biosuccinium®

sustainable succinic acid

enabling sustainable materials

POLYESTER POLYOLS AND THERMOPLASTIC POLYURETHANES DATA SHEET

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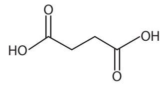
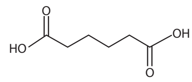
INTRODUCTION

Biosuccinium™ sustainable succinic acid is a 100% bio-based raw material that enables production of polyester polyol (PESP) and polyurethane (PU) products with substantially lower environmental footprints. Biosuccinium™ offers an alternative to conventional fossilbased chemicals—such as adipic acid—for the polyester polyol and polyurethanes industry.

To date, very limited practical work has been published to evaluate the effect of succinic acid in polyester polyols and polyurethanes. Therefore, Reverdia has conducted experiments that can give direction to development of Biosuccinium™ enabled sustainable (thermoplastic) 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	$C_4H_6O_4$	$C_6H_{10}O_4$
Molecular mass [g/mol]	118,09	146,14
Melting temperature [°C]	184	152

REPLACING FOSSIL-BASED ADIPIC ACID

Biosuccinium™ is a "shorter carbon chain" molecule compared to adipic acid, thus, succinic acid polyester polyols will have a higher density of ester groups. It can be expected that this will influence PESP and PU properties to some extent. The renewable content of a polyester polyol using Biosuccinium™ is approximately 50%. To increase the renewable content even further, one may replace the commonly used petro-based 1,4-butanediol with bio-based 1,3-propanediol. Since the 1,3-propanediol molecule is shorter and has a different tacticity than 1,4-butanediol, final TPU properties may be affected.

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	Diol	Renewable content {%w}	Mn [g/mol]	Acid value [mg KOH/g]	OH value [mg KOH/g]	Viscosity [cPoise @75°C]	MeltTemp [°C]
BS	Biosuccinium™	BDO	~50	2000 1880	1.1 1.9	53.9 53.7	Solid Solid	113 108
BA	Adipic acid	BDO	0	2117	0.1	52.9	733	60
EBS	Biosuccinium™	BDO+EG(1)	~55	2004	1.1	54.9	1284	55
EBA	Adipic acid	BDO+EG(1)	0	2004	1.3	54.7	579	17(2)
PS	Biosuccinium™	PDO	100	1979	0.75	56.7	1960 (70°)	48

(1): BDO / EG ratio 50 / 50 mol %
(2): measured using DSC (10°C/min heating rate)

The main difference between adipate and succinate polyols is related to the degree of crystallinity of the polyol, which in turn affects the melting temperature and the viscosity. The BS polyols have a high melting temperature and are solid at conventional processing temperatures, meaning that higher processing temperatures are required. The PS polyols have a melting temperature similar to their benchmark adipate polyols, but their viscosity is still relatively high.

THERMOPLASTIC POLYURETHANE SYNTHESIS

Thermoplastic polyurethanes with varying hard block content have been prepared by reacting Biosucccinium™ polyester polyols with isocyanate (4,4-MDI) and chain extender. Both a one-shot and a prepolymer method have been investigated (table 3). The synthesis of most TPUs were completed without incidence with one exception. It was not possible to prepare prepolymer-based TPU of 2000 g/mol BS polyols with the available lab equipment. Prepolymers based on EBS or EB polyols with different molecular weight might be feasible but have not yet been tested.

Table 3: Conclusion on TPU syntheses with Biosuccinium™-based polyester polyols(1)

Polyol	Chain extender	Conclusion on TPU synthesis: One-shot method	Conclusion on TPU synthesis: Prepolymer method
BS	BDO	Higher temperature used (120°C), good reactivity, no additional gelling catalyst needed	Too high viscosity with 2000 g/mol polyol for processing in lab equipment
PS	PDO or BDO	Similar to conventional polyol, gelling catalyst used	Quasi prepolymer (NCO/OH 3/1) used because of high viscosity of regular prepolymer (NCO/OH 2/1)
EBS	BDO	Similar to conventional polyol	n.a.

(1): MDI has been used in all cases

THERMOPLASTIC POLYURETHANE PROPERTIES

Biosuccinium™ in combination with 1,4-Butanediol and Ethyleneglycol

TPUs based on BS polyols (table 2) exhibited very high hardness at relatively low hard segment concentrations, e.g. 55 ShoreD at 24% hard segment concentration. This is related to the high crystallinity of the 2000 g/mol BS polyol. The effect is less manifest for 1000 g/mol BS polyols or for polyols based on a combination of 1,4-butanediol and ethyleneglycol. The crystalllinity effect disappears at higher (e.g. > 40 %) hard segment concentrations.

The mechanical properties of TPUs based on Biosuccinium™—both BS and EBS polyols—are quite similar to the conventional adipate polyolsbased TPUs (table 4). Only exception is the abrasion resistance of the BS-based TPU which is slightly lower. The chemical resistance of the Biosuccinium™ TPUs is significantly better than the adipate versions for both apolar and polar solvents.

Table 4. Formulation and physical properties of TPU based on Biosuccinium™ and 1,4-Butanediol and Ethyleneglycol

Polyol type	Chain extender	Renewable content [%]	Hard block [%]	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 ~25	48 36	93 70D(1)	41.9 -	1200 -	61 -	5 -	23 -
BA	BDO	0	48	93	46.8	1500	34	16	54
EBS	BDO	~35 ~35	48 36	94 88	53.3 32.3	1350 1600	70 -	3 -	29 -
EBA	BDO	0	48	90	23.1	1500	66	11	45

(1): This TPU shows thermoplastic behaviour rather than elastomeric behaviour. This effect is less for polyols of Mw = 1000 g/mol
(2): Tensile test on ISO 37-3 samples; test speed 200mm/min
(3): Taber abrasion resistance: 500 rotations, 1000gram, H18 wheels
(4): Done by exposure of the TPU to toluene (apolar solvent) and MEK (polar solvent), for 48 hours at 23°C

Biosuccinium™ in combination with 1,3-Propanediol

The use of bio-based 1,3-propanediol (e.g. from DuPont Tate&Lyle Bio Products) instead of 1,4-butanediol in the polyester polyol further increases the renewable content of TPU. The properties of these PS polyol-based TPUs are shown in table 5. The hardness range that can be made for this type of TPU appears to be similar to PA polyol-based TPUs although the fringes of the range have not been investigated. The overall retention of stress-strain properties at elevated temperatures is acceptable. Resilience was low (10%), but can be improved by using BDO as a chain extender instead of PDO and/or by using a pre-polymer method (see table 6).

Table 5. Formulation and properties of TPU based on propylene succinate polyols

Polyol type	Chain extender	Renewable content [%]	Hard block [%]	Hardness [ShoreA]	Strength at break [MPa](2)			Elongation at break [%](1)	Resilience [%]
					RT	50°C	70°C		
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	-

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

Prepolymer method

TPUs prepared using prepolymers in general show better overall properties compared to the one-shot TPU production method. This also holds for PS polyol-based TPU (table 6): the tensile strength is significantly higher compared to both one shot TPU (table 5) and BA prepolymer-based TPU. Other mechanical properties as well as the retention of the tensile modulus are all in the same range compared to conventional BA polyol-based prepolymer TPU. The abrasion resistance of the PS-based prepolymer TPU is very good.

Table 6. Formulation and physical properties of propylene succinate polyols (quasi-prepolymer method)

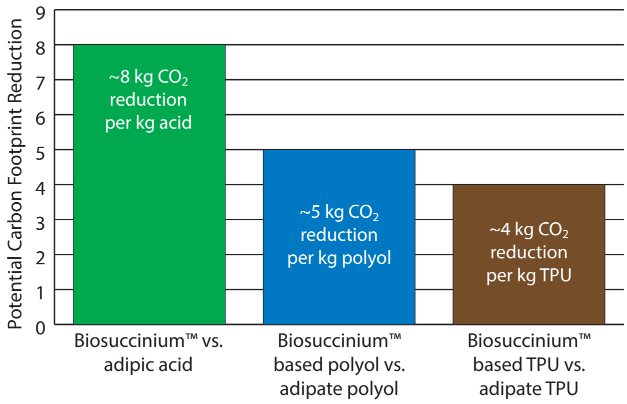
Polyol type	Chain extender	Renewable content [%]	Hard block [%]	Hardness [ShoreA]	Strength at break [MPa](2)			Elongation at break [%](1)	Abrasion [w% loss](4)	Resilience [%]
					RT	50°C	70°C			
PS	PDO	~60	31	87	39.3	17.9(1)	13.6 (1)	690	0.21	20
BA(3)	BDO	0	30	83	28	-	-	654	-	49

(1) Samples reached maximum oven height and did not break; (2) Tensile test acc. ASTM D-412; test speed 200mm/min;
(3) from Miller (2011); (4) 2000 rotations, 500g, 60%vac, H-22 wheels.

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 CO_2 per kg acid, polyol and TPU, respectively) Enabled by Using Biosuccinium™ instead of Adipic Acid



References

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