FUNCTIONAL AND TAILOR-MADE WHEAT GLUTEN BASED MATERIALS
Properties and Applications

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Conventional plastics from fossil resources (PE, PET…)

Increasing interest for eco-friendly products

Abundant, renewable, biodegradable

Natural biopolymers from agricultural origin

= raw material for the development of bioplastics
1. Protein based materials: Structure and general properties
1. Protein based materials

Proteins = Heteropolymers

⇒ Large spectrum of chemical functionalities and high variety of polymer network structures

VEGETAL
- Corn zein
- Wheat gluten
- Soy proteins
- Sunflower proteins

ANIMAL
- Caseins
- Whey proteins
- Gelatin, Collagen
- Myofibrillar prot.

SOLVENT OR THERMOPLASTIC PROCESS

Coatings - Films - Molded materials
1. Protein based materials

**Processing : 3 main steps**

1. Destructuring of the raw materials involving the disruption of intermolecular bonds

2. Shaping of the material in the desired shape

3. Stabilization of interactions in a three dimensional network
1. Protein based materials
1. Protein based materials

Wheat gluten: co-product of starch industry

KEY ADVANTAGES OF WHEAT GLUTEN-BASED MATERIALS

😊 Good Film forming properties
1. Protein based materials
1. Protein based materials

Wheat gluten: by-product of starch industry

KEY ADVANTAGES OF WHEAT GLUTEN-BASED MATERIALS

- Good Film forming properties
- High availability at low price
- Biodegradability and non-ecotoxicity
1. Protein based materials

After 8 days

After 38 days
1. Protein based materials

### Energy input and Green house gas emissions of biopolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Energy use [MJ/kg]</th>
<th>GHG emissions [kg CO₂-eq]</th>
<th>Analysis scope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low density polyethylene</td>
<td>80.6</td>
<td>5.04</td>
<td>Incineration</td>
</tr>
<tr>
<td>Starch</td>
<td>18.5</td>
<td>1.08</td>
<td>Cradle to gate</td>
</tr>
<tr>
<td>Thermoplastic starch</td>
<td>18.9</td>
<td>1.10</td>
<td>Cradle to gate</td>
</tr>
<tr>
<td>Mater-Bi foam grade</td>
<td>32.4</td>
<td>0.89</td>
<td>Composting</td>
</tr>
<tr>
<td>Polylactic acid</td>
<td>57</td>
<td>3.84</td>
<td>Incineration</td>
</tr>
<tr>
<td>Polyhydroxyalcanoates by fermentation</td>
<td>81</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Polyhydroxyalcanoates, various processes</td>
<td>66-573</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Wheat gluten (preliminary data)</td>
<td>10 (– 17)</td>
<td>0.72</td>
<td>Cradle to gate</td>
</tr>
</tbody>
</table>
1. Protein based materials

**Wheat gluten** : by-product of starch industry

**KEY ADVANTAGES OF WHEAT GLUTEN-BASED MATERIALS**

- ☑ Good Film forming properties
- ☑ High availability at low price
- ☑ Biodegradability and non-ecotoxicity
- ☑ Unique promising functional properties:
  - Adhesive properties
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  - Viscoelasticity, High grease barrier
  - High gas barrier properties and gas perm-selectivity
### 1. Protein based materials

#### OXYGEN AND CARBON DIOXIDE PERMEABILITIES OF VARIOUS FILMS
(adapted from Cuq et al. 1995).

<table>
<thead>
<tr>
<th>Film</th>
<th>O2 Permeability (x10^{18} mol.m^{-2}.s^{-1}.Pa^{-1})</th>
<th>CO2 Permeability (x10^{18} mol.m^{-2}.s^{-1}.Pa^{-1})</th>
<th>T (°C)</th>
<th>aw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low density polyethylene</td>
<td>1003</td>
<td>4220</td>
<td>23</td>
<td>0</td>
</tr>
<tr>
<td>High density polyethylene</td>
<td>285</td>
<td>972</td>
<td>23</td>
<td>0</td>
</tr>
<tr>
<td>Polyester</td>
<td>12</td>
<td>38</td>
<td>23</td>
<td>0</td>
</tr>
<tr>
<td>Ethylene-vinyl alcohol</td>
<td>0.2</td>
<td>--</td>
<td>23</td>
<td>0</td>
</tr>
<tr>
<td>Methylcellulose</td>
<td>522</td>
<td>29900</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>Corn zein</td>
<td>35</td>
<td>216</td>
<td>38</td>
<td>0</td>
</tr>
<tr>
<td>Wheat Gluten</td>
<td>1</td>
<td>7</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>High density polyethylene</td>
<td>224</td>
<td>--</td>
<td>23</td>
<td>1</td>
</tr>
<tr>
<td>Cellophane</td>
<td>130</td>
<td>--</td>
<td>23</td>
<td>0.95</td>
</tr>
<tr>
<td>Polyester</td>
<td>12</td>
<td>--</td>
<td>25</td>
<td>0.95</td>
</tr>
<tr>
<td>Ethylene-vinyl alcohol</td>
<td>6</td>
<td>--</td>
<td>23</td>
<td>0.95</td>
</tr>
<tr>
<td>Wheat Gluten</td>
<td>1290</td>
<td>36700</td>
<td>25</td>
<td>0.95</td>
</tr>
<tr>
<td>Starch</td>
<td>1085</td>
<td>--</td>
<td>25</td>
<td>0.95</td>
</tr>
</tbody>
</table>
1. Protein based materials

- Very high selectivity $f(T, RH)$
  \[ S = \frac{P(CO2)}{P(O2)} \]

  $\Rightarrow$ From 3 to 50 when RH varies from 0% to 100% and T from 5°C to 45°C
1. Protein based materials

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KEY DRAWBACKS OF WHEAT GLUTEN-BASED MATERIALS

😊 Poor water resistance
😊 Poor mechanical properties
1. Protein based materials

Mechanical properties of wheat gluten based materials

- Wheat gluten based materials
- Biodegradable Polyesters
- Conventional polymers

Tensile strength at break (MPa) vs. Strain at break (%)

- PS
- PP
- PLA
- PEHD
- PEBD
- PCL
2. Modulation of properties

2.1. Crosslinking phenomena

2.2. Composites

2.3. Nanocomposites
2. Modulation of properties: Crosslinking phenomena

- Protein = heteropolymer with large possibilities for chemical modifications, network structure and crosslink density changes
- Thermo mechanical energy can replace chemicals for reactivity
- Crosslinking: SS/SH interchange and isopeptidic bonds
2. Modulation of properties

2.1. Crosslinking phenomena

2.2. Composites

2.3. Nanocomposites
2. Modulation of properties: Composites

Paper = mechanical support

Protein = functionality

Biodegradability Compatibility

Coating + Drying

Protein = coating agent for paper
2. Modulation of properties: Composites

Gas Permeability and selectivity in relation to relative humidity

\[ S = \frac{P(CO2)}{P(O2)} \]

High selectivity (S)

Composite material
Paper + wheat gluten coating

\( \text{O}_2 \) and \( \text{CO}_2 \) Permeability
(10\(^{-18}\) mol·s\(^{-1}\)·m\(^{-1}\)·Pa\(^{-1}\))

<table>
<thead>
<tr>
<th>Relative humidity (%)</th>
<th>Paper</th>
<th>Paper/gluten</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>70</td>
<td>60000</td>
<td>50000</td>
</tr>
<tr>
<td>75</td>
<td>65000</td>
<td>52000</td>
</tr>
<tr>
<td>80</td>
<td>70000</td>
<td>55000</td>
</tr>
<tr>
<td>85</td>
<td>75000</td>
<td>58000</td>
</tr>
<tr>
<td>90</td>
<td>80000</td>
<td>60000</td>
</tr>
</tbody>
</table>

Selectivity
2. Modulation of properties: Composites
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Controlled release of volatil antimicrobial compounds

**Volatile AM compounds:**
- Carvacrol
- Menthol
- Cinnamaldehyde
- AITC
- Eugenol
- ...

Antimicrobial coated paper

Antimicrobial effect by emission (<organoleptic threshold perception)
2. Modulation of properties

2.1. Crosslinking phenomena

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2. Modulation of properties: Nanocomposites

Wheat gluten / montmorillonite casted nanocomposites

MMt powder: peaks at $2\theta = 9^\circ$ (basal spacing between sheet layers) and between $18^\circ$ – $23^\circ$ (permanent crystalline structure of MMt)

Nanocomposite: disappearance of the (001) peak, indicating that the structure is intercalated or even exfoliated.
2. Modulation of properties: Nanocomposites

Water sensitivity (casted nano composites)

Matrix without MMT (●)
2. Modulation of properties: Nanocomposites

Other functional properties (casted nano composites)

- Higher stress at break and Young modulus
- No effect on gas permeability ($O_2$, $CO_2$)
- Decrease in water vapor and aroma permeabilities
Conclusion
Conclusion

- Protein can be used to develop original active and smart materials.
- Homogeneous, transparent, quite strong, highly permeable to water vapor and highly gas selective protein based materials can been obtained either by "casting" or by "thermoplastic processing".
- Low to medium costs (0.3 to 2 US$ / Kg) raw material as a result of a larger availability of plant protein as co-products of biofuels (ethanol/diesters) production
- Environmental benefit is high compared to conventional polymers and to other “bioplastics”.
- The protein aggregation obtained by controlling the thermomechanical treatments allows obtaining materials with a large range of mechanical / functional properties (without chemicals).
Conclusion

- **Specific / original functional properties** opening new fields of application in the domain of “active packaging”
- High potential for the development of *composite and nanocomposite materials*
- **Significant effect of nanofillers on wheat gluten based material functionalities**
  - Lower water sensitivity
  - Higher barrier properties towards water vapor
  - Improved mechanical properties
  - Unmodified optical properties (transparency maintained)
I thank you for your attention

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Carole GUILLAUME
Nathalie GONTARD
Marie-Hélène MOREL