CHEMICAL RECYCLING OF POLYURETHANE

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ROME, 10th October 2019
Summary and purposes

- Polyurethane market and wastes;
- The need of a circular economy strategy;
- Chemical recycling of polyurethane by glycolysis;
- Application of the glycolysis product in the synthesis of new rigid PU foams.
Polyurethane Market

Distribution of European plastic converter demand by resin type (2017)

51.2 mt
Total converter demand

18.4 mt
Polyurethane converted in the world

3.6 mt
Polyurethane converted in EU in 2017

Source: PlasticsEurope Market Research Group (PEMRG) / Consultic Marketing & Industrieberatung GmbH
Polyurethane disposal

- Thermosetting material
- High volumes
- Mixed with other materials (e.g., coatings in insulation panels)
- Presence of blowing agents and flame retardants
- High cost for disposal
- EU restrictions in landfill disposal
Waste legislation and policy of the EU Member States shall apply as a priority order the following waste management hierarchy:
Disposal of polyurethanes
Glycolysis process

PU scraps

PU powder waste

Synthesis of new PU rigid foams

Recycled polyol

Glycolysis process
**MAIN REACTIONS:**

**TRANSESTERIFICATION** through a glycol

All these reactions lead to the formation of products with end groups reactive with isocyanate.
SIDE REACTIONS:

HYDROLYSIS

\[
\text{Urethane} + \text{Water} \xrightarrow{\Delta, \text{cat}} \text{Polyol} + \text{Amine} + \text{Carbon dioxide}
\]

PYROLYSIS

\[
\text{Urethane} \xrightarrow{\Delta} \text{Amine} + \text{Carbon dioxide} + \text{Unsaturated polyol}
\]

All these reactions lead to the formation of products with end groups reactive with isocyanate.
Glycolysis parameters

- **Glycol type**
- **Glycol/polymer ratio**
- **Catalyst type**
- **Catalyst/polymer ratio**
- **Temperature**
- **Boiling point vs Viscosity and nOH**
- **Selectivity vs Activity**
- **Fast cinetic vs side products formation**
Glycolysis analysis

FT-IR Spectroscopy

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Glycolysis can be extended to different classes of polyurethanes or materials:

**Polyurethane rigid foams**

**Polyurethane rigid blocks**
Polyisocyanurate rigid foams lead to a liquid glycolysis product with highly branched oligomers.
Glycolysis: materials

Reinforced injection molding (RIM) polyurethane or polyurea

Flexible foams
Reinforced injection molding (RIM) polyurethane or polyurea

Polyurea basic molecular structure:

Polymerization:

Oligomers + Glycol

+ Glycol

diethyl toluene diamine (DETDA)
Glycolysis: MDA formation

\[
\begin{array}{c}
\text{H}_2\text{N} & & \text{H}_2\text{N} \\
\downarrow & & \downarrow \\
\text{4,4’-methylene dianiline (MDA)} & & \\
\end{array}
\]

CONSEQUENCES:
• Can cause skin irritation and liver damages;
• Labelling costs for the handling and transport;
• Amines catalyse PU synthesis, so bad reaction control.

SOLUTIONS:
• Prevent MDA formation
  o Use a more selective catalyst towards glycolysis;
  o Optimize the catalyst concentration;
  o Dehydrate the reactants before glycolysis.
• Abate MDA through a deaminating agent
Product properties

- Viscosity ($\mu$)
- Hydroxyl number ($nOH$)
- Amine content (HPLC)
- Molecular weight (GPC)
The liquid product obtained by glycolysis can be used in the production of **new rigid foams**.

**Ratio recycled/virgin polyol:**

- 0/100
- 25/75
- 50/50
- 75/25
- 100/0
New foams performances

Glycolysis product from polyurethane rigid blocks

<table>
<thead>
<tr>
<th>Glycol/PU</th>
<th>Viscosity [cP]</th>
<th>nOH [mgKOH/g]</th>
</tr>
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<tbody>
<tr>
<td>40/60</td>
<td>2500</td>
<td>560</td>
</tr>
</tbody>
</table>

Density 46 kg/m³

Mechanical properties

Thermal properties

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New foams performances

Glycolysis product from reinforced injection molding (RIM) polyurethane or polyurea

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Density 38 kg/m³

Mechanical properties

Thermal properties
Thank you for your attention