Keep an eye on green solutions: Bio-based Polyester Polyols for reactive PUR Hot Melts

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Outline

1. Motivation
2. Challenges
3. Developments
State of the art Polyester Polyols – like the DYNACOLL® 7000 series of Evonik – are tailor-made polyester polyols based on conventional monomers. They are used to formulate one-component moisture-curable hot melt (RHM) adhesives and sealants.

Characteristics:
- Medium molecular weight ($M_n$ 2,000 – 8,000 g/mol)
- Linear
- Hydroxyl end groups

Conventional Polyester Raw Materials

<table>
<thead>
<tr>
<th>Petrochemical Raw Materials</th>
<th>Petrochemical-based Monomers</th>
<th>Conventional Polyester-Polyols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas, Natural oil</td>
<td>Aromatic &amp; aliphatic diesters, dicarboxylic acids &amp; diols</td>
<td>Not bio-based, but possibly biodegradable</td>
</tr>
</tbody>
</table>
Polyester Polyols as building block system for RHM formulations

Building block system

- Amorphous PES-grades
- Liquid PES-grades
- Crystalline PES-grades

Reactive Hot Melt Design

RHMs are reaction products of solid polyol mixtures with excess diisocyanates (e.g. MDI).

Building block systems of amorphous & liquid & crystalline Polyester grades allow a precise formulation of the RHM.

Formulation example

To adjust RHM setting time:

- 40 ppw - amorphous grade A 7150
- 30 ppw - liquid grade L 7250
- 30 ppw - crystalline grade C 73XX

& 4,4’ MDI [OH/NCO 1/2.2]
Why should Polyester Polyols go green?

**Ecological Reasons**

**Megatrend Resource Efficiency**
- Slow-down of general climatic change due to less greenhouse gases
- Lower Carbon Footprint (CF) leads to less Global Warming Potential (GWP)

**Economical Reasons**

**Megatrend Sustainability**
- Renewable raw materials support sustainable raw material feed
- Petrochemical sources might become scarce and therefore expensive
- Resource Efficiency is a growth driver
Challenge 1: Identification of suitable bio-based monomers

Most conventional monomers currently used for polyester synthesis are not available from renewables

- Simple substitution of monomers (“drop-in”) is not possible
- Continuous market screening for bio-based diacids, diesters and diols is necessary
- Testing of monomer samples is essential

Questions to be answered

- Does the monomer survive the harsh reaction conditions of polyester synthesis (high temperatures and long reaction time)?
- Is the monomer incorporated into the polymer?
Challenge 2: Meet or improve current PES- and RHM-properties

Bio-based polyester polyols should …

- … contain ≥ 30 ppw of renewable monomers
- … allow a modular combination of amorphous, liquid and crystalline polyesters
- … have specifications comparable to established state of the art polyesters

Reactive Hot Melts (RHM) based on bio-based polyester polyols should …

- … have well-balanced and versatile adhesion properties on different substrates
- … meet customers requirements regarding melt viscosity, softening point, open and setting time.
First bio-based Polyester Polyols are successfully introduced to the market

With its DYNACOLL® Terra product range Evonik offers polyester polyols made from renewable raw materials also as a building block system:

<table>
<thead>
<tr>
<th>Properties:</th>
<th>Portion of renewables [%]</th>
<th>Softening Point (R&amp;B) [°C]</th>
<th>Melt Viscosity [Pa s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous grades</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A 1</td>
<td>&gt; 30</td>
<td>85</td>
<td>35 (130°C)</td>
</tr>
<tr>
<td>A 2</td>
<td>&gt; 30</td>
<td>85</td>
<td>32 (130°C)</td>
</tr>
<tr>
<td>Liquid grades</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L 1</td>
<td>&gt; 85</td>
<td>-</td>
<td>4 (80°C)</td>
</tr>
<tr>
<td>L 2</td>
<td>&gt; 75</td>
<td>-</td>
<td>4 (80°C)</td>
</tr>
<tr>
<td>Crystalline grades</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C 1</td>
<td>100</td>
<td>65</td>
<td>2 (80°C)</td>
</tr>
<tr>
<td>C 2</td>
<td>100</td>
<td>75</td>
<td>3 (80°C)</td>
</tr>
</tbody>
</table>

OH value approx. 30 mg KOH/g and Acid value <2 mg KOH/g
RHM formulation and performance in flat lamination application

Building block system offers a broad variety of RHM formulations:

Formulation-example RHM3:
- A2 bio-polyol: 30 ppw
- L1 bio-polyol: 30 ppw
- C1 bio-polyol: 40 ppw
- & 4,4’ MDI [OH/NCO 1/2.2]

Characteristics of RHM3:
- Viscosity 130°C: 17 Pa s
- Open Time: 840 sec
- Setting Time: 150 sec

Application Example: Flat Lamination
Three times resource efficiency in woodworking applications

By using bio-based Polyester Polyols in RHMs for e.g. sandwich bonding of wood-based substrates **Resource Efficiency** is supported by:

(1) **Energy Savings** by usage of RHMs, which allow low application temperatures and short cycle times due to high green strengths

(2) Formulation of RHM on **bio-based** raw material

(3) Bonding of wood which is a **renewable** substrate
Need for further portfolio optimization was identified

<table>
<thead>
<tr>
<th>Scope</th>
<th>Preliminary bio-based Polyester Portfolio does not show satisfying results in formulation of very fast setting RHMs, e.g. for edge banding purposes.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>To achieve shorter setting times a higher crystalline bio-based Polyester Polyol is needed.</td>
</tr>
<tr>
<td>Issue</td>
<td>Higher crystalline Polyesters generally show very poor compatibility to amorphous Polyester Polyols.</td>
</tr>
</tbody>
</table>

Recent Research Results: The bio-based Polyester Portfolio is extended by two new amorphous and one new crystalline Polyesters
Properties of the two new amorphous bio-based Polyesters

A new bio-based monomer was identified and two new Polyesters were developed with improved compatibilities.

Properties:

<table>
<thead>
<tr>
<th></th>
<th>Portion of renewables [%]</th>
<th>Softening Point (R&amp;B) [°C]</th>
<th>Melt Viscosity [Pa s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 1</td>
<td>&gt; 30</td>
<td>85</td>
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<td>A 2</td>
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<td>85</td>
<td>32 (130°C)</td>
</tr>
<tr>
<td>A 3</td>
<td>&gt; 35</td>
<td>90</td>
<td>17 (130°C)</td>
</tr>
<tr>
<td>A 4</td>
<td>&gt; 30</td>
<td>95</td>
<td>15 (130°C)</td>
</tr>
</tbody>
</table>

This new monomer gives access to modified Glass Transition Temperature and Hydroxyl Numbers:

Achievement

Broader variety of bio-based Polyester Polyols for more versatile RHM formulations
RHM formulation results with the new amorphous grades

Composition of test formulation:
- 33 ppw - amorphous grade AX
- 33 ppw - liquid grade L2
- 33 ppw - crystalline grade C2
- & 4,4' MDI [OH/NCO 1/2.2]

RHM properties:
- Open Time
- Setting Time

Compatibility results:
- Phase separation
- Opaque
- Cloudy
RHM with faster setting for edge banding applications

New highly crystalline bio-based Polyester was developed

Properties:

<table>
<thead>
<tr>
<th></th>
<th>Portion of renewables [%]</th>
<th>Softening Point (R&amp;B) [°C]</th>
<th>Degree of crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1</td>
<td>100</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>C 2</td>
<td>100</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>C 3</td>
<td>&gt; 60</td>
<td>80</td>
<td></td>
</tr>
</tbody>
</table>

Application Example: Edge Banding

Guide formulation Edge banding:
- 35 ppw - amorphous grade A4
- 20 ppw - liquid grade L2
- 10 ppw - crystalline grade C2
- 25 ppw - crystalline grade C3
- 10 ppw - HM PES S1402
- & 4,4’ MDI [OH/NCO 1/2.0]
Summary

Keep an eye on green solutions!

New bio-based Polyester Polyols offer new opportunities!

- Support of resource efficiency by using green components
- Modular combination of Polyesters in RHM formulation possible
- Well-balanced and versatile adhesive properties
- Implementation of new properties possible