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

Karita Kinnunen-Raudaskoski
Foam as a carrier phase – a multipurpose technology for industrial applications

Karita Kinnunen-Raudaskoski

A doctoral dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Aalto University School of Chemical Technology for public examination and debate in Auditorium KE2 (Komppa Auditorium) at the Aalto University School of Chemical Technology (Espoo, Finland) on the 12th of May, 2017, at 12 noon.

Aalto University
School of Chemical Engineering
Department of Bioproducts and Biosystems
Supervising professors
Professor Jouni Paltakari
Aalto University, Finland

Thesis advisors
D.Sc. (Tech.) Tuomo Hjelt
VTT Technical Research Centre of Finland, Finland

Preliminary examiners
Professor Markku Kataja
Department of Physics
University of Jyväskylä, Finland

Professor Tetsu Uesaka
Department of Chemical Engineering
MidSweden University, Sundsvall, Sweden

Opponents
Professor Mark Martinez
Director, Pulp and Paper Centre
Director, Advance Papermaking Initiative
University of British Columbia, Vancouver, Canada
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

ISSN-L 1799-4934 ISSN (printed) 1799-4934 ISSN (pdf) 1799-4942
Location of publisher Helsinki Location of printing Helsinki Year 2017
Pages 190

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

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>979-952-60-7402-3</td>
<td>979-952-60-7401-6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ISSN-L</th>
<th>ISSN (painettu)</th>
<th>ISSN (pdf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1799-4934</td>
<td>1799-4934</td>
<td>1799-4942</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Julkaisupaikka</th>
<th>Painopaikka</th>
<th>Vuosi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helsinki</td>
<td>Helsinki</td>
<td>2017</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sivumäärä</th>
<th>urn</th>
<th>ISBN: 979-952-60-7401-6</th>
</tr>
</thead>
</table>
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 Kaljumen and Erkki Saharininen. 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 Katajainen 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, lilo 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.


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


Contents

Preface ............................................................................................................................................... i
List of publications............................................................................................................................ iii
Author’s contributions ....................................................................................................................... iv
Supporting publications ..................................................................................................................... v
List of symbols and abbreviations .................................................................................................... ix

1. Introduction ..................................................................................................................................... 1
   1.1 Background ............................................................................................................................... 1
   1.2 Thesis objectives and scope ...................................................................................................... 6

2. Foam properties and foam technologies ....................................................................................... 9
   2.1 Foam as a material .................................................................................................................... 9
       2.1.1 Aqueous foam .................................................................................................................. 9
       2.1.2 Pseudoplastic nature of foam ......................................................................................... 15
       2.1.3 Particles in foam ............................................................................................................. 16
   2.2 Foam technologies .................................................................................................................. 17
       2.2.1 Foam coating ................................................................................................................... 17
       2.2.2 Foam forming .................................................................................................................. 18

3. Materials ....................................................................................................................................... 20
   3.1 Fibrillated cellulose .................................................................................................................. 20
   3.2 Materials in foam coating ....................................................................................................... 20
   3.3 Materials in foam forming and foam assisted dewatering ..................................................... 24

4. Methods ....................................................................................................................................... 27
   4.1 Foam coating ........................................................................................................................... 27
       4.1.1 Measuring of foam stability ......................................................................................... 27
       4.1.2 Foam coating trials to the dry web .............................................................................. 28
       4.1.3 Foam coating trials to the wet web ............................................................................ 32
   4.2 Foam forming .......................................................................................................................... 33
       4.2.1 Laboratory scale studies .............................................................................................. 33
       4.2.2 Dynamic semi-pilot scale studies ................................................................................ 34
   4.3 Foam assisted dewatering ....................................................................................................... 37
4.3.1 Static setup ................................................................. 37
4.3.2 Dynamic setup .......................................................... 38
4.4 Characterization methods ................................................. 41
  4.4.1 Foam coating .......................................................... 41
  4.4.2 Foam forming and foam assisted dewatering .................. 41

5. Results and discussion .......................................................... 45
  5.1 Foam coating .................................................................. 45
    5.1.1 Foam quality .......................................................... 46
    5.1.2 Improvements of surface using native cellulose nanofibrils .................................................................. 48
    5.1.3 Functionalization of paper surface .............................. 52
    5.1.4 Barrier properties with foam coating ......................... 57
    5.1.5 Foam coating of wet web .......................................... 61
  5.2 Foam forming ................................................................. 69
    5.2.1 Improvement of formation ......................................... 69
    5.2.2 Improved dewatering ............................................... 72
    5.2.3 Slower decrease of strength, when grammage is reduced .................................................................. 75
    5.2.4 Better bulk strength ratio using CMF .......................... 76
    5.2.5 Drawbacks ............................................................. 82
  5.3 Foam assisted dewatering .................................................. 82
    5.3.1 Improved dewatering in filtration, better holdout of small particles ................................................. 82
    5.3.2 Dynamic Thickening ................................................ 85

6. Conclusions and future perspectives ....................................... 89
  6.1 Future research recommendations ..................................... 93

Appendix A: Test methods of foam coated paper ....................... 109
Appendix B: Publications I-VI .................................................. 115
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
NO₂ nitrogen dioxide
NOₓ The generic term NOₓ includes NO and NO₂
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
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>°SR</td>
<td>Schopper-Riegler value (drainability of a pulp suspension)</td>
</tr>
<tr>
<td>SW</td>
<td>softwood kraft pulp</td>
</tr>
<tr>
<td>TiO₂</td>
<td>titanium dioxide</td>
</tr>
<tr>
<td>TMP</td>
<td>thermo mechanical pulp</td>
</tr>
<tr>
<td>tDS/a</td>
<td>tons dry solids/year</td>
</tr>
<tr>
<td>VTT</td>
<td>Technical Research Centre of Finland</td>
</tr>
<tr>
<td>WVTR</td>
<td>water vapour transfer rate</td>
</tr>
<tr>
<td>WWTP</td>
<td>waste water treatment process</td>
</tr>
<tr>
<td>ZnO</td>
<td>zinc oxide</td>
</tr>
</tbody>
</table>
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.](image)

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 treat-
ment 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 (Impopola et al., 2011). The fibrous foam is produced using an injection mixing station. In addition to the aforementioned pa-

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, whereas 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 de-
watering, 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 pres-
sure.

Our foam research in the year 2005 was started by efforts to find companies us-
ning 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 dy-
namic research, were a crucial requirement. We contacted several manufacturers
and performed pilot scale trials using different applicator designs, e.g. open cham-
bers 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 pa-
per (Saharininen 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 theTekes 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 chal-
genches 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 na-
tive 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 ‘Effi-
cient Networking towards Novel Products and Processes’ (EffNet) (Kinnunen and
Hjelt, 2013). Outside conventional fibers (pulp, synthetic) we have shown the foam


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 knives 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.

<table>
<thead>
<tr>
<th>Research questions</th>
<th>Surface treatment</th>
<th>Forming</th>
<th>Dewatering of sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td>The interest towards foam technology is growing, why now?</td>
<td>Papers I-III</td>
<td>Paper IV</td>
<td>Paper VI</td>
</tr>
<tr>
<td>What are the main foam properties as a carrier phase, which ensure the proper functioning of foam processes?</td>
<td>Paper I</td>
<td>Paper IV</td>
<td>Paper VI</td>
</tr>
<tr>
<td>What are the main benefits of foam forming technology to paper and board processes? How to maintain the strength properties in bulky structures?</td>
<td>Papers IV, V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>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?</td>
<td>Papers I-III</td>
<td></td>
<td></td>
</tr>
<tr>
<td>How foam affects the dewatering of paper, board and sludge?</td>
<td>Paper III</td>
<td>Paper V</td>
<td>Paper VI</td>
</tr>
</tbody>
</table>

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.

![Surfactant schematic](image)

**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](image)

**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](image)

**Figure 5.** An image from Prof Stubenauch’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 \( \approx 109.43 \) 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 \( \phi \) 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 \( \phi_c \) the bubbles lose contact with each other, and the foam loses its rigidity (Figure 6).

![Figure 6](image)

**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 \( \phi_c \) 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 \( \phi \). 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 \( \mu m \), with none larger than 100 \( \mu m \) or smaller than 10 \( \mu m \). The average radius R was 55 \( \mu m \). 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, $\phi$. The shear modulus $G$ (circles) and the non-linear modulus $G_{nl}$ (triangles) are shown as a function of $\phi$. The continuous lines represent the Mason’s $\phi$ dependence formula, while the dashed line is Princen’s formula. More details on $G_{nl}$ 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 $\mu$m 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 $\mu$m and the foam is like a stable shaving cream.
Figure 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 non-woven 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/m².

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, described by patents (Gatward and Radvan, 1966; Gatward et al., 1972; Robertson, 1972; Radvan and Green, 1973; Wallace and Willis, 1987; Wiggins 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 furnish 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 (Wiggins Teape, 1971). After drainage they had a normal papermaking process system. Tringham (1974) reported further development of the process.

![Flow chart of the Radfoam process](image)

**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 cellulosates are novel bio-based materials, which have potential for numerous applications. Two types of fibrillated cellulosates 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.

<table>
<thead>
<tr>
<th>Web</th>
<th>Materials</th>
<th>Solids %</th>
<th>Applied amount, g/m²</th>
<th>Foaming agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>dry</td>
<td>Native CNF (Table 4)</td>
<td></td>
<td></td>
<td>SDS</td>
</tr>
<tr>
<td></td>
<td>CNF with TiO₂/ZnO (Table 5 and Table 6)</td>
<td></td>
<td></td>
<td>SDS</td>
</tr>
<tr>
<td></td>
<td>Mowiol 40-88 (PVA1)¹)</td>
<td>6.8</td>
<td>Up to 8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Exceval AQ-4104 (EVOH)¹)²)</td>
<td>16.0</td>
<td>Up to 8</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Base paper and board⁴)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>wet</td>
<td>PVA1⁵) (degree of hydrolysis 88%, viscosity 30-42 mPa·s²)</td>
<td>7.0</td>
<td>1.8</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>PVA2⁵) (degree of hydrolysis 99%, viscosity 26-30 mPa·s³)</td>
<td>10.8</td>
<td>2.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>EVOH⁵) (degree of hydrolysis 98-99%, viscosity 3.8-4.5 mPa·s³)</td>
<td>10.8</td>
<td>2.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Guar gum, non-ionic, commercial</td>
<td>0.9</td>
<td>0.2</td>
<td>SDS⁵)</td>
</tr>
<tr>
<td></td>
<td>Starch, cationic, cooked</td>
<td>2.1</td>
<td>0.5</td>
<td>SDS⁵)</td>
</tr>
<tr>
<td></td>
<td>CMF by Masuko collider device at VTT</td>
<td>2.8</td>
<td>0.7</td>
<td>SDS⁵)</td>
</tr>
<tr>
<td></td>
<td>Pre-refined softwood pulp from a Finnish pulp mill, SR² 19</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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/m² 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/m² 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.

<table>
<thead>
<tr>
<th>Grammage g/m²</th>
<th>Bulk cm³/g</th>
<th>Gloss %</th>
<th>Roughness PPS, μm</th>
<th>Air permeance μm/Pas</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>1.2</td>
<td>5.8</td>
<td>4.9</td>
<td>5.8</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Pre-treatment</th>
<th>CNF-CTP</th>
<th>CNF-TE/CTP</th>
<th>CNF-TE/PTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homogenization</td>
<td>Enzymatic</td>
<td>TEMPO oxidized</td>
<td>TEMPO oxidized</td>
</tr>
<tr>
<td>Solids content</td>
<td>micro fluidizer</td>
<td>micro fluidizer</td>
<td>Cavitron</td>
</tr>
<tr>
<td></td>
<td>by CTP</td>
<td>by CTP</td>
<td>by PTS</td>
</tr>
<tr>
<td>Gel type</td>
<td>opaque, viscous</td>
<td>transparent, solid</td>
<td>white, fluent</td>
</tr>
<tr>
<td>Zeta potentials</td>
<td>-25.0 mV</td>
<td>-69.5 mV</td>
<td>-55.5 mV</td>
</tr>
</tbody>
</table>

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 TiO₂ and ZnO were produced by Colorobbia, Italy.
Table 5. Physico-chemical characteristics of inorganic nanoparticles delivered by INNOHUB, Italy.

<table>
<thead>
<tr>
<th></th>
<th>±</th>
<th>TiO₂</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (%w/w)</td>
<td>0.5</td>
<td>6.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.05</td>
<td>1.20</td>
<td>1.12</td>
</tr>
<tr>
<td>Viscosity (25°C) (mPa/sec)</td>
<td>0.1</td>
<td>2.00</td>
<td>ND</td>
</tr>
<tr>
<td>Particles Dimension (nm)</td>
<td></td>
<td>40.0</td>
<td>45.0</td>
</tr>
<tr>
<td>(DLS Malvern Instruments)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polydispersity Index</td>
<td>0.05</td>
<td>0.25</td>
<td>0.20</td>
</tr>
<tr>
<td>pH</td>
<td>0.5</td>
<td>1.0</td>
<td>ND</td>
</tr>
<tr>
<td>Cationic surfactant (%w/w)</td>
<td>0.05</td>
<td>0.1</td>
<td>-</td>
</tr>
</tbody>
</table>

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 TiO₂ (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 TiO₂ 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-TiO₂ (2.8% dry weight) and 15 kg of CNF-ZnO-TiO₂ (4.8% dry weight) were produced. The concentrations of TiO₂ and ZnO in the final nanocomposites were determined by ICP analysis. Table 6 shows the mixing ratios and the TiO₂ and ZnO contents of the prepared CNF composites.
Table 6. Analysis of CNF/inorganic nanoparticles suspensions (TiO₂ and ZnO determined by ICP analysis by INNOHUB, Italy).

<table>
<thead>
<tr>
<th>Nano-composite</th>
<th>Solids content, %</th>
<th>Initial mixing ratio of the preparations (as dry weight)</th>
<th>TiO₂ content (% dry weight)</th>
<th>ZnO content (% dry weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNF-TiO₂</td>
<td>2.8</td>
<td>1 : 1</td>
<td>24</td>
<td>-</td>
</tr>
<tr>
<td>CNF-ZnO&amp;TiO₂</td>
<td>4.8</td>
<td>10 : 1 : 10</td>
<td>42</td>
<td>2</td>
</tr>
</tbody>
</table>

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.

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

![Optical microscopy images of the fibrillated cellulose samples.](image)

**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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shear viscosity, mPas·s</th>
<th>Transmittance, % (800 nm, 0.1% conc.)</th>
<th>Content of smallest fraction (FR4), %</th>
<th>Content of nanosized fraction, %</th>
<th>Visual appearance (optical microscopy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTT coarse</td>
<td>23176</td>
<td>34</td>
<td>3.5</td>
<td>5.6</td>
<td>Coarse/fine, few large fragments, slightly heterogeneous, film-like fibril network</td>
</tr>
<tr>
<td>VTT fine</td>
<td>22502</td>
<td>60</td>
<td>4.8</td>
<td>6.9</td>
<td>Fine, homogeneous, film-like fibril network</td>
</tr>
<tr>
<td>Daicel</td>
<td>15777</td>
<td>8</td>
<td>1.3</td>
<td>2.6</td>
<td>Coarse, long slender fibrils, heterogeneous, film-like fibril network</td>
</tr>
<tr>
<td>P1</td>
<td>3654</td>
<td>26</td>
<td>4.7</td>
<td>20</td>
<td>Coarse, large fragments, heterogeneous, porous and bulky fibril network</td>
</tr>
<tr>
<td>P2</td>
<td>2784</td>
<td>25</td>
<td>0</td>
<td>50.7</td>
<td>Coarse, un fibrillated fibers, heterogeneous, porous and bulky network</td>
</tr>
</tbody>
</table>
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), origi-
nally 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 °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 calendared using a nip load of 100 kN/m, two nips and temperature of 55 °C. Base paper for the reference was calendared under the same conditions.

The trials of CNF functionalized with nanoparticles (ZnO and TiO₂) 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/m².

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](image)

**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/m².
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%.

![Image of foam applicator and papermaking equipment](image)

**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/m²
- 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 m²) 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/m² 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 suc-
tion 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.

![Image](image1.png)  ![Image](image2.png)

**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 m³ and the water tower volume 1.0 m³. The volumes in the white water chest varied between 0.1 and 0.8 m³. 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 fibre 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](image)

**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 (Formulaaction; 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.

<table>
<thead>
<tr>
<th>Property</th>
<th>Equipment</th>
<th>Standard/Method</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Coating of dry web, coated with</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNF</td>
<td>Surface layer</td>
<td>Hitachi S-3400N scanning electron microscope (SEM)*)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Surface layer</td>
<td>Thermo Scientific’s Noran System Six EDX spectrometer.</td>
<td></td>
</tr>
<tr>
<td>Gloss (75°)</td>
<td>Elrepho2000</td>
<td>ISO 8254-1:2009</td>
<td></td>
</tr>
<tr>
<td>Air permeance</td>
<td>Parker-Print Surf (20 kPa pressure)</td>
<td>ISO 5636/1: 0-14 μm Pas</td>
<td></td>
</tr>
<tr>
<td>Roughness</td>
<td>PPS S10</td>
<td>ISO 8791-4:2007</td>
<td></td>
</tr>
<tr>
<td>Hydrophobicity</td>
<td>CAM 200 (Contac angle of water, 2 μl drop size )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Func. CNF</td>
<td>TiO₂/ZnO element map</td>
<td>SEM/EDS *) **)</td>
<td>App. A</td>
</tr>
<tr>
<td></td>
<td>Antimicrobial activity</td>
<td></td>
<td>App. A</td>
</tr>
<tr>
<td></td>
<td>Photocatalytic activity</td>
<td></td>
<td>App. A</td>
</tr>
<tr>
<td>PVA, EVOH</td>
<td>Pinhole</td>
<td></td>
<td>App. A</td>
</tr>
<tr>
<td></td>
<td>KIT-test</td>
<td>Tappi T559 cm-12</td>
<td>App. A</td>
</tr>
<tr>
<td></td>
<td>Grease barrier</td>
<td>Mod. TAPPI 507 T cm-09</td>
<td>App. A</td>
</tr>
<tr>
<td></td>
<td>Water Vapour Transfer rate</td>
<td>Mod. ASTM E-96</td>
<td>App. A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Coating of wet web</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile strength, relaxation</td>
<td>IMPACT-fast tensile test rig</td>
<td></td>
<td>See 1)</td>
</tr>
<tr>
<td>Internal bonding strength</td>
<td>Huygen Internal Bond Tester</td>
<td>TAPPI T569 om-09</td>
<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>Moisture analyser</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*) 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 Size 1.06 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.

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

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.

![Diagram of IMPACT-fast tensile test rig](image)

**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 cellulosics 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).
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.

![Graph showing bubble distribution](image)

**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.

<table>
<thead>
<tr>
<th>Test points (length of the hose, air content, temperature)</th>
<th>Bubble size, μm</th>
<th>Bubble size, μm from images</th>
</tr>
</thead>
<tbody>
<tr>
<td>3m, 90%</td>
<td>75</td>
<td>68</td>
</tr>
<tr>
<td>3m, 90%, 16.5 °C</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>3m, 90%, 55 °C</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>5m, 90%</td>
<td>81</td>
<td>84</td>
</tr>
<tr>
<td>7m, 90%</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>10m, 90%</td>
<td>88</td>
<td>88</td>
</tr>
<tr>
<td>10m, 94%</td>
<td>80</td>
<td>81</td>
</tr>
<tr>
<td>10m, 90%, 16.5 °C</td>
<td>78</td>
<td></td>
</tr>
</tbody>
</table>
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).

![Calculated coat weight](image)

**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/m². 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/m². 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 calendaring 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 TiO$_2$ 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.
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 $10^8 - 10^7$ CFU (6-7 log).
Table 12. Antibacterial activity of foam-coated paper samples under conditions of light exposure.

<table>
<thead>
<tr>
<th>Paper samples (coat weight)</th>
<th>ZnO ppm</th>
<th>TiO₂ ppm</th>
<th>Staphylococcus aureus</th>
<th>Klebsiella pneumoniae</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Bacteriostatic activity (log reduction)</td>
<td>Bactericidal activity (log reduction)</td>
</tr>
<tr>
<td>Untreated paper</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CNF-TiO₂ (0.4 g/m²)</td>
<td>-</td>
<td>340</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CNF-TiO₂ (0.9 g/m²)</td>
<td>-</td>
<td>1670</td>
<td>1.3</td>
<td>0</td>
</tr>
<tr>
<td>CNF-TiO₂ (1.8 g/m²)</td>
<td>-</td>
<td>2910</td>
<td>Total bacteriostatic 1.0</td>
<td>1.8</td>
</tr>
<tr>
<td>CNF-ZnO &amp; TiO₂ (0.6 g/m²)</td>
<td>38.4</td>
<td>1150</td>
<td>0.7</td>
<td>0</td>
</tr>
<tr>
<td>CNF-ZnO &amp; TiO₂ (1.3 g/m²)</td>
<td>104.6</td>
<td>3070</td>
<td>Total bacteriostatic 0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>CNF/ZnO (0.8 g/m²)</td>
<td>180</td>
<td>-</td>
<td>Total bacteriostatic 0.3</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Significant antibacterial activity was obtained for paper samples treated by CNF-TiO₂ 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-TiO₂ 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 TiO₂ 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).

<table>
<thead>
<tr>
<th>Paper samples</th>
<th>ZnO ppm</th>
<th>TiO&lt;sub&gt;2&lt;/sub&gt; ppm</th>
<th><strong>Staphylococcus aureus</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Bacteriostatic activity</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(log reduction)</td>
</tr>
<tr>
<td>Untreated paper</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>(control)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNF-TiO&lt;sub&gt;2&lt;/sub&gt; (1.8 g/m&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>-</td>
<td>2910</td>
<td>1.7</td>
</tr>
<tr>
<td>CNF-ZnO (0.8 g/m&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>180</td>
<td>-</td>
<td>1.2</td>
</tr>
</tbody>
</table>

5.1.3.3 Photocatalytic Activity of the Foam-Coated Papers

Photocatalytic efficiency of the paper samples foam-coated by nanocomposites: CNF-TiO<sub>2</sub>, CNF-ZnO, CNF-ZnO&TiO<sub>2</sub> are reported in Table 14.

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

<table>
<thead>
<tr>
<th>Sample (coat weight)</th>
<th>ppm ZnO dry weight on paper (ICP analysis)</th>
<th>ppm TiO&lt;sub&gt;2&lt;/sub&gt; dry weight on paper (ICP analysis)</th>
<th>% NO degradation after 105 min</th>
<th>% NOx degradation after 105 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated paper</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CNF-TiO&lt;sub&gt;2&lt;/sub&gt; (0.4 g/m&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>-</td>
<td>80</td>
<td>16.8</td>
<td>12.6</td>
</tr>
<tr>
<td>CNF-TiO&lt;sub&gt;2&lt;/sub&gt; (0.9 g/m&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>-</td>
<td>1670</td>
<td>72.6</td>
<td>46.0</td>
</tr>
<tr>
<td>CNF-TiO&lt;sub&gt;2&lt;/sub&gt; (1.8 g/m&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>-</td>
<td>2910</td>
<td>79.9</td>
<td>61.6</td>
</tr>
<tr>
<td>CNF-ZnO&amp;TiO&lt;sub&gt;2&lt;/sub&gt; (0.6 g/m&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>38.4</td>
<td>1150</td>
<td>81.7</td>
<td>64.9</td>
</tr>
<tr>
<td>CNF-ZnO&amp;TiO&lt;sub&gt;2&lt;/sub&gt; (1.3 g/m&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>104.6</td>
<td>3070</td>
<td>90.9</td>
<td>78.5</td>
</tr>
<tr>
<td>CNF/ZnO (0.8 g/m&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>180</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
The results show that paper samples foam-coated by nanocomposites containing TiO₂ display photo activity for the degradation of volatile compounds at a TiO₂ 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 TiO₂ content of the paper. The NOx photo degradation in gaseous phase by CNF-TiO₂ foam-coated paper is shown in Figure 33. Within 100 minutes, around 70% NOx oxidation occurred, this shows that foam-coated paper with CNF-TiO₂ had a significant effect on the oxidation of NO and NOx. In a coat weight of 0.9 g/m², the corresponding TiO₂ dry weight on paper was 0.162% (1620 ppm), this was enough to have an influence of 72.6% NO degradation after 105 min.

![Graph showing NOx, NO, and NO₂ concentrations over time](image)

**Figure 33.** The NOx photo degradation in gaseous phase by CNF-TiO₂ foam-coated paper. Note: coat weight below 1 g/m².
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/m² of PVA1 or 8.2 g/m² 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/m²: KIT-value = 7
- PVA2 coated, coat weight 8 g/m²: KIT-value = 8.

5.1.4.4 Grease barrier tests

The grease barrier was tested first according to the standard (4h at 60°C). 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 60°C). Top: 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/m² of PVA2. Also 3 g/m² of PVA1 gave a very good result.
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\(^2\)).
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/m² (PVA2 and EVOH).

The effect of SDS spray was not studied. The SDS foam slightly enhanced de-watering. 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. $\Delta P$ 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:

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

(1)

where V is the interface velocity, $\varepsilon$ is the sheet porosity, and $\mu$ 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:

$$\int_0^L -xdx = \int_0^t \frac{K \Delta P}{\varepsilon \mu} \, dt'$$

resulting in

$$t = \frac{\varepsilon \mu L^2}{2K \Delta P}$$

(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).](image)

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.

![HiVac vacuum level](image)

**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.

![Wet pressing load 1200 kN/m.](image)

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.

![Graph showing T.E.A index and Scott Bond delamination energy for different additives.]

**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/m² 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/m².

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).

![Dryness increase as a function of bulk change, reference in point (0,0)](image)

**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/m² 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/m² (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 furnish 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.

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Foam forming</th>
<th>Water forming</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Consistency,</td>
<td>Grammage,</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>g/m²</td>
</tr>
<tr>
<td>Spruce-CTMP</td>
<td>1.45</td>
<td>108</td>
</tr>
<tr>
<td>Pine</td>
<td>1.30</td>
<td>82</td>
</tr>
<tr>
<td>Birch</td>
<td>1.38</td>
<td>84</td>
</tr>
</tbody>
</table>

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® lyocell 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/m³, 80% BSK and 20% lyocell was 0.54 \( \sqrt{g/m} \). 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/m³. 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.

<table>
<thead>
<tr>
<th>Method</th>
<th>Furnish</th>
<th>Ratio</th>
<th>Refining</th>
<th>Retention chemicals</th>
<th>Head box consistency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (Jakkula, 2012)</td>
<td>SW/HW</td>
<td>30/70</td>
<td>refined</td>
<td>yes</td>
<td>0.26</td>
</tr>
<tr>
<td>Foam</td>
<td>SW/synthetic PP fibers, 6 and 12 mm</td>
<td>70/30</td>
<td>Unrefined SW (SR° 13)</td>
<td>no</td>
<td>0.61</td>
</tr>
</tbody>
</table>
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) sug-
gested 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 °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/m² – 135 g/m². 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/ m² 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.
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 Gaward, 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 50. Tensile index of refined chemical SW pulp (20 °SR) sheets as a function of grammage. The results are presented as a geometric mean value of the machine and cross-sectional directions.

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 cm\(^3\)/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 cm³/g. The reference (no CMF added) has the bulk value of 10 cm³/g. However, the acquired z-directional strengths were reached in unpressed samples with CMF addition in high bulk levels of ca. 6 cm³/g, by wet pressing the target was possible to reach in bulk levels of 2-3 cm³/g. Remarkable in these results compared with the results showed in Figure 54, is that in bulk values above 6 cm³/g the samples have Scott bond values above 50 J/m², whereas in the wet pressing case all Scott bond values were below 50 J/m².

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.

![Diagram](image)

**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 de-watering 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).

![Graph showing turbidity and dry solids content](image)

**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.

![Boiler efficiency as function of moisture content](image)

**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 furnish, 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 roll 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.
Foam coating of wet web

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 de-watering 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.
Acknowledgements

The research leading to the results from application of functionalized CNF received funding from the European Community’s Seventh Framework Programme under Grant Agreement No 228802.

The research leading to these results was performed as part of the “Efficient Networking towards Novel Products and Processes” (EffNet) research programme of Forestcluster Ltd. The EffNet programme has received funding from Tekes – the Finnish Funding Agency for Technology and Innovation and Forestcluster Ltd.
References

Abhishek, J., Nitin, A., Cost effectiveness in textile processing, 


The report is in Finnish, and freely downloadable from: http://www.metla.fi/julkaisut/workingpapers/2009/mwp122.htm


structures. Pat. WO2013144449 A, publication date 3 October 2013, application
number FI2013050342, application date 27 March 2013, priority
FI20125353 (27 March 2012).

A1Method and apparatus for in-line production of milk of lime into an in-
line production process of pcc arranged in connection with a fibrous web
machine.


during the application of foam to fabrics and its effects on product quality.

Jahangiri, P. Korehei, R., Zeinoddini, S., Madani, A., Sharma, Y., Phillion, A.,
Martinez, M., and Olson, J. (2014): On filtration and heat insulation prop-
erties of foam formed cellulose based materials, Nord Pulp Paper Res J,


Jehad M. Yousef, Enas N. Danial. (2012). In Vitro Antibacterial Activity and Mini-
um Inhibitory Concentration of Zinc Oxide and Nano-particle Zinc oxide

Jenkins, B. (1975). US Patent 4184 914, Foam coating of paper employing a hy-
drolyzed protein foaming agent.


Juvonen, M, Hiltunen, J., Jetsu, P., Gestrianius, M., Harlin, M., Kunnari, V., Lattu,
J., Kinnunen, K., Hjelt, T., Numinen, I., Saharainen, E., Lamminen, H.
Pat. WO2014080084 A, publication date 30 April 2014, application number
FI2013051097, application date 22 November 2013, priority
FI201262227 (22 November 2012).

(2014). Characterization of fibrillated cellulos. A short review and eval-
Res J. 29(1) 2014.


Lindsay, J.D. (1991). Displacement dewatering to maintain bulk, IPSTL Technical paper series, number 377, Institute of Paper Science and Technology, Atlanta, Georgia.


Liu, A.J., Nagel, S.R. (2010). The jamming transition and the marginally jammed solid. University of Rochester, Department of Physics and Astronomy,


tion number FI2014050769, application date 9 October 2014, priority
FI20136006 (9 October 2013).

Pugh, R., J. (2016): Bubble and Foam Chemistry, Chapter 8: Particle stabilized

Punton, V. W. (1975a). Fibre distribution in foam and foam-laid paper. International-
Paper Physics Conference, pp.135-139.

Punton, V. W. (1975b). The use of an aqueous foam as a fibre-suspending medi-
um in quality papermaking. Foams, Proceedings of a Symposium organ-
ized by the Society of Chemical Industry, Colloid and Surface Chemistry
Group, Brunel University, September 8-10, pp 179-195.

Radvan B., Gatward A.P.J. (1972). The formation of wet-laid webs by a foaming
process, Tappi Vol. 55 No. 5 May (1972) p. 748.


Rand, P. B. (1984) “Stabilized aqueous foam systems and concentrate and meth-

and relaxation of wet webs. Transactions of the 14th Fundamental Re-
search Symposium, Pulp and Paper Fundamental Society, Lancashire,
UK.

Riddell, M.C., Jenkins, B. (1976). The use of non-surfactant foaming agents in the

Riddell, M. C., Jenkins, B. (1977). The white wet-end concept by the use of foam.

Riddell, M., Jenkins, B. (1978). EUCEPA Symp. Chemistry in Papermaking (War-
saw), Stowarzyszenie Inz. Tech. Prem. Papier., Lodz, Poland, pp. 234-
243, Sept.

lishers, 353, 851-854.


Robertson, N.G.D. (1972). GB1395757, Apparatus for producing a foamed fibre
dispersion.

FI121241 B, publication date 14 November 2006, application number
FI20050511, application date 13 May 2005, priority FI20050511 (13 May 2005).


Weaire, D., Cox, S.J., Brakke, K., Liquid Foams, Research Gate.


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+ \textit{Staphylococcus aureus} and gram- \textit{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) (Figure 1). 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.

![Photocatalytic Activity of the Foam-Coated Papers](image)

**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.

![Pinhole Test Image]

**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 organophobic 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, 60°C) (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 °C, 50% RH and 4 hours. Rapeseed oil is used as the test oil. Five parallel samples are measured.

![Grease Barrier Test Diagram]

**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 (Figure 6). 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.](image)

**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 80°C 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 23°C and at 50% RH.
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.