

BIO-BASED POLYESTER POLYOLS FOR REACTIVE PUR HOT MELTS

The search for bio-based monomers has been successful

The first polyester polyols based on renewable raw materials have been developed and are ready for the market. What were the challenges of developing bio-based polyester and producing the first guide formulations for reactive PU hot melt adhesives? The following article provides some information and compares the property profiles of various RHM model formulations based on these new polyester polyols.

SABINE THÜNER, GABRIELE BRENNER,
DR. CHRISTINA DIEHL

The development of tailored hydroxyl group-based polyester polyols already had a major effect on the technology of one-component moisture-curing hot melt adhesives several years ago. Since then, the amorphous, liquid, and crystalline copolyesters, which can be combined according to a building block concept, have allowed specific formulations of reactive PUR hot melts (RHM) for many applications in the adhesive and sealant industries. Market analysis confirm rapid and significant growth in the past: global demand for polyester polyols grew by an average of 5.4% per annum between 2005 and 2008 /1/.

The one-component PUR hot melts based on polyester polyols are very resistant to high temperatures, have high final strengths, low processing temperatures, and a broad adhesion spectrum on many different substrates. Very high initial strengths also enable rapid further processing - the advantages are obvious: short cycle times translate into energy efficiency and high levels of productivity.

Green policy shift

While in the past conventional polyester polyols were almost all based on petro-

chemical monomer building blocks (Figure 1), for several years the R&D departments of the polymer designers have been facing new challenges.

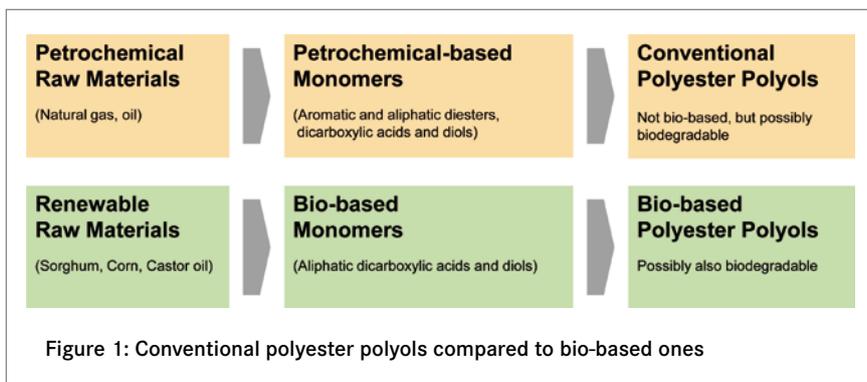
Demand for the increased use of renewable raw materials in the chemical industry has increased constantly since the adoption of the Kyoto Protocol in 1997 and now extends well beyond simply developing bio-fuels. The entire chemical industry has been undergoing a green policy shift for many years and is continuously strengthening its profitable sustainability image. Resource efficiency is regarded as one of the growth drivers of the future. This is confirmed, for example, in an analysis carried out by management consultant Frost & Sullivan /2/ in 2008, according to which sales in the global market for chemicals from renewable

raw materials will grow by 28% between 2007 and 2015 (Figure 2).

Renewable raw materials are defined as agricultural and forestry products that are used by humans to generate heat, electricity or fuel, or to manufacture base chemicals. As opposed to petrochemical substances, renewable raw materials are not finite and thus help to provide sustainable resources.

Identifying bio-based monomers

The challenges of material use begin with identifying suitable monomers. The petrochemical-based aromatic and aliphatic diesters, dicarboxylic acids, and diols used to produce polyester polyols are generally not available as bio-based materials. Consequently, they cannot simply be replaced, which means that innovative, bio-based



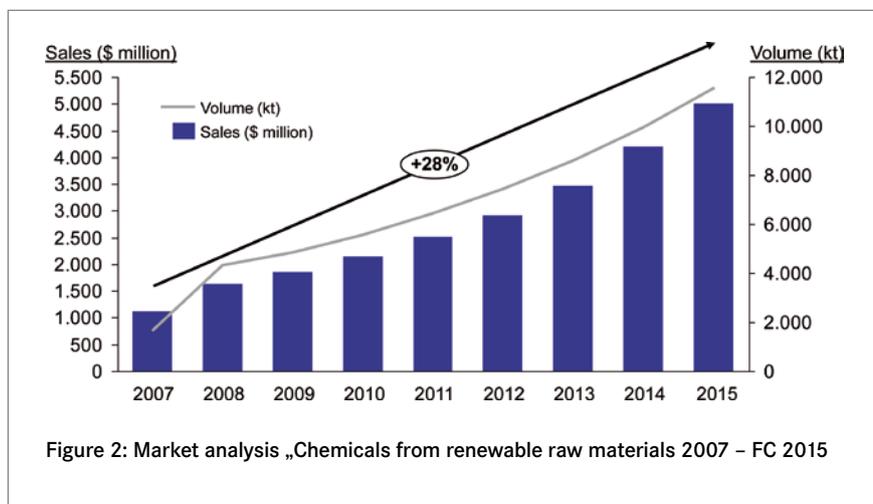


Figure 2: Market analysis „Chemicals from renewable raw materials 2007 – FC 2015

When the polyester has been developed on the basis of bio-based monomers, several other questions are raised. Does it also fulfill the requirements profile that is needed for reactive PUR hot melts? In other words, does the polyester have the desired necessary physical properties, especially regarding melting point and glass transition temperature? These properties can be set specifically by selecting the right monomers and also through the relative composition of the monomers. In particular, viscosity, melting point and glass transition temperature essentially determine the property profile of the formulated PUR hot melts.

monomers have to be identified and tested according to their suitability for polyester synthesis. The main focus of the research is the basic suitability of bio-based dicarboxylic acids or diols, for example, from sorghum, corn, or castor oil: is there sufficient reactivity in the polycondensation reaction and are they incorporated in the polyester? Do they have sufficient stability under the harsh reaction conditions of melt polymerization so that decomposition or other secondary reactions can be excluded?

If these elementary requirements are fulfilled, basically many novel monomers are suitable, which, in some cases are not even accessible via petrochemicals. This could enable access to innovative polyesters for the formulation of adhesives with improved properties. For example, long-chain linear monomers that could be recovered from fats and oils are recommended for synthesizing high-crystalline polyesters with increased initial strength.

Two objectives should be pursued in the development of bio-based polyester polyols:

- The action spectrum of the adhesive formulators must not be restricted; in other words, a diverse combination of amorphous, liquid, and crystalline polyesters based on the building block concept must also be possible with the bio-based types.

- A high share of bio-based monomers in the polyester is desirable; the minimum content should be 30% by weight.

Bio-polyester: status quo

The first bio-based polyester polyols that fulfill these requirements have been developed and marketed under the brand

Bio-based polyester types	Share of bio-based monomers	OH-value	Acid value	Glass transition temperature	Melting Point	Softening Point (R&B)	Melt viscosity
	[%]	[mg KOH/g]	[mg KOH/g]	[°C]	[°C]	[°C]	[Pa s]
Amorphous							
A 1	> 30	30	max. 2	30	-	85	35 (130°C)
A 2	> 30	30	max. 2	30	-	90	32 (130°C)
Liquid							
F 1	> 85	30	max. 2	-38	-	-	4 (80°C)
F 2	> 75	30	max. 2	-41	-	-	4 (80°C)
Crystalline							
K 1	100	30	max. 2	-45	55	60	2 (80°C)
K 2	100	30	max. 2	-20	65	80	3 (80°C)

Figure 3: Characteristics of bio-based polyester types

RHM based on bio-polyesters	Melt viscosity 130°C	Softening point (R+B)	Open time	Setting time	Tensile strength*)	Elongation*)
	[Pa.s]	[°C]	[sec]	[sec]	[N/mm ²]	[%]
Amorphous						
A1	400	105	< 5	< 5		brittle
A2	350	100	< 5	< 5		brittle
Liquid						
F1	5	(-)	> 24h	> 24h	10	1100
F2	4	(-)	> 24h	> 24h	15	1200
Crystalline						
K1	6	61	660	150	27	600
K2	4	78	100	50	28	500

*) after 7 d of moisture-curing at 20°C and 65% relative humidity

Figure 4: Properties of reactive hotmelts based on bio-based polyester polyols

name Dynacoll Terra. Adhesive formulators can currently be provided with six different bio-polyesters - two amorphous, two liquid, and two crystalline types. To achieve sufficient cross-link density and, at the same time, good, manageable viscosities, an OH value of 30 was chosen. Figure 3 contains an overview of the properties of these bio-based polyester types.

In model experiments the polyester polyols were combined with each other in terms of a building block system in many different mixing ratios and the physical and adhesive properties of the reactive hot melts were tested. Depending on the selection and the mixing ratio of amorphous, liquid, or crystalline types the properties of the reactive hot melts (RHMs) can be tailored using known methods.

RHM formulations with bio-polyesters

An analysis of the important properties of hot melts, such as viscosity, open time, setting behavior, initial strength, and cohesion provide the first information in the development of guide formulations.

The manufacture of moisture-curing hot melt adhesives in the melt is done by converting the polyols and mixtures of them with pure 4,4'-diphenylmethane diisocyanate (MDI) in an OH/NCO ratio of 1/2.2.

To determine the open time, paper strips are applied to the adhesive film at defined intervals and are then pulled off again as soon as the surface is tack-free. The open time is the point in time when the last removed paper strip exhibits fiber tear. With setting time the point in time when two T-shaped bonded 2-cm wide beech wood substrates can be loaded with a 500-g weight is determined.

Initially, the properties of reactive hot melts were determined on the basis of the individual polyester polyols. As Figure 4 shows, the amorphous polyesters have shorter open times and setting times, while the liquid types allow formulation of highly flexible adhesives. The crystalline products control the setting behavior and increase cohesion of the adhesive.

In other experiments the RHM properties of binary and ternary polyol mixtures of selected polyester types were investigated. Based on RHM 1, which is based on polyester K1, the addition of the liquid polyester F1 prolongs the open time and the setting time of reactive hotmelt RHM 2. On the other hand, the RHM formulations 3 and 4, based on ternary mixtures of A2, F1, and K1, exhibit long open times and a relatively short setting time. With the addition of an amorphous type the relatively long

open time remains but the setting time is shortened. To shorten the setting time even more and to increase the initial strength for applications such as profile wrapping the higher crystalline polyester K2 (formulations RHM5 and RHM6) is suitable (Figure 5).

Adhesion requirements

Apart from the physical properties of a formulation, naturally the adhesive must also fulfill adhesion requirements. Ternary mixture RHM 3 exhibited especially good adhesion properties on many different substrates after being cured for 7 days at 20°C and 65% relative humidity (Figure 6).

The versatility of the adhesion spectrum is very important, since reactive hot melts processed with standard equipment (such as roller application systems) are used in joining techniques in many different industries. While the focus in the woodworking industry is on edge banding, profile wrapping, and flat lamination, in the automotive industry hot melt adhesives are used mainly in car interiors to adhere many different substrates. Other areas of application for reactive PUR hot melts are book spines, sandwich bonding in the construction industry (Figure 7) and bonding in the textile industry, such as breathable membranes.

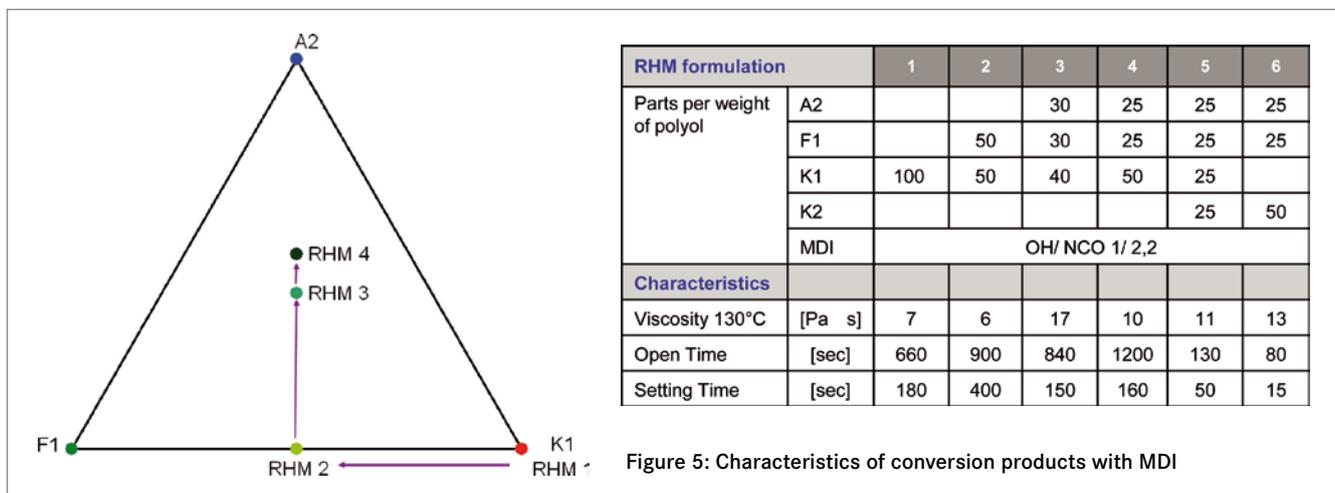


Figure 5: Characteristics of conversion products with MDI

Shorter setting time for flat lamination

With consideration of using bio-based polyester polyols in reactive PUR hot melts, the RHM3 formulation produced especially positive results in the flat lamination of wooden materials (Figure 8).

In many cases, reactive hot melt adhesives formulated exclusively with conventional polyester polyols do not fulfill the requirements profile for flat lamination as regards very long open times to ensure sufficiently long handling times in combination with a good initial strength and relatively short setting time. With a suitable combination of the innovative bio-polyesters it is now possible to formulate reactive hot melts with the desired improved properties.

The idea of “green chemistry” is especially obvious in the lamination of wooden surfaces, since ecological sustainability takes place in the form of a three-level cascade:

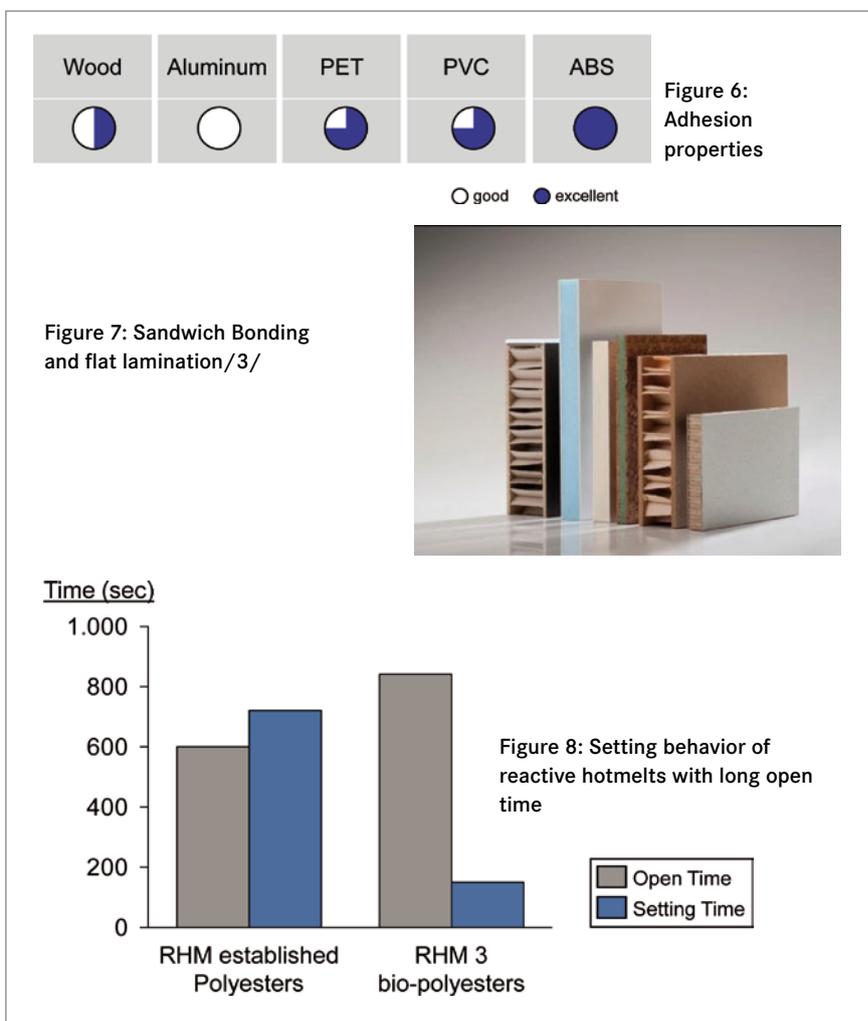
- Use of energy-efficient reactive hot melt (RHM)
- Formulating the RHM on the basis of bio-based polyester polyols
- Bonding on the renewable material, wood.

Other applications are following: first decorative materials based on renewable raw materials are available within the automotive industry.

Outlook

Apart from the many different activities from researchers and developers in the industry, several institutes are also working intensively in the field of “chemistry from renewable raw materials”. In close collaboration between companies and institutes, research is being carried out into new solutions for the sustainable use of resources.

In spite of the first successes with bio-based polyesters to formulate reactive PU hot melts, development work in this field is still in its infancy. Continuous monitoring of the market



with the focus on new, commercially available raw materials is a requirement for complete raw material screening to discover bio-based monomers for polyester synthesis. Apart from the sustainable replacement of petrochemical monomers another focus is on the use of novel monomers which are only available from renewable sources. In this way it will be possible to synthesize polyester polyols that are not only bio-based but that also have improved property profiles for use in reactive hot melts. This will enable new fields of application to be opened up. ■

The authors References

Sabine Thüner (sabine.thuener@evonik.com) is Marketing Manager Hot Melts at Evonik Industries AG in Marl, Germany. Gabriele Brenner (gabriele.brenner@evonik.com) manages Applied Technology Reactive Hot Melts, and Dr. Christina Diehl (christina.diehl@evonik.com) manages Innovation Management Adhesive Polyesters.

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