Characterization of Fucopol Films for Food Packaging

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State of art

Plastics:
- Global plastics production increased to 288 million tonnes in 2012.
- European production was 57 million tonnes and collected post-consumer was 25 million tonnes.

Packaging sector, on Europe, uses 18 million tonnes of plastic.
- PE-LD & PE-LLD
- PE-HD
- PP
- PET

Plastic packaging is essential for processing, storing, transporting, protecting and preserving food.

[Source: PlasticsEurope - Association of plastic manufacture 2013]
State of art

Food Industry:

- Packaging materials by natural compounds

The natural polysaccharides are polymer materials biologically produced, that exhibit unique functional properties and are environmentally friendly.

Polysacharides:

<table>
<thead>
<tr>
<th>Plants</th>
<th>Algae</th>
<th>Animals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch</td>
<td>Carrageenan</td>
<td>Chitin</td>
</tr>
<tr>
<td>Pectin</td>
<td>Alginate</td>
<td>Chitosan</td>
</tr>
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</table>

Biopolymers

- Extracted from biomass: e.g. Pectin, starch, chitosan
- Synthesized through bio-monomers: Polylactic acid (PLA)
- Produced by microorganisms: Polysaccharides PHAs
State of art

**Advantages**
- Higher production rate
- Favorable to manipulation growth and/or production
- New/improved properties

**Microorganisms**
- Xanthan
- Bacterial alginate

**Need to find low-cost substrates**
- Disadvantages
  - Cost of substrates

**Glycerol byproduct from biodiesel industry:**

- 10% of biodiesel production is glycerol.
FucoPol production and characterization

Fucose-containing exopolysaccharide (FucoPol)

- The FucoPol is produced by Enterobacter strain A47 (DSM 23139).
- Carbon source: Glycerol byproduct from biodiesel industry.

Operating conditions:
- Batch and fed-batch mode
- Temperature 30.0±0.1°C
- pH 6.8±0.05
- Aeration rate 0.125 vvm
- Stirring rate 400 – 800 rpm

Microscopic observation of Enterobacter sp. broth sample
FucoPol production and characterization

FucoPol characteristics:

- Heteropolysaccharide
- Anionic character
- Molecular weight: \(0.9 \times 10^7 - 1.3 \times 10^7\)

Purification method: Diafiltration
FucoPol production and characterization

**FucoPol characteristics:**

- Heteropolysaccharide
- Anionic character
- Molecular weight: $0.9 \times 10^7 - 1.3 \times 10^7$

**Chemical composition:**

- Fucose
- Galactose
- Glucose
- Acyl groups
  - Pyruvate
  - Acetate
  - Succinate
Results – Films preparation

1\textsuperscript{st} • Dissolve dried FucoPol in deionized water

2\textsuperscript{nd} • Add citric acid

3\textsuperscript{rd} • Transfer to Teflon Petri dishes
• Dry at 40ºC during 12h

- Flexible films
- Bending without breaking
- Homogeneous
- Biodegradable

International Conference “Eco-sustainable Food Packaging Based on Polymer Nanomaterials”
COST ACTION FA0904, 26-28 February 2014
## Results – Films characterization

### Transparency:

<table>
<thead>
<tr>
<th>Material</th>
<th>Transparency</th>
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<tbody>
<tr>
<td>FucoPol (Present work)</td>
<td>3.7 ± 0.4</td>
</tr>
<tr>
<td>Chitosan 1% (w/w)*</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>GalactoPol (From Pseudomonas Oleovorans)</td>
<td>5.9 ± 0.7</td>
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</tbody>
</table>

\[
Transparency = -\frac{\log T_{600}}{\chi}
\]

*Rivero, S.; Composite and bi-layer films based on gelation and chitosan; 2009; J. Food Eng. 90.*
Results – Films characterization

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Colour alteration:

- Colour alteration is perceived by human eye ($\Delta E_{ab} > 3$)
- Decrease in colour saturation

Parameters $a^*$ and $b^*$ of the CIELAB system for coloured paper sheets uncovered (diamonds) and covered (circles) by the test films and calculated colour differences.
Results – Films characterization

Water vapour sorption isotherm:

- Water vapour sorption ability similar to pectin from citrus fruits, except for $a_w > 0.8$.
- The isotherm behavior is very similar to another bacterial polysaccharide (GalactoPol).

GAB model

$$X = \frac{m_m \cdot C \cdot a_w}{(1 - K \cdot a_w)(1 - K \cdot a_w + C \cdot K \cdot a_w)}$$

<table>
<thead>
<tr>
<th>$m_m$</th>
<th>$C$</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.071±0.008</td>
<td>2.223±1.057</td>
<td>0.930±0.009</td>
</tr>
</tbody>
</table>

- High solubility in liquid water
- Film disintegration

Contact angle:

- FucoPol films contact angle: 61±4°
- Hydrophilic surface
Results – Films characterization

Water vapour permeability:

<table>
<thead>
<tr>
<th></th>
<th>Salt</th>
<th>Water activity at 30ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desiccator</td>
<td>CH3COOK</td>
<td>0.225</td>
</tr>
<tr>
<td>Petri dish</td>
<td>NaCl</td>
<td>0.769</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>ΔRH (%)</th>
<th>WVP ($10^{-11}$ mol m⁻¹s⁻¹Pa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FucoPol (Present work)</td>
<td>76.9 - 22.5</td>
<td>1.0±0.2</td>
</tr>
<tr>
<td>GalactoPol*</td>
<td>64.8 - 22.0</td>
<td>1.1±0.8</td>
</tr>
<tr>
<td>Chitosan**</td>
<td>65 - 0</td>
<td>1.1±0.1</td>
</tr>
</tbody>
</table>

Mechanical properties:

- **Tensile test**
  - **Malleable films:** High elongation at break, Low Young modulus

<table>
<thead>
<tr>
<th></th>
<th>Conditioned at (%)</th>
<th>Stress at break (Mpa)</th>
<th>Elongation at break (%)</th>
<th>Young modulus (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FucoPol</td>
<td>44.3% RH</td>
<td>3.1±0.3</td>
<td>54.9±4</td>
<td>2.8±0.2</td>
</tr>
</tbody>
</table>

*V.D. Alves et al. Carbohydrate Polymers 83 (2011) 1582–1590
**M. Pereda et al. Food Hydrocolloids 25 (2011) 1372-1381
Results – Films characterization

Gas barrier properties:

- Good barrier properties to oxygen and carbon dioxide.
- Better selectivity than synthetic polymers.

<table>
<thead>
<tr>
<th>Film</th>
<th>RH (%)</th>
<th>$O_2$ Permeability $10^{-16}$ (mol m/m² s Pa)</th>
<th>$CO_2$ Permeability $10^{-16}$ (mol m/m² s Pa)</th>
<th>Selectivity ($\alpha$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FucoPol</td>
<td>32.4</td>
<td>0.7 ± 0.3</td>
<td>42.7 ± 5.6</td>
<td>62</td>
</tr>
<tr>
<td>Starch*</td>
<td>100</td>
<td>10.9</td>
<td>264.1</td>
<td>24</td>
</tr>
<tr>
<td>Carrageenan /pectin**</td>
<td>_</td>
<td>0.4</td>
<td>39.0</td>
<td>98</td>
</tr>
<tr>
<td>Chitosan***</td>
<td>50</td>
<td>2.3 ± 0.1</td>
<td>24.3 ± 2.7</td>
<td>11</td>
</tr>
<tr>
<td>LDPE*</td>
<td>0</td>
<td>10.03</td>
<td>42.2</td>
<td>4</td>
</tr>
<tr>
<td>PET*</td>
<td>0</td>
<td>0.12</td>
<td>0.38</td>
<td>3</td>
</tr>
</tbody>
</table>

$*N.~\text{Gontard}~\text{et al.}~\text{J. of Agricultural and Food Chemistry}~44~(1996)~1064-1069$

$**V.\text{D. Alves Procedia Food Science}~(2011)~240-245$

$***P.~\text{Fajardo J. of Food Engineering, 101 (2010)}~349-356$
Results – Blends preparation

Blends preparation:

- Blends of FucoPol and Chitosan (maintaining constant the overall polymer concentration).

1st
- Dissolve dried FucoPol in 1%wt acetic acid solution
- Dissolve Chitosan in 1%wt acetic acid solution

2nd
- Add glycerol (plasticizer)
- Add citric acid

3rd
- Transfer to Teflon Petri dishes
- Dry at 40ºC during 12h

FucoPol Film

FucoPol/Chitosan film
Results – Blends characterization

Blends solubility:

- **FucoPol**: Totally soluble in water
- **Fucopol/Chitosan film**:
  - Solubility in water: $33.1 \pm 7.7$ % (w/w)
  - Swelling in water: $4.7 \pm 0.9$ % (w/w)

<table>
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<th>Transparency</th>
<th>Contact angle (º)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FucoPol Films</td>
<td>$3.7 \pm 0.4$</td>
<td>$61 \pm 4$</td>
<td>$57 \pm 4$</td>
</tr>
<tr>
<td>Blends of Fucopol and Chitosan</td>
<td>$4.1 \pm 1.9$</td>
<td>$43 \pm 10$</td>
<td>$55 \pm 12$</td>
</tr>
</tbody>
</table>
FucoPol was able to produce cohesive films, either alone, or blended with Chitosan when dissolved in acidic solutions.

Both films are transparent, flexible and ductile, due to the plasticizing effect of citric acid.

FucoPol films are hygroscopic with low water vapour barrier properties, hydrophilic and soluble in water. However they present good barrier properties to gases.
On going work

Blends of FucoPol and Chitosan

Bi-layer of FucoPol and Chitosan

Characterization:
- Surface morphology
- Optical properties
- Barrier properties
- Mechanical properties

Applications:

- Packaging material – Layer in a multilayer film
  - Ductile mechanical properties
  - Hydrophilic character
  - Good barrier properties to gases

Fruits
- Fresh
- Fresh-cut
- Dehydrated

- Slow down respiration rate and dehydratation
- Avoid enzymatic browning
Acknowledgements

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Thank you!