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

Gabriele Brenner
Dr. Christina Diehl, Sabine Thüner
Paris, 2012-09-20

Outline

1. Motivation
2. Challenges
3. Developments

State of the art
Polyester Polyols

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.

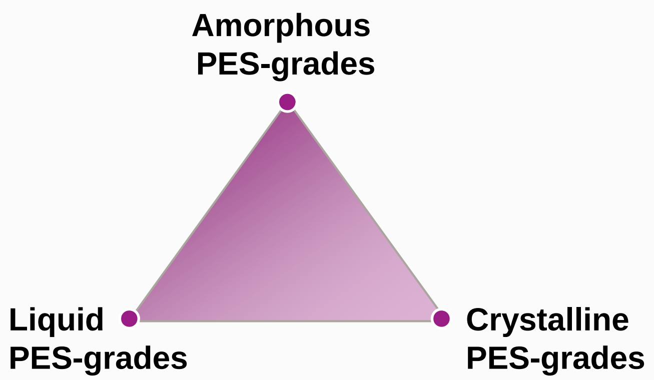
Characteristics:
- Medium molecular weight (M_n 2.000 – 8.000 g/mol)
- Linear
- Hydroxyl end groups

Conventional Polyester Raw Materials

Petrochemical Raw Materials	Petrochemical-based Monomers	Conventional Polyester-Polyols
Natural gas, Natural oil	Aromatic & aliphatic diesters, dicarboxylic acids & diols	Not bio-based, but possibly biodegradable

Polyester Polyols as building block system for RHM formulations

Building block system



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

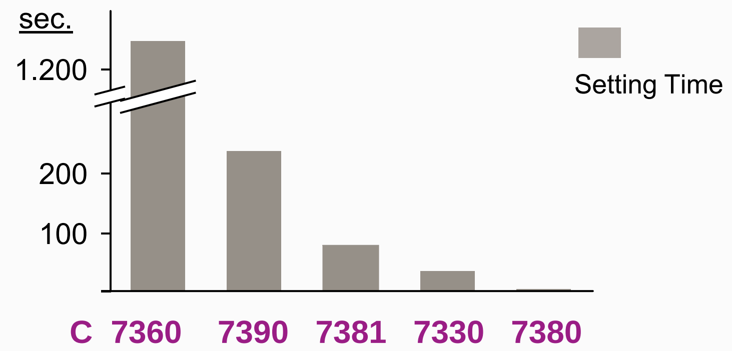
allow a precise formulation of the RHM.

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]

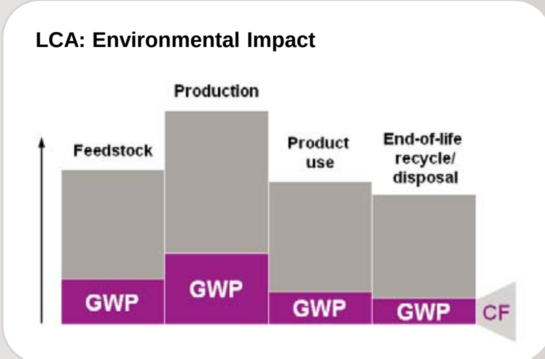


Why should Polyester Polyols go green?

Ecological Reasons

Megatrend Resource Efficiency

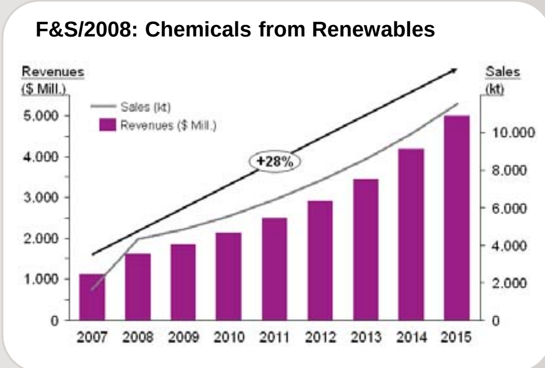
- Slow-down of general climatic change due to less greenhouse gases
- Lower Carbon Footprint (CF) leads to less Global Warming Potential (GWP)



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

Renewable Raw Materials	Bio-based Monomers	Bio-based Polyester-Polyols
Millet, Corn, Ricinus Oil, Sugar	Aliphatic Diacids & Diols	Possibly additionally biodegradable

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:

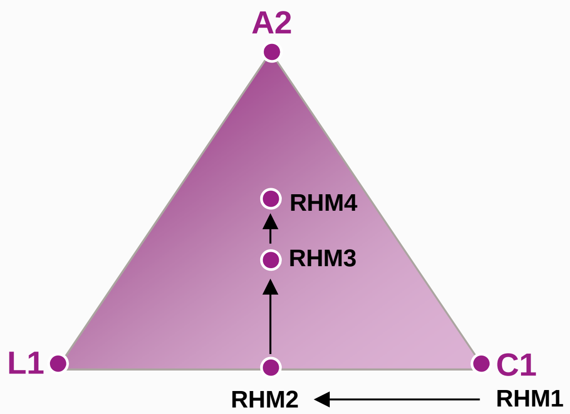
DYNACOLL® ***Terra***

	Properties:	Portion of renewables [%]	Softening Point (R&B) [°C]	Melt Viscosity [Pa s]
Amorphous grades	A 1	> 30	85	35 (130°C)
	A 2	> 30	85	32 (130°C)
Liquid grades	L 1	> 85	-	4 (80°C)
	L 2	> 75	-	4 (80°C)
Crystalline grades	C 1	100	65	2 (80°C)
	C 2	100	75	3 (80°C)

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:

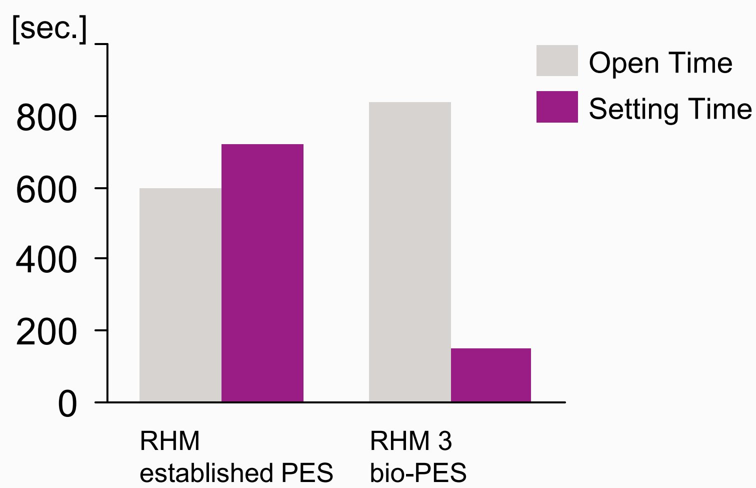
A2 bio-polyol:	30 ppw
L1 bio-polyol:	30 ppw
C1 bio-polyol:	40 ppw

& 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



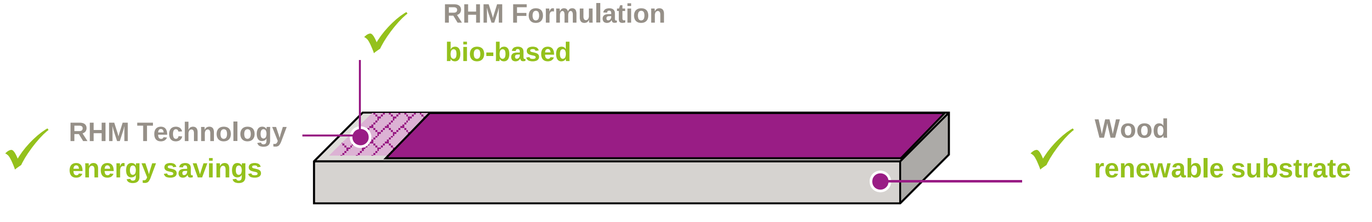
Three times resource efficiency in woodworking applications

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

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

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

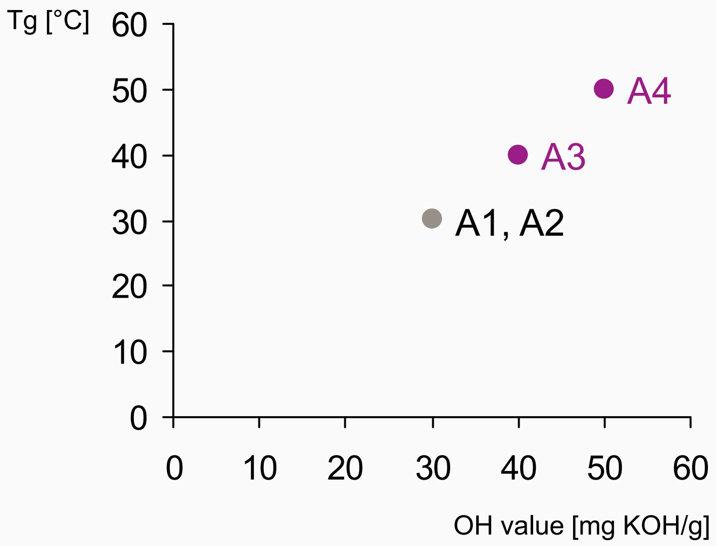
Properties of the two new amorphous bio-based Polyesters

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

Properties:

	Portion of renewables [%]	Softening Point (R&B) [°C]	Melt Viscosity [Pa s]
A 1	> 30	85	35 (130°C)
A 2	> 30	85	32 (130°C)
A 3	> 35	90	17 (130°C)
A 4	> 30	95	15 (130°C)

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

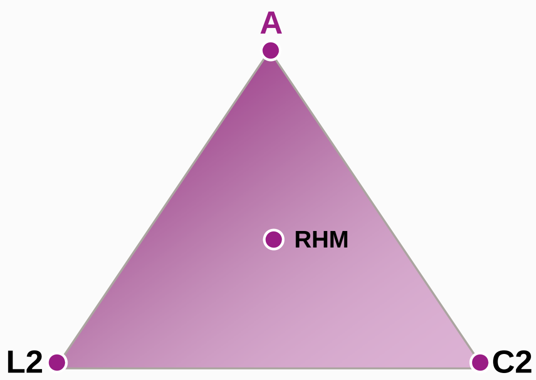


Achievement

Broader variety of bio-based Polyester Polyols for more versatile RHM formulations

RHM formulation results with the new amorphous grades

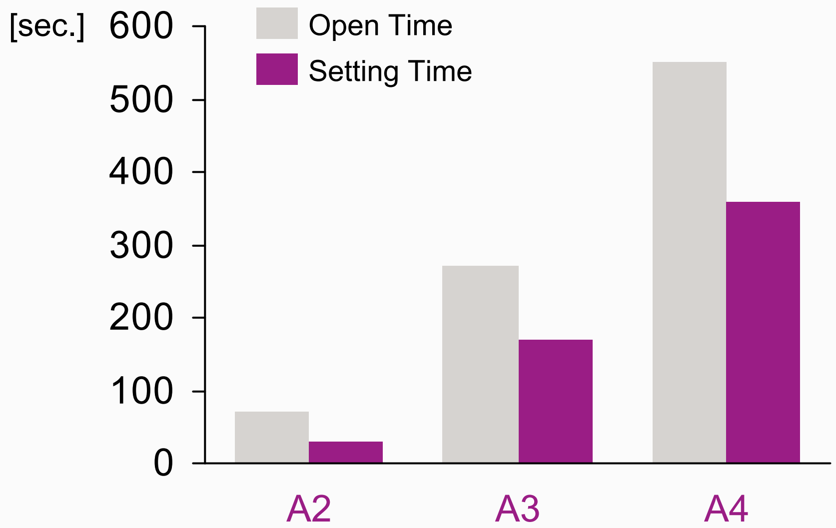
Composition of test formulation



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



Compa-tibility results

Phase separation | **Opaque** | **Cloudy**

RHM with faster setting for edge banding applications

New highly crystalline bio-based Polyester was developed

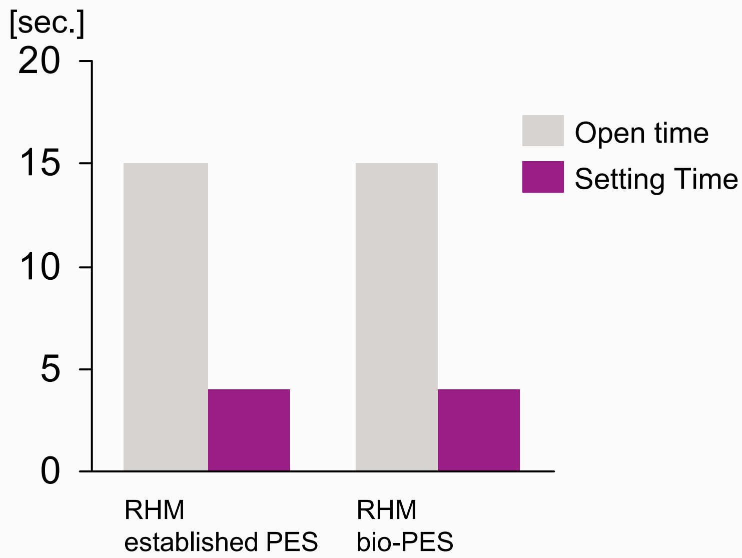
Properties:

	Portion of renewables [%]	Softening Point (R&B) [°C]	Degree of crystallinity
C 1	100	65	
C 2	100	75	
C 3	> 60	80	

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]

Application Example:
Edge Banding



Summary

EVONIK INDUSTRIES

Keep an eye on green solutions!

New bio-based Polyester Polyols offer new opportunites!

- ✓ 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

EVONIK
INDUSTRIES