Hemicellulosic gels from Sitka Spruce

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- Centre for Water Soluble Polymers – NEWI Wrexham
  - Dr Rob English
- BioComposites Centre - UW Bangor
  - Dr Paul Fowler
SILVICHEM PROJECT

- Funded by the Engineering and Physical Sciences Research Council, with support from Forest Research

- Industrial partners were Shotton Paper, BSW Timber, and A.W. Jenkinson
Silvicichemicals

- Timber is a *sustainable* source for chemicals

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Percent by mass</th>
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</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>40-45</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>25-35</td>
</tr>
<tr>
<td>Lignin</td>
<td>26-34</td>
</tr>
<tr>
<td>Extractives</td>
<td>0-5</td>
</tr>
</tbody>
</table>
Use of Hemicellulose

- Economic viability of process dependent on extraction of material with high intrinsic value

- Utilisation
  - adhesives
  - thickeners
  - stabilizers
  - emulsifiers
Hemicellulose

- Polysaccharides derived from several different monosaccharide units.
  - e.g. glucose, xylose, mannose

- Much lower degree of polymerisation (DP) than cellulose
  - Cellulose DP – 10,000
  - Hemicellulose DP - Up to 200
Softwood Hemicellulose

Softwood contains two main types of hemicellulose

- 60% of softwood hemicellulose is Galactoglucomannan
  (contains about 70% mannan)

- 40% of softwood hemicellulose is arabino-4-O-methylglucuronoxylan
  (contains about 65% xylan)
Xylan

Consists of alternating β-D-xylose with 1:4 ether linkages with side chains of arabinose units and some glucouronic acid groups

---4-β-D-xyloβ--- 4-β-D-xyloβ--- 4-β-D-xyloβ---
| α-L-Araf
Glucomannan

Glucomannan is made up of glucose and mannose units joined by 1:4 ether bonds with side chains of galactose units

\[ \text{--4-β-D-Glu}\rho\text{--1-4-β-D-Man}\rho\text{--1-4-β-D-Man}\rho\text{--} \]

\[ \text{α-D-gal}\rho \]
Scope of the investigation

The principle was to extract hemicellulose from softwoods using low environmental impact processes. An important aspect was to avoid the use of pre-bleaching of the wood substrate.

Sitka spruce was chosen as a model timber for the investigation.
Extraction Method

- Atmospheric refiner
- Water throughput to reduce thermal damage
- Fibre length/width reduced by 50%

Fibre → Extraction → Pulp

Extraction Method:
- Alkaline peroxide
  - 60°C
  - ± sodium borate

Isolation:
- Neutral pH
- Excess Ethanol
- Centrifugation
Resultant gels

Four gels were produced based on the substrate and whether borate was added

- Fibre
- Fibre with borate
- Pulp
- Pulp with borate
Monosaccharide analysis of hemicellulose

Hemicelluloses were initially analysed on the basis of their monosaccharide composition

- Acid hydrolysis of gel
- High performance anion exchange chromatography with pulsed amperometric detection (HPAEC – PAD)
Hemicellulose yield and purity

<table>
<thead>
<tr>
<th></th>
<th>Fibre</th>
<th>Pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monosaccharide content of gel</td>
<td>59%</td>
<td>58%</td>
</tr>
<tr>
<td>Actual yield of monosaccharide (mg/g dry wt)</td>
<td>142</td>
<td>116</td>
</tr>
</tbody>
</table>

Yield compares well with standard determination of hemicellulose content (206 mg/g dry weight)
Comparison of monosaccharide composition of fibre and pulp derived gels

- Arabinose
- Rhamnose
- Galactose
- Glucose
- Xylose
- Mannose

Fibre
Pulp
Effect of borate on hemicellulose monosaccharide composition

Monosaccharide Composition (%)

Arabinose  Rhamnose  Galactose  Glucose  Xylose  Mannose

No borate  With borate

Graph showing the comparison of monosaccharide composition with and without borate.
Summary

- Good yield and purity obtained
- No significant difference in monosaccharide composition between fibre and pulp derived gels
- Addition of borate an easy method of changing composition by altering xylan/glucomannan ratio
Further analysis

- Dynamic Light Scattering
- Nitrogen gas sorption analysis
- Fourier Transfrom Infra-red (FTIR) spectrophotometry
Dynamic light scattering (DLS)

- Used to determine diffusion co-efficients
- Gives indication of shape and molecular mass
- Limit of resolution between peaks is a factor of 2 in hydrodynamic diameter
  - Corresponds to factor of 8 in molecular mass
DLS plots for Fibre derived gel

Diffusion distribution(s)

Relaxation time distribution(s)
Summary

- Two species of significantly different molecular mass are present
Nitrogen sorption analysis

- Determination of surface area
  - Brauner, Emmet and Teller (BET) Theory

- Pore size distribution
  - Barrett, Joyner and Halenda (BJH) theory
Gas analysis

- Use different partial pressures of nitrogen
- Surface sorbs nitrogen molecules
- Layers of nitrogen molecules cover the material surface
- Surface is in equilibrium with gaseous nitrogen at each partial pressure
- Volume of Nitrogen related to surface area by the BET theory
Surface area of gels

BET surface area (m²/g)

Pulp  Pulp + borate  Fibre  Fibre + Borate  Wood Fibre  Wood Pulp
Sorption/desorption isotherms

- Sorption/desorption cycle gives isotherm curves
  - Large pores desorb at different pressure compared to sorption
  - Difference gives rise to hysteresis
  - Larger pores therefore give larger hysteresis effect
- Also allows determination of pore size distribution
Model isotherm

Vol. Adsorbed (cm$^3$/g) STP

SED Celulose

\[
\text{Vol. Adsorbed (cm}^3/\text{g) STP}
\]

\[
\frac{P}{P_0}
\]

- Adsorption
- Desorption
Nitrogen absorption analysis - isotherms

Pulp

Fibre

Pulp + borate

Fibre + borate
Pore size distribution

Pore volume (cm³/g·Å)

Pore diameter (Å)

- **Pulp**
  - **Pulp + borate**

- **Fibre**
  - **Fibre + borate**
Summary

- Gels have a large surface area
- Isotherms show very little porosity
- Pore distribution shows possibility of large macropores
- Gels have large open structure but are non-porous
FTIR

Presence of specific chemical functional groups can be detected based on infrared bands.
FTIR spectra of pulp derived gel
Comparison of FTIR spectra of pulp and pulp + borate derived gels
Comparison of FTIR spectra of pulp + borate and fibre + borate derived gels
Summary

- There are subtle differences between the spectra of the gels
- The fibre + borate gel shows bands not shown in other gels
- Lignin indicators are present in all gels
- Cellulose indicators are present in all gels
Conclusions

- Extraction method is effective
  - Needs refinement and scale up
- Gels produced are complexes of hemicellulose sugars with lignin residues.
  - Lignin residues potentially very useful for modification of gel
- The gels have an open structure and a large surface area
- Altering extraction parameters can change the sugar profile of the gel
The future

- Considerable research is still required

- High potential for exploitation of this complex and naturally sustainable material
Thank You