Paper – A fibre-based bio-composite for high performance materials
Structural changes in the European paper industry - The need for new products

Possible strategies

- Reduction of over-capacities
- Significant improvement in terms of use of energy/resources/chemicals
- Innovative products with high added value
Solutions for all partners of the value chain

Supplying industry → Paper producer → Paper converter → End user → End customer

Intersectoral solutions provided by PTS

Other industries: food, construction, ceramics, automotive ...

End user → End customer

Resources & Eco-design
The paper making process – a versatile tool for tailoring new materials

- Efficient and cost effective production method for 2D materials
  - High homogeneity
  - Variable in thickness and porosity
- Simple process for mixing of various components (fibres, fillers, matrix materials)
- Multi-layer systems and/or coatings possible
- Subsequent processing by standard paper conversion techniques
Paper-based fibre composites - Biomaterials for industrial applications

- Development of new materials for light weight construction
  - automotive industry, construction industry
- New production processes for ceramic, metals and polymer-based materials
- New paper-based products with adsorptive properties
  - water treatment, heat storage
- Paper-based fire prevention and protection equipment
- Paper-based solutions for electromagnetic shielding
From the traditional use of fillers to highly filled papers

<table>
<thead>
<tr>
<th></th>
<th>Traditional Use of Fillers</th>
<th>Innovative Use of Fillers</th>
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</thead>
<tbody>
<tr>
<td><strong>Type</strong></td>
<td>e.g. kaoline, calcium carbonate, titania</td>
<td>e.g. ceramic powders, metal powders, graphite, silica</td>
</tr>
<tr>
<td><strong>Amount</strong></td>
<td>Up to 30 and 40 wt.-%</td>
<td>Up to 90 wt.-%</td>
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<tr>
<td><strong>Goal</strong></td>
<td>Decrease of production costs Improvement of properties such as surface structure, printability, opacity</td>
<td>Adoption of filler properties by paper</td>
</tr>
</tbody>
</table>
Choosing the building blocks for fibre composites

Fiber Composites

Natural fibers
- e.g. Softwood, hardwood, cotton wool, linters

Synthetic fibers
- e.g. PE, PP, carbon

Functional fillers
- e.g. ATH, silica

Matrix material
- e.g. Melamine

Modified fibers (larger and/or functionalized surface)
- Mechanical treatment (refiner)
- Enzymatic, chemical treatment
- Adding chemically and enzymatically dissolved cellulose
- Micro / nano scale cellulose
- Modified fibers (larger and/or functionalized surface)
- Coating, impregnation

Coating, Impregnation
Application range of highly filled papers

The properties of highly filled papers are determined by the properties of the fillers that are used. Thus, new and innovative applications for paper can be created.

- **Thermal conversion (sintering)**
  - Ceramics
  - Metals
  - Polymers

- **Adsorption**
  - Activated charcoal
  - Zeolites
  - Silica

- **Thermal management**
  - PCMs
  - Graphite

- **Electromagnetic properties**
  - Various metals
  - Ferrites
Paper-based fibre composites for ceramic applications

**Filler:** Ceramics (Al$_2$O$_3$, SiC, Si$_3$N$_4$, …)

**Filler content:** Up to 93 wt.-%

**Function:** Fire resistance, sintering

**Application area:** Fire protection, precursor material for technical ceramics (e.g. hot gas filtration, catalytic converter, high temperature isolation)

Cross section (SEM): Paper filled with 80 wt.-% Al$_2$O$_3$ before and after sintering.

Paper derived ceramic light weight structure used as kiln furniture.
Paper-based fibre composites for metallurgic applications

**Filler:** Metals (Stainless steel, copper, aluminum, silver,...)

**Filler content:** Up to 90 wt.-%

**Function:** Sintering, Electromagnetic shielding

**Application area:** Precursor material for metallurgy (e.g. hot gas filtration, heat exchanger...)

Cross section (SEM): Paper filled with 80 wt.-% copper before and after sintering.

Corrugated paper filled with 80 wt.-% copper.
Paper-based fibre composites for adsorptive applications

**Filler:** Adsorbents (e.g. silica, zeolite, activated charcoal...)

**Filler content:** Up to 75 wt.-%

**Function:** Adsorption

**Application area:** Filtration, quality control for room air, packaging

Crossection (SEM): Paper filled with 70 wt.-% zeolite (top), paper filled with activated charcoal (right).
Paper-based fibre composites for thermal management

**Filler:** Phase-change materials (PCM), graphite

**Filler content:** Up to 70 wt.-%

**Function:** Temperature regulation and adjustment, temperature distribution

**Application area:** Packaging, indoor decoration (e.g. wall hangings), air conditioning

Cross section (SEM): Paper highly filled with PCM capsules, 70 wt.-%

For example a PCM-filled paper with a grammage of 300 g/m² (= 350 µm thickness) provides 210 g PCM/m² resulting in a storage capacity of latent heat of about 23 kJ/m², which is comparable to 5 mm concrete or 15 mm brick.
Summary:
Fibre-based bio-composites for high performance materials

- There is a high demand for new paper-based products with added value
- Paper has a high potential for being a base material for bio-composite materials, since the paper making process offers:
  - Cost-effective production method for continuous production of 2D materials
  - Simple mixing of a vast variety of raw materials
- Highly filled papers are functionalized papers for high performance applications
- Applications at a glance:

<table>
<thead>
<tr>
<th>Ceramic fillers</th>
<th>Metallic fillers</th>
<th>Other functionalized fillers</th>
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</thead>
<tbody>
<tr>
<td>Filters (gases, liquids, particles)</td>
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<td>Room air management</td>
</tr>
<tr>
<td>Kiln furniture</td>
<td>Membranes</td>
<td>Filters (gases)</td>
</tr>
<tr>
<td>Substrates for catalysis</td>
<td>Thermal insulation</td>
<td>Temperature control</td>
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<tr>
<td>Light weight construction</td>
<td>EM shielding</td>
<td>Panel heating</td>
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<td>Substrates for catalysis</td>
<td>Functionalized decorations</td>
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</table>

Microstructure of papers filled with ceramic powders

- 80 wt.-% $\text{Al}_2\text{O}_3$
- 80 wt.-% SiC
Fibre derived pore network in ceramic substrate - µ-CT

Paper-derived $\text{Al}_2\text{O}_3$ ceramic
## Properties of papers filled with aluminum oxide after thermal conversion

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Mass loss:</td>
<td>14.4 – 28.8 %</td>
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<tr>
<td>Shrinkage:</td>
<td>10 – 22.5 %, 10 – 22.6 %, 10 – 26.3%</td>
</tr>
<tr>
<td>Density:</td>
<td>1.44 – 3.47 g/cm³</td>
</tr>
<tr>
<td>Porosity (open):</td>
<td>14.4 – 63.4 vol.-%</td>
</tr>
<tr>
<td>Bending strength:</td>
<td>6 – 162 MPa</td>
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<tr>
<td>Weibull module:</td>
<td>3 – 21</td>
</tr>
<tr>
<td>Elastic modulus:</td>
<td>14.4 – 256.2 GPa</td>
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<tr>
<td>Thermal conductivity:</td>
<td>1.6 – 17.7 W/mK</td>
</tr>
<tr>
<td>Thermal expansion, $\alpha$:</td>
<td>8.3 – 8.6 $10^{-6}$ K$^{-1}$ (100 – 1000 °C)</td>
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<tr>
<td>Max. thermal shock:</td>
<td>35 – 108 K</td>
</tr>
</tbody>
</table>
Production of a paper filled with 83 wt.-% $\text{Al}_2\text{O}_3$ on pilot plant scale
Examples for paper-derived ceramic structures
The principle of metal-filled papers and their conversion to metal products

- **Powder metal**
- **Pulp**
- **Retention aids**
- **Sintered paper structure**

**Sheet formation paper machine**

**Metal powder filled paper**

**Shaping**

**Heat Treatment**

**Green compact**
Microstructure of papers filled with metal powders

Stainless steel, iron, copper, bronze, silver, ...
Example: Paper filled with 71 wt.-% stainless steel powder and 17 wt.-% stainless steel fibres
Properties of papers filled with stainless steel after thermal conversion

- Thickness: 0.2 – 1.0mm, 3.0mm (in process)
- Width: 300mm (pilot plant scale), up to 1400mm (in process)
- Pore size: 10 – 500 µm
- Porosity: 20 – 75%
- Amount of C: ~ 0.05 – 0.3%, amount of O₂: ~0.1 – 0.5%, amount of N₂: <0.01%
Production processes available at PTS – laboratory and pilot plant

Technological paper conversion

Pilot scale (Fourdrinier machine)

Laboratory scale (Rapid Köthen)