Biosuccinium
for sustainable materials

Lawrence Theunissen and **Richard Janssen** of **Reverdia** look at the use of bio-based succinic acid in thermoplastic polyurethanes*

The need to reduce dependency on fossil fuels, a growing world population and an increased concern for the environment are driving companies to supplement oil-based chemicals with plant-based, sustainable, high-quality chemical building blocks. Among the companies active in this field is Reverdia, a JV between DSM and Roquette Frères, which produces the Biosuccinium** band of bio-based succinic acid (bio-SA).

Reverdia has produced Biosuccinium in a 300 tonnes/year capacity demonstration plant at Roquette's site in Lestrem, France, since 2010. This facility is used for process validation and optimisation, in particular towards polymer-grade product quality, as well as to provide tonne-scale quantities of Biosuccinium to customers for internal testing and application development.

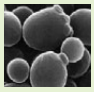
At the end of 2012, Reverdia started operations in the world's first commercial-scale bio-SA facility at Roquette's large biorefinery site in Cassano Spinola, near Genoa's harbour in Italy, with 10,000 tonnes/year capacity. This plant is backward-integrated into the biorefinery that produces the raw material carbon source and will also employ the co-generation of steam and electricity and on-site waste water treatment.

Yeast-based technology

Reverdia is the only company currently employing low-pH yeast technology derived from the parent companies rather than bacteria to produce bio-SA. This has several benefits (Figure 1). The proprietary technology is simple and converts feedstock directly to succinic acid. Bacteria-based processes are indirect and therefore require extra chemical processing, additional equipment and additional energy to convert intermediate succinate salts into succinic acid.

The low-pH yeast process is also much less vulnerable to infection. As a result, production equipment requires less cleaning and handling, which improves product consistency and quality.

Figure 1 - Yeast v. bacteria process comparison

		Yeast 	Bacteria 
Fermentation	Production at pH 3	● (green)	● (red)
	Robustness/phage infection	● (green)	● (yellow)
Recovery	Product purity	● (green)	● (yellow)
	No waste salts	● (green)	● (red)
	Simple purification	● (green)	● (yellow)
Carbon footprint	Compared to petrochemical	● (green)	● (yellow)

It also results in fewer impurities and undesired by-products. Bacterial processes often suffer from mono-acid by-products, which may cause unwanted side reactions in polymerisation reactions that use succinic acid and the formation of certain compounds that lead to undesired discoloration.

Biosuccinium is also produced in an ecologically sensitive way. A life-cycle assessment, performed by CE Consult and validated by Patel and Roes of the Copernicus Institute in the Netherlands, compared the carbon footprint of its production to that of fossil-fuel based adipic acid from public domain and internal validation. Biosuccinium scored 0.9 kg CO_2/kg acid, adipic acid 9.0.

Market potential

Current markets for succinic acid include pharmaceuticals, food, coatings and pigments, but Reverdia believes that the production of a good-quality bio-SA like Biosuccinium will help drive the emergence of new markets and new applications, notably bio-based polybutylene succinate (PBS), polyurethanes, plasticisers, composite and coating resins and 1,4-butanediol (BDO). These materials and intermediates are used in end products as diverse as packaging, footwear, clothing, shopping bags, mulch films and automotive interiors.

For some products, such as PBS, Biosuccinium is positioned as a direct substitute for petrochemical-based succinic acid. In this case, the base molecule is identical, regardless of its origin, so the properties of the end product are identical. This has been demonstrated by our own investigations as well as by feedback from commercial PBS producers.

For many other products, such as polyester polyols, plasticisers and resins, Biosuccinium is an alternative to adipic acid. In this case, the molecule is similar but slightly different from the incumbent, so the performance characteristics of the end product may be different. Biosuccinium is a near drop-in in these cases.

In general there have not been many publications about the use of succinic acid as a substitute for adipic acid and the resulting properties. Reverdia believes that it is important to know and understand the differences between the two in order to drive wider, more value-added potential applications for Biosuccinium.

Table 1 - Composition of polyols

Polyol	Di-acid	Diol	Renewable content (%w)	Mn (g/mol)	Acid value (mg KOH/g)	OH value (mg KOH/g)	Viscosity (cPoise@75°C)	Melt temp. (°C)
BS	Biosuccinium	BDO	~50	2,000 1,880	1.1 1.9	53.9 53.7	Solid Solid	113 108
BA	Adipic acid	BDO	0	2,117	0.1	52.9	733	60
EBS	Biosuccinium	BDO+EG[1]	~55	2,004	1.1	54.9	1,284	55
EBA	Adipic acid	BDO+EG[1]	0	2,004	1.3	54.7	579	17[2]
PS	Biosuccinium	PDO	100	1,979	0.75	56.7	1,960 (70°C)	48

Notes: 1 - BDO/EG ratio 50/50 mol%. 2 - Measured using DSC (10°C/minute heating rate)

Application example

Thermoplastic polyurethanes (TPU) are produced by polymerising isocyanates, typically either MDI or TDI, with polyols. The nature of the polyol is subject to many more variables: they might be distinguished by type (ether, ester, carbonate, etc.) or by physical characteristics, such as molecular weight and functionality.

In order to assess the feasibility of Biosuccinium as a sustainable raw material for TPUs, polyester polyols with a molecular weight of about 2,000 g/mol (Table 1) were prepared and characterised, followed by polymerisation with MDI.

Since succinic acid has only four carbon atoms whereas adipic acid has six, the succinic acid-based polyester polyols have a higher density of ester groups, leading to a higher level of molecular chain interaction which in turn causes a higher melting point and higher viscosity levels. The fully bio-based propanediol-succinate (PS) polyols have a melting temperature similar to their benchmark petrochemical butanediol-adipate (BA) polyols, but their viscosity is still relatively high.

Although the differentiating characteristics of these succinate polyols may have an impact in terms of handling and processing (the BS polyol is solid at typical processing temperatures), the aforementioned polyester polyols could be converted to TPUs according to industry-standard formulations and a standard one-step process.

The various soft segment polyols were finished by reaction with MDI and 1,4-BDO as the chain extender. TPUs were prepared at various percentages of hard segments, leading to materials ranging in hardness from approximately 88 Shore A up to 70 Shore D (Table 2). Based on these results it is expected that also other degrees of hardness can be produced.

Most of the TPUs have properties in line with expectations, and should be able to find their way into suitable applications. There is one exception though: the TPU based on the BS polyol and hard block content of 48%. Due to the high degree of crystallinity of the soft block, this specific TPU shows thermoplastic instead of elastomeric behaviour, being very hard and fairly stiff, with a yield point.

Reverdia has just opened a commercial-scale bio-SA plant in Italy

The apparently high crystallinity in the soft block can be avoided by the incorporation of a certain amount of co-monomers that do not match the 'structure' of succinic acid and BDO, which are both C_4 monomers. These might be alternative diols, like ethylene-glycol or propanediol, or alternative di-acids, like adipic acid or sebacic acid. Some of these co-monomers can also be bio-based, which allows for further increase of renewable content in the final application

The use of bio-based 1,3-propanediol from DuPont Tate & Lyle Bio Products instead of 1,4-BDO in the polyester polyol further increases the renewable content of TPU. The properties of these PS polyol-based TPUs are shown in Table 3.

Summary

Although no attempt has been made to optimise any of the polyols or polyurethanes for specific applications or uses in the work presented above, it clearly demonstrates that Biosuccinium and Biosuccinium-based polyester polyols are a feasible raw material for TPU.

Obviously when replacing one monomer with another, slightly different one, the resulting product may have slightly different performance, but for many applications this performance will still be acceptable and in some cases may even outperform the current option. Reverdia will continue to investigate the performance of Biosuccinium-based materials and applications proactively and communicate the results to the industry.

* - This article is partly based on work done in collaboration with DuPont Tate & Lyle Bioproducts
** - Biosuccinium is a trade mark of Reverdia

■ Contact
Linda van Egmond
Interim Marketing Manager
Reverdia
Tel: +31 6 51 690 916
E-mail: linda.egmond-van@reverdia.com
Website: www.reverdia.com

Table 2 - Formulations & properties of TPU based on Biosuccinium, BDO & EG

Polyol type	Chain extender	Renewable Content (%)	Hard block (%w)	Hardness (ShoreA)	Strength at break (MPa)[2]	Elongation at break (%)[2]	Abrasion (mg loss)[3]	Swell index Toluene (%)[4]	Swell index MEK (%)[4]
BS	BDO	~20	48	93	41.9	1,200	61	5	23
		~25	36	70D[1]	–	–	–	–	–
BA	BDO	0	48	93	46.8	1,500	16	16	54
EBS	BDO	~35	48	94	53.3	1,350	3	3	29
		~35	36	88	32.3	1,600	–	–	–
EBA	BDO	0	48	90	23.1	1,500	11	11	45

Notes: 1 - This TPU shows thermoplastic behaviour rather than elastomeric behaviour. This effect is less for polyols of Mw = 1,000 g/mol. 2 - Tensile test on ISO 37-3 samples, test speed 200 mm/min. 3 - Taber abrasion resistance: 500 rotations, 1,000 gram, H18 wheels. 4 - Done by exposure of the TPU to toluene (apolar solvent) and MEK (polar solvent), for 48 hours at 23°C

Table 3 - Formulations & properties of TPU based on propylene succinate polymers

Polyol type	Chain extender	Renewable content (%w)	Hard block (%)	Hardness (ShoreA)	Strength at break (MPa)[2] RT	Strength at break (MPa)[2] 50°C	Strength at break (MPa)[2] 70°C	Elongation at break (%)[1]	Resilience (%)
PS	PDO	~70	22	64	18.6	8.8[1]	5.6[1]	831	10
		~60	31	~85[1]	15.7	12.3[1]	10.6[1]	559	–
	BDO	~65	23	67	4.25	–	–	656	26
		~50	33	~85	9.99	–	–	562	–

Notes: 1 - Samples reached maximum oven height and did not break. 2 - Tensile test acc. ASTM D-412; test speed 200 mm/minute