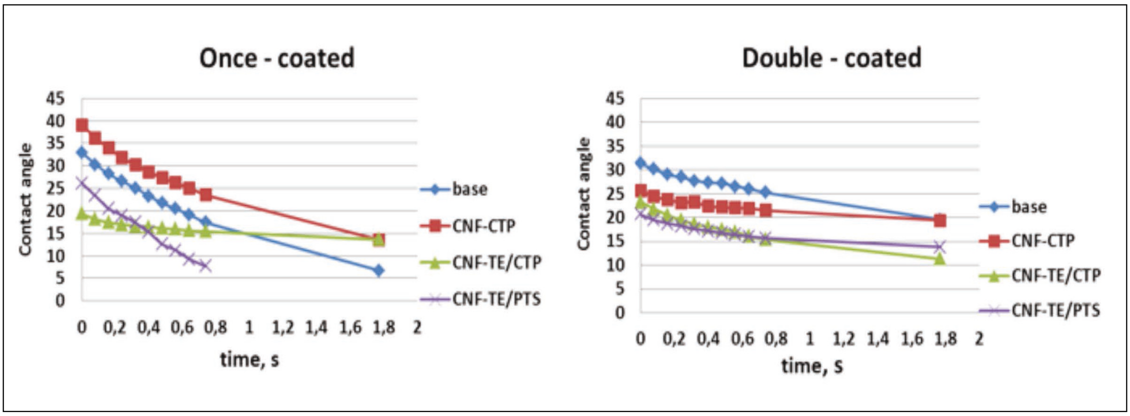
The paper surface structure of double CNF foam-coated paper after on-line calendering was analyzed with scanning electron microscope (SEM) imaging using a secondary electron (SE) detector. Surface images were compared with the base paper (**Fig. 12**). The nanocellulose coating of CNF-TE/CTP did not clearly stand out in the SEM images of 100× magnification, but the CNF-coated surface looks more opaque than the base paper surface. The SEM image shows that the CNF coating has evened out the paper surface and reduced the surface porosity.

CONCLUSIONS

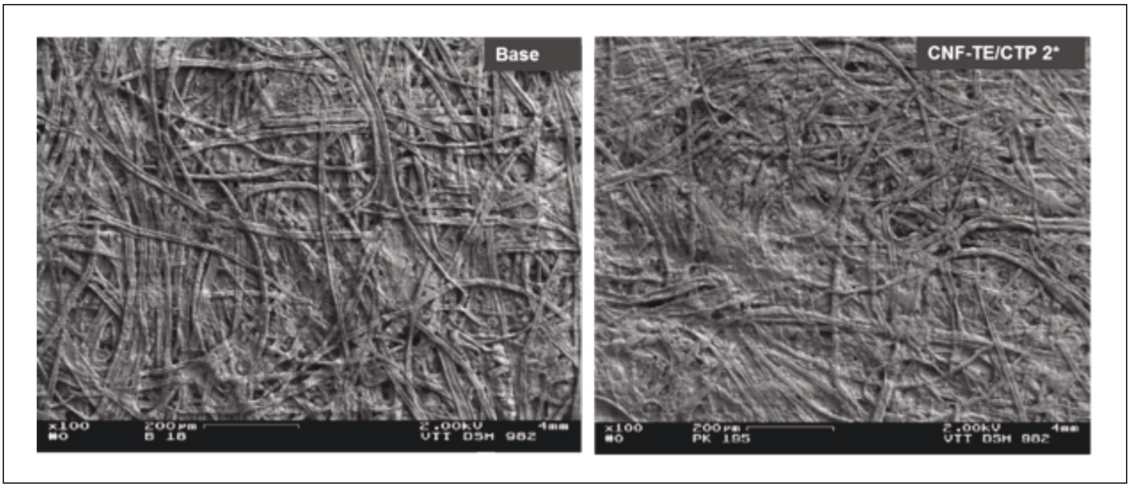
The results presented from our pilot-scale studies clearly show that foam coating is a suitable method for applying cellulose nanofiber onto fiber-based substrates. The technology offers a unique method for applying very light coat weights to the web surface with exceptional uniformity and absence of coating strike-in. Foam application of CNF, specifically, is a viable application method; a standard spray application of CNF at the same consistency would not be possible. Lack of airborne particles during the coating process makes foam application more favorable from an environmental and worker health perspective. For successful foam coating, an important prerequisite is proper foam, with an average bubble size and stability suitable for the process. Our measurements showed that a good foam (as defined in the discussion) is rather in-



10. Air permeance and Parker Print Surf S10 roughness values of base paper and carbon nanofiber-coated samples.



11. Water contact angle values of single- and double-coated papers show that unmodified carbon nanofibers increase paper surface hydrophilicity.



12. Topographic image (secondary electron-scanning electron microscopy [SE-SEM]) of base paper (left) and carbon nanofiber-TE/CTP double-coated paper (right). Magnification 100×.

sensitive to changes in process conditions such as temperature and pressure.

The results obtained showed that even a small amount of nanomaterial could change the surface properties of the paper. A thin layer of unmodified cellulose nanofibers increased hydrophilicity of the paper and closed the paper surface making it smoother and less permeable. The study indicates that when using functionalized coating materials (CNF in this case) it is possible to create functionality in paper by foam coating.

The method is suitable for self-foaming materials and for foamable materials. The foam chemistry and possible binders need to be adjusted to meet the properties and requirements of the starting material and the substrate. Technically, the foam coating method is suitable for materials used in the wet end such as starch, wet strength resin, polyvinyl alcohol (PVA), wet end sizing agents, and direct dyes [19-21], but also for novel materials such as functionalized nanomaterials [30,31]. **TJ**

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ABOUT THE AUTHORS

Our research around foam-based technology started almost 10 years ago when we had a project involving paper structuring; the base from coarse material and the top layer from ground fines. At that time, we did not speak about carbon microfiber or carbon nanofiber; however, the fine material was prepared using a Masuko grinder.

The foam-based technology opened up a totally new research area. Earlier, Kinnunen-Raudaskoski worked as a Fourier transform infrared spectroscopy analyst and also did research work in food contact materials. Now, the focus is totally in foam: foam coating, foam forming, and foam-assisted dewatering.

The most challenging aspect of this research was in the beginning to find co-operation partners, machine suppliers, and of course, to convince research directors and the paper and board industry of the usefulness of foam.

This research has opened up new research topics in foam utilization, and it raised an interest in further developing foam coating technology. The most interesting finding was the applicability of foam technology to paper.


Kinnunen-Raudaskoski


Hjelt


Kenttä


Forsström

We hope this research will further generate rethinking in the paper and board industry: Would this be technology for new materials or can chemicals added at the moment to the wet end be applied this way?

The next step is to show that, using functionalized material, it is possible to create activity on the paper surface and to show the applicability of the foam-based application technology in paper and board machines.

Kinnunen-Raudaskoski, Hjelt, and Kenttä are senior scientists and Forsström is principal scientist with VTT Technical Research Centre of Finland, Espoo, Finland. Email Kinnunen-Raudaskoski at karita.kinnunen@vtt.fi.

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II

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Novel thin functional coatings for paper by foam coating

KARITA KINNUNEN-RAUDASKOSKI, TUOMO HJELT, ULLA FORSSTRÖM,
PATRIZIA SADOCCO, AND JOUNI PALTAKARI

ABSTRACT: Conventional coating methods are currently being challenged by newly developed technologies that can result in products with interesting properties and competitive prices. Versatile foam coating is one such promising technology. Foam coating is carried out using different foam application methods, and the viscoelastic nature of the foam allows the use of a large variety of materials. Paper was coated with nanomaterials on a pilot scale using a method based on slot die application combined with foam destruction by absorption and infrared drying. A thin layer of titanium dioxide/zinc oxide (TiO_2/ZnO) functionalized cellulose nanofibrils (CNF) creates antimicrobial properties in the paper, and a thin layer of CNF-TiO_2 alone has substantial ability to oxidize nitric oxide (NO) and nitrogen oxides (NOx). These results illustrate methods that can be used to create novel functional properties for different end-use applications. Thin functional layers could bring added value to current products and also create opportunities to introduce novel products for several industrial areas using web-type manufacturing processes.

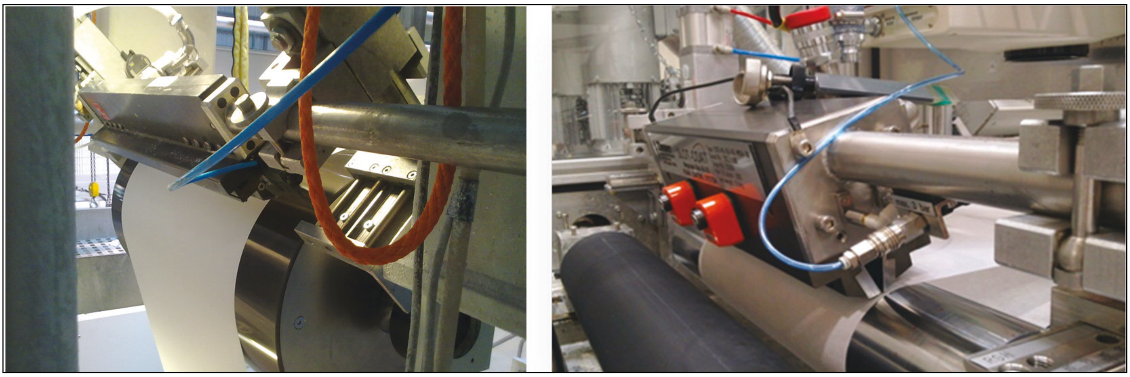
Application: The versatile foam coating method, using foam as a transferring media, allows manufacturers to modify web surfaces with a large variety of materials, from nanoparticles to highly viscous material such as cellulose nanofibers.

In foam coating, foam is commonly used as a carrier phase for applied chemicals or dispersions. In the textile industry, a wide variety of foam application techniques have been developed [1-9]. The foam application method reduces the problems caused by large amounts of liquid medium used in conventional treatments [10]. In paper applications, dispersions containing microcapsules with the natural foaming agents, gelatin, casein, and soybean extract have been applied [11]. Materials such as starch, wet strength resin, polyvinyl alcohol, wet end sizing agent, and direct dyes, as well as correction of an inherent curl in one-side-coated papers by water, have been applied using the foam coating method [12-14]. This system, referred to as the Foamcote system, is described in patents [15,16]. Eklund and Hobbs presented a more flexible application system for applying foamed starch to a paper web at high speeds [17].

Our earlier work [18-24] clearly shows that foam coating is a suitable method for applying nanoscale material to fiber-based substrates, and the method has several benefits compared with spray or film transfer technologies [21]. The technology offers a unique method for applying very light coat weights to the web surface with exceptional uniformity and absence of coating strike-in. Our earlier studies also showed that even a small amount of organic nanomaterial could change the surface properties of the paper [21]. The characterization of the coating layer having a small amount of material on the surface is challenging; however, in the case of inorganic particles, a combination of microscopic and spectroscopic procedures can be used for the analysis [23]. A thin layer of unmodified cellulose nanofibrils (CNF) increased hydrophilicity of paper and closed the paper surface, making it smoother and slightly less permeable [20,21].

Silver has been known to be an antimicrobial agent. Polycrystalline titanium dioxide (TiO_2) powders, on the other hand, have been intensively used as white pigments in diverse applications, including papermaking [25]. The photocatalytic properties of TiO_2 were first discovered 40 years ago [26]. TiO_2 is also a photoactive material with the ability to promote oxidation of organic adsorbates at the surface because of photogenerated electron-hole pairs after ultraviolet irradiation [27, 28]. The optical activity of TiO_2 has also been intensively exploited in the field of heterogeneous photocatalysis and solar energy conversion. Moreover, extended studies have been carried out on photodegradation of volatile organic compounds. More recently, there has been great interest in TiO_2 as a photoactive antimicrobial agent. In addition, the antimicrobial properties of zinc oxide were considered to be of interest [29].

In this paper we describe how the aforementioned properties of TiO_2 and zinc oxide (ZnO) were exploited for the first time in CNF-based products by foam coating of paper [24]. In addition, we tested the thin layer of CNF-TiO_2 alone for the oxidation of nitric oxide (NO) and nitrogen oxides (NOx).



1. The narrow slot-type foam applicator. The left side applicator has a labyrinth design, and the foam enters the applicator chamber in the middle of the unit. The right side applicator has a chamber design, and the foam enters the applicator from both ends.

2. Cellulose nanofibrils (CNF) with solid content 2.9 % (left), and foamed CNF containing 90% air (right).

EXPERIMENTAL

In the foam coating process, dry foam with air content greater than 80% and preferably 90%–95% (corresponding to foam densities of 50–200 g/L) is used as a carrier phase for the coating material. The coating material is located in the bubble pockets (vertices) and on the bubble surfaces. The main components in a foam coating line are a foam generator and a foam applicator. These trials used the Top-Mix type 60 foam generator (Hansa Industrie-Mixer GmbH & Co. KG; Stuhr, Germany). The starting material feeding capacity of the generator is 6–60 kg/h, and it can produce foam with densities of 50–400 g/L. The generator is connected to the compressed-air pipeline of the pilot plant. The coating material and foaming agents are mixed with pressurized air in a mixing head equipped with a rotor-stator unit.

For the application of the foam, two different Magnojet narrow slot-type applicators (J. Zimmer Maschinenbau GmbH; Klagenfurt, Austria) were employed and are shown in **Fig. 1**.

Foam coating trials

In the trials of CNF functionalized with nanoparticles, we used a noncontact, curtain-type foam application method, where foam collapses through the absorption of the paper web and through infrared (IR) drying. This method is suitable especially for small application amounts with hydrophilic substrates with fast absorption properties.

The trials were performed at the Zimmer coating line in Austria. The chamber-type applicator was used in the trials. A 400-µm gap between the slot and the moving web was used. The IR drying, with the dryers on both sides of the web, was followed by drying with hot-air ovens at a temperature of 150°C. The maximum speed of the line is around 180 m/min, but the coatings were applied at 100 m/min. This coating speed allowed for the low consistency of CNF coating to achieve the desired coat weights, while providing enough speed to obtain a good quality coating layer. The applied coat weights in trials at Zimmer were 0.4–1.8 g/m^2. The maximum speed we have obtained so far with the KCL pilot coater is 400 m/min (KCL Pilot Plant; Espoo, Finland). Technical improvements are nonetheless needed to increase the speed and to improve the evenness of the coating layer.

Property	±	TiO_2	ZnO
Concentration, %w/w	0.5	6.0	1.0
Density, g/cm³	0.05	1.20	1.12
Viscosity (25°C), mPa/sec	0.1	2.00	ND
Particle dimension, nm	-	40.0	45.0
Polydispersity index	0.05	0.25	0.20
pH	0.5	1.0	ND
Cationic surfactant, %w/w	0.05	0.1	-

I. Physicochemical characterization of inorganic nanoparticles (TiO_2 = titanium dioxide; ZnO = zinc oxide).

Materials

Functionalized cellulose nanofibrils

This work was carried out as part of the European SUNPAP (Scaling Up Nanoparticles in Modern Paper Making, 2009-2012) project targeting CNF applications. However, other nanomaterials, such as silica, can be used as a carrier for the functional materials. CNF are nanosized cellulose fibrils with a high aspect ratio (length-to-width ratio). The width of fibrils is typically 5–20 nanometers and the length ranges widely from tens of nanometers to several microns. The more nanoscale particles present in the CNF material, the more viscous and transparent the material will be. The benefit of foam coating is that high-viscosity CNF does not need to be diluted for the coating process. **Figure 2** shows the case where the starting CNF had a solids content of 2.9% and did not flow by itself into the screw pump. However, the foamed CNF from the generator (with an air content of 90%) was a suitable material for the coating process. The foamed CNF was pushed manually to the pump through the pipe (10 cm length and 4 cm diameter), combining the feeding tank and the screw pump.

The CNF for the trials was produced by the Centre Technique du Papier, Gières, France (CTP). The CNF fibers were produced by an initial enzymatic pretreatment of cellulose fibers followed by low consistency refining. Then, the pretreated and refined fibers were disintegrated to nanoscale particles by running them through a homogenizer several times. This produced CNF with a solids content of 2.3%, which was then functionalized by Innovhub (Milan, Italy). For functionalization of the CNF, inorganic nanoparticles TiO_2 and ZnO were produced by Colorobbia (Vinci, Italy). **Table I** shows the physicochemical characterization of inorganic nanoparticles.

The functionalization of CNF was achieved on the basis of direct physical adsorption of inorganic nanoparticles to CNF. The nanocomposites were prepared by mixing CNF (2.3% in water) with TiO_2 (6% in water) or ZnO (1% in ethylene glycol), or both, for 15 min. The mixtures were then washed three times with water followed by centrifugation to eliminate non-adsorbed inorganic fillers. CNF and inorganic nanoparticles suspensions were mixed together as supplied by an immersion mechanical blade stirrer. Centrifugations were performed and washings were carried out to eliminate excess TiO_2 or ZnO. After each washing, homogenization by stirring was carried out. The centrifuge took approximately 2 min to reach 7000 rpm, which was then maintained for 5 min. After centrifugation, the water supernatant was discarded. The pellet produced was suspended in the same volume of fresh water that had been removed by ultracentrifugation and then mixed with the mechanical stirrer. For the trials, 25 kg of CNF-TiO_2 (2.8% dry weight) and 15 kg of CNF-ZnO-TiO_2 (4.8% dry weight) were produced. The concentration of TiO_2 and ZnO in the final nanocomposites was determined by inductively coupled plasma analysis. **Table II** shows the mixing ratios and the contents of inorganic nanoparticles in the prepared composites.

The foams were produced by mixing the foaming agent and CNF containing nanoparticles with pressurized air in the mixing head of the foam generator. The air content of the foams was adjusted to 80%–90%, with foam density 100–200 g/L. The anionic foaming agent used was sodium dodecyl sulfate, in a ratio of 0.2% of CNF composite volume. The addition of a surface active agent was on the basis of the liquid volume.

Base paper and paperboard

The base paper used in the CNF trials was 80 g/m² uncoated and uncalendered fine paper produced from hardwood and softwood fiber without hydrophobic sizing agents with fast absorption properties.

Characterization

Using the paper samples coated by CNF-TiO_2 or CNF-ZnO, or CNF- TiO_2 and ZnO, the following tests were performed:

Nanocomposite	Solids Content, %	Initial Mixing Ratio of the Preparations, as dry weight	TiO_2 Content, % dry weight	ZnO Content, % dry weight
CNF-TiO_2	2, 8	1:1	24	-
CNF-ZnO and TiO_2	4, 8	10:1:10	42	2

II. Analysis of CNF/inorganic nanoparticles suspensions (TiO_2 and ZnO determined by inductively coupled plasma analysis).

Data Type	Counts
Image resolution	1024 by 1024
Image pixel size	1.06 µm
Map resolution	256 by 256
Map pixel size	4.24 µm
Alternating current (AC) voltage	12.0 kV
Magnification	100

III. The information of scanning electron microscopy analysis of TiO_2/ZnO modified CNF–containing paper.

- Antimicrobial activity (AATCC Test Method 100 "Quantitative assessment of antibacterial activity") toward gram-positive *Staphylococcus aureus* and gram-negative *Klebsiella pneumoniae* [24].
- Photocatalytic activity by using a device designed by Colorobbia Italy [24].

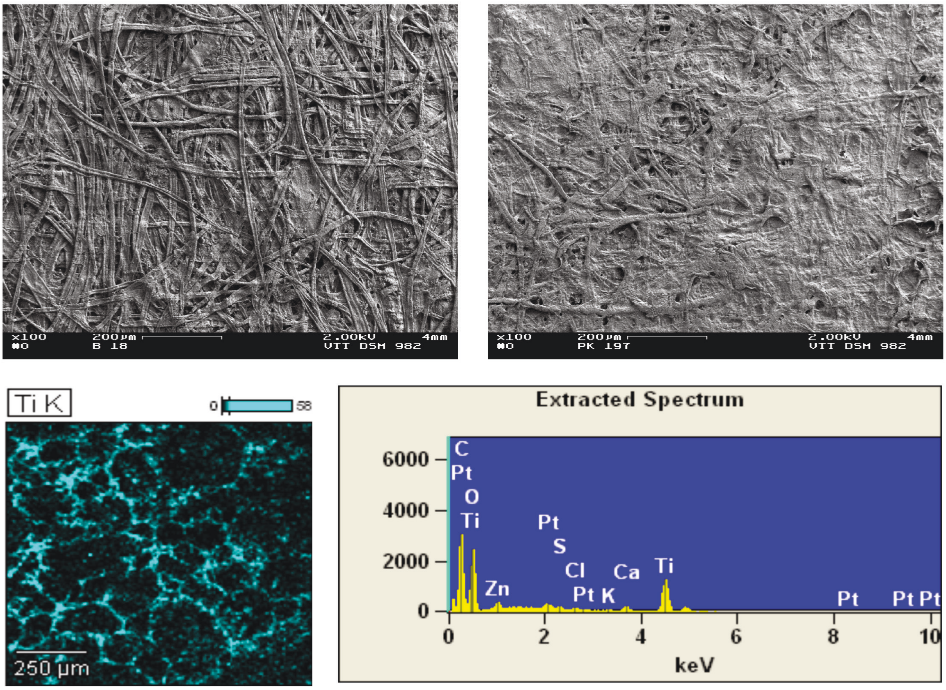
Before the tests, the TiO_2/ZnO modified CNF-containing papers were analyzed with scanning electron microscopy (SEM) imaging using a backscattered electron (BSE) detector and titanium element mapping. The information of SEM analysis is seen in **Table III**.

Titanium element maps show that material on a paper surface is attached on the fiber surfaces to form a structure that resembles a honeycomb (**Fig. 3**).

Antimicrobial activity of the foam-coated papers

Photoactivation

In the presence of TiO_2 and ZnO nanocomposites, the antibacterial tests were carried out on photoactivated samples as follows. The samples were sterilized before testing and the antibacterial tests were conducted by spreading a known number of living cells on the paper surface to yield a population of 10^5 colony forming units (CFU). The paper samples were subjected to light exposure (4 h by standard solar lamp 6000 lux) to induce photoactivation of inorganic nanoparticles (TiO_2 or ZnO, or both). Then the samples were incubated by adopting testing conditions (temperature and nutrients) that promote bacterial growth. In addition, some tests were also run in darkness. The inoculated paper samples were maintained 20 h under optimal nutrient and temperature conditions for bacterial growth. At the end of the test, the paper samples were extracted and the number of living cells determined by plating serial dilution on nutrient agar.



3. Titanium element scanning electron microscopy/energy-dispersive x-ray spectroscopy (SEM/EDS maps) from calendered TiO_2/ZnO modified CNF–containing paper showing that material on the paper surface is attached on the fiber surfaces (top left–base; top right–coated surface).

4. The photodegradation kinetics of nitrogen oxides (NOx) in gaseous phase by foam-coated papers were tested using a photoreactor equipped with chemiluminescence and gas chromatography–mass spectrometry.

Testing conditions

The tests were performed according to AATCC Test Method 100 under static conditions. The foam-coated paper samples were tested for antibacterial activity toward gram-positive *Staphylococcus aureus* and gram-negative *Klebsiella pneumoniae.* The inoculated samples were subjected to overnight incubation (about 18 h) at 30°C or 37°C, depending on the optimal temperature for microbial growth. After incubation, the bacteria were extracted from the samples under investigation by using a neutralizing solution. CFU, the number of living cells in the extracted suspension, was evaluated by the count plate agar method. The antibacterial activity of the sample, as bacteria log reduction, was calculated as follows in Eq. (1):

$$\text{log reduction} = \log \text{CFU } T_{18} \text{ blank (control)} - \log \text{CFU } T_{18} \text{ sample} \quad (1)$$

where CFU T_{18} is the colony forming number corresponding to the bacteria living cells at incubation of 18 h.

In general, two antibacterial effects can be distinguished:

1. Bactericidal — Reduction (killing) of the number of bacteria initially inoculated (CFU at time 0).
2. Bacteriostatic — Inhibition of bacteria growth under testing conditions favorable to bacteria proliferation, evaluated with respect to growth in the blank sample (CFU at time 18 h).

Untreated CNF was used as a blank untreated control (CNF control).

Photocatalytic activity of the foam coated papers

The catalytic activity of the treated paper samples was tested using a device developed by Colorobbia Italy consisting of a glass chamber with a quartz window, in which the treated samples were exposed. In the chamber, a NOx-polluted atmosphere was created and the NOx concentration, humidity, and temperature were measured at fixed sampling time intervals. The measurement of NOx concentrations was carried out by a Model 42i chemiluminescence apparatus (Thermo Fisher Scientific; Waltham, MA, USA) (**Fig. 4**). The samples were continuously irradiated by an Ultravitalux 300W mercury vapor lamp (Osram Light AG; Munich, Germany) to induce photoactivation. The measurements were made by passing the polluted air passed through a closed circuit, including the reaction glass chamber, a bag in which the polluted air was stored, and a pump. During the entire experiment, the lamp remained on for activation of the samples. The data collected were used to assess the kinetics of the photocatalytic process.

RESULTS AND DISCUSSION

Antibacterial activity of the foam coated papers

Table IV reports the results obtained with the different paper samples (logarithmic reduction of the number of living cells) for tests run under light exposure conditions. Bacteria grown on the untreated reference is at a level of 10^6–10^7 CFU (6–7 log). One sample from earlier trials at KCL, namely the CNF/ZnO (0.8 g/m^2) sample, was tested at the same time with these new samples because the preparation procedure of modified CNF and the base paper were the same.

The results reported in Table IV show substantial antibacterial activity for paper samples treated by CNF-TiO_2 for TiO_2 content around 0.3%, while for paper samples treated by CNF-ZnO, a much lower inorganic filler content is needed to obtain similar effects. In general, bacteriostatic activity was obtained while bactericidal activity was not detected with these amounts of inorganic particles. Bacteriostatic activity was also demonstrated for CNF-TiO_2 foam-coated papers under conditions of darkness with respect to *Staphylococcus aureus*, as reported in **Table V**. The results show that in the absence of light, TiO_2 or ZnO modified CNF coated papers had only a slight effect on bacteria growth; that is, they need light exposure to show antibacterial activity.

Photocatalytic activity of the foam coated papers

The paper samples foam coated by nanocomposites CNF-TiO_2, CNF-ZnO, and CNF-ZnO and TiO_2 were characterized for their photocatalytic efficiency. As shown in **Table VI**, paper samples foam coated by nanocomposites containing TiO_2 display

Paper Sample (coat weight)	ZnO, ppm	TiO_2, %	*Staphylococcus aureus*		*Klebsiella pneumoniae*	
			Bacteriostatic Activity, log reduction	Bactericidal Activity, log reduction	Bacteriostatic Activity, log reduction	Bactericidal Activity, log reduction
Untreated paper	-	-	0	0	0	0
CNF-TiO_2 (0.4 g/m^2)	-	0.034	0	0	0	0
CNF-TiO_2 (0.9 g/m^2)	-	0.167	1.3	0	0	0
CNF-TiO_2 (1.8 g/m^2)	-	0.291	Total bacteriostatic	1.0	1.8	0
CNF-ZnO and TiO_2 (0.6 g/m^2)	38.4	0.115	0.7	0	0	0
CNF-ZnO&TiO_2 (1.3 g/m^2)	104.6	0.307	Total bacteriostatic	0.1	0.2	0
CNF/ZnO (0.8 g/m^2)*	180	-	Total bacteriostatic	0.3	2.1	0

* A sample from KCL coating machine trials. The procedure of CNF/ZnO composite preparation and the base paper were the same as in Zimmer trial samples.

IV. Antibacterial activity of foam-coated paper samples, under conditions of light exposure.

Paper Sample (coat weight)	ZnO, ppm	TiO_2, %	*Staphylococcus aureus*	
			Bacteriostatic Activity, log reduction	Bactericidal Activity, log reduction
Untreated paper (control)	-	-	0	0
CNF-TiO_2 (1.8 g/m^2)	-	0.291	1.7	0
CNF-ZnO (0.8 g/m^2)	180	-	1.2	0

V. Antibacterial activity of foam-coated paper samples, under conditions of darkness. Bacteria grown on untreated reference: 106–107 (6–7 log).

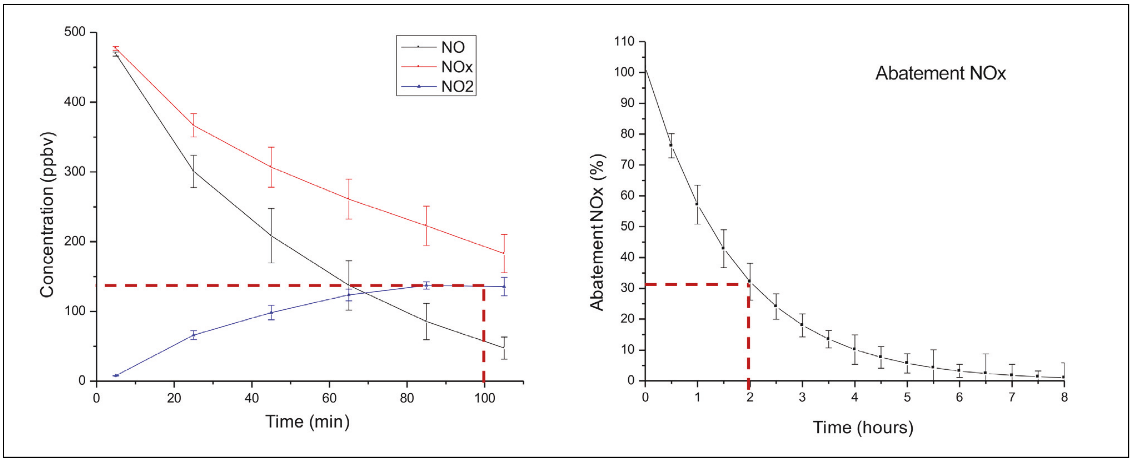
photoactivity for the degradation of volatile compounds at TiO_2 content higher than 0.1%. In contrast, ZnO presence seems to have little influence on the photoactivity of the paper. Photo-oxidation of volatile substances depends only on the TiO_2 content of the paper.

Figure 5 shows the NOx photodegradation in gaseous phase by CNF-TiO_2 foam-coated paper. Around 70% NOx oxidation occurred within 100 min, showing that foam-coated paper with CNF-TiO_2 had significant activity for the oxidation of NO and NOx. At a coat weight of 0.9 g/m^2, the corresponding TiO_2 dry weight on paper was 0.162%; this was enough to have an influence of 72.6% NO degradation after 105 min.

Photo-oxidation of NOx has important applications for the control of air pollution. In the case of active paper it could be used for wallpaper, for example, to control indoor pollution. However, the photo-oxidation by TiO_2 can also work to oxidize or breakdown organic volatile compounds (not only for inorganic materials such as NOx). These could include formaldehyde or other air pollution organic compounds (e.g., acetaldehydes) or ethylene produced by fruits that are responsible for the ripening and fast spoilage of fruits and vegetables in packaged produce systems.

CONCLUSIONS

Foam coating technology offers a unique opportunity to apply coating to a web surface thinly enough to be economically viable. The method is suitable for production of functional construction materials, filters, and disposable textile materials for hospital use or for active packaging solutions with antimicrobial, photoactivity, or barrier properties. The results ob-



5. NOx photodegradation in gaseous phase by CNF-TiO_2 foam-coated paper. Note: coat weight below 1 g/m^2.

Paper Sample (coat weight)	ZnODry Weight on Paper*, ppm	TiO_2Dry Weight on Paper*, %	NO Degradation (after 105 min), %	NO Degradation (after 105 min), %
Untreated paper	-	-	0	0
CNF-TiO_2 (0.4 g/m^2)	-	0.008	16.8	12.6
CNF-TiO_2 (0.9 g/m^2)	-	0.167	72.6	46.0
CNF-TiO_2 (1.8 g/m^2)	-	0.291	79.9	61.6
CNF-ZnO and TiO_2 (0.6 g/m^2)	38.4	0.115	81.7	64.9
CNF-ZnO and TiO_2 (1.3 g/m^2)	104.6	0.307	90.9	78.5
CNF/ZnO (0.8 g/m^2)	180	-	0	0

* From inductively coupled plasma analysis.

VI. Nitric oxide (NO) and NOx degradation by foam-coated papers.

tained from the foam coating trials with TiO_2 and ZnO functionalized CNF show that it is possible to create antimicrobial and photocatalytic properties of paper and paperboard.

The results obtained from the foam coating trials with functionalized CNF showed that by using modified CNF, it is possible to activate properties on the paper surface even at extremely low coat weights (i.e., below 1 g/m^2). For the foam coating trials, functionalized CNF was prepared using a physical absorption based method. Nanoscale inorganic particles TiO_2 and ZnO were mixed with CNF to create nanocomposites CNF-TiO_2, CNF-ZnO, and CNF-ZnO and TiO_2 .

The paper coated by the functionalized CNF showed antibacterial activity mainly depending on the TiO_2 or ZnO content, or both. The antibacterial activities obtained were mainly bacteriostatic. The bacteriostatic property of CNF-TiO_2 or CNF-ZnO, or both, was obtained even at low coat weights of modified CNF. The TiO_2 content was around 0.3% dry weight on paper, and ZnO content was even lower.

Regarding the photo-oxidation of NOx compounds in gaseous phases, only paper samples coated by CNF-TiO_2 showed efficient photoactivity. At a coat weight of 0.9 g/m^2, the corresponding TiO_2 dry weight on paper was 0.162%; this was enough to result in a 72.6% NO degradation after 105 min. The degradation depended strongly on the TiO_2 content, while the paper samples containing only CNF-ZnO nanocomposite did not show any photoactivity, indicating that this additive is not sensitive to photoactivation.

Further work with more defined targets for different end applications, including product and process development at high speeds, would serve to optimize the effects reported here. **TJ**

ACKNOWLEDGEMENTS

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ABOUT THE AUTHORS

The paper and board industry needs new tools for renewal. We chose this research topic because foam based technologies in several application areas are such promising tools. This research is a continuation of earlier foam coating research focusing on the application of unmodified cellulose nanofibrils.

The most difficult aspect of this work was finding the facilities for starting the research at pilot scale. It was difficult because no relevant laboratory scale facilities exist. The most interesting finding was that the foam coating technology was able to transfer the effectiveness of the functionalized cellulose nanofibrils to the paper surface. The research shows that the foam based coating technology is very versatile. It allows the use of a wide variety of materials, which might challenge the conventional coating technologies.

For this author (Kinnunen-Raudaskoski), the next step is to continue product development based on foam technologies at Paptic Ltd., a spinoff company of VTT.

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Increased dryness after pressing and wet web strength by utilizing foam application technology

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AND TUOMO HJELT

ABSTRACT: Production cost savings by lowering basis weight has been a trend in papermaking. The strategy has been to decrease the amount of softwood kraft pulp and increase use of fillers and recycled fibers. These changes have a tendency to lower strength properties of both the wet and dry web. To compensate for the strength loss in the paper, a greater quantity of strength additives is often required, either dosed at the wet end or applied to the wet web by spray. In this pilot-scale study, it was shown how strength additives can be effectively applied with foam-based application technology. The technology can simultaneously increase dryness after wet pressing and enhance dry and wet web strength properties. Foam application of polyvinyl alcohol (PVA), ethylene vinyl alcohol (EVOH), carboxymethyl cellulose (CMC), guar gum, starch, and cellulose microfibrils (CMF) increased web dryness after wet pressing up to 5.2%-units compared to the reference sample. The enhanced dewatering with starch, guar gum, and CMF was detected with a bulk increase. Additionally, a significant increase in z-directional tensile strength of dry web and and in-plane tensile strength properties of wet web was obtained. Based on the results, foam application technology can be a very useful technology for several applications in the paper industry.

Application: Foam-based application technology is an interesting tool for developing new cost-efficient solutions for the paper industry. Increased solids content and improved wet strength of the web after pressing imply direct energy savings during drying, improvements in wet web runnability, and possible material saving through improved bulk. The technology may also enable possibilities for chemical savings with respect to the wet end application.

A crucial requirement in papermaking is good runnability of paper machines. This is often evaluated by the number of web breaks in proportion to the production speed. Minimizing web breaks, broke, and downtime, in general, and maximizing the production speed enable increased paper production on the paper machine [1,2].

Many paper machines are forced to run below their design speed due to web breaks. In many cases, the bottleneck is the runnability of the wet web in the press-to-dryer transfer and at the beginning of the dryer section [3-6]. In an open draw at those points, the wet web is transferred from one surface to another without the support of any fabrics, and the stability of the running web depends mainly on web tension. The dryness of the wet web after the press section typically varies between 40%–50%, meaning that the tensile stiffness of the web is only 10%–15% of the stiffness of dry paper. In order to guarantee a stable run of the paper web in the open draw, a considerable speed difference (typically 2%–5%) is required to create enough tension to transfer the web [3,7,8]. After the open draw, the velocity of the web remains constant for a considerable time, whereas the tension created in the open draw lowers rapidly; i.e., tension relaxation occurs. Typically, during the 0.5 s relaxation time, 50%–60% of the tension created in straining is lost. This leads to slackening of the wet paper, causing wrinkling, bagging, fluttering, and weaving of the web and leading to web breaks [3,9]. In order to predict wet web tension behavior at the beginning of the dryer section, both tensile strength and relaxation properties of the wet web should be known.

Savings in raw materials, by using less and cheaper raw materials, result in deterioration of mechanical properties for the wet and dry web. To increase the permanent wet strength of dried papers, a greater quantity of strength additives is often required. Several strength additives are available that serve to: 1) increase or strengthen existing bonds; 2) protect existing bonds; 3) form bonds that are insensitive to water; and 4) produce a network of material that physically entangles with fibers. These traditional wet strength additives do not enhance wet web strength, i.e., the strength of never dried wet web. This is because wet strength additives usually require heating and curing time [10]. However, wet web strength can be improved by chemicals such as retention aids. These materials increase the water removal of pulp, and thus improve the mechanical properties of the wet web by increasing dryness.

Another way to improve wet web mechanical properties is the use of chemical additives that increase interactions between fibers in the wet state. Typically, these strength additives are either dosed at the wet end or applied to the wet web by spray. In this study, a foam-based application technology was used to demonstrate the potential of foam technology in surface treatment of dry paper on a pilot-scale coating machine [11-17].

Foam coating utilizes foam as the carrier phase of chemicals and dispersions. However, there is another effect of foam, namely the ability of the foam to displace liquid water from a porous medium. The well-known phenomenon enhances dewatering by the use of agents that lower the surface tension of the saturating liquid. This procedure forms the basis for the commercial cleaning processes in the coal industry [18]. The static experiments were done by Lauchenauer and, later, dynamic processes were described by him in 1980s patents [19,20]. The patents showed that foam spread over the sheet immediately before the sheet was exposed to the vacuum enhanced dewatering. Skelton et al. [21] reported about the foam assisted dewatering trials done at the former and at the pilot paper machine. Their results showed enhancement in dewatering, thus a drier web — especially when the surface-active agent was used in a foamed state (**Table I**), and the effectiveness of the foam appears to be the same whether it is drawn through the sheet by vacuum or forced into the sheet by external pressure (**Table II**).

According to Skelton, they had applied the foam-assisted-dewatering (FAD) concept to a wide range of products under reasonably close simulations of industrial processes: paper, nonwoven, board and pulp products; mineral sludge; coal tailings; and municipal sludge. With minor exceptions, the addition of foam has been shown to be generally beneficial. The authors have also demonstrated that foam application technology can be used to enhance dewatering of bio-based sludge [22]. The beneficial characteristics of foams are also utilized in secondary or tertiary oil recovery [23].

Condition	Sheet Consistency, %	Consistency Increase
Vacuum alone	40.0	-
Vacuum and foam	49.5	9.5
Vacuum and spray	43.2	3.2

I. Effects of foam and surfactant spray on consistency of vacuum-dewatered sheet [21].

In the paper and board industry, energy efficient dewatering is of great importance. Capabilities of the press section have significantly progressed in the last several decades, allowing ever higher dryness levels to be achieved. In this study, the applicability of foam technology to simultaneously improve dewatering and strength properties of dry and wet paper/board in wet web treatment on paper and board machines was evaluated.

EXPERIMENTAL

Foam application technology

In foam application technology, foam is used as a carrier phase for the application material. The material is located in the bubble pockets (vertices) and on the bubble surface. The main components in the technology are a foam generator and a foam applicator. For the trials, a Top-Mix type 60 foam generator (Hansa Industrie-Mixer GmbH & Co.; Heiligenrode, Germany) was used. This unit had a chemical feeding capacity of 6–60 kg/h and a foam density range of 50–400 g/L. The chemical and foaming agents are mixed with pressurized air in a mixing head having a rotor-stator unit. For the application of the foam, a narrow slot-type applicator, the Magnojet (J. Zimmer Maschinenbau GmbH; Klagenfurt, Austria) was employed. The trials were performed at VTT's pilot papermaking research laboratory. The application point was prior to the high vacuum suction boxes (HiVac) (**Fig. 1**). The dryness level of the web was around 22.8% ± 0.4% at the application point.

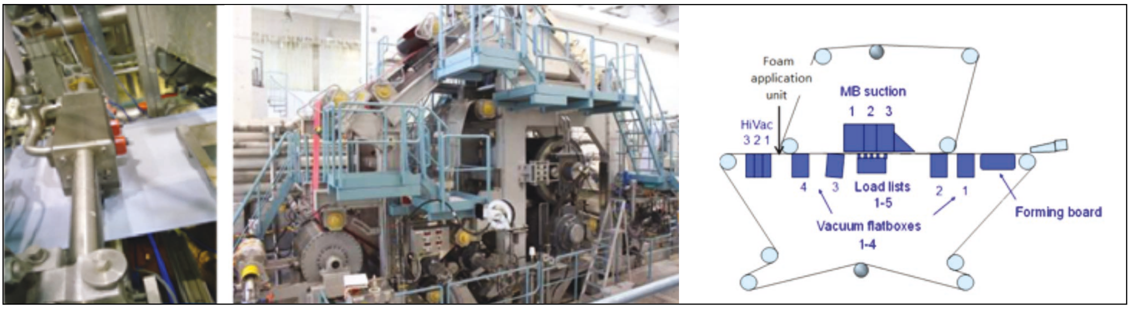
The following process setup was used in the trials:

- Headbox: Optiflow
- Former: Hybrid former
- Wet press: 1 shoe press: 400 and 1200 kN/m
- Paper machine speed: 300 m/min
- Grammage: 80 g/m^2
- Material feeding speed to the foam generator: 55 L/h
- Foam density: 200 g/L; with polyvinyl alcohol (PVA) and ethylene vinyl alcohol (EVOH), 300 g/L

The VTT research equipment is able to run either as a loop, returning the formed web back to the process or with the taking of wet web samples after the press section. The latter was used for these trials. The experiments were performed using a one-after-another procedure: the studied additive was poured

Condition	Consistency, %		Consistency Change, %
	No Foam	Foam	
Foam applied at former, sampled at couch	23.4	26.8	3.4
Foam applied at former, sampled after press	39.5	40.9	1.4
Foam applied at press nip, sampled after press	44.9	46.2	1.3

II. Effects of foam on sheet consistency [21].



1. The foam applicator (left), VTT's papermaking research laboratory (middle), and a schematic of the addition point in the line (right).

to the feeding tank, foamed, the foam quality checked, and foam applied to the web. After a couple of seconds, the wet sample was taken after the press section by rolling the web. After sampling, the web was led to the pulper and a new chemical was changed in to the feeding tank. The addition amounts differed between the polymers. The basic idea was to apply a reasonably high amount of the polymers in order to see their impacts on the wet web properties, taking into account the limits defined by the polymers, e.g., solids content. The retention of the polymers in the trials was unknown and more research is needed to quantify this. Thus, the applied amounts were not the amount retained into the web structure. The addition amounts were calculated from the trial parameters: material solids content, material density, pumping speed of the foam generator, application width, and web speed.

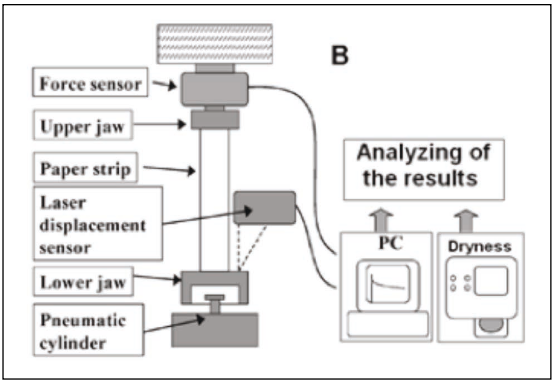
MATERIALS

Pre-refined bleached softwood pulp suspension was obtained from a Finnish pulp mill. The Schopper-Riegler value of the pulp was 19. **Table III** shows the applied additives.

The PVA and EVOH grades foamed well without any external foaming aid. With guar gum, starch and the CMF commercial surface active agent, sodium dodecyl sulfate (SDS) was used as a foaming agent. The amount of added SDS was 0.2 vol-%.

CHARACTERIZATION

The IMPACT-fast tensile test rig (**Fig. 2**) was applied for paper tensile strength and relaxation tests. The strain rate used was 1 m/s. The relaxation tendency of wet paper was estimated by straining the paper to 2% elongation followed by 0.475 s of relaxation. In addition to the tensile and relaxation test instrument, an essential instrument in the test procedure is a moisture analyzer, with which the dryness of wet paper



2. Schematic illustration of IMPACT-fast tensile-and relaxation test rig [24].

Strength Additive	Solids Content, %	Applied Amount, g/m²
PVA1 (degree of hydrolysis 88%, viscosity 30–42 mPa.s*), cooked	7.0	1.8
PVA2 (degree of hydrolysis 99%, viscosity 26–30 mPa.s*), cooked	10.8	2.7
EVOH (degree of hydrolysis 98%–99%, viscosity 3.8–4.5 mPa.s**), cooked	10.8	2.7
Guar gum, non-ionic, commercial	0.9	0.2
Starch, cationic, cooked	2.1	0.5
CMF manufactured by Masuko collider device at VTT	2.8	0.7

* of a 4% aqueous solution at 20°C determined by Höppler-viscometer (DIN 53015)
** of a 4% aqueous solution at 20°C determined by Brookfield synchronized motor rotary type viscometer

III. The applied chemicals, their solids content, and the amounts applied to the wet web.

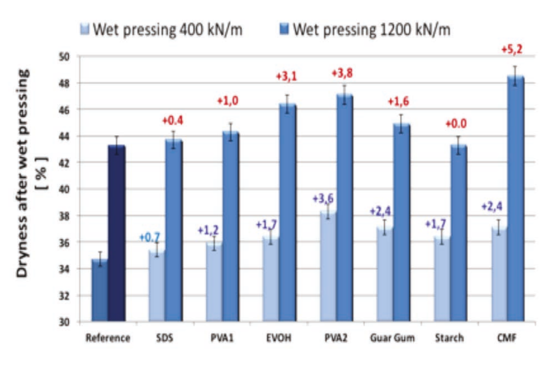
samples was measured after tests. Z-direction strength (Scott bond internal bonding strength, modified Scott, J/m²; Huygen Internal Bond Tester; Huygen, Crystal Lake, IL, USA) was measured according to TAPPI Standard Test Method T 569 om-09 "Internal bond strength (Scott type)."

RESULTS AND DISCUSSION

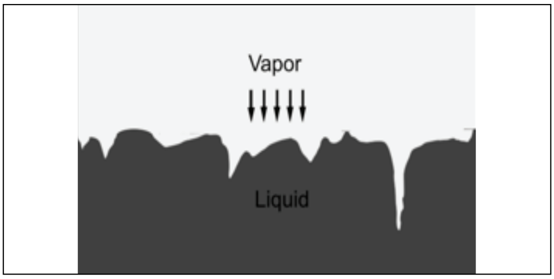
Dryness after wet pressing

Drying of paper and board consumes approximately 2/3 of the total energy consumed on the machine line [24]. Paper/board entering the dryer section typically contains approximately 50% water. At these conditions, a 1%-unit increase in dryness after wet pressing reduces roughly 4% of the drying energy required [24]. Foam-based chemical application in our trials increased dryness of wet pressed samples on average by 2.3%-units (**Fig. 3**) and 5.2%-units in the best case (CMF, 1200 kN/m). Based on the given assumption, foam application could be estimated to give in average approximately 10% (up to 21% with CMF application) savings in drying energy compared to the situation when foam is not applied with 1200 kN/m wet pressing load.

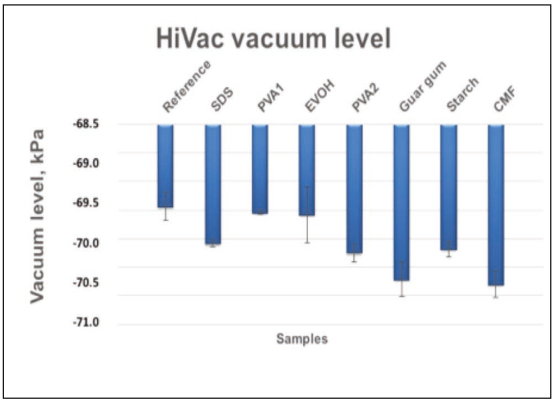
The effect of SDS spray was not studied. The SDS foam slightly enhanced dewatering. The effect of SDS foam on dewatering was lower than the effect of the other studied foams, which were more viscous than the SDS foam. The foams were more viscous due to the higher viscosity of the liquids used to make the foams. The result of the SDS foam is similar to the findings made by Lindqvist et al. [25], who showed that addition of surfactants to pulp suspensions reduces surface tension forces and thus enhances water removal in forming and wet pressing. Skelton [21] suggested that there is also an additional effect attributable to the properties of foam, which enhances dewatering during forming. He claims that small air bubbles remove liquid water from the porous paper structure more efficiently than a stream of free air. According to Lindsay [26,27], the analogy to oil recovery would appear to provide at least part of the explanation. Due to the highly viscous foam, the viscous fingers become "self-sealing" to some extent, making the interface more stable. The stability of the displacement process in suction is increased and water removal becomes more efficient. Lindsay describes one proposed means of achieving this objective, namely through displacement dewatering in which a pressurized gas phase is used to drive liquid water out of a mechanically compressed sheet [26,27]. However, in practice the displacement process faces some inherent instability that reduces its efficiency. In a porous medium, when a liquid is displaced by another fluid of lower viscosity, the interface between the phases is often unstable. The disturbances on a smooth interface create "fingers" that penetrate into the phase being displaced (**Fig. 4**). This phenomenon is called "viscous fingering" [26,27,28]. A uniform interphase assures less viscous fingering.



3. The effect of applying different additives by foam technology on web dryness after wet pressing. The 80 g/m² samples from 100% bleached softwood (SW) kraft pulp were produced on a pilot paper machine running at 300 m/min. The dryness level in the former section at the foam application point was 22.8% ± 0.4%. The applied amounts of additives were between 0.2 (guar gum) and 2.7 g/m² (polyvinyl alcohol [PVA] sample 2 [PVA2] and ethylene vinyl alcohol [EVOH])

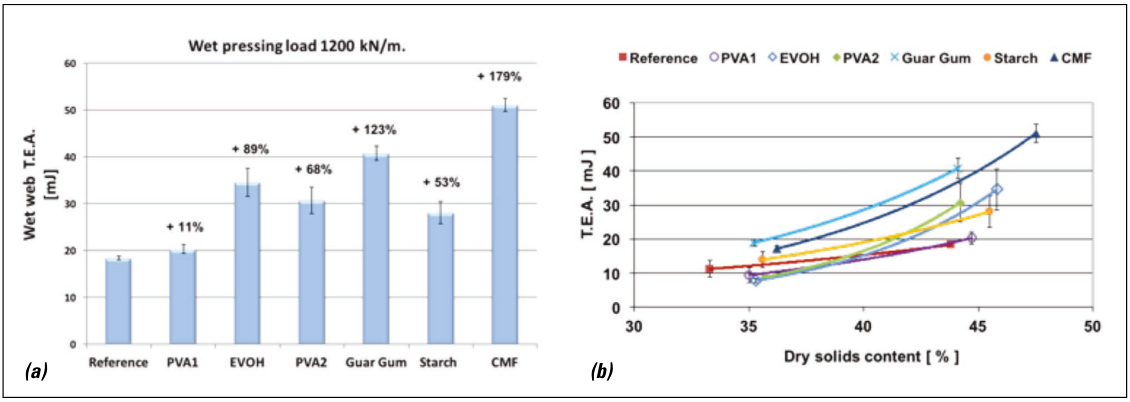


4. Viscous fingering in a porous medium as a gas displaces a liquid [29].

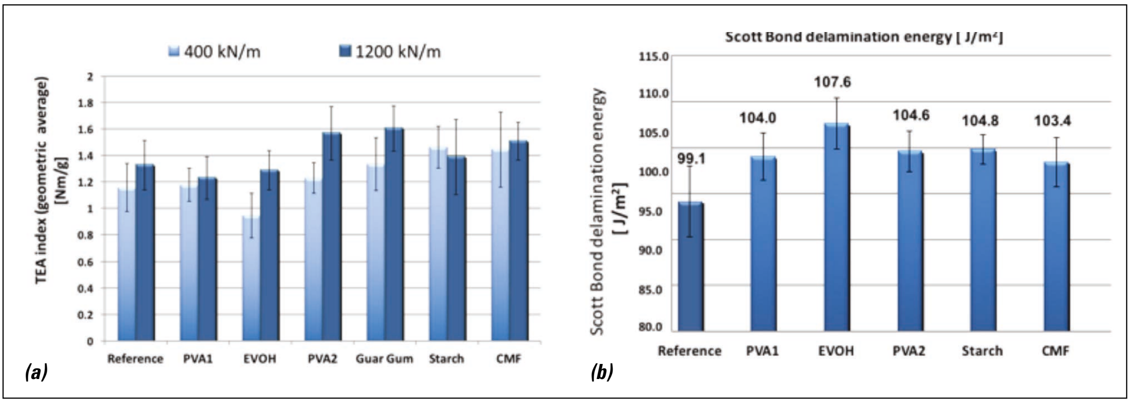


5. The vacuum levels of the high vacuum suction boxes (HiVac) in foam applications.

This phenomenon means that a gas phase will tend to simply blow through certain paths, leaving much of the water behind. Lenormand et al. [29] numerically examined a displacement process for a wide variety of conditions. The con-



6. The effect of applying different additives by foam technology on wet web tensile energy absorption after constant (line load 1200 kN/m) wet pressing conditions (left) and as a function of dryness. The 80 g/m^2 samples from 100% bleached SW kraft pulp were produced on a pilot paper machine running at 300 m/min. The dryness level in the former section at the foam application point was 22.8% ± 0.4%. The applied amounts of additives were between 0.2 (guar gum) and 2.7 g/m^2 (PVA2 and EVOH).



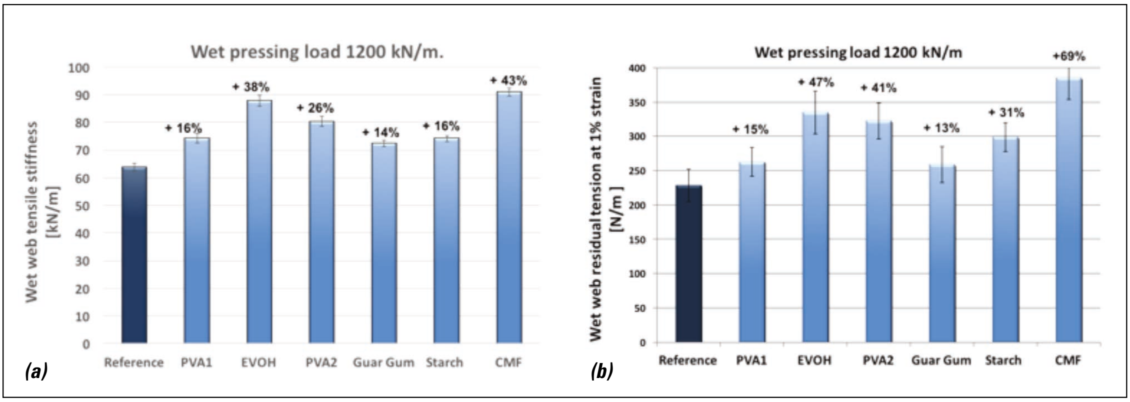
7. The effect of applying different additives by foam technology on dry paper tensile energy adsorption (left) and Scott bond delamination energy. The 80 g/m^2 samples from 100% bleached hardwood (HW) kraft pulp were produced on a pilot paper machine running at 300 m/min. The dryness level in the former section at the foam application point was 22.8% ± 0.4%. The applied amounts of additives were between 0.2 (guar gum) and 2.7 g/m^2 (PVA2 and EVOH).

ditions typical to air-water displacement in paper clearly fall in a regime where significant viscous fingering likely happens.

In our trials, the foam applications were done to the web above the high vacuum suction boxes (HiVac), where the web dryness level was 22.8% ± 0.4% at the application point. The self-sealing phenomenon of foam can be seen from the vacuum levels, which were all higher compared to the reference (**Fig. 5**). Vacuum level comparison between the test points and applied foams need more extensive studies.

Mechanical properties of wet web

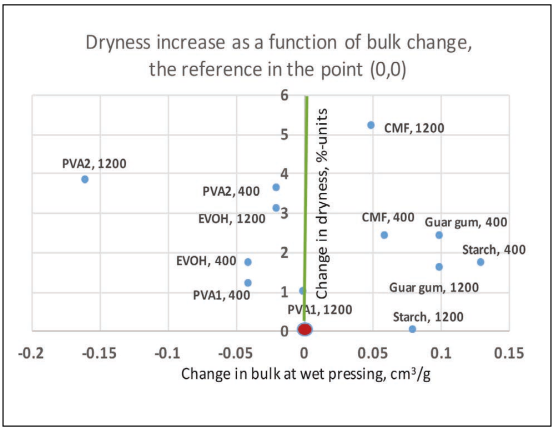
Seth et al. [30,31] showed that simultaneous increases in wet web strength and stretch (failure envelope curve) reduces web breaks on a paper machine. **Figure 6** (left) shows that wet web tensile energy adsorption (T.E.A., which also combines the stretch and strength of paper) was significantly increased at a given wet pressing level, but also at a given dryness level (right). Figure 6 (left) shows that application of additives increased wet web T.E.A. significantly (11% to 179%) after the constant wet pressing line load of 1200 kN/m. Figure 6 (left) reveals that the development of wet web T.E.A. as a function of dryness was greatly dependent on the applied additive. Application of starch and PVAs had only a minor effect on T.E.A. at dryness levels below 40%, but the effect strongly increased with increasing dryness. The addition of PVA increased wet paper strength and also dry paper strength (**Fig. 7**), which is in line with the earlier studies [32,33,34]. It is likely that PVA and EVOH as high-molar-mass polymers having high affinity to fibers may increase molecular-level interaction between fibers in a wet state. Poly and ethylene vinyl alcohols are hydrophilic polymers carrying a hydroxyl group on each of their repeating units. This permits the develop-



8. The effect of applying different additives by foam technology on wet web tensile stiffness (left) and residual tension (right) after constant (line load 1200 kN/m) wet pressing conditions. The 80 g/m² samples from 100% bleached SW kraft pulp were produced on a pilot paper machine running at 300 m/min. The dryness level in the former section at the foam application point was 22.8% ± 0.4%. The applied amounts of additives were between 0.2 (guar gum) and 2.7 g/m² (PVA2 and EVOH.

ment of hydrogen bonds with hydroxyl and carboxylic groups of cellulose fibers, thus enhancing the tensile strength of dry paper [35]. Guar gum and CMF also had a clear effect on wet web T.E.A. at lower dryness levels. In the case of CMF, an increase of surface fibrous area is believed to increase the surface tension forces in the network [36], which could also explain the increase of T.E.A. at low dryness levels. The applied amounts of guar gum and CMF, 0.2 and 0.7 g/m² respectively, compared with poly and ethylene vinyl alcohols, 1.8 g/m² of PVA1 and 2.7 g/m² of PVA2 and EVOH, make the result even more significant.

Wet web tensile stiffness and residual tension after constant wet pressing conditions are given in **Fig. 8**. Wet web tensile stiffness describes the tension response when paper is strained. For a paper having high stiffness, a lower amount of straining is needed to create a certain tension on open draws. Residual tension describes tension existing in the wet web at a certain time after straining. The effect of applied additives on wet web tensile stiffness and residual tension was quite similar and the effect of additives was lower than in the case of the wet web T.E.A. Earlier studies have given clear indications that the addition of chemicals increases the strength of fiber-fiber joints. This augments wet web strength and strain. According to our results, 0.7 g/m² addition amount of CMF has a significant influence on wet web elastic tensile stiffness and residual tension at low strain levels compared with the other applied additives.



9. The dryness increase as a function of bulk change. The wet pressing load is marked after the applied additive. The reference is marked as a red oval in the point (0,0) and the results of the applied additives are compared as a change to the reference. The 80 g/m² samples from 100% bleached HW kraft pulp were produced on a pilot paper machine running at 300 m/min. The dryness level in the former section at the foam application point was 22.8% ± 0.4%. The applied amounts of additives were between 0.2 (guar gum) and 2.7 g/m² (PVA2 and EVOH).

Mechanical properties of dry paper

The effect of the studied additives on dry paper T.E.A. was not so clear as in the case of wet web. Figure 7 (left) shows the dry paper T.E.A. The results show that when applying CMF, starch, guar gum, or PVA having a high hydrolysis level, there is a minor effect on the in-plane tensile properties of dry paper, but a stronger effect on out-plane strength properties. Application of additives increased 4% to 9% of Scott bond delamination energy (Fig. 7, right). An increase of Scott bond delamination energy indicated that polymers have also penetrated the web structure in the z-direction. However, this does not indicate how even the distribution of each additive in the web structure has been. The applied amounts of the additives must be taken into account in comparison of Scott bond improvement. Based on that, CMF and starch applied at amounts of 0.7 and 0.5 g/m², respectively, enhanced out-plane strength significantly more than poly and ethylene vinyl alcohols, which were applied amount at amounts of 1.8 and 2.7 g/m^2. Also, starch and guar gum enhanced dewatering with a positive effect on bulk (**Fig. 9**).

Increased bulk with higher dryness

The applied poly and ethylene vinyl alcohols enhanced dewatering, but densified the web structure compared to the reference sample. The strongest influence on dewatering was reached with CMF, which has a minor positive effect on bulk. Also, starch and guar gum enhanced dewatering with a positive effect on bulk.

CONCLUSIONS

The effects of applying polymers to the wet web utilizing a foam-based application technology were examined on a pilot scale. The main findings of the study can be summarized as follows:

- Foam application of polymers to the wet web provides a possibility to simultaneously improve dewatering and strength properties of dry and wet paper/board.
- Foam application could provide a significant reduction in drying energy.
- CMF, starch, and guar gum enhanced dewatering and had a positive impact on bulk.
- Poly and ethylene vinyl alcohols enhanced dewatering, but had a negative impact on bulk.
- Foam application could enable higher retention of different polymers through high mechanical retention, thus reducing the cost of polymers for a mill. It could also make possible the use of polymers having no cationic charge.
- Polymers significantly improved tensile strength, TEA, tensile stiffness, and residual tension of wet paper .
- The highest increase in wet web mechanical properties was obtained with the CMF mixture, guar gum, and PVA having a high hydrolysis level.
- The effects on dry paper mechanical properties were relatively smaller compared to those on wet web.

The foam-based application method might open up several benefits for paper and board manufacturing. Increased solids content of the web after pressing implies direct energy savings during drying or possible material savings through improved bulk. Foam application may also enable possibilities for wet end chemicals savings. The results also suggest that improvements in wet web runnability and some increases in the strength of the end product may be obtained. The versatile foam application method allows the use of a large variety of materials at relatively high consistency. It is an occupationally safe method because there are no airborne particles (which might be the case with spray application) and hence no extensive safety precautions and equipment are needed. Combined, these aspects make foam-based application technology an interesting tool for developing new cost-efficient solutions for the paper industry.

LITERATURE CITED

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The paper and board industry needs new tools for renewal, and foam-based technologies are such promising tools in several application areas, which we have studied. This research is a continuation of earlier foam coating research, but we applied foam coating to the wet web instead of the dry web.

The most difficult aspect in foam coating research was finding the facilities for starting the research at pilot scale, because no relevant laboratory scale facilities exist. Our most interesting finding in this study was that foam application of polymers to the wet web simultaneously improved dewatering and strength properties of dry and wet paper/board -- and in some cases without bulk loss!

This research shows that foam based coating technology is very versatile and can be used for different purposes. VTT has projects and is starting new ones in the area of foam technology, and Kinnunen-Raudaskoski will continue her work in the area at Paptic Ltd., a spin-off company of VTT.

Kinnunen-Raudaskoski (formerly of VTT) is research director at Paptic Ltd., Espoo, Finland. Salminen is team leader, Lehmonen is senior scientist, and Hjelt is senior scientist at VTT Technical Research Centre of Finland, Espoo, Finland. Email Kinnunen-Raudaskoski karita.kinnunen@paptic.fi.

IV

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Benefits of foam forming technology and its applicability in high NFC addition structures

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Abstract

In paper and board industry there is a strong need for a radically more resource-efficient production technologies, which would also enable the manufacture of sustainable and value-added fibre products. In this paper we introduce foam forming method, where foam is used as a transporting media of furnishes. The technology enables to make structures with excellent formation in higher headbox consistencies and a very high bulk. When this is combined with the good water drainage properties, which allows the high addition levels of strengthening agents as nano fibrillar cellulose (NFC), one can make products with very big bulk and still have an adequate strength value. We studied different NFC grades and they seem to behave rather similarly in bulk vs. strength comparisons. However, some difference is obtained leaving room for optimization of best NFC grade on certain product.

Introduction

In the traditional paper making, foam is found typically to cause problems such as aggregating soluble chemicals. Therefore, from a historical point of view, much more attention has been given to the development and the usage of foam control agents than to foaming agents. There are a number of publications and books dealing with foam problems in processes and foam control [1]. However, in the 1970's technology based on usage of foam was demonstrated in a pilot scale based on the Radfoam process [2,3,4,5]. The Radfoam process was found to enhance product properties and especially formation in non-woven and paper applications [4,5]. In the foam-laid technology aqueous foam is used (instead of water) as a process fluid and flowing medium. This kind of foam has an air content of 60-70% and it contains small, spherical air bubbles with diameters below 100 μm. Aqueous foams are pseudoplastic, having very high viscosity at low shear conditions, but low viscosity at high shears. Due to these characteristics aqueous foams are excellent material to transport particles and fibres in a dispersed state leading to the excellent formation of the paper [5, 6]. In additions, these foams allow the use of wide variety of different raw materials, from nanoparticles up to 200 mm long fibres and also low density materials.

The foam forming technology is used in non-woven production, but after the 1970's in paper making it was forgotten due to the lack of economical drives like savings in energy and raw material consumptions. At the moment paper industry is facing such demanding, and there is a strong need for a radically more resource-efficient production technology, which would also enable the manufacture of sustainable and value-added fibre products.

In this paper we re-introduce this foam forming method, because it provides many interesting benefits for the properties of the paper, as well as for the processing phase. For the studies foam formed paper sheets were made using a laboratory scale foam handsheet mould and a semi-pilot scale dynamic former. The former was modified from a water former based on the knowledge of the Radfoam process.

In the Radfoam process a paper making furnish was mixed with a prefabricated foam. The foam was generated under controlled, high shear conditions from a surfactant-water solution. On the paper machine wire, foam was broken down by physical means to form a foamy-water medium; this could be done by vacuum or by pressure in the nip of any configuration [6]. Under the influence of suction, these foam-fibre mixtures drained rapidly producing sheets of a higher uniformity than that of a water slurry of the same weight consistency [5]. In our semi-pilot scale studies enchantments in formation, dewatering and headbox fibre consistencies were obtained. The paper made by the Radfoam process had high bulk and low strength characteristics in an unpressed state compared with a comparable water-laid paper, but the strength could be regained by beating or by pressing. Pressing raised the strength to the water-laid level whilst correspondingly reducing the bulk [2].

In our laboratory scale studies we show another way to increase the strength, namely a usage of nano fibrillated cellulose (NFC) as strength additive to enhance sheet strength to the acquired level, for example, to the level suitable for normal packaging applications. We used six different types of nanofibrillated celluloses, isolated from the wood-based fibres in our laboratory scale studies, in order to study their capability to increase strength of paper sheets made from chemical or mechanical pulp. In water forming high NFC addition is not an option, as fine material influences on dewatering, but the open structure of the foam formed sheets enables the high NFC usage. Our studies show that NFC enables the strength enhancement without a bulk lost. It also shows that the grade of NFC must be chosen based on the application and product requirements.

Experimental

Materials

The forming studies were carried out using a refined chemical pine pulp, chemical birch pulp and chemi thermo mechanical (CTMP) spruce pulp [7]. The average fibre length of pine pulp was 2.19 mm, coarseness was 141.7 µg/m and shopper value was 26 °SR. The average fibre length of birch pulp was 0.91 mm, coarseness was 101.9 µg/m and shopper value was 26 °SR. The average fibre length of spruce-CTMP pulp was 1.60 mm, coarseness was 220,3 µg/m and Canadian Standard Freeness value was 566 ml. Tap water was used as process water. Sodium dodecyl sulphate was used as a foaming agent. Nanofibrillated cellulose was used as a strength additive. NFC is a material composed of nanosized cellulose fibrils with a high aspect ratio (length to width ratio). Width of fibrils is typically 5–20 nanometres and length is in a wide range from 10s of nanometres to several microns. The more nanoscale the material is, the more viscous and transparent it is. We used six different types of nanofibrillated celluloses isolated from the wood-based fibers in our trials. The background information of the NFCs available is the following and

Figure 1 shows the light microscope images of the NFCs and Table 1 the characteristics available from the NFCs:

- NFC1, NFC2: made of bleached hardwood kraft pulp. They are ground to different coarseness levels having viscous structure higher than the other grades. These grades have also the highest transmittance levels. Material was delivered in the consistency of 3%
- NFC3: made of dissolving pulp with high cellulose content. The dissolving pulp is originally from softwood. Material was delivered in the consistency of 10%.
- NFC4: is produced via acid hydrolysis of kraft pulp cellulose polymer, and refined with varied setups. Material has relatively low viscosity.
- NFC5: micro fibrillated material that consists of wide selection of unfibrillated and fibrillated material that form medium viscosity in the scale of available grades.
- NFC6: micro fibrillated material that consists of stiff fiber fragments and fibrils that form medium viscosity in the scale of available grades

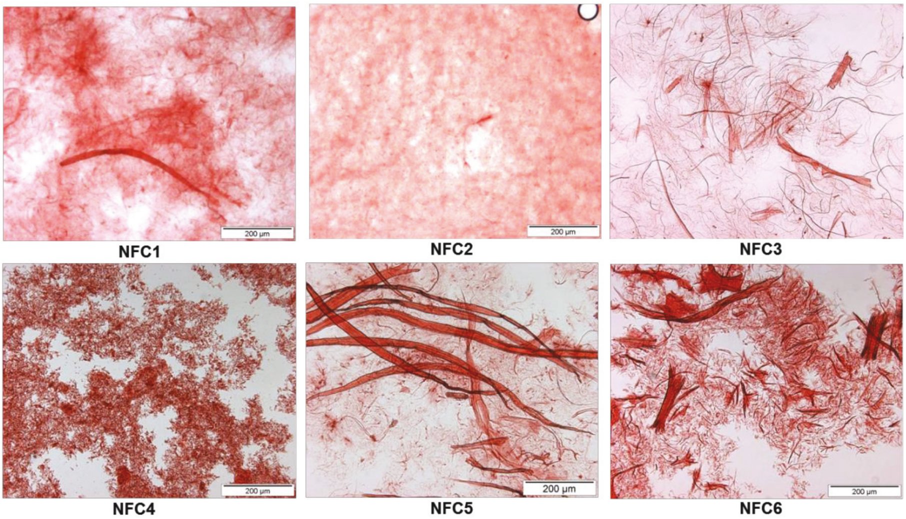

Figure 1.The light microscope images of the nanofibrillated celluloses used in the studies.

Table 1. The characteristics available from the the nanofibrillated celluloses used in the studies.

Sample	Viscosity, mPas·s 10 rpm 1.5% conc.	Transmittance, % 800 nm 0.1% conc.	Sedimentation volume, mm	Visual appearance (optical microscopy)
NFC1	23176	34.3	35	Coarse
NFC2	22502	60.2	42	Fine
NFC3	15777	8.1	16	Coarse, long fibrils
NFC4	400	0.5	32	Coarse
NFC5	3654	26.2	13	Coarse
NFC6	2784	24.9	23	Coarse

Material characterization

The pulp properties were characterised using the Fibre Quality Analyser (Fibre-Master). The Schopper-Riegler value was determined according to ISO standard 5267-1:1998 and the Canadian Standard Freeness value, in accordance with ISO standard 5267-2:2001. The grammage of the paper samples was determined according to ISO standard 536:1995. Thickness of the samples was determined according to ISO standard 534:1998. Density and bulk are based on the measured values of the grammage and sheet thickness. The tensile strength properties of paper samples were measured using a Lloyd tensile tester, in accordance with ISO standard 5270:1998. The z-strength property was measured according to ISO standard 15754:2009. Internal bonding strength, modified Scott bond was measured using Huygen Internal Bond Tester, in accordance with TAPPI T569.

Based on the β-formation measurement for the current study, a storage phosphor screen (SPS) was exposed to β-radiation through the paper sample, with Carbon-14 as the radiation force. This was done in order to evaluate the radiation absorption map. Thereafter, the screen was scanned with a Fuji BAS-1800 II SPS reader. Then, the measured values were converted into a grammage map. The size of the scanned area was 100 mm x 100 mm and the scanning resolution was 100 µm. Following this, the resolution was transformed to the Ambertech resolution (Ø 1 mm). The characteristics of the nanofibrillated celluloses were delivered with the samples.

The static foam forming equipment

The static forming studies were performed using refined chemical pine pulp and chemi thermo mechanical (CTMP) spruce pulp. The foam laid handsheets were made using a method and an equipment set-up adopted from the glassfiber industry (Figure 2).

Figure 2. The foam forming handsheet mould and the equipment set-up.

The procedure of the foam laid handsheets is as follows:
Aqueous fiber suspension is mixed with the prefabricated foam, which was produced by stirring water and surface active agent (sodium dodecyl sulphate, SDS) at 3500 rpm. The ratio of SDS should be 0.15-0.2 g/L for 60-70% air content of the foam. When the fiber foam state is stabilized, it is decanted into the handsheet mould using tilted plate as shown in Figure 3 (centre). There is a one centimetre slit between the plate end and the mould wall. This restricts the spreading speed to the wire and also forced the foam to spread from one end of the mould to another end of it. This movement is enough to orient fibres in a flow direction. After foam is settled it is filtered through a wire using a vacuum chamber. In the filtration we use same wire material as used in paper machines. The sheet filtrated is detached with the transferring wire from the mold and pre-dried on a special suction table. The suction table has a 5-mm–wide suction slit that sucks air through the sheet with a 0.2 bar vacuum. The picture series below show the working procedure (Figure 3). The sheets formed were fixed between a metal plate and a fabric to be dried in an air tunnel for one night, stored and analysed in a standard conditioned room at RH 50% and 23°C.

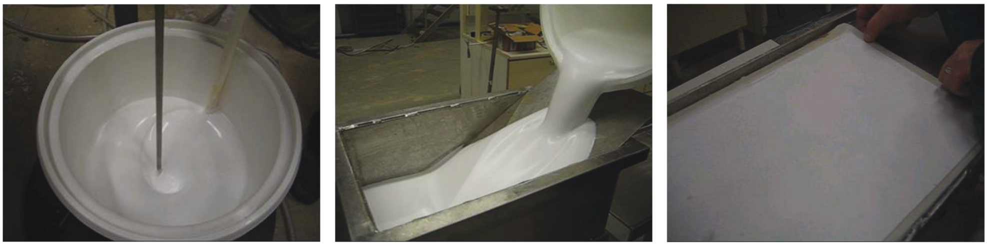

Figure 3. The procedure of the foam laid handsheet making. (1) An aqueous fiber suspension is mixed with a prefabricated foam produced from water and sodium dodecyl sulphate (SDS) in ratio 0.15-0.20g/L. (2) The fiber foam is decanted into the handsheet mould and filtrated through a wire using a vacuum chamber. (3) The sheet is pre-dried on a suction table (0.2 bar vacuum).

The dynamic foam forming equipment

The dynamic forming studies were performed using refined chemical pine pulp, chemical birch pulp and chemi thermo mechanical (CTMP) spruce pulp. The average process temperature in the foam forming studies was around 27 ˚C. The water-laid fibre webs from the pulps were produced using the semi-pilot scale former. The foam forming studies were performed using the same former modified to a foam forming mode [7]. The schematic picture of the modified water-laid semi-pilot scale former is presented in Figure 4. The main principle of the foam-laid process is that the process foam recirculates in the flow loop and raw materials are mixed with the process foam in a machine chest.

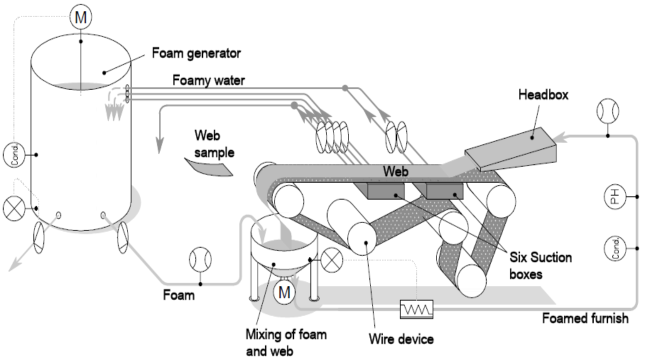

Figure 4. Schematic picture of the water-laid process research environment.

Results

Dynamic forming studies

One of the major benefits of using the foam forming technology is the excellent formation of products formed. The formation potential of the foam-laid forming technology for different kinds of wood-fibres has been studied in the case of chemical pine pulp, chemical birch pulp and spruce-CTMP pulp. Paper samples were formed using selected web-forming conditions [7]. The average grammage of spruce-CTMP pulp was 108 g/m^2 for foam and 107 g/m^2 for water, forming consistencies were 1.45% for foam and 1.15% for water, for pine pulp respectively grammages 82 g/m^2 and 84 g/m^2, consistencies 0.67% and 1.30%, and for birch 84 g/m^2 and 83 g/m^2, consistency 1.38% and 0.72%.
The selected forming points were formed with optimal forming conditions determinated to reach the appropriate formation level and the tensile-strength ratio approximately to the same level in both cases, e.g. in the case of pine pulp a jet-to-wire ratio of 1.1 for the water-laid paper and with 2.2 for the foam-laid paper, the formation 1.9 for water-laid paper and 0.7 for foam-laid paper and the tensile-strength ratio approximately 2.2 in both cases.

In the water forming method the formation is dependent on fibre length; good formation can be achieved with short fibres like birch, but when the fibre length and fibre coarseness increase the formation start to deteriorate [8]. In the foam forming the formation is independent of fibre properties, and a significantly better formation was achieved with all pulps than in the case of water-laid paper (Figure 5 [7]). When fibres are mixed to the foam, the foam bubbles attached to the fibre surface thus forming a bubble layer. This layer prevents fibres touching each other before dewatering phase, thus preventing flocculation.

The formation difference was greatest in the case of spruce-CTMP, due to relatively stiff fibre compared to chemical pine and birch pulps.

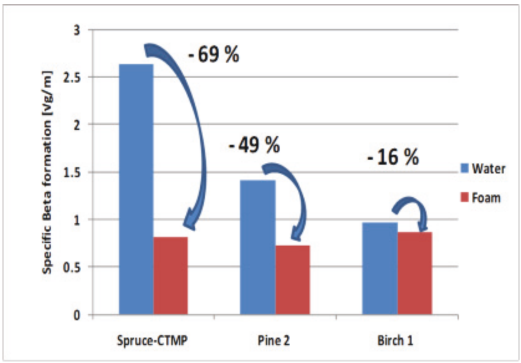

Figure 5. Comparison of specific formation number of water formed samples (blue) and foam formed samples (red) using spruce-CTMP, pine and birch [7].

Given that the headbox consistencies in the foam forming trials were higher compared to the water forming trials, the formation results are even more impressive. The consistencies are shown in Figure 6. In all cases there is a significant increase in the headbox consistencies. The limitations to the consistencies in the foam forming in our dynamic former come from the mixing procedure of fibres to the foam. In the Wiggins Teape Radfoam process even higher headbox consistencies were used. They managed to raise it up to 3 – 5% [4].

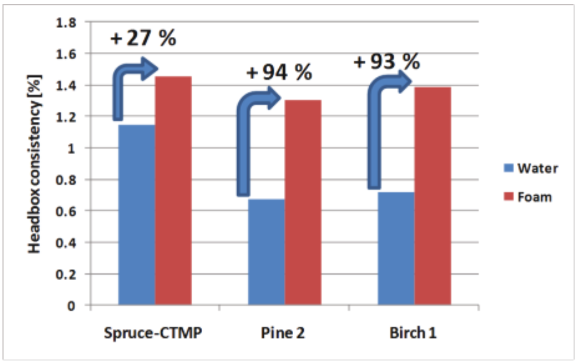

Figure 6. Comparison of headbox consistency of the water formed samples (blue) and the foam formed samples (red) using spruce-CTMP, and chemical pine and birch pulps [7].

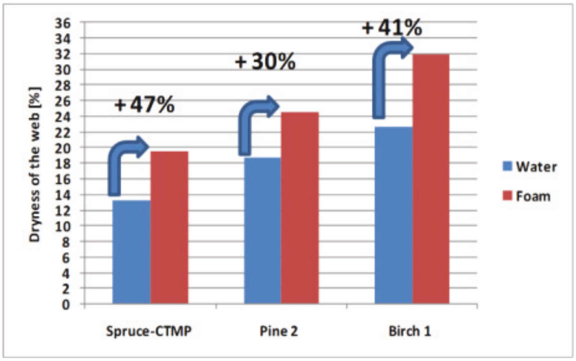

Figure 7. Comparison of the dryness of the web before wet pressing of the water formed samples (blue) and the foam formed samples (red) using and chemical pine and birch pulps [7].

In foam forming, the dewatering in a wire section is more effective than in the case of water forming. The dryness of the web before wet pressing for each pulp is shown in Figure 7. In all case the dryness was increased. However, this is partly due the fact that in foam forming the drainage capacity of the machine needs to be higher than for conventional papermaking [5], therefore higher vacuum levels are needed than in water forming. The used vacuum levels are presented in Figure 8.

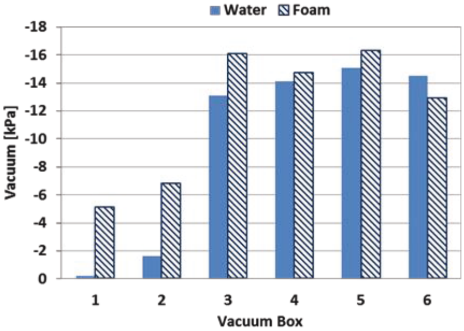

Figure 8. Vacuum levels in the forming section in the water and foam forming trials [7].

Another reason for improved dewatering properties is due to the difference in pore size distribution in the paper structures as shown in Figure 9. In that figure is shown the analysis of the x-ray microtomography images of water and foam formed samples [10].To characterise the pore network of the samples, we applied a distance transform to a binary sample image. Each local maximum in the distance transform is represented as a sphere of corresponding radius. In Figure 9, all spheres of a radius larger than 52 µm are plotted. The sphere colour indicates the z-directional position of the sphere in the structure, with red being top and blue bottom. In the foam-formed sample, big pores construct channels through the structure in the z-direction, whereas in the water-formed sample, large pores are almost isolated. The channels in the foam-formed samples are very beneficial for drainage properties.

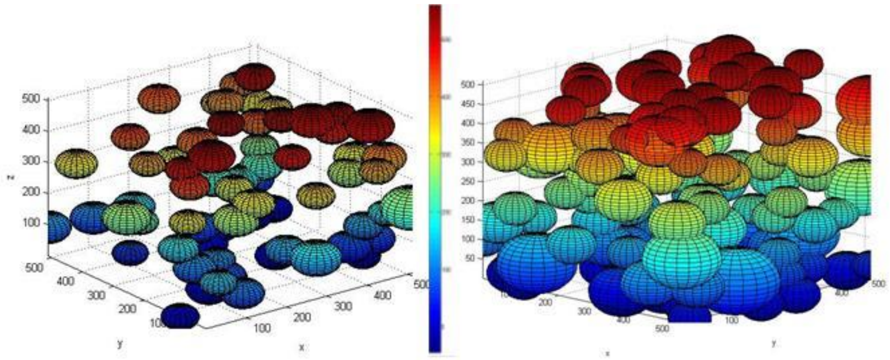

Figure 9. Characterisation of the pore network by balls of radius larger than 52 µm. The figure on the left-hand side is a water-formed sample and on the right-hand side a foam-formed sample. The red colour indicates that pores are at the top of the paper and blue that pores are at the bottom [10].

Application of high amount of nano fibrillated cellulose

The paper made by the foam forming process has high bulk and low strength characteristics in an unpressed state compared with a comparable water-laid paper. The strength lost is possible to regain by beating or by pressing [2], in latter case at the expense of the bulk. In paper physics it is well known fact that there is strong correlation with porosity of a structure and strength of a structure [9]. In normal water forming method the strength required is attained using strong enough wet pressing. The example of this behaviour is shown in Figure 10. The green triangles are shown the typical values for the current CTMP pulp obtained from the KCL pilot paper machine trials. In the same figure the blue squares are the results of the water formed sheets and the brown diamonds the results of the foam formed sheets, both sheet forming done in the laboratory scale.

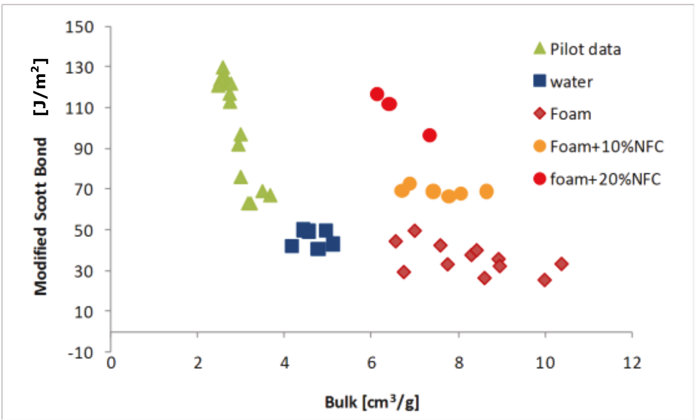

Figure 10. Scott bond values CTMP sheets as a function of bulk. The green triangles are the typical values for the sheets made from typical CTMP pulp obtained from the KCL pilot plant tests. The blue squares and red diamonds are values from water-formed and foam-formed laboratory handsheets, respectively. The circles show the values of the foam formed samples with different nano fibrillar cellulose contents.

In the first experiments we used the same CTMP as in the dynamic trials. The water formed handsheets were wet pressed according to ISO 5269-1 (2005-02-01), which says that the pressing is 400 kPa +/- 10 kPa. The sheet size was 16.5 cm x 16.5 cm. The foam formed sheets were wet pressed using a couch roll 1 time or 10 times. The method is rather crude, but enables sheets with different bulk values. Part of the foam formed sheet was left unpressed in order to see the bulk potential. The couch roll used in wet pressing has a mass 13.0 kg, length 178 mm, diameter 102 mm as said in the standard ISO 5269-1 (2005-02-01).

The results clearly show that the foam forming enables much higher bulk values compared to the water forming. The Scott bond values of the laboratory scale water and foam formed samples go into the same curve than the pilot scale results showing that by reducing the bulk in the foam formed sheets to the level 2-3 cm^3/g with wet pressing, the rapid increase in the Scott bond is obtained leading to the acquired level in z-directional strength.

Maintaining the bulk, and increasing the Scott bond values to the acquired level suitable for normal packaging applications, is possible to do using some strength additives. The amounts used can be reasonable high due to the open structure of the foam formed samples explained earlier. This is not an option in the water forming, because the water drainage properties would be compromised too much. In our foam forming studies the addition amounts of NFC, 10% and 20%, did not effect on water drainage times on a static foam former. Figure 10 shows the bulk and Scott bond values of the samples containing 10% (yellow circles) or 20% of NFC (red circles. These results show that structures with extremely high bulk and acquired strength properties are possible to produce by foam forming. This is very advantageous especially in board applications. The ability to use reasonable high amount of NFC addition opens up a wide window of different kind of optimization of the end properties. It also makes the selection of the suitable NFC grade very important, because the price of the NFC varies quite a lot. In these first tests we used NFC3.

As a consequence of this next test series were run in a laboratory scale using six different grades of nano or micro fibrillated celluloses in order to see their effect on both z-directional and plane strength properties. The pulps used in the study were the pine kraft pulp and the mechanical spruce CTMP pulp and addition amounts of NFCs 0% (a reference), 5% and 15%. The sheets prepared were dried after forming without any wet pressing. The results from CTMP series are shown in Figure 11.

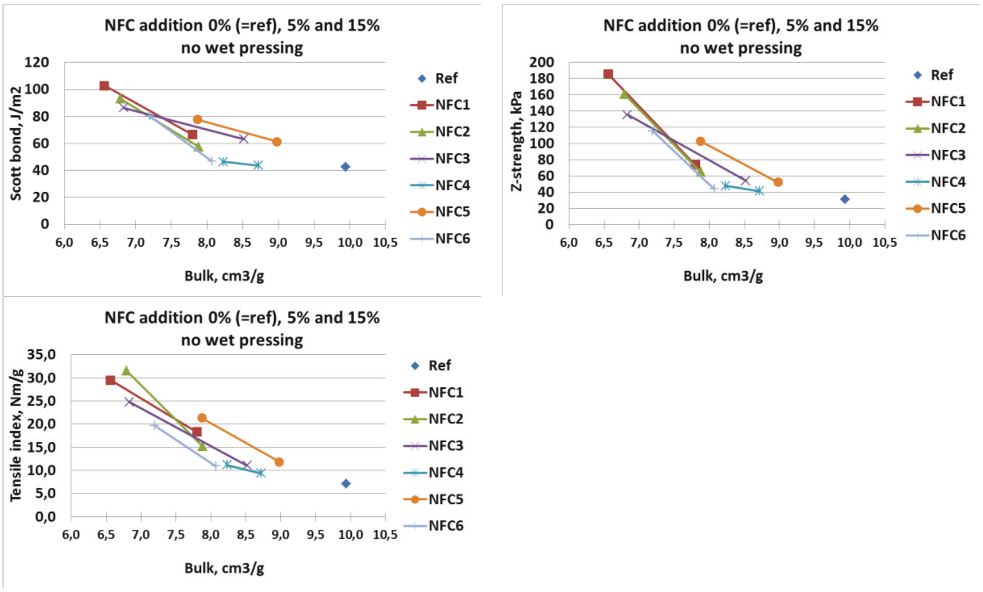

Figure 11. Effects of addition of six different NFC grades to the spruce-CTMP pulp. Above left: Modified Scott bond as function of bulk. Above right: Z-strength as function of bulk. Below: Tensile index as a function of bulk. The right edge of the line equates the 5% addition amount and the left edge 15% addition amount.

We measured both z-strength and modified Scott bond, because the latter is dependent on the formation. The similar results indicate good formation. The general trend of effects of different NFC/MFC on strength properties is rather similar. The results show that NFC made the sheet structure denser leading to the bulk lost from bulk value of 10 cm^3/g (a reference, no NFC) to values of 6.5-9 cm^3/g. However, the acquired z-directional strengths were reached in unpressed samples with NFC addition in high bulk levels of ca. 6 cm^3/g, by wet pressing the target was possible to reach in bulk levels of 2-3 cm^3/g. Remarkable in these results compared with the results showed in Figure 10 is that excluding NFC4 all others in the bulk values above 6 cm^3/g have Scott bond values above 50 J/m^2, whereas in the wet pressing case all Scott bond values were below 50 J/m^2. Another interesting result is to compare NFC1 and NFC2. Especially, in the case of the z-directional strength comparison NFC1 gives the highest Scott bond, even though it is more coarse (and cheaper) than NFC2. This shows that by choosing the most suitable NFC for certain application one can save substantial amount of money. The addition of NFC increases also plane strength of CTMP sheets significantly. However, in this comparison NFC2 gave highest tensile index value showing that the selection of NFC depends on needed property.

The same study was done using the pine kraft pulp. The results are shown Figure 12. The general trend of effects of different NFC/MFC on z-directional strength properties is rather similar that in CTMP series, except the behaviour of NFC5. With chemical pulp the influence of NFC5 is extremely interesting; the z- directional strengths were doubled without any bulk lost likewise the stretch. The mechanism behind this behaviour is unclear to us and needs more investigations.

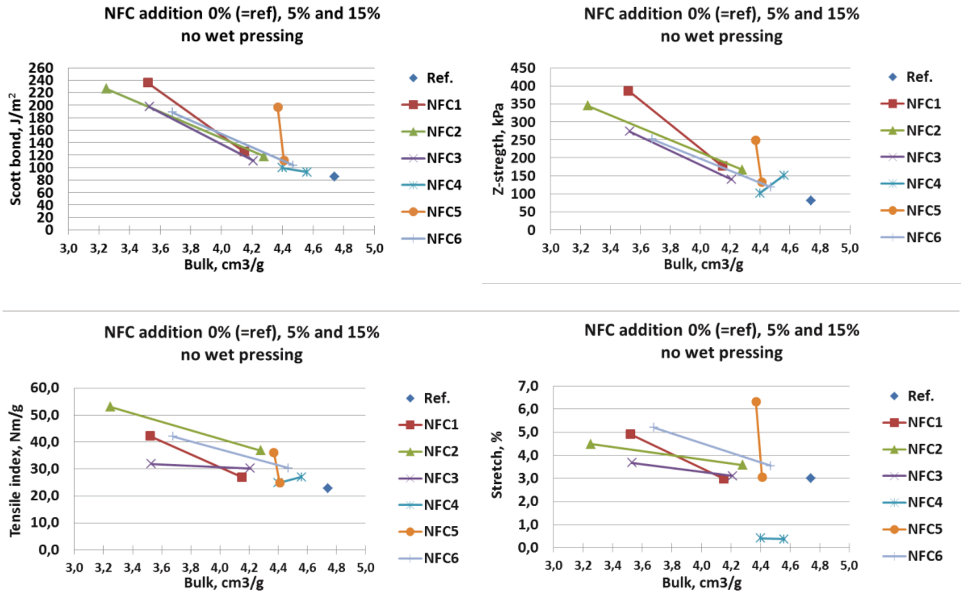

Figure 12. Effect of addition of six different grades of NFC to the kraft pine pulp. Above left: Modified Scott bond as function of bulk. Above right: Z-directional strength as function of bulk. Below left: Tensile index as a function of bulk. Below right: Stretch as function of bulk. The right edge of the line equates the 5% addition amount and the left edge 15% addition amount.

Conclusion

In this paper we have introduced the main benefits of the foam-laid technology. The main focus of the paper is in packaging applications, but also other application areas benefits from the process and paper properties improvements the foam-laid technology offers.

Good formation is needed in many paper and board application. Using the foam-laid technology the formation is independent of fibre properties or head box consistency. In all cases studied we obtained improvement in beta formation. Even using much coarse fibre such as spruce-CTMP we obtained slightly better formation than in the water formation using birch kraft. In addition, the headbox consistency was increased at the same time.

When water removal properties before wet pressing were compared, the foam-laid technology gave higher dryness levels. Because vacuum levels used were not exactly same, the direct comparison is not exact. However, the results from the pore size distribution of the paper samples show clear difference. In the foam-laid samples there are much more big pores that are beneficial in a water removal process. That makes it possible to use high addition levels of strengthening agents.

With the foam-laid technology one is able to make structures with very high bulk. When this is combined with the good water drainage properties, which allows the high addition levels of strengthening agents such as NFC, one can make products with very big bulk and still have an adequate strength value. That can be utilized in the savings on raw material especially in packaging applications.

There exists a lot of different kind of NFC grades that one can choose from. We compared the performance of some of them. Different NFC grades seem to behave rather similarly in bulk vs. strength comparisons. However, in case of modified Scott bond the coarser and cheaper NFC gave slightly higher value compared to more refined and expensive NFC. On the other hand more refined NFC gave higher tensile index value. This example illustrates that NFC used have to be chosen depending of paper properties needed.

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Potential of foam-laid forming technology in paper applications

Jani Lehmonen, Petri Jetsu, Karita Kinnunen and Tuomo Hjelt.

KEYWORDS: Foam-laid forming, Water-laid forming, Aqueous foam, Tensile strength, Formation, Consistency.

SUMMARY: The target of the work was to study the potential of foam-laid technology used conventionally in the non-woven industry for paper and board. Foam-laid technology can offer several benefits to the paper and board industry, in processing as well as product quality terms. Foam-laid technology utilises small spherical air bubbles containing aqueous foam instead of water as a process fluid and flowing medium. For the purposes of the study, a water-laid semi-pilot-scale process, formerly used for water-laid forming, was modified for foam-laid forming. Such modification included the processes used for foam production, mixing of furnish and foam, and the recovery, recirculation and refoaming of the process foam and foamy water. When using foam-laid technology, a higher forming consistency and improved formation were also achieved. The excellent formation results confirmed the potential of foam-laid technology in forming different kinds of wood-fibres. The mechanical properties of the resulting paper samples indicated that the average tensile strength was somewhat higher and the z-directional was higher in the case of water-laid paper than for foam-laid paper, when both had the same bulk level.

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Foam is an advanced material that can be applied in several industrial-scale applications; foams have been used conventionally by the long fibre based non-woven industry (Hanson 1977). In non-woven applications, typical products manufactured using foam-laid forming technology include specialty paper e.g. filter materials and various kinds of technical textiles. In addition, foam based applications can be found in the food, petroleum and gas industries, particularly in enhanced oil recovery (Weaire, Hutzler 1999). Foams are also used in fire-fighting applications (Kruglyakov 1999).

In the case of foam-laid forming technology, small spherical air bubbles containing aqueous foam are used, instead of water, as a process fluid and flowing medium (Smith, Punton 1975). Furthermore, aqueous foam is known to be excellent at transporting particles in a dispersed state (Smith, Punton 1975). In paper applications, foam typically causes problems related to aggregation. Foam-laid forming technology, on the other hand, utilises the properties of dispersive foam. In the paper industry, foam-laid forming technology was demonstrated in 1970, in a pilot-scale project based on the Radfoam process (Radvan, Gatward 1972; Punton 1975). This process was found to enhance important product properties, particularly formation in non-woven and paper applications (Kidner 1974; Smith, Punton 1975; Smith et al.1974).

In the paper making process, shear conditions vary greatly during different unit operations. In these kinds of processes, pseudo plastic material can be effectively utilised as foam. During the fibre mixing phase and the dewatering phase in the forming section, high shear conditions are applied which create a viscosity reduction in the foam. As a consequence of viscosity reduction, the dispersal of fibres becomes easier. Dewatering is also effective in creating a higher dryness level after the forming section (Smith et al. 1974; Wiggins Teape 1973). When the foamed materials are pumped into a pipeline, the transport properties of aqueous foams are unique because their air bubbles effectively prevent fibre entanglement. This behaviour leads to a minor reflocculation tendency in the fibres, thereby minimising the need for turbulence (Wiggins Teape 1971).

For the paper and board industry, which uses high amounts of fresh water in wet end unit operations, foam-laid forming technology enables possibilities to reduce the circulation of water, compared to the water-laid system. It is also possible to obtain a higher forming consistency and improved formation in the case of foam-laid technology (Smith, Punton 1975). A higher forming consistency gained with foam-laid technology enhances possibilities to achieve improvements in the reduction of the circulation of water. Foam forming technology also provides the possibility of widening the range of product properties, or even generating new ones for paper and board products. This could help in the renewal of the paper and board industry.

In this study, the possibility of applying foam-laid forming technology to paper applications was investigated using a semi-pilot scale former. The studies were carried out using open slice-jet-based headbox geometry.

Materials and Methods

Materials

Forming studies were performed using refined chemical pine pulp, chemical birch pulp and chemithermo-mechanical (CTMP) spruce pulp. The average process temperature in foam forming studies was ~ 27°C, while the average fibre length of pine pulp was 2.19 mm, the coarseness was 141.7 µg/m and the shopper value was around 20 °SR. The average fibre length of birch pulp was 0.91 mm, its coarseness was 101.9 µg/m and the shopper value was around 20 °SR. The average fibre length of spruce-CTMP pulp was 1.60 mm, its coarseness was 220.3 µg/m and the Canadian Standard Freeness value was around 570 ml. Tap water was used as process water. The stock was prepared by dispersing pulp and tap water within the pulper until forming was achieved.

Methods

Material characterization

The pulp properties were characterised using the Fibre Quality Analyser (Fibre-Master). The shopper value was determined according to ISO standard 5267-1:1998 and the Canadian Standard Freeness value, in accordance with ISO standard 5267-2:2001.

Paper testing

The formed paper web was sampled after the forming section without wet pressing, using a sampling apparatus or through simultaneous, gentle wet pressing using a roll nip. Afterwards, unpressed paper samples were wet pressed at wet pressure levels of 0.5 bar, 1.5 bar and 3.5 bar. Paper samples were wet pressed according to ISO standard 5269:1. Unpressed and gentle pressed samples were dried with a cylinder drying device (Kodak rotary drum dryer) and the wet pressed paper samples were dried on the plates. All paper samples were stored and analysed in a standard conditioned room at RH 50% and 23oC. The grammage of the paper samples was determined according to ISO standard 536:1995, while their thickness was determined according to ISO standard 534:1998, and their density and bulk based on the measured values of the grammage and sheet thickness. The tensile strength properties of paper samples were measured using a Lloyd tensile tester, in accordance with ISO standard 5270:1998. The z-directional tensile strength properties of paper samples were measured according to ISO standard 15754:2009.

Based on the β-formation measurement for the current study, a storage phosphor screen (SPS) was exposed to β-radiation through the paper sample, with Carbon-14 as the radiation force. This was done in order to evaluate the radiation absorption map. Thereafter, the screen was scanned with a Fuji BAS-1800 II SPS reader. Then, the measured values were converted into a grammage map. The size of the scanned area was 100 mm x 100 mm and the scanning resolution was 100 µm. Following this, the resolution was transformed to the Ambertech resolution (Ø 1 mm).

Water-laid process

Water-laid studies were carried out with a Short Circulation Device, which provides a dynamic semi-pilot scale research environment for forming studies. A schematic picture of the water-laid process is presented in *Fig 1*. The former unit consists of one-sided dewatering with seven adjustable vacuum box elements. The orientation level of web samples can be controlled using a jet-to-wire ratio. The machine chest volume was 0.5 m^3 and the water tower volume 1.0 m^3, while the white water chest volumes varied between 0.1 – 0.8 m^3. The temperature range could be varied between 20 – 60°C. A retention agent and filler feed systems were also included in the research environment. Online pH, conductivity, turbidity and temperature measurements could be used to characterise the chemical state of the process. Dewatering velocities and vacuum levels were also measured in the forming section. In the case of the water-laid process, the average forming speed of the web was 210 m/min. In the current experiments, the wire speed was constant and the speed of the slice jet varied from 190 m/min to 263 m/min, with the corresponding jet-to-wire ratio values ranging from 0.90 to 1.25.

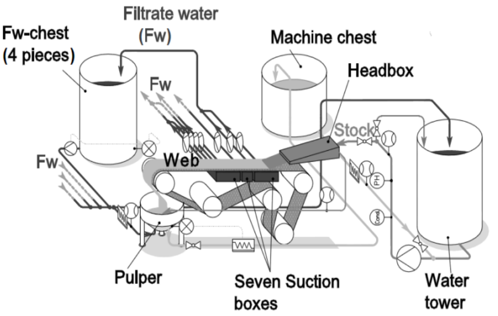

Fig 1. Schematic diagram of the water-laid process research environment.

The surface velocity of the slice jet was characterised using a laser and a camera, and by applying the triangulation method. In order to define the surface velocity, the recurrent structures of two sequential profiles were examined by using the cross-correlation in the machine direction. The surface velocity of the slice jet was characterised after the slice opening.

In these experiments, one row turbulence generator with four tubes was used. The tube diameter was changed from 10 mm to 13 mm, and then again to 25.5 mm, in two steps. The tube outlet was rectangular in shape. With a nozzle length of 800 mm, the height of the nozzle varied from 19 mm to 10 mm. The slice opening was 9 mm. In the case of water-laid forming studies, the volume flow rate was measured by using an electromagnetic flow sensor. For water-laid forming studies the average flow rate was varied between 4.6 l/s – 5.5 l/s.

The forming section covers two suction decks. While the first suction deck consisted of two suction sections with two suction slots, the second consisted of four suction sections with two suction slots. In both suction decks, the width of the suction slot was 160 mm and the length of the suction slot was 10 mm.

Foam-laid process

Foam-laid forming studies were carried out with a modified water-laid semi-pilot scale former. A schematic picture of the modified water-laid semi-pilot scale former is presented in *Fig 2*. The main principle of the foam-laid forming process consisted in the process foam being recirculated within the flow loop and the raw materials being mixed with the process foam in a pulper. In the case of the foam-laid process, the average forming speed of the web was changed from 36 m/min to 125 min, while corresponding jet-to-wire ratio values were changed from 3.0 to 0.9. The average speed of the slice jet was 110 m/min. Due to the limited feeding capacity of the

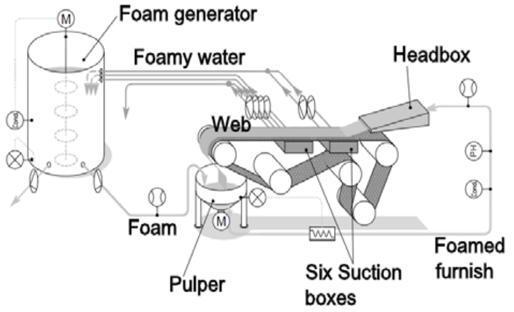

Fig 2. Schematic diagram of the foam-laid process research environment.

headbox feeding pump and the headbox geometry used, a higher forming speed could not be attained for foam-laid technology. The capacity of the used headbox feeding pump was limited to pumping a higher amount of dispersed air containing suspensions.

In the case of foam-laid forming studies, an electromagnetic flow sensor could not be used for measuring the volume flow rate, because of the high amount of dispersed air involved. For this reason, the volume flow rate for foam suspension was determined using a scale and by defining the amount of foam suspension as a function of time. The average flow rate was 2.5 l/s for foam-laid forming studies.

When upgrading the water-laid former into a foam-laid former, a closed flow loop was built for the recovery, recirculation and refoaming of the process foam and foamy waters. Dosing systems were also implemented for the surface active agent used in foam generation. In the forming section, the same dewatering elements as in the water-laid process were used for the drainage of both process foam and water. The intensity of the process foam drainage level was adjusted using vacuums. A vacuum-assisted water separator and foam generator were included in the flow loop.

The quality of new and recovered process foam was controlled online, by adjusting mixing conditions within the foam generator. A continuously working flow-through generator formed the basis of the foam generator's operating principle. The amount of process water and the conductivity of process foam were measured within the foam generator. Based on earlier studies, it is known that the air content of the foam correlates with conductivity measurements (Kruglyakov 1999; Weaire, Hutzler 1999). Mixing conditions in the foam generator were adjusted on the basis of these foam conductivity measurements. The average mixing speed of the foam generators' mixer was around 2,000 rpm. In the case of the foam-laid process, in order to maintain the air content at a constant level, the amount of process water must be balanced. The foam-laid process was stabilised by removing any extra process water. Furthermore, part of the process water must be replaced with fresh water in order to avoid excessive levels of surfactants in the water circulation. This ensures that the foaming process remains stable. Extra process water originates from various locations, for example sealing water used for pumps and cleaning water used for forming fabrics.

The dosage of a surface active agent depends on issues such as the type of foaming agent, the raw materials used and mixing conditions. For this reason, the correct amount of surface active agent must be defined during experiments of the kind undertaken in the study.

Process foam

In the production of process foam, foam-laid forming technology typically utilises surface active agents. The surface tension of the flowing medium can be lowered using surface active agents that enhance air dispersion into the medium (Nicolaysen, Borgin 1954; Riddel, Jenkins 1976; Touchette, Jennes 1960). In the current study, anionic natrium dodecyl sulphate supplied by Sigma-Aldrich was used as a surface active agent.

The stability of the foam forming process is based on process foam of uniform quality. According to reports, 60% – 70% can be regarded as favourable air content. For foams utilised in the foam forming processes, the average bubble size is between 20 µm – 100 µm (Smith, Punton 1975; Smith et al. 1974). Conductivity and density measurements in a process scale can be used to characterise the quality of process foam. In the current studies, process foam was produced continuously in the foam generator, at a height of 1.28 m and a diameter of 0.59 m. The average surfactant dosage was 3 – 3.5 kg/tn. The average density of the process foam was 330 kg/m^3 ± 20 kg/m3, while the average mixer energy consumption per foam volume was estimated to be □□7.4 kW/m^3. In terms of its average consistency, average mixer energy consumption per fibre weight was estimated to be around 154 kWs/kg. The characterised Sauter mean radius r[3,2] bubble size of the process foam was 58 µm (Lappalainen, Lehmonen 2012).

Results and Discussion

Jet-to-wire series

A jet-to-wire ratio series was run using both forming technologies. In the web forming studies, the average grammage was 80 g/m^2 and refined chemical pine pulp was used as a fibre raw material. The results for tensile strength ratio and specific β-formation as a function of the jet-to-wire ratio are presented in *Fig 3* and *Fig 4*. In the case of the water-laid technique, the results adhere to the conventional water forming results of the fourdrinier process. The lowest tensile strength ratio value was achieved at a speed difference of zero between the jet and wire. This so-called unity point is located near a jet-to-wire ratio of 1.06, rather than a jet-to-wire ratio of 1, because the speed of the slice jet decreases before it impacts on the wire, causing an error in estimating the jet-to-wire ratio.

At first, a greater speed difference results in higher tensile strength ratios, but after a certain point the tensile strength ratio begins to decrease rapidly. This behaviour can be explained by the existence of shear forces at the forming point that are too high, leading to a deterioration in formation and strength properties both under rush and drag conditions. The tensile strength ratio varied from 2.2 to 2.6 in the relevant area of the jet to wire ratio.

However, the tensile strength ratio slope can be much deeper at higher machine speeds. At best, water-laid

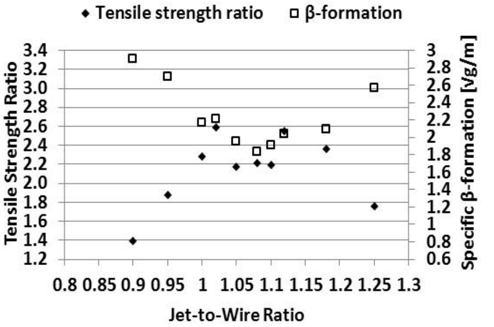

Fig 3. Tensile strength ratio and specific β -formation in the case of water-laid paper, as a function of the jet-to-wire ratio.

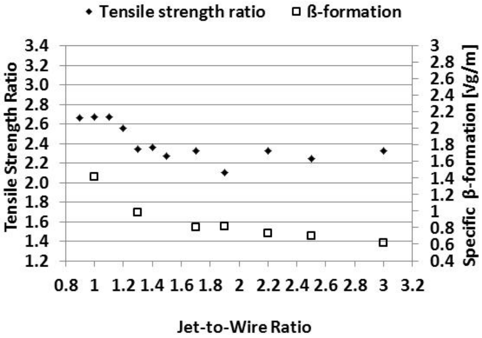

Fig 4. Tensile strength ratio and specific β-formation in the case of foam-laid paper, as a function of the jet-to-wire ratio.

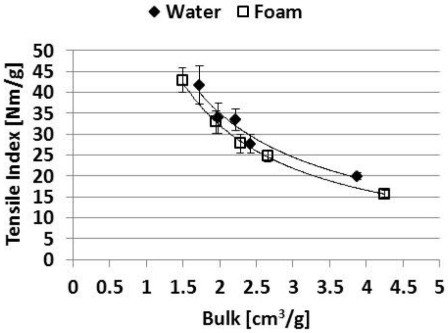

Fig 5. Tensile strength of water-laid and foam-laid paper, as a function of bulk.

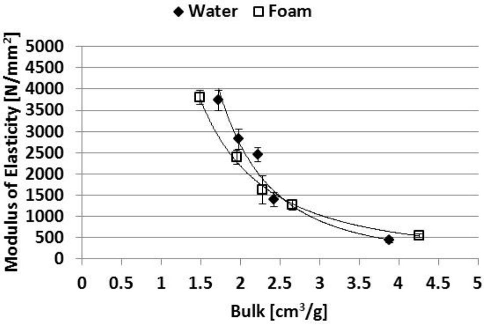

Fig 6. Modulus of elasticity in the case of water-laid and foam-laid paper, as a function of bulk.

paper formation of 1.9 √g/m was achieved, with a tensile strength ratio of 2.2. In general, the best formation values in fourdrinier processes occur close to the unity point, with formation deteriorating rapidly as the speed difference increases.

In the case of foam-laid forming, the tensile strength ratio decreased as a function of the jet-to-wire ratio, until it evened out under rush conditions, from a starting jet-to-wire ratio of 1.3. It is most likely that this clear unity point also exists in foam-laid forming but, perhaps due to the very slow speeds applied in these experiments, the rising slope cannot be observed during rush conditions. The tensile strength ratio of foam-laid paper varied from 2.1 to 2.7 when the jet-to-wire ratio varied from 0.9 to 3.0. The formation of foam-laid paper was improved using a higher speed difference, with the best formation values at 0.6 – 0.7 √g/m, a significant improvement in formation was achieved with foam-laid forming technology. In the case of foam-laid forming technology, the optimum range of the jet-to-wire ratio was 1.7 – 3.0, which was much wider than in the case of water-laid forming.

Paper web samples with optimal forming conditions were formed using both forming technologies in further processing. Optimal forming conditions were determined in such a way that the formation of paper samples was at the appropriate level and the tensile-strength ratio was at approximately the same level in both cases. The selected forming points were formed with a jet-to-wire ratio of 1.1 for water-laid paper and a jet-to-wire ratio of 2.2 for foam-laid paper. The vacuum profile of vacuum boxes in the machine direction was 0.2 kPa, -1.6 kPa,- 13.1 kPa, -14.1 kPa, -15.1 and -14.5 kPa for water-laid paper. Correspondingly, the vacuum profile of vacuum boxes in the machine direction was -5.1 kPa, -6.8 kPa -16.1 kPa, -14.7 kPa, -16.3 kPa and -12.9 kPa for foam-laid paper. Whereas the formation of selected points was 1.9 for water-laid paper and 0.7 for foam-laid paper, the tensile-strength ratio was approximately 2.2 in both cases. In the case of water-laid paper, the forming consistency was ~ 0.80% by weight. For foam-laid paper, the equivalent figure was ~ 1.30% by weight. A higher forming consistency and better formation were achieved simultaneously, using the foam-laid process. The average increase in forming consistency was ~ 63% and the average improvement in specific β-formation was ~ 69%. Enhanced forming consistency and formation levels were achieved in the case of foam-laid paper. These results verified the statements related to formation and forming consistency in the case of the foam-laid process.

The mechanical properties of the paper samples are presented in *Figs 5 –7*, as a function of bulk. These results are presented as a geometric mean value of the machine and cross-sectional direction. They indicate that the average tensile strength was somewhat higher for water-laid paper at the same bulk level. Based on earlier laboratory-scale studies, it has been reported that the tensile strength of a foam-laid paper sheet decreased by

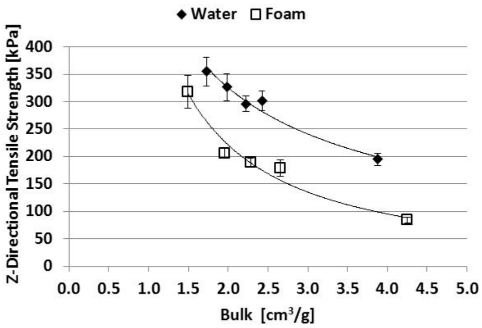

Fig 7. Z-directional tensile strength in the case of water-laid and foam-laid paper, as a function of bulk.

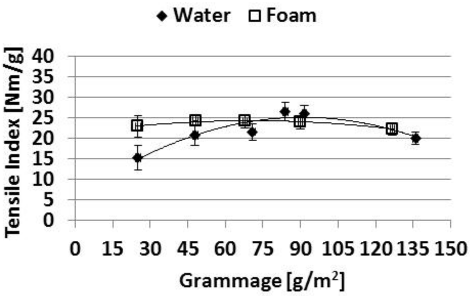

Fig 8. Tensile index as a function of grammage.

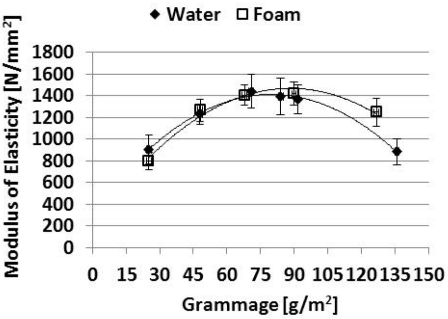

Fig 9. Modulus of elasticity as a function of grammage.

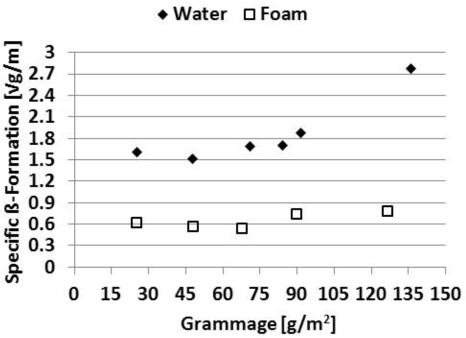

Fig 10. Specific β-formation of water-laid and foam-laid paper as a function of grammage.

up to 50% compared to a water-laid paper sheet, but could be regained by e.g. drying a foam-laid paper sheet under pressure (Smith, Punton 1975). In the current studies, the same wet pressing and drying methods were applied to water-laid and foam-laid paper, leading to the same kind of tensile strength behaviour as a function of bulk.

The water-laid paper was slightly stiffer at bulk levels lower than 2.5 cm^3/g, but at bulk levels higher than this foam-laid paper was as stiff as water-laid paper. In general, with respect to the effect of wet pressing on the modulus of elasticity, results similar to those of our study have been reported (Niskanen 1999).

The z-directional strength of the paper samples is presented in *Fig 7* as a function of bulk. The z-directional strength was weaker in the case of foam-laid paper. It is possible that the reason for this lies in the difference between the pore size distribution of the paper samples. It has been shown that foam-formed samples have a significantly large number of large pores compared to water formed samples (Hjelt et al. 2011). These large pores could act as weak points in the structure, thereby lowering the z-directional strength.

The effect of grammage on strength properties

The effect of grammage on the strength properties of water-laid and foam-laid paper was studied under selected web forming conditions. Refined chemical pine pulp was used as a fibre raw material when studying the effect of grammage on strength. The starting point for web forming studies consisted of utilising optimised web forming conditions of 80 g/m^2 paper. Other grammage level papers were formed in the same forming conditions. Water-laid papers were formed with a jet-to-wire ratio of 1.1 for water-laid paper and foam-laid papers were formed with a jet-to-wire ratio of 2.2. In this, the grammage range of paper alternated between 135 g/m^2 – 25 g/m^2 (*Figs 8–10*). Grammage was adjusted by changing the forming consistency. The average forming consistency varied between 0.26% – 1.24% by weight for water-laid paper and 0.48% – 1.77% by weight for foam-laid paper.

Based on earlier studies, it can be concluded that the tensile index of water-laid paper weakens if the grammage falls sufficiently (Seth et al. 1989). At higher grammage levels, the tensile index of water-laid paper was almost constant. In the current studies, the tensile index of water-laid paper began to fall notably at a grammage level of lower than ~45 g/m^2. Correspondingly, the results showed that the tensile index of foam-laid paper remained almost constant throughout the studied grammage range. The modulus of elasticity was at roughly the same level for both water-laid and foam-laid paper.

One of the reasons for the enhanced tensile index properties of low grammage foam-laid paper can be found in the significant improvement in the formation of foam-laid paper compared to water-laid paper, as seen in *Fig 10*. Good formation means fewer weak points in foam-laid paper, which has a positive effect on its strength properties, particularly in the low grammage area.

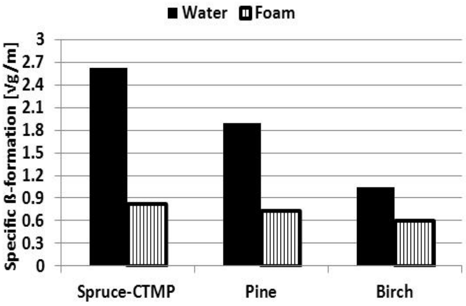

Fig 11. Specific β-formation values of wood-fibre pulps in the case of water-laid and foam-laid paper.

Formation

It has been claimed that one advantage of foam-laid forming technology lies in its suitability for a wide variety of fibres (Smith et al. 1974). The formation potential of foam-laid forming technology for different kinds of wood-fibres has been studied in the case of chemical pine pulp, chemical birch pulp and spruce-CTMP pulp. Paper samples were formed using optimal web-forming conditions for chemical pine pulp. Foam-laid papers were formed with a jet-to-wire ratio of 2.2 and water-laid papers were formed with a jet-to-wire of ratio1.1. The average grammage of spruce-CTMP pulp was 108 g/m^2 for foam and 107 g/m^2 for water. Correspondingly, the forming consistency for foam was 1.45%, while for water it was 1.15%. The average grammage of pine pulp was 82 g/m^2 for foam and 84 g/m^2 for water. Correspondingly, its forming consistency was 0.67% for water foam and 1.30% for foam. The average grammage of birch pulp was 84 g/m^2 for foam and 83 g/m^2 for water, while the related forming consistency was 1.38% for foam and 0.72% for water. The formation results confirmed the potential of foam-laid forming technology for use within different kinds of wood-fibres (*Fig 11*). For every pulp type, the formation of foam-laid paper was significantly better than in the case of water-laid paper. The formation difference was greatest in the case of spruce-CTMP, due to relatively stiff fibre compared to chemical pine and birch pulps. In earlier studies, it has been shown that stiff fibres are a challenging material to form, since their coarseness affects the specific β-formation of water-laid paper (Niskanen 1999). The current studies and results confirmed the validity of the above mentioned statement in the case of water-laid paper, whereas for foam-laid paper excellent formation is obtained independent of the fibre properties in question.

Conclusions

The aim of the study was to evaluate the potential of using foam-laid technology in paper applications. Foam-laid technology was compared to the current forming technology used in the paper industry, water-laid technology. The process parameters used in water-laid forming studies are not applied to production paper machines, leading to poorer paper quality than for production scale activities. However, process parameters, such as speed and consistency, utilised in water-laid forming are more favourable to the achievement of high paper quality than those used in foam-laid forming. This is what makes a comparison possible.

Foam-laid technology offers an improvement in terms of reduced water circulation and uniform web structure. A higher forming consistency gained with foam-laid technology enhances possibilities to achieve improvements in the reduction of the circulation of water. Formation was also improved in the case of foam-laid technology. Average forming consistency increased by 63% while the average improvement in specific β-formation was 69%, in comparison to water-laid technology. It can be concluded that, these results verified the statements presented in earlier studies related to formation and forming consistency in the case of the foam-laid process.

The mechanical strength results of the water-laid and foam-laid papers indicated that the average tensile strength was somewhat higher and the z-directional higher in the case of water-laid paper. However, the results also showed that foam-laid paper enables a stronger light-weight web structure compared to the corresponding water-laid web structure. This is advantageous in the case of very thin paper products. Such characteristics could enable raw material savings in paper and board production.

Based on the results achieved, foam-laid technology has clear potential in the forming of different kinds of wood fibres. The formation of foam-laid paper was excellent for every type of wood-fibre studied, including for stiff and long fibres. This could enable the range of product properties to be broadened, or even the creation of new features in paper and board products.

Acknowledgements

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FOAM-AIDED SLUDGE TREATMENT

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Both industry and domestic households produce huge amounts of wastewater and, as a result, effective sludge management is required. One route is to reduce the amount of water in the final sludge cake. This paper introduces a foam-assisted thickening method to improve the effectiveness of biosludge dewatering. The method, foam-assisted dewatering (FAD), has previously been used in a paper production process in the 1980s. The current work shows that in both static and dynamic experiments, FAD is also applicable for sludge treatment. Foam addition to the dewatering process of biosludge from a paper mill increased the dry solids content of the wet cake and shortened the dewatering time. In addition, the turbidity of the filtrate fell indicating enhanced microparticle retention. Results could be utilised in industrial belt thickening and the vacuum filtration of slurries. The expected benefits could be higher dry solids content of filter cakes, a faster dewatering rate and lower flocculent consumption.

INTRODUCTION

Municipal wastewater plants produce 11 million tons of dry solids sludge per year, even in the EU. Stricter legislation and increased industrial production have led to increased quantities of sludge, high treatment costs and high landfill costs. In the EU, organic matter such as wastewater sludge will soon not be allowed to be landfilled at all[1]. Thus, a lot of effort is focused on minimising the amount of sludge. Two routes are available, either to reduce the generation of sludge in the wastewater treatment process (WWTP) or to reduce the amount of water in the final sludge cake. Reducing the amount of water can, for example, be achieved by using different filter aids in order to create 'water channels' inside the filter cake during filtration. In addition to commercial filter aids, residue-based fly ash, classified ash, cement kiln dust, gypsum, fine coal, lignite, rice hull ash, plant derived aid, bagasse, wood chips, wheat dregs, char, recycled fibres and cationised/anionised recycled fibres have been used as skeleton builders together with flocculants in order to form porous, permeable and rigid lattice structures for sludge cake filtration[2-16].

In the paper and board industry energy efficient dewatering is of great importance and capabilities of the press section have progressed significantly in the last several decades, allowing ever higher dryness levels to be achieved. Lindsay describes one proposed means of achieving this objective, namely through displacement dewatering whereby a pressurised gas phase is used to drive liquid water out of a mechanically compressed sheet[17,18]. The theory of displacement dewatering is presented in the following.

The length of time the gas pressure must be applied is the key issue in displacement dewatering. The motion of a stable gas-liquid interface driven by constant gas pressure is considered as a one-dimensional motion through a uniform porous medium of thickness L and permeability K. The gas liquid interface is at position x, with $x = 0$ at the flow exiting side of the sheet, and ΔP is the pressure drop across the sheet. If the inertial effects and the viscosity of the gas phase are neglected, Darcy's law can be applied to determine the interface velocity:

$$V = -\frac{dx}{dt} = \frac{K\Delta P}{\varepsilon \mu x} \qquad (1)$$

where V is the interface velocity, ε the sheet porosity and μ the liquid viscosity. The time required for the interface to move across the entire porous medium beginning at the upper surface ($x = L$) is given by integration:

$$\int_L^0 -x dx = \int_0^t \frac{K\Delta P}{\varepsilon\mu} dt' \qquad (2)$$

resulting in

$$t = \frac{\varepsilon\mu L^2}{2K\Delta P} \qquad (3)$$

where t is the required time.

As shown in equation (3), a thick or less permeable web requires more time than a thin and porous web. However, in practice the displacement process faces some inherent instabilities that reduce its efficiency. In a porous medium, when a liquid is displaced by another fluid of lower viscosity, the interface between the phases is often unstable. Disturbances on a smooth interface create 'fingers' that penetrate into the phase being displaced (see Figure 1), a phenomenon known as 'viscous fingering'[17-19]. This phenomenon means that a gas phase will tend to simply blow through certain paths, leaving much of the water behind. Lenormand *et al.*[20] numerically examined a displacement process for a wide variety of conditions. The conditions typically found with air-water displacement in paper clearly fall in a regime where significant viscous fingering is liable to happen.

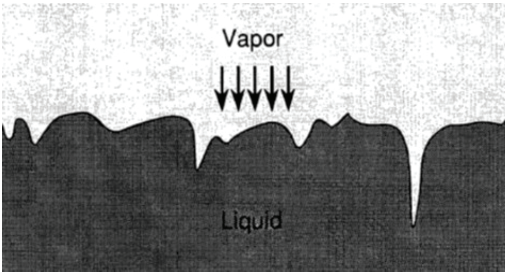

Figure 1: Viscous fingering in a porous medium as a gas displaces a liquid.[19]

The stability of the displacement process can be enhanced, for instance, by using a displacing phase with higher viscosity. One option is the use of foams, which are mostly low viscosity air, but due to their structure the foam behaves like a fluid with a very high viscosity. Such a benefit is utilised in secondary or tertiary oil recovery[21]. In the paper industry, foam assisted technology is validated on a pilot paper machine[22]. Skelton[22] reports that the application of foam to paper increases water removal by suction. In the experiments, Skelton compared dewatering by vacuum alone with applications of surface-active agents to the paper web in several process stages. The surface-active agent was used in both unfoamed and foamed states. The foam layer applied to the surface of the paper web was sucked through the sheet by vacuum or forced in by external pressure. The results of the tests showed enhancement in dewatering and thus a dryer web, particularly when the surface active agent was used in a foamed state. Skelton[22] wrote that the reasons for this effect were unknown.

According to Lindsay[17,18], the analogy to oil recovery would appear to provide at least part of the explanation. Due to the high viscous foam, the viscous fingers become 'self-sealing' to some extent, making the interface more stable. The stability of the displacement process in suction is increased and water removal becomes more efficient.

In our study, the experimental result from the paper machine – i.e. foam displaces liquid more effectively than a stream of free air – was applied to the thickening of biosludge from a paper mill. The method is applicable to sludge treatment, because vacuum filters and thickening devices are widely used in dewatering sludge in wastewater plants and industry.

METHODS

Static Setup

The first experiments performed to test whether FAD is applicable to sludge treatment used a static vacuum filtration setup. Figure 2 shows the measurement arrangement which consisted of a funnel-based filtration device, a scale and a filtrate bowl. The average vacuum level in the funnel was 0.5 bar. The effectiveness of dewatering was characterised by measuring the amount of filtrate as a function of time. The sludge used in the tests was biosludge from a mill producing both pulp and paper. The dry solids content of the sludge was 1.2%. Fennopol K1390 was used as a flocculation polymer at a dose of 5 kg/t DS. The foam was made separately from water, surface active agent (sodium dodecyl sulphate, SDS) and pressurised air using a mixer. The amount of SDS added was 2.5 g/l and the density of the foam produced was 100 g/l.

The procedure applied was as follows. Firstly, the sludge was flocculated with polymer and 200 g of flocculated sludge was poured into the funnel. The foam was made separately and 36 g of it was dosed to the top of the sludge. Subsequently, an underpressure of 0.1 bar was applied and the sludge was drained through a filter cloth. An example of the filtrate cake is shown in Figure 3. In static studies the filtrate was only analysed visually, without verifying the observations with analytical methods.

Dynamic Setup

The results obtained in the static experiments were

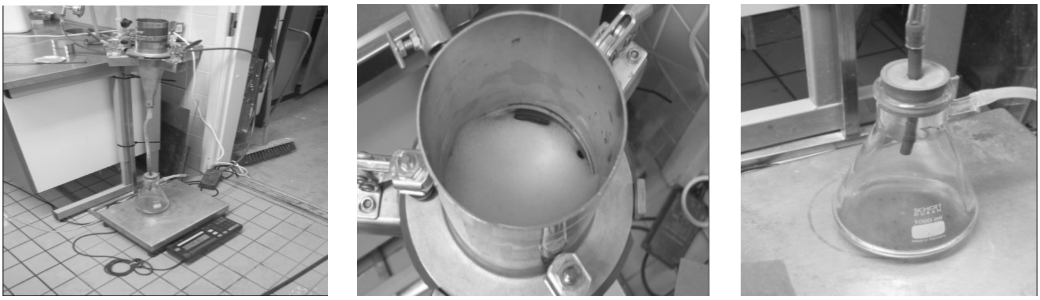

Figure 2: Foam assisted dewatering (FAD) arrangement in the sludge dewatering studies. Funnel based filtrate device, scale and filtrate bowl (*left*); foam layer on top of the sludge (*middle*); Filtrate bowl on the scale (*right*).

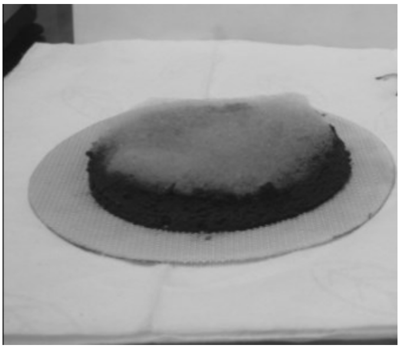

Figure 3: An example of the filter cake produced by using a foam-assisted thickening technique in the treatment of biosludge from a paper mill.

confirmed in dynamic conditions using a dynamic filter unit. The filter unit consisted of a feeding chest, a feeding line with a feed pump, free and vacuum assisted dewatering sections, an adjustable wire device and a unit for the filtrate collection. The dynamic set-up is shown in Figure 4. The length of the free dewatering section was 90 mm, and the length of the vacuum assisted dewatering section was 410 mm. The length of the sludge web was 95 mm. The average vacuum level used in the sludge dewatering was rather low, namely around 2 kPa. Thus, in these conditions dynamic filtration was actually thickening due to the insignificant vacuum pressure.

In the first test performed with the dynamic setup, the focus was on finding the optimum foam application point and the application direction. For these tests, a new batch of biosludge was obtained from the mill. Fennopol K1390 was used as a flocculation polymer as in the earlier tests; the application dose needed to produce proper flocculation was 4 kg/t DS. The polymer was dosed online before a headbox feed pump. Foam with an average density of 100 g/l was produced online from water, SDS and pressurised air by a foam generator based on a stator-rotor mixing system; SDS was used at a dosage of 2.5 g/l, as in the static studies. The flocculated sludge from the feeding chest was pumped to the filter cloth, and a foam layer was applied to the surface of the sludge web with a separately

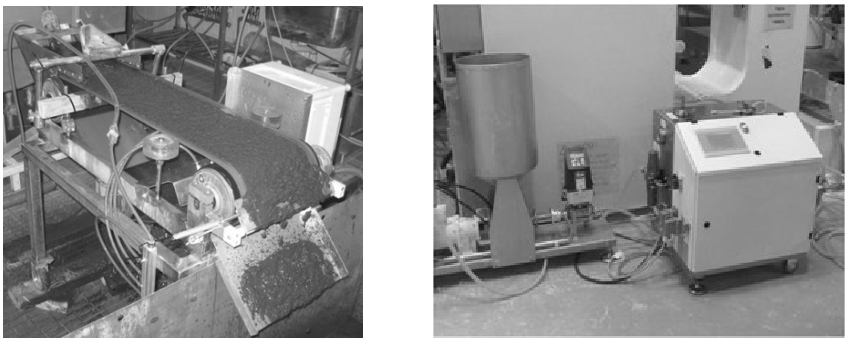

Figure 4: The dynamic setup comprised of a dynamic thickening unit (*left*) and a foam generator (*right*).

mounted foam applicator.

The applicator was easily transferable, and during the thickening process several application possibilities of applying foam onto the sludge web were tested in order to find the optimum foam application point. It was not possible to test the optimum foam amount due to the foam generator having too high a pumping capacity. In order to decrease the foam amount, a by-pass flow was constructed without any measuring devices. This set-up enabled only a 'less – more' estimation of the amount of applied foam. In addition, the different application directions - downstream and upstream - were tested. For reference, the flocculated sludge was thickened without using the foam. The turbidity and dry solids content of the filtrates were measured so as to evaluate the filtering results.

Based on these results, another test series was run with a new batch of biosludge. The experiments were performed at two different polymer dosage levels, namely 0.95 kg/t DS and 1.9 kg/t DS. The polymer dosing, foam generation and sludge application were carried out as in the earlier tests. The position of the foam application was just before the dewatering section, the position where the highest dry solids content was achieved in the first test series. For reference, the flocculated sludge was thickened without using the foam. The dry solids content of the filter cakes and the turbidity of the filtrates were measured so as to evaluate the thickening results.

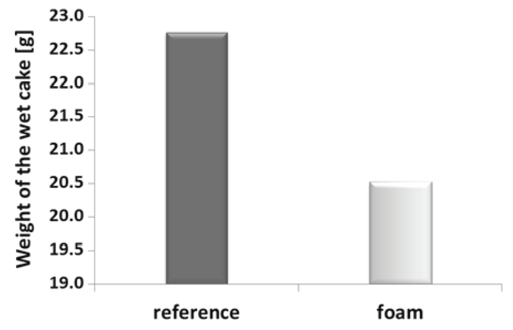

Figure 5: Effect of FAD in the static filtration studies. The dry solids content of the cake was around 10% and the foam was applied to the top of the sludge before filtering.

RESULTS AND DISCUSSION

Static Filtration

The target in static filtrations was to demonstrate that the reported ability of the foam to displace liquid water from a porous medium[22] was also applicable in sludge treatment. According to our experiments, an enhancement in a dewatering process was obtained with a dryer sludge cake. Figure 5 shows the effect of FAD on the weight of the cake. When foam was applied to the top of the sludge before dewatering, the foam layer worked as a 'lid' on the cake surface, thereby enhancing water removal. The viscous foam increased the interface stability and no 'viscous fingers' from the surface were observed. The foam applied prevented the gas phase from blowing through the cake, because of the missing paths, and water was removed evenly from the cake. Comparing the foam assisted filtration with the conventional filtration, the dry solids content of the cake clearly increased, as the weight of foam-assisted cake was lighter. The average difference in dry solids content of the cake was around 10%.

The influence of the stable displacement process could also be seen in the dewatering time. The stable displacement process, where no paths leading through the cake exist, removed water effectively and faster from the cake compared to the reference. Figure 6 shows the dewatering rates of the samples. The sample treated with foam was dewatered very quickly – in 20 s 95% of the total filtrate amount was removed from the sludge sample; correspondingly only 60% of the total filtrate amount was removed from the reference sample in 20 s (Figure 6, *left*). Figure 6, *right*, shows

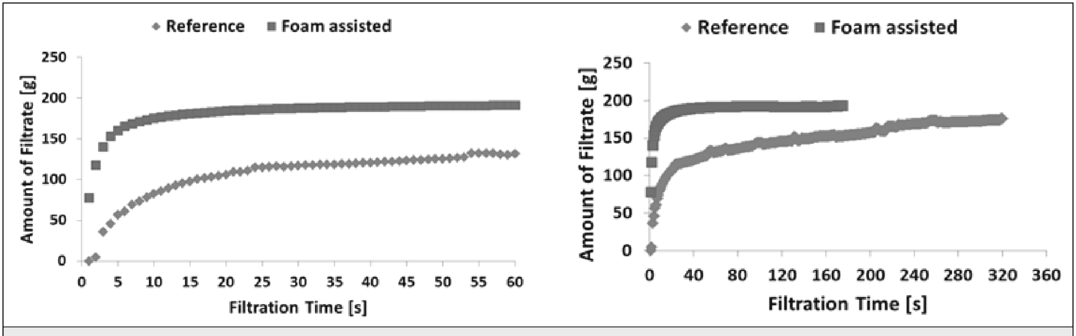

Figure 6: Effect of foam on dewatering rate and the amount of water removed in static vacuum filtration.

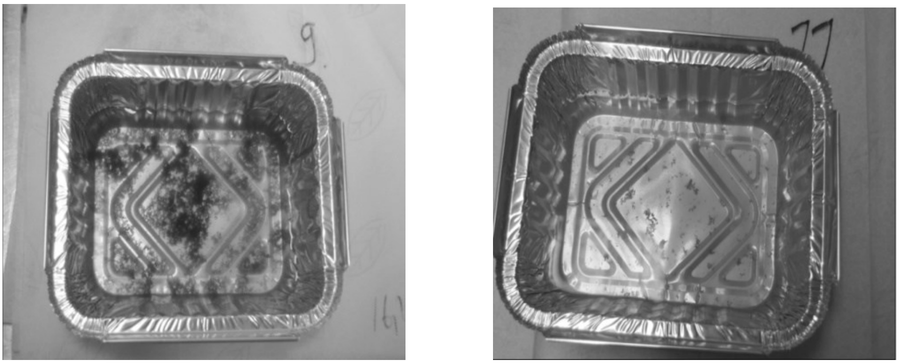

Figure 7: The effect of foam on filtrate properties. Filtrate from sludge vacuum filtration without foam (*left*) and with foam (*right*).

the overall picture of the filtration process; in the foam case the process was very fast and happened in less than one minute. In the reference case, the filtration process was notably slower and took six times longer. In spite of the longer filtration time, the total filtrate amount was 10% smaller in the reference case than in the foam-assisted case.

An interesting result was observed when examining the filtrates. Visually the filtrates from foam-assisted filtration were much cleaner, containing fewer large particles, and were also more transparent (Figure 7). According to these observations, it seems improvement in solids retention and enhanced dewatering are simultaneously possible. The amount of sludge used in the filtration tests was the same in both cases.

Dynamic Thickening

Figure 8 shows the basic concept of the foam-assisted thickening process in dynamic conditions. The left-hand picture is an example of the reference result, where the flocculated sludge was thickened without using the foam. The right-hand picture is an example of the corresponding sludge web after applying a 3-6 mm layer of foam with an air content of 90% on the sludge surface.

In the first experiment, the influence of the application point, amount and the way foam was applied to the sludge surface was tested. Based on the results, the optimum position for the foam application was found to be just before the dewatering section, where foam aid was strongest, producing the highest dry solids content of the sludge cake. The amount of foam needed at that application point was only tested roughly by increasing the bypass flow of the foam. The results of these experiments show that neither foam amount nor the application direction have the expected results on dry solids content of the sludge web (Figure 9). Regardless of the dry solids content results, the foam treatment had a significant effect on the turbidity of filtrates in all foam cases (Figure 10).

The second set of experiments was performed at two different polymer dosage levels, namely 1.9 kg/t DS and 0.95 kg/t DS, in order to clarify whether the first

Figure 8: An example of the sludge web before (*left*) and after (*right*) applying foam in the dynamic filtration process.

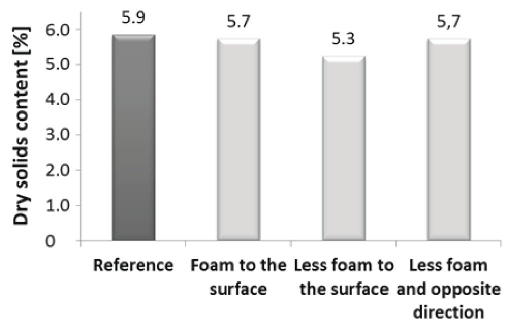

Figure 9: Foam did not (more or less) have any positive effect on dry solids content of the sludge dewatering in the dynamic conditions of the first experiments.

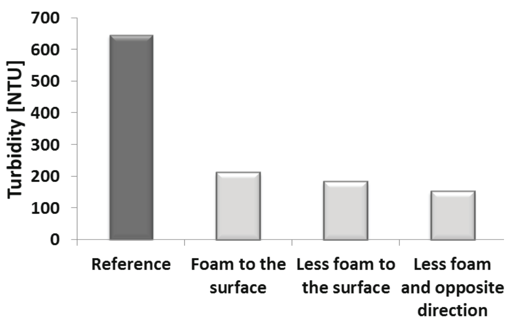

Figure 10: Effect of foam on filtrate turbidity in dynamic thickening. The addition of foam decreased turbidity.

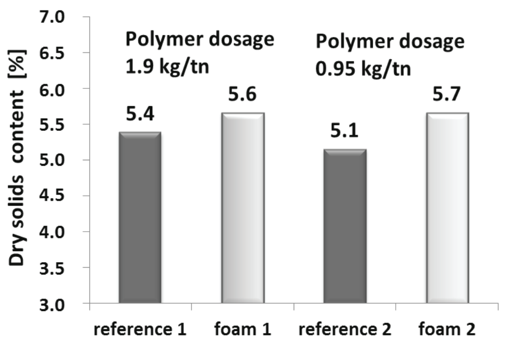

Figure 11: Effect of foam on the dry solids content of the filter cake in dynamic thickening. The increase in dry solids content at the lower polymer addition level was around 10%, the same as that observed for static vacuum filtration.

experiment's dry solids content results were caused by disturbances in the flocculation stage. The results from this second experiment showed that dry solids content without foam usage was 5.4% and 5.1%, respectively. When the foam was used, the dryness was increased to 5.6% and 5.7% (Figure 11). The increase in the lower polymer addition level was around 10%, the same as in the case of static filtration.

Results from the filtrate turbidity measurements were congruent with results from the first experiments and showed a large decrease in turbidity when foam was used (Figure 12). This indicates that the retention of microscale particles was enhanced effectively. With the higher polymer dose of 1.9 kg/t DS, the decrease was almost 50%, from 80 NTU to 43 NTU, and with the lower polymer dose of 0.95 kg/t DS the decrease was over 59%, from 215 NTU to 89 NTU. The latter result indicates the possibility of chemical optimisation in sludge foam-assisted thickening. The thickness of the applied foam layer (90% air content) was 5-10 mm. This corresponded to a 0.1-1 mm water layer, so there was no dilution effect caused by extra water.

The turbidity results were confirmed by measuring the dry solids content of the filtrates (Figure 13). The results show that when using foam-assisted thickening an enhancement of the retention of micro-sized particles was achieved.

CONCLUSIONS

Foam-assisted dewatering (FAD) technology is applicable to sludge thickening and vacuum filtration.

In static filtration, the dry solids content of the filter cake using foam as a filtering aid was increased by 10% compared to filtration without foam. In addition, the rate of dewatering was significantly increased, indicating savings in dewatering energy or an increase in filter capacity. The same 10% difference in cake dry solids content was obtained for dynamic thickening conditions. In the dynamic FAD experiments, turbidity of the filtrate clearly decreased which indicates an enhancement in micro-sized particle retention.

The results obtained in this study may be valuable in the dewatering of WWTP sludge and industrial slurries. More experiments need to be performed using industrial slurries and different dynamic belt filtering techniques. The expected benefits could be a higher dry solids content in filter cakes, cleaner filtrates, faster dewatering rates and lower flocculant consumption.

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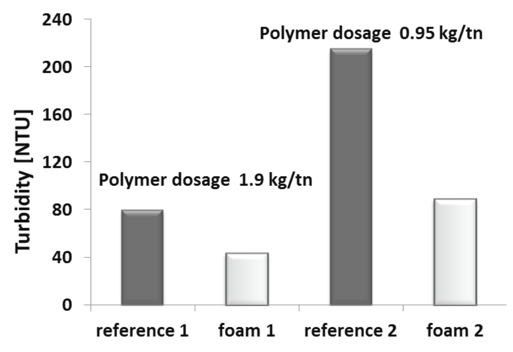

Figure 12: Effect of foam on filtrate turbidity in dynamic sludge thickening. With a higher polymer dose of 1.9 kg/t DS the decrease in turbidity was almost 46%, and with a lower polymer dose of 0.95 kg/t DS the decrease was over 59%.

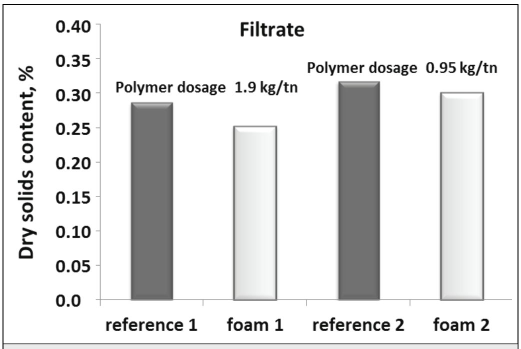

Figure 13: Dry solids content of the filtrates.

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Foam as a carrier phase – a multipurpose technology for industrial applications

In the 1970s foam was explored for the first time as a replacement for water in papermaking, but the foam technique was not able to break through in the field of paper and board production. A renewed interest in foam technology has been raised now. One of the most important reasons for this is the force to renew the paper and board industry. Also the driving forces of savings in energy and raw materials, lead the paper and board industry to search for solutions to meet challenges. The newly developed materials may challenge the conventional processes and their full potential may not be achieved in traditional processes. New technologies are needed for that. The main aim of this thesis was to study the applicability of foam technology in industrial applications: in web forming, chemical dosing, coating and biosludge treatment. Furthermore, the potential of foam technology in nanomaterial application was also assessed.

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