VEGETABLE-BASED BUILDING BLOCKS FOR THE SYNTHESIS OF RENEWABLE POLYURETHANES AND POLYESTERS

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SFEL 2012
A greener future for polymeric materials

Source: European bioplastics/Probip 2009

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Bio-based raw materials

Methyl oleate

~90% in high oleic sunflower oil

Methyl ricinoleate

Between 85 and 95% in castor oil

Pyrolysis of methyl ricinoleate

Methyl 10-undecenoate

Isosorbide

Starch

succinic acid

1,4-Diaminobutane

1,3-Propanediol

Glycerol

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Bio-based raw materials


Bifunctional building blocks for polyurethanes

\[ X = -O- \text{ or } -\text{NH}- \]

Poly(ester urethane)s
Poly(amide urethane)s
Poly(ester amide urethane)s
Synthetic route to the fatty-based diols

Transesterification and/or Amidation

$X = \text{-O- or -NH-}$

Thiol-ene reaction

$X = \text{-O- or -NH-}$
Particular case of diamide diol

Bio-based well-defined difunctional building-blocks

Bio-based Thermoplastic polyurethanes & polyesters

Structure of bio-based diols
**Bifunctional building blocks for polyurethanes**

X = -O- or -NH-

Poly(ester urethane)s
Poly(amide urethane)s
Poly(ester amide urethane)s

\[
M_n = 30,000 \text{ g.mol}^{-1} \\
M_w = 50,000 \text{ g.mol}^{-1} \\
D = 1.6
\]
Synthetic route to the poly(amide urethane)

0.1wt% DBTDL
80°C
Bulk or DMF
4wt% LiCl (UndBdA-diol)

OCN

MDI

PU-dA-2
Amorphous polyurethanes

Glass transitions from -26.8°C to 51.5°C

DSC thermograms – Second cycle, 10°C.min⁻¹
Semi-crystalline polyurethanes

X = -O- or -NH-

\[ \text{OCN} - \text{MDI} \]

\[ \text{IPDI} / \text{MDI} \]

\[ \text{+ MDI} \]

\[ \text{+ MDI} \]

\[ \text{+ MDI} \]
Semi-crystalline polyurethanes

DSC thermograms – Second cycle, 10°C.min⁻¹

Flexibility
High hydrogen bonding
Polyurethanes
Mechanical properties via tensile experiments

<table>
<thead>
<tr>
<th>Samples</th>
<th>Young's modulus (MPa)</th>
<th>Ultimate strength (MPa)</th>
<th>Maximum strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU-dE-2</td>
<td>287 ± 35</td>
<td>17.4 ± 2.4</td>
<td>266 ± 24</td>
</tr>
<tr>
<td>PU-EA-2</td>
<td>314 ± 33</td>
<td>23.2 ± 1.4</td>
<td>269 ± 26</td>
</tr>
<tr>
<td>PU-dA-1</td>
<td>770 ± 68</td>
<td>58.1 ± 3</td>
<td>41 ± 2</td>
</tr>
<tr>
<td>PU-dA-2</td>
<td>775 ± 51</td>
<td>48.3 ± 3</td>
<td>44 ± 13</td>
</tr>
</tbody>
</table>

Ester → Amide

Tensile experiments: Tensile stress versus strain curves
2. Poly (ester/amide urethane)s

Thermal stability

- Typical multiple step degradations behavior
- Urethane functions, thiocarbon chains, ester and amide linkages
- Mostly $T_{5\%} > 280^\circ C$

TGA thermograms – $N_2$, 10°C.min⁻¹
Polyesters : Our strategy to more robust fatty-acid based materials

Polyesters

- biodegradable
- Poor thermomechanical properties

Poly(ester-amide)s

- biodegradable
- Good thermomechanical properties

Castor oil

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Our strategy to more robust fatty-acid based materials

Polyesters

$$\text{HO-S-\text{carboxylate}}-\text{S-OH}$$

$$\text{HO-S-\text{glycol unit}}-\text{S-OH}$$

Poly(ester-amide)s

$$\text{HO-S-\text{carboxylate}}-\text{S-OH}$$

$$\text{HO-S-\text{ester unit}}-\text{S-OH}$$
Polyesters using diol precursors

Dynamic mechanical analysis (compression mode)

\[ \tan \delta = \frac{E''}{E'} \]

Storage Modulus: \( E' \)
Loss Modulus: \( E'' \)

DSC – 10°C/min

Low increase of glass transition (10°C) with incorporation of Isosorbide

<table>
<thead>
<tr>
<th>Diol</th>
<th>ester:amide ratio</th>
<th>Mn (g/mol)</th>
<th>Mw (g/mol)</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE 1</td>
<td>UndPdE</td>
<td>1:0</td>
<td>18 400</td>
<td>35 000</td>
</tr>
<tr>
<td>PE 2</td>
<td>UndIdE</td>
<td>1:0</td>
<td>8 900</td>
<td>13 300</td>
</tr>
</tbody>
</table>

SEC in THF, PS calibration
Our strategy to more robust fatty-acid based materials

Polyesters

Bio-based well-defined difunctional building-blocks

Bio-based Thermoplastic polyesters & poly(ester-amide)s
Poly(ester-amide)s: promising bio-based materials

<table>
<thead>
<tr>
<th>Entry</th>
<th>Monomer</th>
<th>ester:amide ratio</th>
<th>Mn (g/mol)</th>
<th>Mw (g/mol)</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE 1</td>
<td>UndPdE</td>
<td>1:0</td>
<td>18 400</td>
<td>35 000</td>
<td>1.9</td>
</tr>
<tr>
<td>PEA 1</td>
<td>UndPEA</td>
<td>3:1</td>
<td>17 500</td>
<td>33 100</td>
<td>1.9</td>
</tr>
<tr>
<td>PEA 2</td>
<td>UndPmA</td>
<td>2:1</td>
<td>10 902</td>
<td>19 500</td>
<td>1.8</td>
</tr>
<tr>
<td>PEA 3</td>
<td>UndBdA</td>
<td>1:1</td>
<td>19 300</td>
<td>29 000</td>
<td>1.5</td>
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SEC in THF, PS calibration - For PEA3, trifluoroacetic anhydride was used to dissolve the polymer using standard method.
Poly(ester-amide)s: promising bio-based materials

Thermal degradation begins between 300 and 350°C

Ester functions degradation

Amide functions degradation

TGA 10°C/min
Poly(ester-amide)s: promising bio-based materials

High increase of melting point with hydrogen bond density
36°C < Tm < 126°C

Modulated DSC 2°C/min
30min Annealing 10°C/minute

DSC 2nd heating run 10°C/minute

Heat Flow (mW/g)

PE1
PEA1
PEA2
PEA3

Fats & Oils expertise

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Poly(ester-amide)s: promising bio-based materials

Chemical structure comparable to Nylon

**α form**: hydrogen bonds between antiparallel chains

**γ form**: hydrogen bonds between parallel chains

Metastable pseudohexagonal structures which vary continuously in size, perfection, and structural parameters

amide-amide intermolecular H-bonded chains (~4.8 Å)

van der Waals packed sheets (~3.7 Å)

Disappearance of pseudohexagonal reflection by heating = Melting of pseudohexagonal form which crystallize in the α-form
Poly(ester-amide)s: promising bio-based materials

Tensile tests

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<tr>
<th>Entry</th>
<th>Young’s Modulus (MPa)</th>
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<tr>
<td>PE1</td>
<td>93.0 ± 10.4</td>
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<tr>
<td>PEA1</td>
<td>82.7 ± 15.2</td>
<td>5.4 ± 1.2</td>
<td>11.1 ± 2.4</td>
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<tr>
<td>PEA2</td>
<td>131.5 ± 17.5</td>
<td>3.5 ± 0.3</td>
<td>3.4 ± 0.7</td>
</tr>
<tr>
<td>PEA3</td>
<td>363.0 ± 89.1</td>
<td>10.0 ± 3.5</td>
<td>3.3 ± 0.7</td>
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Poly(ester-amide)s: promising bio-based materials

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Conclusion

Hydroxyesters → Polyester

AB type condensation

Polyesters

Ester and/or amide diol precursors

Diol + Diester condensation

Poly(ester-amide)s with improved thermo-mechanical properties

Poly(ester-amide)s urethanes with improved thermo-mechanical properties
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