DSM & Chemelot Site, Geleen

DSM Mission:
Our purpose is to create brighter lives for people today and generations to come.

Enabled by bright sciences

Centre court, ready 2016

19,000 m² office & labs

2014: 21000 people, net sales 9.2 billion €, EBITDA 1.2 billion €

See also: www.dsm.com
Why a polyamide?
The amide link

- Directional H-Bond (30 kJ/mol)
- High dipole
- Stiff C-N due to double bond character

Strong interaction between chains

- The amide link explains PA’s special properties
Nature's also chooses polyamides: Amino acids building units for proteins

Combination of H-bonding and non bonding interactions

- Triple-helix

β-sheet

Glycine
Hydroxyproline
Proline
Alanine
Hydroxyproline
Proline
Reducing CO₂ emission with PA 46 (Stanyl®)

High $T_m$ of 295°C

Special aspects:

- Fast crystallization
- High crystallinity
- High concentration interactions between chains

→ Low friction

Chain Tensioner: investment <1€ per g/km CO₂ reduction!
(Per 100 000 km 100 kg CO₂)
Why bio-based?
Outlook availability petrochemical resources

Oil and gas use

1000 2000 3000

Live of the land

A brief moment in history

Live of the land

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Aachen-Dresden-itec 2015
Why bio-based? Reducing CO\textsubscript{2} emission by monomer choice PA 410 (EcoPaXX\textsuperscript{®})

- Long sebacic acid moiety is bio-based with a low CO\textsubscript{2} carbon footprint.
- Short diamine limits petro based C content to 30%
- EcoPaXX\textsuperscript{®} is the DSM brand name for our PA 410.
Polyamides and Amide density

**PA XY**

Amide / methylene ratio \( L/CH_2 = 2/(4+4) = 0.25 \)

**PA Z**

Amide / methylene ratio \( L/CH_2 = 1/5 = 0.20 \)
Why bio-based monomers: Enabling good properties

- Current commercial bio-based polyamides are based on fatty acids.
- They find their way in the market because of their special properties.
$T_m$ of linear aliphatic PA’s

![Graph showing $T_m$ of linear aliphatic PA’s](image-url)
$T_m$ of linear aliphatic PA’s

D. Steiger, T. Tervoort, C. Weder, P. Smith, Macromol. Rapid Commun. 21, 405-422, 2000
$T_m$ of linear aliphatic PA’s
$T_m$ of linear aliphatic PA’s
What monomers to choose? Different monomer combinations for the same isomer

- 8 Isomers of PA 410 (even CH₂ numbered monomers)
Relation $T_m$ point and amide density

Polyamide isomers with $L/CH_2 = 0.17$

- Combining short and a long chain monomer leads to a higher $T_m$
- Linear relation between amide density and $T_m$ per class of polyamide

Experimental data of PA 410 isomers obtained by B. Noordover, TU/e
Molecular modeling of the H-bond fraction

L/[CH₂]=1/6 modeling of H-bond fraction \( X_b \) at 300 °C

- Correlation between hydrogen bond density and \( T_m \) of isomers

\( X_b \) data obtained by molecular modelling, B. Coussens, DSM
How to obtain a high Tensile Modulus?

Tensile modulus (Mpa) - dry and conditioned (50% RH)

Short aliphatic nylons ... EcoPaXX® ... Long-chain aliphatic nylons
How?: Building a market position in Automotive Engine Covers

Application Requirements

- Surface quality in combination with dimensional stability
- Noise reduction from Engine
- CUT = 210°C with peak temperature resistance up to 230 °C
- (HDT-B at 0.45 MPa = 235°C)
- Optical appearance (no painting)
- Sustainability (based on LCA figures)

Success at Daimler: After A-class, CLA, GLA, now also M177 in AMG ...
Also in various BMW models and Bentley

Aachen-Dresden-itc 2015
How?: Building a market position in Industrial Brushes

- Application by Hahl-Pedex as abrasive fibers AbraMaXX™ in abrasive brushes. EcoPaXX® shows excellent combination of abrasion resistance and heat resistance.

- Potential application as high performance fibers in PIGS (oil-pipe cleaning). Abrasion resistance, wet-bend recovery and high temp resistance needed...

Key characteristics:
- Chem. resistance
- Heat resistance
- Wet-bend recovery
- Abrasion resistance
How can we increase hydrophobicity?

- Generally copolyamides have higher moisture uptake and lower melting points.
- With long aliphatic comonomers, moisture uptake can be reduced.
- Melting point depression can be reduced by controlling the polymer structure by synthetic strategies.

Approach:
Polymerize a mix of diaminobutane, sebacic acid and C36 dimerized fatty acid.
PA 410/436 (76/24 mol/mol) copolymer

<table>
<thead>
<tr>
<th></th>
<th>PA 410</th>
<th>PA 410/436 (76/24)</th>
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</thead>
<tbody>
<tr>
<td>L/(C-L)</td>
<td>0.17</td>
<td>0.11</td>
</tr>
<tr>
<td>$T_m$ (°C)</td>
<td>246</td>
<td>236</td>
</tr>
<tr>
<td>$\Delta H_m$ (J/g)</td>
<td>92</td>
<td>49</td>
</tr>
<tr>
<td>[H$_2$O]$^*$ (wt.%)</td>
<td>5.9</td>
<td>2.0</td>
</tr>
<tr>
<td>$T_g$ DSC (°C)</td>
<td>54</td>
<td>33</td>
</tr>
<tr>
<td>$T_g$ DMTA (°C)</td>
<td>63</td>
<td>42</td>
</tr>
<tr>
<td>$E$ 24°C (GPa)</td>
<td>2.91</td>
<td>1.55</td>
</tr>
</tbody>
</table>

* In water at 40°C (equilibrium)

- Bio-based content increased from 70 to 80 wt. %
Conclusions

- Polyamides are a good material class for the production and development of bio-based materials with a good property profiles

- The pairing of the amide bonds combined with the good thermal properties of longer bio-based dicarboxylic acids make diaminobutane a good enabler for superior properties

- This results in the excellent high temperature stiffness under moist conditions for PA 410

- Good value propositions in various markets have led to successful commercial introduction of EcoPaXX®