Reactive extrusion of cellulose fibres as a feasible way to process value added products

Nikita Polikarpov

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Sustainable development in paper industry

Paper industry is looking for

- new markets
- new products
- new approaches

Is it possible to imagine…

- Cellulose as a source for bioplastics?
- Cellulose fibres as reinforcement in composites?
- Cellulose fibre as thermoplastic?

Yes, but there are some issues…

- Cellulose esters (bioplastic) are costly.
- Poor interactions between hydrophilic cellulose fibres and hydrophobic thermoplastics.
- Cellulose decomposes below its glass-transition temperature.
PTS Platform Technology Reactive Extrusion

New approach

Pulp

Various monomers and reactive compounds

Surface modified pulp fibres (hydrophobic, thermoplastic)

Surface modified microfibrillated cellulose

Amorphous cellulose derivatives

New markets / products

• Thermoplastic paper based products
• Reinforcement in composites / Light weight construction
• Masterbatches
• Injection moulding
Twin Screw Extruder

Source: Coperion

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EXAMPLE 1
CELLULOSE ACETYLATION
Cellulose Acetate

Dominant thermoplastic cellulose based product is cellulose acetate (~80,000 t/p.a.)

- Properties depend on substitution degree DS and polymerisation degree DP

<table>
<thead>
<tr>
<th>DS</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8–1.9</td>
<td>Composite fabrics</td>
</tr>
<tr>
<td>2.2–2.3</td>
<td>Lacquers, plastics</td>
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<tr>
<td>2.3–2.4</td>
<td>Acetate rayon</td>
</tr>
<tr>
<td>2.5–2.6</td>
<td>Safety films</td>
</tr>
<tr>
<td>2.8–2.9</td>
<td>Insulation foils</td>
</tr>
<tr>
<td>2.9–3.0</td>
<td>Fabrics</td>
</tr>
</tbody>
</table>
Esterification in Extruder

- ZSK 26 Mc
- Pulp + acetic acid
- Acetic anhydride + catalyst
- Cellulose acetate

< 1 min reaction time (compare with 1h in batch reactor)
FTIR – Results of Acetylation

DS ~3.0
DS 2.4 (commercial product)
DS ~2.2
DS ~0.9

normalisation to band at 1431 cm$^{-1}$
Pulp Acetylation in Extruder

NBSK pulp

Acetylated pulp, DS 0.9–1.6

Cellulose acetate, DS ~3.0

L(I) c ~ 0.2-0.5 mm

L(I) c < 0.05 mm
Producing Cellulose Triacetate in Extruder

Solvent casting of CTA films
Producing Acetylated Pulp in Extruder

Hand sheet from acetylated pulp and its thermoplastic properties
Hand Sheets – Hot Pressing

Cross-sectional SEM image of thermoplastic paper before hot pressing

SEM image of thermoplastic paper upon hot pressing. Fibre network structure of the non-heated area (top left) is observable

Cross-sectional SEM image of thermoplastic paper upon hot pressing
EXAMPLE 2
FIBRE BASED MASTERBATCHES
Fibre-Polymer Masterbatches in Extruder

ZSK 26 Mc

Pulp

1-2 min reaction time

Various reactive modifiers/monomers

Fibre-Polymer Masterbatches
Fibre-Polymer Masterbatches in Extruder

\[ \text{Fibre} + \text{O} \xrightarrow{\text{kat.} \Delta} \text{Polymer} + \text{PCL} \]
Fibre-Polymer Masterbatches for Thermoplastic Paper

Before hot pressing

Upon hot pressing
Contact Angle Measurements

Water drop on a NBSK + PTS-Masterbatch hand sheet, **before hot pressing**

- **0.0 s**: ~56°
- **0.5 s**: ~17°

Water drop on a NBSK + PTS-Masterbatch hand sheet, **upon hot pressing**

- **0.0 s**: ~85°
- **0.5 s**: ~65°
- **1.0 s**: ~60°
Conclusions

- Reactive extrusion of cellulose fibres is a feasible way to produce cellulose derivatives, fibres and microfibrillated cellulose with added-value properties

- Example 1. Cellulose acetylation
  - Reaction time < 1 min
  - Both homogeneous and heterogeneous acetylation was achieved by reactive extrusion
  - Various typical for cellulose acetate properties were demonstrated

- Example 2. Fibre-Polymer-Masterbatches
  - Potential application as paper additive (thermoplastic and barrier properties)
  - Potential application as composite additive (as reinforcement)
Contact

Papiertechnische Stiftung, IZP
Dr. Nikita Polikarpov
Pirnaer Str. 37
01809 Heidenau
Telefon: 03529-551-640
nikita.polikarpov@ptspaper.de
http://www.ptspaper.de

Papiertechnische Stiftung, IZP
M.Sc. Tiemo Arndt
Pirnaer Str. 37
01809 Heidenau
Telefon: 03529-551-643
tiemo.arndt@ptspaper.de
http://www.ptspaper.de