Biotechnological modification of polyester surfaces

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Enzymes in Textile and Polymer Biotechnology

- **Vast potential in the industrial production**
  - ~200 million euros **enzymes** in textile processing
    - Industrial applications in textiles ~10% of the industrial enzymes
      - Detergents ~34% of the industrial enzymes
        - today mainly amylases, cellulases
        - increasing importance and potential and new developments
          - pectinases, catalases, proteases, cutinases, ...
          - chemo-enzymatic approaches
  - Novel technology and processes
  - BIOTEX roadmap (EuropaBio, Euratex)
Enzymes in Textile and Polymer Biotechnology

The importance and potential of biotechnology in textiles has been assessed in the last 10-20 years.

• Biocatalysis has already proven to be very profitable in industrial textile pre-treatment processes of natural fibers.
• Application of enzymes is not limited to biological materials: relatively recently it has been demonstrated enzymes are able to modify the surfaces of synthetic textile materials as well (PET, PA, ..).
• Synthetic fibers form an important part of the textile industry
  Global annual production (2008) of fibers and yarns was estimated (Oerlikon) to be:
  30.3 million tons of polyester
  3.6 million tons of polyamide
  1.9 million tons of acrylics
  23.6 million tons of cotton
• The production volume of PET fibers and yarns justifies research into effective production.
Biotechnological surface modification and functionalisation

Motivation

• Manipulation of surface characteristics is of fundamental importance in the production of functional textiles.
• Research efforts often focus on chemical or physical modification or structuring of the surfaces.
• The introduction of functionalities using biotechnology is a relatively unexplored and modern scientific area.
• Innovative enzymatic processes to functionalize textile surfaces

Need for a concerted multi-disciplinary approach.
Surface modification of PET

- surface modification to improve (yarns, films, ….)
  - hydrophilicity (wetting and absorbency)
  - electrostatic charge
  - dyeability
  - washability
  - wear comfort
- improved functionalisation
  - coating
  - introduction functional groups
- **not** to change the bulk properties
Achieving hydrophilicity

Incorporate hydrophilic groups
- Co-polymerization
- Co-crystallisation

Generate hydrophilic groups
- Plasma treatments
- Alkali treatment
- Enzymes

- affecting bulk properties
- strength, pitting corrosion
- hydroxide
- temperature
  + durable
  + incubation time
  + mild reaction conditions
  + not affecting bulk properties
  + durable
  - longer incubation time
Cutinase hydrolysis of PET

Model substrates, films, fabrics, yarns, fibers, oligomers

Cutinase
Polyesterase
Lipase

1 2 3 4

2 3 TPA (terephthalic acid)
1 4 BHET (bis(2 hydroxyethyl) terephthalate)
1 3 or 2 4 MHET (mono(2 hydroxyethyl) terephthalate)
Cutinase in PET modification

- Cutinase exhibits significant hydrolytic activity towards amorphous regions. (ratio TPA, MHET, BHET is function of enzyme concentration and substrate)
  

- Model substrates vs ‘real’ substrates
- Introduction of carboxyl and hydroxyl groups in PET surface / endo mechanism

- Serine hydrolase
- 45/30/30 Å
- Ser 120, Asp175, His188
- No interfacial activation
- Absence of flap
Enzymes or NaOH

untreated  
cutinase 20 U/mg 2 h, 40°C
NaOH, 1M 2 h, 40°C

Contact angle  
(water/PET amorphous)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Contact Angle</th>
<th>Mechanism</th>
<th>Effect on New Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>~75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cutinase</td>
<td>~58</td>
<td>endo</td>
<td>introduction new groups</td>
</tr>
<tr>
<td>NaOH</td>
<td>~45</td>
<td>hydrolysis</td>
<td>little or no introduction new groups</td>
</tr>
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Functionalisation with 2-(bromomethyl)naphthalene (BrNP)

To evaluate the effect total photoluminescence intensity was measured using an integrating sphere.

The emission spectra of the 6 samples (the spectra are corrected detector sensitivity).

A= PET-Cr + BrNP, B=PET-Cr + Enzyme + BrNP,
C=PET-Am + Enzyme + BrNP, D=PET-Cr + Enzyme + BrNP,
E=PET-Am + Enzyme + BrNP and F=PET-Cr + NaOH + BrNP.

Biotechnologically functionalised materials

Challenges

Today’s challenge is to make the enormous potential of modern biotechnology for production and synthesis of materials with advanced functionalities an opportunity for textile and polymer industry.

• Novel processes for textiles exhibiting the desired functionalities.
• Novel enzyme technology for structuring and functionalisation of surfaces.

To contribute to the transition towards a biobased economy
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