Title: High performance polymers based on isoidide

Author: Rutger Knoop

Contact details: Rutger Knoop
Scientist polymer chemistry
Wageningen Food & Biobased Research
P.O. Box 17
6700 AA Wageningen
The Netherlands
T +31 317 480127
E rutger.knoop@wur.nl

Curriculum: After his master polymer chemistry at the state University Groningen, Rutger Knoop obtained his PhD at the University of Technology Eindhoven in 2009. In December 2008 he joined Wageningen Food & Biobased Research to start up polymer chemistry research. Since then, he was involved in many projects in the field of renewable polymer synthesis, polymer characterisation and polymer modification. He is (co)inventor on 7 patent applications, e.g. polyisoidide furanoate thermoplastic polyester and copolymesters and the use thereof for hot fill applications, and a polymer composition comprising an impact modifier and method of making the same.

Abstract: Isohexides are a versatile class of monomers suitable for the development of engineering plastics. Isohexides are advocated as a potential monomer to replace bisphenol-A for food packaging applications mainly due to the rigid structure of isohexides. Three different isomers of isohexides exist of which isosorbide is well explored due to its commercial availability. At Wageningen Food & Biobased Research, a technique was developed to transform isosorbide into isoidide, a more reactive and symmetrical isohexide. In this presentation, some insights in the benefits of isoidide over isosorbide will be shown. This will be illustrated with some examples obtained in the BPM-HIPPIE project. This project was a collaborative research project together with ADM, DuPont and Holland Colours.
HIPPIE: High Performance Polymers from Isoidide

June 19th 2019, Willem Vogelzang, Rutger Knoop, Jacco van Haveren
Outline

- Introduction
  - Project partners
  - Aim of Hippie
  - Isohexides
    - Applications
    - Furandicarboxylic acid (FDCA)
- Results
  - Co-diol isoidide polyesters
- Conclusions
- Future outlook
Partners

- BPM-2 Project
- 3 Partners
  - Archer Daniels Midland (ADM): large agri-food processor
  - DuPont: was the world's fourth-largest chemical company based on terms of sales\(^1\)
  - Holland Colours (HCA): SME, Coloring & Barrier solutions for consumer packaging

\(^1\) https://en.wikipedia.org/wiki/DowDuPont
Introduction (Aim of the project)

1: Develop materials for food packaging applications from isoidide with:
   - Glass transition temperature \( (T_g) > 120^\circ C \)
   - Semi-crystalline; Melting temperature \( (T_m) \leq 260^\circ C \)
   - High barrier properties

- Target markets/applications:
  - BPA-PC alternatives and BPA-free food packaging

2: Develop carrier for additives based on isoidide with
   - \( T_m > 100^\circ C \)
   - High crystallization rate
Introduction (Background information)

- Bisphenol-A based materials are under debate.
  - Potentially endocrine disruptive
  - Potentially impair the immune systems of (unborn) children

- Bisphenol-A based materials are found in:
  - Construction materials
  - Electronics
  - Bottles
  - Food packaging
  - Medical devices
  - Coatings
Introduction (Commercially available alternatives)

• Mitsubishi DURABIO™ (left) and Eastman Tritan (right)
Introduction (Monomers of interest)

Biomass (starch cellulose)

\[ \text{H}_2\text{O} \]
\[ \text{Catalyst} \]

\[ \text{fructose} \]
\[ \text{H}_2 \]
\[ \text{Catalyst} \]

\[ \text{D-mannitol} \]

\[ \text{D-sorbitol} \]

\[ \text{glucose} \]
\[ \text{H}_2 \]
\[ \text{Catalyst} \]

\[ \text{L-iditol} \]

isomannide

isosorbide

isoidide
Introduction (Monomers of interest)

- Development of catalytic method to obtain isoidide from isosorbide
  - Resulted in patent application\textsuperscript{1a} and scientific paper\textsuperscript{1b}


Introduction (monomers of interest)

Cellulose / Starch

Glucose ↔ Fructose ↔ Inulin

HMF

HMFA

2,5-FDCA

DHMF
Introduction (Monomers of interest)

- 2,5-FDCA is advocated as alternative for terephthalic acid.

- Poly(ethylene terephthalate) vs Poly(ethylene furanoate)¹
  - PEF oxygen barrier is 10 times better than PET
  - PEF carbon dioxide barrier is 4 times better than PET
  - PEF water barrier is 2 times better than PET
  - The Tg of PEF is 86°C compared to the Tg of PET of 74°C
  - The Tm of PEF is 235°C compared to the Tm of PET of 265°C

¹)https://www.avantium.com/yxy/products-applications/
Introduction (Monomers of interest)

- Research questions
  - Can isoidide increase the glass transition temperature of 2,5-FDCA based polyesters?
  - Can isoidide improve the barrier properties of 2,5-FDCA based polyesters?
  - Does isoidide outperform isorbide in polyesters?
Results isosorbide vs isoidide

- Poly (isosorbide furanoate)

- Poly (isoidide furanoate)

<table>
<thead>
<tr>
<th>GPC</th>
<th>DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn (g/mol)</td>
<td>Mw (g/mol)</td>
</tr>
<tr>
<td>1,700</td>
<td>3,800</td>
</tr>
<tr>
<td>2,100</td>
<td>3,600</td>
</tr>
</tbody>
</table>
Results homo-polymerization

Fox, T.G.; Flory, P.J., "Second-order transition temperatures and related properties of polystyrene"
Results homo-polymerization

- Molecular weight increment by solid state post condensation

<table>
<thead>
<tr>
<th>Entry</th>
<th>$T_{SSPC}$ (°C)</th>
<th>Time (h)</th>
<th>GPC</th>
<th>DSC</th>
<th>PIIF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mn (g/mol)</td>
<td>Mw (g/mol)</td>
<td>PDI</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>1,500</td>
<td>4,000</td>
<td>1.7</td>
</tr>
<tr>
<td>2</td>
<td>230</td>
<td>4</td>
<td>14,200</td>
<td>30,700</td>
<td>2.2</td>
</tr>
<tr>
<td>3</td>
<td>230</td>
<td>16</td>
<td>19,800</td>
<td>44,100</td>
<td>2.2</td>
</tr>
</tbody>
</table>
Results co-polymerization

- Semi-crystalline and amorphous co-polyesters based on isoidide and 2,5-FDCA
Results co-polymerization

- Glass transition temperature as function of isoidide content in
  - poly(ethylene-co-isoidide furanoate)
  - poly(propylene-co-isoidide furanoate)
  - poly(butylene-co-isoidide furanoate)
Results co-polymerization
Intermediate conclusions

- Homo-polymerization of isoidide and 2,5-FDCA.
  - Highly crystalline polyester with:
    - $T_g$: 169-175°C
    - $T_m$: >250°C (slightly high for processing)

- Homo-polymerization of isosorbide and 2,5-FDCA
  - Amorphous polyester with:
    - $T_g$: 169-175°C

- Co-polymerization of isoidide with aliphatic diols.
  - Glass transition temperature increases with isoidide content
  - Remain semi-crystalline for
    - 15%<isoidide content (mol %)<85%
Intermediate conclusions

- Development of isoidide based polyesters
  - Resulted in patent application on polyisoidide furanoate (PIIF) homo-polyester and co-polyesters
  - Solid State Postcondensation (SSPC) was used to increase MW
  - Concept proven that isoidide allows for producing semi-crystalline polymers

1) polyisoidide furanoate thermoplastic polyester and copolyesters and the use thereof for hot fill applications. (WO20156607 A1)
Reduction of the melting temperature

- The melting temperature of isoidide based polyesters is slightly too high for processing.
  - Reduction of melting temperature by introduction of additional co-monomers
Results co-polymerization

PIIF[85]-co-[15]

Mn: 27,900 Da
Mw: 56,300 Da
PDI: 2.1

phase 1

Quenching

285-290 °C

PIIF[85]-co-[15]

Mn: 19,800 Da
Mw: 40,900 Da
PDI: 2.1

phase 2

Compression moulding

250 °C

PIIF[85]-co-[15]

Mn: 26,600 Da
Mw: 54,300 Da
PDI: 2.0

Mn: 32,000 Da
Mw: 72,000 Da
PDI: 2.1

Retaining 70-75% initial MW after compression moulding
# Tensile properties of polyesters

## PIIF copolyester A

<table>
<thead>
<tr>
<th>Polymer</th>
<th>E-modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Stress at break (%)</th>
<th>T(_g) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIIF copolyester A</td>
<td>2.6</td>
<td>21</td>
<td>0.7</td>
<td>160</td>
</tr>
<tr>
<td>PIIF copolyester B</td>
<td>2.6</td>
<td>55</td>
<td>2.5</td>
<td>140</td>
</tr>
<tr>
<td>BPA-PC(^1)</td>
<td>2.0-2.4</td>
<td>55-75</td>
<td>80-150</td>
<td>150</td>
</tr>
</tbody>
</table>

1) [https://en.wikipedia.org/wiki/Polycarbonate](https://en.wikipedia.org/wiki/Polycarbonate)
# Tensile properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>E-Modulus (MPa)</th>
<th>Stress-max (MPa)</th>
<th>Strain at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WVHIP55</td>
<td>PiIF[85]-co[15]</td>
<td>2640 [191]</td>
<td>20.9 [4.6]</td>
<td>0.7 [0.2]</td>
</tr>
<tr>
<td>WVHIP60</td>
<td>PiIF[85]-co[15]</td>
<td>2562 [115]</td>
<td>54.7 [5.6]</td>
<td>2.5 [0.4]</td>
</tr>
</tbody>
</table>
Conclusions

- Polyesters based on isoidide and 2,5-FDCA in combination with other co-monomers can result in materials with a $T_g > 125^\circ C$

- Semi crystalline materials for compositions for II and
  - FDCA : other co-monomer = 80:20 up to 100:0

- All co-polyesters with other co-monomers show slow crystallization rates

- All co-polyesters with other co-monomers can be processed into:
  - Foils
  - Tensile bars

- Mechanical properties of all co-polyesters can be tuned by composition of c-monomers
Acknowledgements

Willem Vogelzang
Wouter Teunissen
Herman de Beukelaer
Guus Frissen
Rutger Knoop
Daan van Es
Jacco van Haveren