BiMaC Innovation Stage 4

The proposed research activities within Stage 4 are divided into five work packages (WP), as shown in Figure 1. Each work package consists of several activities, where at least two competence areas are involved.

Competence building research

The basic idea in Stage 4 is that PhD students will work within competence-building research activities. Hence, all PhD students that are currently enrolled in BiMaC Innovation will be engaged in 1 or 2 projects.

Implementation projects

Implementation projects that are used to increase the TRLs of the projects will be run. These will be performed by senior researchers and/or as in-kind activities by the partners. The expectation is that the partner companies will contribute heavily to these projects. It is important that the project can access relevant pilot facilities and characterization labs.

Figure 1. BiMaC Innovation consists of four proposed work packages, and their relations to the competence areas.
Personnel

Giada Lo Re is since January 16th, 2016, enrolled within BiMaC Innovation Stage 4 as a postdoctoral researcher. After receiving her PhD from University of Palermo, Italy, she has also been in charge of national projects and Project Leader of European Projects (FP7) for the UMONS University in Belgium. Her research is focused on processing and compatibilization of thermoplastic nanocomposite materials based on cellulose. In BiMaC Innovation she is working together with Lars Berglund et al. in the fibre-based composites activity. Her main competence areas are melt processing, synthesis, chemical modification and characterization of biopolymers and corresponding nanocomposites for eco-friendly applications. Her understanding spans from hybrid materials to polymer rheology, reactive processing and structure-property relationships at both molecular and nanoscale level.

Doctoral dissertations

Emma Larsson
Thermoresponsive cellulose-based composites by polymer modification

Abstract
The interest in utilizing cellulose based materials has grown rapidly in recent years, due to the growing environmental concerns about utilizing fossil based material. One potential application of cellulose is in thermoresponsive materials, which are attracting attention due to their ability of altering conformation when exposed to changes in external temperature. In this study, a variation of cellulose substrates have been utilized; both as the main component and as reinforcing fillers in thermoresponsive composites.

Photoinduced controlled radical polymerization was utilized to graft the thermoresponsive polymer poly(di(ethylene glycol) ethyl ether acrylate) (PDEGA) from the surface of filter paper. The method showed to be efficient to graft large amounts of polymer from the cellulose surface in short reaction times, while utilizing smaller amounts of catalyst than typically employed in controlled radical polymerizations.

Di-, tri, and star block copolymers of quaternized poly(2-(dimethylamino)ethyl methacrylate) (qPDMAEMA) and poly(di(ethylene glycol) methyl ether methacrylate) (PDEGMA) were synthesized by atom transfer radical polymerization (ATRP), and
adsorbed to cellulose nanofibrils (CNFs) in a water dispersion. This provided a simple route for the preparation of thermoresponsive CNF based composites.

Thermoresponsive cryogels of poly(N-isopropylacrylamide) (PNIPAAm), synthesized by free radical polymerization (FRP), were reinforced by the addition of cellulose nanocrystals (CNCs). Two types of CNCs were investigated: neat CNC and CNC with acrylic, polymerizable, groups attached to its structure. The CNC addition showed to be an efficient way to modify the mechanical properties of the cryogels.

All materials synthesized in this project displayed thermoresponsive properties. Cellulose can therefore be considered to be a promising material for the production of more environmentally friendly thermoresponsive composites.

Publications

Eric Linvill and Sören Östlund
“Parametric study of hydroforming of paper materials using the explicit finite element method with a moisture- and temperature-dependent constitutive model”

Abstract

A moisture- and temperature-dependent constitutive model for paper materials was proposed and implemented into a finite element model of the paper hydroforming process. The proposed model, which also included the effects of drying, captured the extent of forming of all experimental results within reasonable accuracy. The phenomenon of drying was found to be the reason why the application of temperature had a much greater effect on the degree of forming than hydroforming at various moisture contents. A simulation-based parametric study was conducted in order to identify the importance of various process and material parameters. This parametric study confirmed many previous empirical findings and was capable of quantifying the extent to which these process and material parameters affect the 3-D formability of paper. The coefficient of friction was identified as one of the most important factors when determining the extent of forming. One interesting result from the parametric study was the discovery that an increase of the stiffness of the forming balloon increased the extent of forming.

Anton Hagman och Mikael Nygårs
“Short compression testing of multi-ply paperboard, influence from shear strength”

Abstract
The influence of the through-thickness shear strength profiles on the short span compression test was examined. This was done both with experiments and finite element simulations on five industrial produced paperboards. It was concluded that the short span compression test is governed by in-plane stiffness and through thickness delamination. The delamination damage was in turn dependent on the local transverse shear strength and in-plane stiffness gradients. Furthermore, it was concluded that the pre-delamination mechanisms were elastic. Finally it was possible to alter the results from the test by altering the shear strength of the paperboard; this should be done uniformly over the entire middle ply of the board if an increased SCT value was what was sought after.

Mikael S. Magnusson
"Investigation of interfibre joint failure and how to tailor their properties for paper strength"

Abstract
The key property for the load carrying capacity of paper materials is the interfibre joint strength. Due to the difficulty of testing the strength of such microscopic entities, the typical approach is to test isolated fibre-fibre crosses. In such experiments the joint is but one component of the tested structure and the flexural compliance of the long fibre segments results in a mixed mode of loading. Furthermore, the details of the failure mechanisms of such joints are as of yet unknown. A continuum description of the paper sheet is often insufficient to explain governing mechanisms when properties of the underlying structure are changed by mechanical or chemical modifications. Therefore network models are often used to take into account the underlying mechanisms. However, network models in turn rely on the properties of the fibres and of the interfibre joints.

This paper aims to characterize the damage behaviour of isolated fibre-fibre crosses from three approaches: identifying typical damage features from an extensive number of mechanical tests of isolated fibre-fibre crosses; study the applicability of using cohesive zones to model the failure behaviour of inter-fibre joints; and, to study the influence of fibre and joint properties to the load carrying capacity of fibre-fibre crosses.

The results indicate that the strength in the normal direction is significantly lower than in the shear direction and means on how to tailor the properties of fibres and joints for increasing the load carrying capacity is suggested.

E. Larsson, A. Boujemaoui, E. Malmström, A. Carlmark
"Thermoresponsive cryogels reinforced with cellulose nanocrystals"

Abstract
Herein, we report the first study of thermoresponsive cryogels with cellulose nanocrystals (CNCs) incorporated into the structure. Free radical polymerization was utilized to synthesize cryogels of poly(N-isopropylacrylamide) (PNIPAAm), resulting in thermoresponsive gels after the cryo-polymerization. Two types of CNCs were investigated: one which had reactive vinyl groups on the surface, enabling covalent incorporation and crosslinking with the cryogel network; and one which had no reactive groups on the surface, rendering it physically embedded in the network. The degree of crosslinking of the cryogels was controlled by varying the addition of N,N'-methylenebisacrylamide (MBAm). The cryogels were analyzed by FE-SEM and were all found to be macroporous. The morphology of the gels was largely dependent on the reaction conditions and the presence of CNC. The swelling properties of the freeze-dried gels were investigated and all gels exhibited a thermoresponsive behavior. Our study showed that the incorporation of CNCs is an effective method to alter both the morphologies and the mechanical properties of a cryogel, although the final properties of the cryogels depend on several different parameters. Due to the complexity of the system, a clear trend regarding the CNC incorporation is difficult to conclude, but compression testing showed that a cryogel having 1 wt% of crosslinkable CNC was far superior to the other gels in terms of mechanical properties, exhibiting that the presence of crosslinkable groups on the surface of CNCs could have a large influence over the final properties.

Andrew Marais, S. Pendergraph, L. Wågberg
"Nanometer-Thick Hyaluronic Acid Self-Assemblies with Strong Adhesive Properties"

Abstract
The adhesive characteristics of poly(allylamine hydrochloride) (PAH)/hyaluronic acid (HA) self-assemblies were investigated using contact adhesion testing. Poly(dimethylsiloxane) spheres and silicon wafers were coated with layer-by-layer (LbL) assemblies of PAH/HA. NO increase in adhesion was observed when surfaces covered with dried LbL films were placed in contact. However, bringing the coated surfaces in contact while wet and separating them after drying resulted in an increase by a factor of 100 in the work of adhesion (from one to three bilayers). Herein we discuss the adhesion in PAH/HA and PAH/poly(acrylic acid) assemblies. PAH/HA assemblies have potential application as strong biomedical adhesives.

Johan Tryding, Gustav Marin, Mikael Nygårds, Petri Mäkelä and Giulio Ferrari
"Experimental and theoretical analysis of in-plane cohesive testing of paperboard"
International Journal of Damage Mechanics, in press

Abstract
In-plane cohesive failure of paperboard was characterized by short-span uniaxial tension tests. Six paperboards qualities were experimentally investigated, from which cohesive stress-widening curves were extracted. A fracture energy was defined, expressed in the tensile strength and maximum slope of the cohesive stress-widening relation. Analytical cohesive relations were derived based on the tensile strength and maximum slope, utilizing the Morse potential for diatomic molecules. It was experimentally found that the maximum slope and fracture energy depend on the tensile strength. The ratio of the maximum slope and the elastic modulus (stable length) was shown to be independent of the tensile strength.

Reports
Elisabet Horvath and Mikael Nygårs
Impact of Chemical Additives on Strainability of Paper - A StratEx trial
Inventia Report No. 706

Abstract
Different chemistry systems are used to give strength in papermaking. The most common strength additive in papermaking is starch, but cellulose micro fibrils (CMF) has also becoming of interest as a strength additive. The objective of this work has been to use different strength additives in an up-scaled pilot trial on StratEx. Seven paper rolls were produced; one reference with bleach softwood pulp, and 6 where the pulp was mixed with the chemical additives: PLA-latex (PL-1000, PL-2000, PL-3000), PVAm, cationic starch and CMF. A web of roughly 5 meters of paper was be made for each trial point. Thereafter, the papers were creped to different levels in a lab nip.

The strain at break could be increased from 8% to 17% by creping. However, the tensile strength decreased with increased strain at break. The addition of 5% CMF best maintained the strength of papers with high strain at break, although starch (1%) and PVAm (0.5%) also showed good potential. The strength of the creped papers with PLA-latex were higher than for the reference, both lower than for the papers with the other chemical additives.

Patents
P. Larsson, L. Wågberg
Material, useful in food or liquid package, comprises oxygen barrier polymer film comprising polymer obtainable by oxidizing cellulose fibers to obtain crosslinked cellulose, and then homogenizing to obtain fibrils
Patent number: WO2015034426-A1

Abstract
NOVELTY - Package material comprises either an oxygen barrier polymer film, or a base material and an oxygen barrier film comprising crosslinked fibrillated cellulose. The polymer film comprises a polymer obtainable by a process comprising (a) oxidizing cellulose fibers to ultimately obtain crosslinked cellulose, and (b) homogenizing the product of step (a) to obtain fibrils in a width of 1-150 nm.

USE - The material is useful in a package, preferably food or liquid package (all claimed).

ADVANTAGE - The packaging material ensures that the cellulose based film has improved oxygen and water-vapor-barrier properties at 80% or 90% relative humidity, and low moisture sensitivity.
## KTH-researchers in BiMaC Innovation

In the table below you will find e-mail and telephone number to all BiMaC Innovation researchers at KTH.

<table>
<thead>
<tr>
<th>Executive office</th>
<th>Phone</th>
<th>Email</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Daniel Söderberg</strong> (Head of centre)</td>
<td>08-790 7196</td>
<td><a href="mailto:dansod@kth.se">dansod@kth.se</a></td>
</tr>
<tr>
<td>Micael Stehr (Deputy Head of centre)</td>
<td>08-790 9046</td>
<td><a href="mailto:stehr@kth.se">stehr@kth.se</a></td>
</tr>
<tr>
<td>Tom Lindström</td>
<td>08-790 9035</td>
<td><a href="mailto:toml@kth.se">toml@kth.se</a></td>
</tr>
<tr>
<td>Mikael Nygårds (Project manager)</td>
<td>08-676 7193</td>
<td><a href="mailto:nygards@kth.se">nygards@kth.se</a></td>
</tr>
<tr>
<td>Svetlana Borodulina (graduate student)</td>
<td>08-790 7550</td>
<td><a href="mailto:sveisbo@kth.se">sveisbo@kth.se</a></td>
</tr>
<tr>
<td>Andreas Gabriëlsson (researcher)</td>
<td>08-676 7126</td>
<td><a href="mailto:andreas.gabriellson@innventia.com">andreas.gabriellson@innventia.com</a></td>
</tr>
<tr>
<td>Ulf Gedde (researcher)</td>
<td>08-790 7640</td>
<td><a href="mailto:gedde@polymer.kth.se">gedde@polymer.kth.se</a></td>
</tr>
<tr>
<td>Anton Hagman (graduate student)</td>
<td>08-790 7550</td>
<td><a href="mailto:antonhag@kth.se">antonhag@kth.se</a></td>
</tr>
<tr>
<td>Elisabet Horvath (researcher)</td>
<td>08-676 7138</td>
<td><a href="mailto:elisabet.horvath@innventia.com">elisabet.horvath@innventia.com</a></td>
</tr>
<tr>
<td>Artem Kulachenko (researcher)</td>
<td>08-790 8944</td>
<td>arte@<a href="mailto:m@kth.se">m@kth.se</a></td>
</tr>
<tr>
<td>Eric Linvill (graduate student)</td>
<td>08-790 8986</td>
<td><a href="mailto:linvill@kth.se">linvill@kth.se</a></td>
</tr>
<tr>
<td>Mikael Magnusson (researcher)</td>
<td>08-676 7192</td>
<td><a href="mailto:mikael.magnusson@innventia.com">mikael.magnusson@innventia.com</a></td>
</tr>
<tr>
<td>Andrew Marais (graduate student)</td>
<td>08-790 8296</td>
<td><a href="mailto:marais@kth.se">marais@kth.se</a></td>
</tr>
<tr>
<td>Jonas Sundström (researcher)</td>
<td>08-676 7106</td>
<td><a href="mailto:jonas.sundstrom@innventia.com">jonas.sundstrom@innventia.com</a></td>
</tr>
<tr>
<td>Lars Wågberg (researcher)</td>
<td>08-790 8294</td>
<td><a href="mailto:wagberg@kth.se">wagberg@kth.se</a></td>
</tr>
<tr>
<td>Sören Östlund (researcher)</td>
<td>08-790 7542</td>
<td><a href="mailto:soren@kth.se">soren@kth.se</a></td>
</tr>
<tr>
<td>Linda Fogelström (Project manager)</td>
<td>08-790 9758</td>
<td><a href="mailto:lindafo@kth.se">lindafo@kth.se</a></td>
</tr>
<tr>
<td>Lars Berglund (researcher)</td>
<td>08-790 8118</td>
<td><a href="mailto:blund@kth.se">blund@kth.se</a></td>
</tr>
<tr>
<td>Anna Carlmark (researcher)</td>
<td>08-790 8027</td>
<td><a href="mailto:annac@kth.se">annac@kth.se</a></td>
</tr>
<tr>
<td>Per Larsson (researcher)</td>
<td>08-790 8109</td>
<td><a href="mailto:perl5@kth.se">perl5@kth.se</a></td>
</tr>
<tr>
<td>Farhan Ansari (graduate student)</td>
<td>08-790 8109</td>
<td><a href="mailto:mfansari@kth.se">mfansari@kth.se</a></td>
</tr>
<tr>
<td>Veronica Lopez (graduate student)</td>
<td>08-790 8109</td>
<td><a href="mailto:vld@kt.se">vld@kt.se</a></td>
</tr>
<tr>
<td>Eva Malmström (researcher)</td>
<td>08-790 7225</td>
<td><a href="mailto:mavem@kth.se">mavem@kth.se</a></td>
</tr>
<tr>
<td>Torbjörn Pettersson (researcher)</td>
<td>08-790 8160</td>
<td><a href="mailto:torbj@kth.se">torbj@kth.se</a></td>
</tr>
<tr>
<td>Lars Wågberg (researcher)</td>
<td>08-790 8294</td>
<td><a href="mailto:wagberg@kth.se">wagberg@kth.se</a></td>
</tr>
<tr>
<td>Giada Lo Re (researcher)</td>
<td>08-790 8109</td>
<td><a href="mailto:7giada.lre@gmail.com">7giada.lre@gmail.com</a></td>
</tr>
<tr>
<td>Fabiola Vilaseca (researcher)</td>
<td>08-790 8118</td>
<td><a href="mailto:vilaseca@kth.se">vilaseca@kth.se</a></td>
</tr>
</tbody>
</table>