Biopolymers as sustainable fillers for elastomers

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What are biopolymers and why are they sustainable?

- Biopolymers are polymers synthesised by plants (and animals)
  - Carbohydrates
    - Starch
    - Cellulose
    - Lignin
  - Proteins

- Structure or storage

- Sustainable
  - not derived from fossil fuel
  - carbon comes from carbon dioxide recently in the atmosphere
Why might biopolymers be suitable as fillers for rubber?

- Much higher modulus than rubber (2 GPa)
- Can be particulate materials

- Isotropic fillers
  - “natural” e.g. starch grains
  - Spray dried particles
- Fibres

- Other advantages
  - Low density
  - Low cost
  - Special functionality?

What happens if you use them “as received”?

- Behave as non-reinforcing fillers
- Can use as partial replacement for a reinforcing filler – usually only about 10-15% replacement possible with acceptable properties
- Example: SBR tyre sidewall compound with carbon black replaced by rapemeal protein
Why don’t biopolymers work as reinforcing fillers?

- Problems with surface chemistry and particle size

### Surface chemistry “problems” with biopolymers similar to silica

- Saturated bonds (not double bonds)
- Many polar functional groups
  - Starch, cellulose, lignin
    - -OH and -O-
- Proteins
  - -OH, -NH2, - COOH
  - depends on protein, complex chemistry
- Leads to weak non-specific interactions, potentially strong polar interactions

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Average %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alanine</td>
<td>1.53</td>
</tr>
<tr>
<td>Arginine</td>
<td>2.12</td>
</tr>
<tr>
<td>Aspartate</td>
<td>2.55</td>
</tr>
<tr>
<td>Cysteine</td>
<td>6.94</td>
</tr>
<tr>
<td>Glutamate</td>
<td>6.43</td>
</tr>
<tr>
<td>Glycine</td>
<td>1.75</td>
</tr>
<tr>
<td>Histidine</td>
<td>1.13</td>
</tr>
<tr>
<td>Isoleucine</td>
<td>1.41</td>
</tr>
<tr>
<td>Leucine</td>
<td>2.39</td>
</tr>
<tr>
<td>Lysine</td>
<td>2.62</td>
</tr>
<tr>
<td>Methionine</td>
<td>0.77</td>
</tr>
<tr>
<td>Methionine + cysteine</td>
<td>1.71</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>1.54</td>
</tr>
<tr>
<td>Proline</td>
<td>2.23</td>
</tr>
<tr>
<td>Serine</td>
<td>1.44</td>
</tr>
<tr>
<td>Threonine</td>
<td>1.50</td>
</tr>
<tr>
<td>Tryptophan</td>
<td>0.46</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>1.65</td>
</tr>
<tr>
<td>Valine</td>
<td>1.71</td>
</tr>
</tbody>
</table>
Strategies for dealing with surface chemistry

1. Blend into rubbers that can undergo specific interactions with the biopolymer

   - polar interactions,
   - hydrogen bonding,
   - chemical reaction,
   - ionic bonding

Polar interactions: Starch in nitrile rubber
Polar interaction/chemical reaction: Starch in ENR

<table>
<thead>
<tr>
<th>Unaged Properties</th>
<th>NBR 28 / Carbon Black</th>
<th>NBR 48 / Starch</th>
<th>ENR 50 / Starch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (MPa)</td>
<td>10.5 minimum</td>
<td>5.5 (0.17)</td>
<td>15.1 (1.22)</td>
</tr>
<tr>
<td>Elongation at Break (%)</td>
<td>350.0 minimum</td>
<td>610.5 (34.5)</td>
<td>520.0 (20.5)</td>
</tr>
<tr>
<td>Crescent Tear (N/mm)</td>
<td>15.0 minimum</td>
<td>14.8 (2.32)</td>
<td>14.3 (1.86)</td>
</tr>
<tr>
<td>Hardness (Shore A)</td>
<td>50 ± 3</td>
<td>57</td>
<td>53</td>
</tr>
</tbody>
</table>

Hydrogen bonding/ionic interaction: rapemeal protein in XNBR

Rapemeal protein is rich in carboxylic acid groups

Ionomer type structure

Hydrogen bonding and other polar interactions
2. For non-polar rubbers - need coupling agents

- Resorcinol formaldehyde resin (RFH)
- Malic anhydride grafted polybutadiene (PBMAH)
- TESPT (Si69)

Effect of coupling agents (36 phr starch)
Coupling Mechanisms


D. De and B. Adhikari, *Journal of Applied Polymer Science*. 2006, **101**, 3151

**Ways of reducing particle size**

- Pre-treatment
  - Mechanical grinding
  - Hydrolysis
  - Spray drying
  - Freeze drying
  - Precipitation

- During mixing
  - Plasticisation
  - Aqueous phase mixing
Particle size reduction - Hydrolysis

Hydrolysed with hydrochloric acid

0 days
8 days
16 days

Hydrolysed starch "cements" particles together

Particle size reduction – Spray Drying

Rapemeal protein

spherical particles – some hollow
5 µm - 20 µm
Particle size reduction – Freeze Drying

Rapemeal protein

Flake-like particles 20µm x < 1µm

After mixing into rubber (XNBR) particle size 1-2 µm

Particle size reduction - Precipitation

Starch can be precipitated by cooling a dilute solution very slowly

Micro-sized particles with nano-sized structures

Crystalline – probably a good thing

Low yields – 7-12%, time consuming

Particle size reduction – In-mix plasticisation

- Most biopolymers are very hygroscopic and owe a lot of their hardness to hydrogen bonding between molecules.
- A plasticiser can be added to break down the intermolecular bonds – makes the material softer and able to be broken down during mixing (like blending 2 polymers).
- BUT want to remove plasticiser afterwards otherwise no reinforcement.
- Can require longer mixing (low temps) and energy is required to remove the water.

**State diagram of starch (1 atm)**

- Melting (END)
  \[ T_m = T_p + \frac{R \cdot T_p \cdot \Delta H_m}{\Delta S_m} \]
- Evaporation
  \[ T_e = T_p - \frac{R \cdot T_p \cdot \Delta H_e}{\Delta S_e} \]
- Freezing
  \[ T_f = T_p - \frac{R \cdot T_f \cdot \Delta H_f}{\Delta S_f} \]
- Glass transition

Water content % (w/w w.b.)
Particle size reduction – In-mix plasticisation

(ENR + 36 phr starch + water)

ENR mixed with as received starch

ENR mixed with Starch Plasticised with 50% water

Particle size reduction – In-mix plasticisation (water)

Stress, MPa

Elongation, %

100 µm

100 µm

1.5-

2.5-

60

20

40

Water content, %

100% modulus, MPa

200

400

25% 50% 75% 0%
To reduce inhomogeneity can plasticise (gelatinise) the filler before mixing

Problem of reduced compatibility due to extra water

No incorporation unless a small amount of silica (3.6 phr) was added, as a compatibiliser
Biopolymer solution (dispersion) is blended with rubber in latex form.

- low energy required for mixing
- energy required for drying
- most elastomers start out as latex
- most compounding not as latex

Aqueous phase mixing:

\[
\begin{align*}
\text{pH} &= 10 \\
9\% \text{ protein in water} &\rightarrow \text{heat} \\
75^\circ C, 15 \text{ min} &\rightarrow \text{latex}
\end{align*}
\]
**Blend with Latex then Dry**

- Heat 40°C 36h
- Heat 85°C 6h
- Not rubbery

**Moulding and Reworking**

- 150°C 3 min, 10 tonne
- Hot press
- Plastic-like
- 2-roll mill – several passes
- Rubbery
Effect of re-milling (42 phr, 97% purity)

1. Re-milling reduces stiffness and strength suggesting the breakdown of a continuous protein matrix.

2. Properties stabilise after a single milling.

Aqueous phase mixing results in very fine dispersion

Conventional mixing

Latex mixing
Reinforcement can be obtained …..

Problem of “set”:
- possibly the ionic bridges

Is dispersion too good?
Would more phase separation be better?

Conclusions

- Biopolymers can potentially be used as reinforcing fillers for elastomers, but the particle size must be reduced, and the interaction between filler and elastomer optimised by either selection of a suitable elastomer or by use of a coupling agent.

- RF resin and maleic anhydride grafted polybutadiene are potentially good coupling agents. Silane coupling agents have not worked so far.

- Particle size reduction methods, in order of decreasing effectiveness:
  1. Aqueous phase (latex/solution) blending
  2. Pre-gelatinisation
  3. In-mix plastisisation
  4. Precipitation
  5. Freeze drying
  6. Spray drying = natural grain size (starch)

Apart from basic mechanical properties, many other properties need to be tested, set, resistance to fluids, aging …….
Acknowledgements

Project sponsorship
- MRPRA (PhD sponsorship – Mazlina Mustafa-Kamal)
- EPSRC (Valorape project)

Materials and technical help :-
- Avon rubber - Materials Development Centre (Artis)
- Clwyd Compounders
- Central Science Laboratories
- Columbian Chemicals,
- Cray Valley Sartomer,
- Degussa
- Flexsys
- National Starch Company,
- Synthomer
- Tun Abdul Razaak Research Centre,