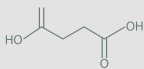
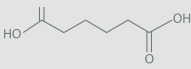


ENABLING SUSTAINABLE MATERIALS

INTRODUCTION

BIOSUCCINIUM®, a 100% bio-based raw material, enables production of polyester polyol (PESP) and polyurethane products with substantially lower environmental footprint. BIOSUCCINIUM® offers an alternative to conventional fossil-based chemicals, such as adipic acid, for the polyester polyol and polyurethanes industry. Up to today, very limited practical work has been published to evaluate the effect of succinic acid in polyester polyols and polyurethanes. Therefore, experiments have been conducted that can give direction to the development of BIOSUCCINIUM®, enabling sustainable microcellular polyurethanes. No attempt has been made to optimize any of the polyols or polyurethanes for specific applications or uses.

Table 1: Properties of succinic and adipic acid

	Succinic acid	Adipic acid
Molecular structure		
Molecular formula	C ₄ H ₆ O ₄	C ₆ H ₁₀ O ₄
Molecular mass [g/mol]	118.09	146.14
Melting temperature [°C]	184	152

REPLACING FOSSIL-BASED ADIPIC ACID

BIOSUCCINIUM® is a shorter molecule, with less carbon atoms, compared to adipic acid. Consequently, succinic acid polyester polyols will have a higher density of ester groups, which is expected to influence polyol and polyurethane properties to some extent. The renewable content of a polyester polyol using BIOSUCCINIUM® is about 40-60 % and can be increased further by using biobased glycols like bio-based EG, 1,3-PDO or 1,4-BDO.

POLYESTER POLYOLS

Polyester polyols have been synthesized with a molecular weight of 2000 g/mol. Preparation of these polyols was completed without problems and the resulting properties are shown in table 2.

Table 2: Formulation and properties of 2000 g/mol BIOSUCCINIUM® and adipate polyols

Polyol	Di-acid	Diols ¹	Renewable content (%w)	Molecular mass [g/mol]	Acid value [mg KOH/g]	OH value [mg KOH/g]	Viscosity [cPoise @75C]	Oven temperature ⁴ [°C]
EDS	BIOSUCCINIUM®	EG + DEG	-57	2044	0.5	54.5	1405	70
EDSS	BIOSUCCINIUM® +Sebacic acid ³	EG + DEG	-63	1941	0.5	57.3	1292	50
EDA	Adipic acid	EG + DEG	0	1908	1.1	57.7	502	50
P716	Adipic acid	EG + DEG	0	~2000	< 0.5	~56.1	520	50
EDSS-mix	BIOSUCCINIUM® +Sebacic acid ³	EG + DEG ²	-62	1300 2150	0.4 0.4	87 48	480 @70C 1320 @70C	50

(1): EG / DEG ratio 60 / 40 mol %

(2): EG / DEG ratio 50 / 50 mol %

(3): succinic acid / sebacic acid ratio 85 / 15 mol%

(4): oven temperature used to melt the polyol

The main difference between adipate and succinate polyols relates to the tendency of succinate polyols to crystallize, which in turn affects the melting temperature and the viscosity. This is especially noticeable in the polyol with BIOSUCCINIUM® as the sole dicarboxylic acid, which is solid at conventional processing temperatures, meaning that higher processing temperatures are required. The incorporation of some sebacic acid strongly suppresses that effect, resulting in an amorphous polyol but still with a higher viscosity than the adipate polyol.

POLYURETHANES FOR SINGLE DENSITY UNIT SOLE

First, a polyol blend has been prepared by blending each of the above polyols (86w%) with an activator blend (14w%, catalyst, surfactant, water).

Microcellular polyurethane elastomers have been prepared by heating the components to 40°C, and mixing the polyol blend with an MDI prepolymer (NCO-content = 19%), at a mixing ratio of polyol: prepolymer of 100 : 88 w/w. Reactivity was compared using 200ml polystyrene cups for various ratios (2% steps). Table 3 shows the process characteristics at the “best molded ratio”. Gel time was not recorded since all formulations started to cream during mixing.

Table 3. Reactivity evaluation of microcellular PU elastomers

Elastomer	Polyol	Mix ratio P:I = 100: ..	Tack free time [s]	Rise time [s]	Pinch time [s]	Cup cure ¹ @ 2 min	Slab demould ¹ @ 4 min	Corner bend @ 4 min
PU1	EDS	82	45	45	65	Good	Good	No cracks
PU2	EDSS	84	50	50	85	Good	Good	No cracks
PU3	EDA	84	40	40	90	Quite good	Quite good	No cracks
PU4	P716	86	60	40	80	Good	Good	No cracks

(1): On a scale of Good (full recovery), Quite good, Slightly soft, Soft (no recovery)

Microcellular PU elastomers were moulded into 6mm slabs at a target density of 0,6g/cm³, at the best molded ratio +/- 2%. Table 4 shows physical properties of the elastomers at the best molded ratio.

The mechanical properties of elastomers based on BIOSUCCINIUM[®], both EDS and EDSS polyols, are quite similar to the conventional adipate polyols based elastomers (table 2). Only exception is the abrasion resistance of the EDS based elastomer which is slightly better.

Table 4. Physical properties of microcellular PU elastomers

Elastomer	Polyol	Mix ratio P:I = 100: ..	Renewable content ¹ %	Density [g/cm ³]	Hardness ShoreA	Tensile strength [MPa]	Strain at break [%]	Tear strength [N/mm]	Abrasion resistance [mg weight loss]
PU1	EDS	82	>28	0.56	46	3.5	235	26	15.0
		84	>28	0.60	48	5.0	270	31	n.d.
PU2	EDSS	84	>30	0.51	37	3.7	280	22	18.3
PU3	EDA	84	0	0.56	46	4.3	340	32	19.1
PU4	P716	86	0	0.47	38	3.7	300	24	18.4

(1): Biocontent originating from the di-carboxylic acids only. Using biobased EG or DEG will further increase biocontent.

(2): Tensile test on ISO 37-3 samples; test speed 500mm/min

(3): Taber abrasion resistance: 1000 rotations, 1000gram/wheel, H18 wheels

POLYURETHANES FOR MID SOLE AND OUTER SOLE

In a separate study, a similar comparison was made for elastomers targeted at shock absorbing middle sole as well as abrasion resistant outer soles. In these studies a blend of EDSS polyols has been used (Mn=1300 and Mn = 2150), which is compared against a similar blend of EDA polyols (also Mn=1300 and Mn = 2150).

Using a standard process setup, the bio-based polyols were reacted with an NCO-prepolymer (NCO-content = 20%) used to produce biobased shoe soles with comparable properties to petro-based shoe soles.

Table 5. Reactivity evaluation of microcellular PU elastomers

Sole type	Elastomer	Polyol	Mix ratio P:I = 100: ..	Process temperature P/I [°C]	Gelation time [s]	Rise time [s]	Free rise density [g/cm ³]	Demol- ding time [s]	Mould temperature [°C]
Mid sole (bio)	PU5	EDSS-mix	79	45 / 40	~6	53	~0.22	5 min	~50
Mid sole (petro)	PU6	EDA-mix	81	45 / 40	~6	59	~0.22	5 min	~50
Outer sole (bio)	PU7	EDSS-mix	94	45 / 40	~6	~29	~0.27	5 min	~50
Outer sole (petro)	PU8	EDA-mix	92	45 / 40	~6	~30	~0.27	5 min	~50

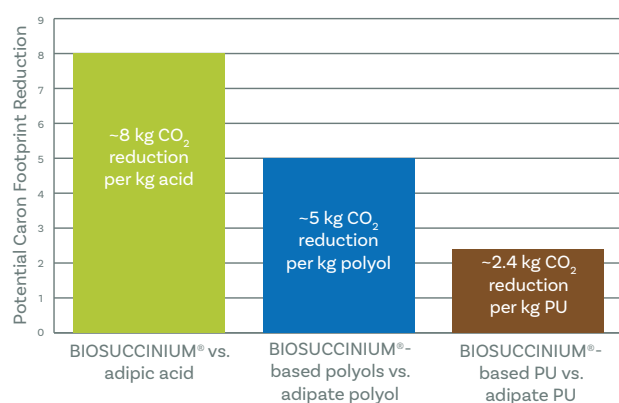
Table 6. Properties of microcellular PU elastomers

Sole type	Elastomer	Polyol	Renewable content1 %	Density [g/cm3]	Hardness ShoreA	Tensile strength [MPa]	Strain at break [%]	Tear strength [N/mm]	Abrasion resistance [mg weight loss]
Mid sole (bio)	PU5	EDSS-mix	~30	0.5	29	2.7	489	17	-
Mid sole (petro)	PU6	EDA-mix	0	0.5	47	2.9	543	18	-
Outer sole (bio)	PU7	EDSS-mix	~27	0.65	64	11.1	553	55	43
Outer sole (petro)	PU8	EDA-mix	0	0.65	66	11.4	570	58	46

SUSTAINABILITY IMPACT

BIOSUCCINIUM® sustainable succinic acid is a potential alternative for (fossil-based) adipic acid as raw material for polyester polyols and polyurethanes. This enables an improvement of the sustainability characteristics of polyester polyols and polyurethane materials (figure 1).

Figure 1. Indicative examples of carbon footprint reduction (kg CO₂ per kg acid, polyol and PU, respectively) enabled by using BIOSUCCINIUM® instead of adipic acid



* Data courtesy of Huafon New Material, China
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HOW TO ORDER BIOSUCCINIUM®

Production

BIOSUCCINIUM® is available in commercial quantities from the first large scale commercial production plant, located in Cassano, Italy. Samples for evaluation are available, as well. The biotechnology process to produce BIOSUCCINIUM® was developed by Reverdia, a joint venture between DSM and Roquette. Since Reverdia's dissolution in April 2019, Roquette now manufactures and sells BIOSUCCINIUM® under licence from DSM. Please contact Roquette at www.roquette.com for more information.

USDA CERTIFICATION

Roquette has earned the U.S. Department of Agriculture (USDA) Certified Biobased Product label. The product, BIOSUCCINIUM® succinic acid, is now able to display a unique USDA label that highlights its percentage of biobased content. It shows that BIOSUCCINIUM® contains 100% USDA certified biobased content.



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