

Evaluating the properties and performance of Susterra 1,3-propanediol and Biosuccinium sustainable succinic acid in TPU applications

Susterra propanediol (PDO) and Biosuccinium sustainable succinic acid (SA) have been evaluated as potential alternatives for 1,4-butanediol (BDO) and adipic acid (AA) in polyester polyols for thermoplastic polyurethanes (TPU). Biosuccinium and Susterra are unique 100 % bio-based offerings from their respective suppliers, Reverdia and DuPont Tate & Lyle Bio Products. Their use makes it possible to yield a final polyester polyol and polyurethane product with a substantial renewable content of up to 100 % and 70 % respectively. Susterra reduces greenhouse gas emissions by more than 56 % compared to petro-based PDO and Biosuccinium has a 90 % carbon footprint reduction potential compared to adipic acid. The work presented here is intended to be a reference for a first technical evaluation of use of these bio-based raw materials in a straightforward standard formulation of polyester polyol and thermoplastic polyurethane. No attempt was made to optimise or to improve the products.

PDOSA and BDOSA polyols were synthesized without problems and their properties were within expectations of standard PDOAA type of polyols. However, the BDOSA polyol exhibited a higher melt temperature – ~100–110 °C vs. 48 °C and 65 °C for PDOSA and BDOAA respectively – this leads to a higher viscosity requiring a higher processing temperature. Reduction of the melt temperature is possible by adjusting the formulation. TPUs were produced via a prepolymer and one shot method at 20–30 % hard segment concentration. BDOSA TPU could only be produced via a one shot method because BDOSA prepolymers could not be processed in available lab equipment. PDOSA TPU is relatively soft and elastomeric at the chosen hard segment concentration. BDOSA TPU is very hard due to the crystalline morphology of the soft block. This is in line with previous work by Sonnenschein et al. [9] and Theunissen et al. [11, 13]. In general, the PDOSA and BDOSA TPUs exhibit very good heat and abrasion resistance, as well as solvent and moisture resistance. The resilience of these TPUs is low but can be altered by selection of chain extenders.

This was a first evaluation of polyurethanes based on Biosuccinium and Susterra using formulations optimized for adipic acid and 1,4-butanediol. The next step in any application will be to improve and optimize the performance portfolio of the polyol and TPU.

1. Introduction

In the last decade a number of global megatrends have intensified the need for products made from “green materials”. Firstly the

need to respect generations to come and use available resources responsibly, leading to more efficient ways to use, reduce, re-use and recycle materials, and also to using renewable raw materials. Secondly, the strong growth in demand for oil has caused policy making around the world to focus energy security now and in the future. Recent oil price volatility has driven the search for alter-

natives. Finally, environmental concern has risen strongly in the past ten years. The long-term maintenance of the planet’s well-being is at the forefront of many governments, corporations, consumers and non-governmental organizations (NGO) alike. Consumers expect and demand more sustainable products. Renewable materials offer a potential way of improving the sustainable character-

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▼ **Tab. 1:** Overview of formulations

	Label	Diol	Di-acid	Renewable content / %
Polyester polyols	BDOAA	1,4-butanediol	Adipic acid	0
	BDOSA	1,4-butanediol	Biosuccinium	~ 50
	PDOAA	Susterra	Adipic acid	~50
	PDOSA	Susterra	Biosuccinium	100
	Label	Polyol	Chain extender	Renewable content / %
Thermoplastic polyurethanes (TPU)	BDOAA + BDO	BDOAA	1,4-butanediol	0
	BDOSA + BDO	BDOSA	1,4-butanediol	~30
	PDOAA + BDO	PDOAA	1,4-butanediol	~30
	PDOAA + PDO		Susterra	~33–40
	PDOSA + BDO	PDOSA	1,4-butanediol	~60
	PDOSA + PDO		Susterra	~63–70

istics of the products that are made from them.

1.1 Biosuccinium and Susterra brand owners

Biosuccinium is a trademark for bio-based succinic acid, belonging to Reverdia VoF. Susterra is a registered trade name for bio-based 1,3-propanediol belonging to DuPont Tate & Lyle Bio Products Company LLC. Biosuccinium sustainable SA is produced by Reverdia, a joint venture between DSM and Roquette, using a proprietary low-pH yeast process. It is a 100 % bio-based and renewable diacid; bio-based succinic acid being the only available bio-based short chain diacid. Typically, this material can be used to substitute AA and is regarded as a “near drop-in” raw material for the production of polyester polyols and polyurethanes [9, 11, 13]. Reverdia will be the first in the world to have a large scale facility for the commercial production of bio-based SA. It will benefit from a sustainable fermentation production technology which has been in development since 2008. The new facility with a capacity of about 10 kt is located on the Roquette site in Cassano Spinola, Italy, and is scheduled to be operational by the end of 2012.

Susterra 1,3-propanediol (PDO) is produced by DuPont Tate & Lyle Bio Products Company, LLC at one of the largest biomaterials

processing facilities in the world at Loudon, TN, USA. Originally built to meet the global demand for the DuPont Sorona polymer, a renewably-sourced polytrimethylene terephthalate (PTT), the proprietary production process for Susterra ferments corn sugar, a rapidly renewable feedstock, to manufacture a 100 % bio-based PDO. This material has been successfully evaluated as an alternative replacement for 1,4-butanediol as a polyester building block or chain extender in the production of cast elastomers [1, 2, 3] and microcellular elastomers [4, 5]. The commercial success of this product led to the recent announcement that capacity was expanded by 35 % to 65 kt in early 2012.

1.2 Enabling sustainable PU

Biosuccinium and Susterra require less from the earth’s limited fossil resources and deliver a reduction in GHG emissions. The combined use of these materials makes it possible to yield a final polyester polyol and polyurethane product with a renewable content of up to respectively 100 % and 70 % (tab. 1). The sustainability improvement potential has been evaluated for both materials by a life cycle assessment (LCA). The LCA of the bio-based PDO using design data of the cradle-to-gate production versus the production of chemically derived PDO shows significant environmental benefits. The unique manufacturing process consumes up to

42 % less energy and reduces GHG emissions by more than 56 %, saving the energy equivalent of over 15 million gallons (~5.68 million l) of gasoline per year. The LCA has been externally reviewed and Susterra is also certified as readily biodegradable based on an OECD Guideline Test for biodegradation.

The Biosuccinium cradle-to-gate study was executed by the Copernicus Institute of Sustainable Development at Utrecht University, the Netherlands [12]. The production process uses non-fossil raw materials, sequesters carbon dioxide, is energy efficient and does not produce unnecessary by-products.

Figure 1 shows the carbon footprint of Biosuccinium. It has a large potential carbon footprint reduction – of about 8 kg CO₂-equivalent per kg of acid when fossil-based AA is substituted with Biosuccinium. The AA data was supplied by DSM for a best in class plant with 98 % N₂O abatement.

2. Experimental

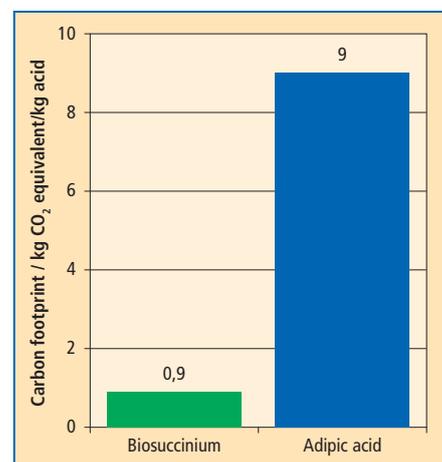
2.1 Materials

The raw materials used in this study are shown in table 2. Polyols, PDO and BDO used in the preparation of NCO-prepolymers, quasi-prepolymers and TPUs were de-moisturized for 24 h under vacuum of 1–3 mm Hg and continuous mixing by magnetic stirrer. The temperature of the polyols during

▼ Tab. 2: Materials

Designation	Identification	Supplier
Susterra	Bio-based 1,3-propanediol	DuPont Tate & Lyle Bio Products
Biosuccinium	Bio-based succinic acid	Reverdia
1, 4-butanediol	1,4-butanediol	Alfa Aesar
Butyltintris(2-ethylhexanoate)	Butyltintris(2-ethylhexanoate)	ChemCruz
Dabco T-12	Dibutyltin dilaurate	Air Products
Mondur M	Diphenylmethane 4,4'-diisocyanate (flaked) NCO % = 33.6	Bayer
Rubinate 44	Diphenylmethane 4,4'-diisocyanate NCO % = 33.6	Huntsman
Water	Distilled water	Kroger
Oil	Vacuum pump oil	Mobil
Toluene	Toluene	Mallinckrodt
Ethyl acetate	Ethyl acetate	Burdick and Jackson
Xylene	Xylene	JT Baker
Methyl ethyl ketone	Methyl ethyl ketone	Jade Scientific
Benzoyl chloride	Benzoyl chloride	Mallinckrodt

Fig. 1: Reduction of the carbon footprint using Biosuccinium vs. petrochemical adipic acid [12]



degassing was kept above melting temperature of the polyol (80 °C for PDOSA 2000 and 110 °C for BDOSA 2000). The water content after drying was checked by Karl Fisher Titrator. Diphenylmethane diisocyanate (MDI) was used as received from the supplier and its isocyanate content was checked by di-n-butylamine titration method (ASTM D-5155).

2.2 Preparations

2.2.1 Polyester polyols

The PDOSA 2000 and BDOSA 2000 polyol samples were both prepared according to the protocol described by Sonnenschein et al. [9].

2.2.2 NCO-prepolymers and NCO-quasi-prepolymers

The prepolymers and quasi-prepolymers based on PDOSA 2000 and BDOSA 2000 were prepared utilizing a laboratory procedure, as follows: MDI melted at 60 °C, was placed in the heated reaction kettle, which was equipped with a stirrer, thermometer and continuous flow of nitrogen. Preheated polyol was added slowly to isocyanate at 60–65 °C and reaction continued at elevated temperature. The NCO % of prepolymers was checked periodically during synthesis. After completion, the prepolymer was degassed under vacuum and continuous mixing. Degassed prepolymer was transferred into glass jars and sealed under dry nitrogen. The NCO % of prepolymers was checked after 24 h.

2.2.3 TPUs via prepolymer method

TPUs were prepared by reacting NCO-prepolymers and quasi-prepolymers with a chain extender at an isocyanate index of 1.02, in the presence of small amount of tin catalyst. TPU sheets and round bottom samples were prepared to test physical and mechanical properties of the elastomers.

The elastomer sheets were prepared using a laboratory compression molding method (Carver press). The NCO-prepolymer was

preheated to 80 °C, weighed into a speed mixer cup and degassed under vacuum at 80 °C for 120 min. The prepolymer was then heated at 90 °C for 15 min in an air circulation oven, chain extender containing catalyst (conditioned at RT) was added to the prepolymer and all components were mixed using a Speed Mixer for 30–60 s at 2,200 rpm and transferred into an aluminum mold covered with Teflon sheet that was preheated at 120 °C. At the gel time the mold was closed and cured for 2 h at 120 °C. Afterwards, the samples were post-cured for 16 h at 100 °C.

Cylindrical “button samples” (6.5 cm² x 1.3 cm) for testing of hardness, resilience, and compression set were prepared by casting of degassed polyurethane system into a Teflon coated mold with multiple cavities which was preheated at 120 °C. The mold was then covered with Teflon coated aluminum plate, transferred into an oven at 120 °C, cured for 2 h and then post-cured for 16 h at 100 °C. The TPU samples were kept in desiccators and aged for seven days at room temperature prior to testing.

2.2.4 TPUs via one-shot method

TPUs were prepared by reacting MDI and a mixture composed of polyester polyol, chain

extender and small amount of tin-gelling catalyst (when used) at an isocyanate index of 1.02. TPU sheets and round bottom samples were prepared as previously described.

3. Testing and test methods

3.1 Polyols

These materials were tested using the following methods:

- Acid value, mg KOH/g, ASTM D 4662-08
- Hydroxyl value, mg KOH/g, ASTM D 4274-05
- Moisture, %, ASTM D 4672-00
- Viscosity, cPs (50 & 70 °C), ASTM D 4878-08
- Glass transition temperature T_g and melt temperature T_m
- GPC analysis, (Mw, Mn, Mw/Mn)

3.2 Prepolymers

- NCO %, ASTM D 5155

3.3 TPU elastomers

The properties of the elastomers were tested using the following:

▼ **Tab. 3:** Formulations and properties of PDOSA and BDOSA, Mw 2000

Type	Methods	PDOSA			BDOSA	
Label		A	B	C	D	E
Formulation /pbw						
Succinic acid		1,000	1,000	1,000	1,000	1,000
1,3-propanediol		708	708	708		
1,4-butanediol					855	855
Dabco T-12		-	-	-	1.9	-
Butyltintris(2-ethylhexanoate)	-	0.065	0.065	0.065	-	0.07
Properties						
Acid value / mg KOH/g	ASTM D 4662-08	1.39	0.75	1.16	1.11	1.92
Hydroxyl value / mg KOH/g*	ASTM D 4274-05	57.4	56.7	57	58.5	59.7
Moisture / %	ASTM D 4672-00	-	0.059	0.066	-	0.023
Viscosity / cPs @50 °C @70 °C	ASTM D 4878-08	5,300 2,680	5,600 1,960	4,601 1,360	Solid Solid	Solid Solid
Glass transition temperature	DSC	-38°C	-	-		
Melt temperature	DSC	+48°C	-	-	99/108 °C	
Solubility in THF		yes	yes	yes	no	no
Average MW	Calculated from OH#	1,955	1,979	1,968	1,918	1,879

*Hydroxyl values adjusted for acidity

- Hardness, ASTM D-2240, Shore A and Shore D
- Tensile properties (tensile strength, tensile modulus and elongation %), ASTM D 412
- Tear strength, Dye C, ASTM D 6240
- Flexural strength and modulus, ASTM D 790
- Abrasion resistance, ASTM D 1044 (H22 wheels, weight load 500 g, 2,000 cycles)
- Resilience, % (Bayshore rebound), ASTM D2632
- Dynamic mechanical analysis, DMA, in bending mode (DMA 2980, TA Instruments)
- Differential scanning calorimetry, DSC (DSC Q 10, TA Instruments)
- Thermo-mechanical analysis, TMA (TMA Q 400, TA Instruments)
- Heat resistance: tensile strength and elongation % at 50 °C and 70 °C was measured by using heat chamber attached to the Instron tester
- Solvent resistance, including water: three elastomer specimens (10x40x2 mm) (cut from the sheet) were weighed together and immersed in a solvent at room temperature. The samples were taken out after 1 day and 7 days of immersion. Their weight and dimension were measured.

PDOSA polyols were soluble in THF. GPC results showed a molecular weight distribution typical for polyester polyols with PDI of 2.74 and 2.51, respectively. DSC results for T_g and T_m are $-38\text{ }^\circ\text{C}$ and $48\text{ }^\circ\text{C}$, respectively (**fig. 2**).

4.1.2 1,4-butanediol succinate polyol (BDOSA)

BDOSA polyols were prepared as shown in **table 3**. Molecular weight of the polyol was controlled by stoichiometry. In the first batch tin catalyst Dabco T-12 was used as catalyst for esterification. In order to decrease reactivity with isocyanates, another batch of BDOSA polyol was prepared using relatively low concentration of butyl tris(2-ethylhexanoate) as a catalyst (**tab. 3**). Molecular weights, calculated from hydroxyl numbers measured on each batch of polyol, were 1,879 and 1,918.

BDOSA polyol was not soluble in THF, which is commonly used as a diluent in GPC for determination of molecular weight distribution. This polyol was not soluble in most common solvents, including MEK, toluene, NMP, and DMF at very low concentrations. However, it was soluble in chloroform which is not practical as an eluent for GPC. Melt temperatures of BDOSA polyol, as determined via DSC, were $99\text{ }^\circ\text{C}$ and $108\text{ }^\circ\text{C}$ (**fig. 3**), which were almost identical to those reported by Sonnenschein et al. [9].

4. Results and discussion

4.1 Polyester polyols

4.1.1 1,3-propanediol succinate polyol (PDOSA)

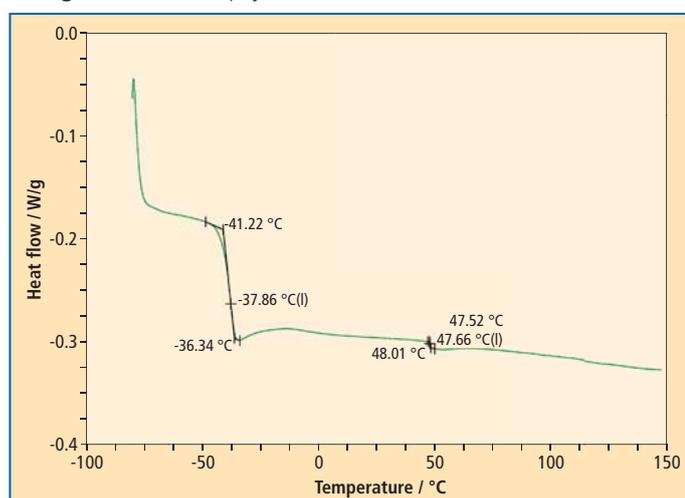
Several batches of PDOSA polyols were prepared (**tab. 3**). Molecular weight was controlled by stoichiometry. First batches were produced using Dabco T-12 (not mentioned in table 3) as a catalyst which proved to be very reactive with the aromatic isocyanate, 4,4'-MDI. In order to decrease reactivity of the polyol, butyltintris(2-ethylhexanoate) was used as a catalyst at very low concentration.

These PDOSA polyols exhibited relatively long gel time in reactivity screening test with 4,4'-MDI.

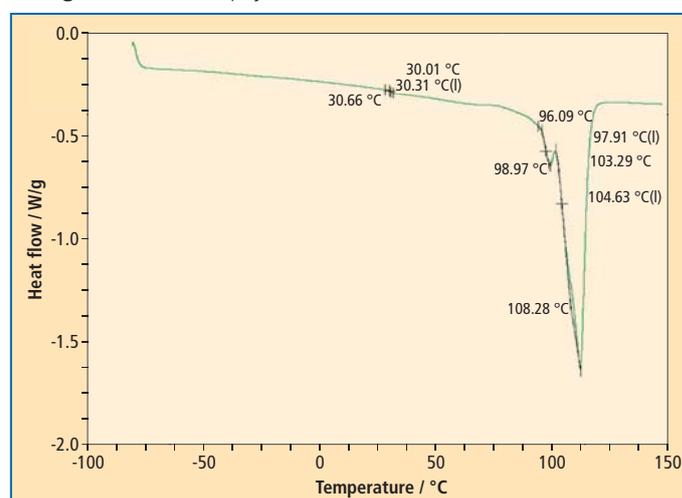
▼ **Tab. 4:** Formulation of quasi-prepolymers (PDOSA)

Label	F	G
NCO/OH Ratio	3:1	3:1
Prepolymer formulation / pbw		
Mondur M	81.50	196.61
PDOSA 2000 (tab. 3 B)	215.56	-
PDOSA 2000 (tab. 3 C)	-	492.11
Benzoyl chloride	5 drops	5 drops
Reaction temperature and time		
Time of polyol addition / min	21	23
Time of reaction / min	30	45
Temperature	65–70 °C	69–87 °C
Properties of prepolymer		
NCO % theoretical	6.15	6.17
NCO % measured	3.76	5.79
Consistency at RT	Solid	Solid
Viscosity at 70 °C / cps	-	6,570

▼ **Fig. 2:** DSC of PDOSA polyol



▼ **Fig. 3:** DSC of BDOSA polyol



4.2 NCO-prepolymer / quasi-prepolymer formulations

4.2.1 PDOSA

The viscosity of the NCO-prepolymer (NCO/OH=2/1) based on 4,4'-MDI and PDOSA 2000 was very high at 120 °C and it was not possible to prepare TPUs using the procedure reported earlier in preparation of PDO adipates [10, 14]. Quasi-prepolymers (3/1 NCO/OH ratio) based on PDOSA 2000 were then prepared (**tab. 4**). The resulting viscosity of the quasi-prepolymers was lower than the straight NCO-prepolymers, due to presence of monomeric 4,4'-MDI.

4.2.2 BDOSA

The viscosity of the NCO-prepolymer (NCO/OH=2/1) based on 4,4'-MDI and BDOSA 2000 were too high at 120 °C and it was not possible to prepare TPUs using the PDO adipates procedure reported [10, 14].

4.3 Polyurethane elastomer formulations

4.3.1 Quasi-prepolymer method using PDOSA + PDO

Thermoplastic polyurethane elastomers were prepared by the quasi-prepolymer method at a 1.02 isocyanate index and hard segment

concentration of approximately 31 %. Formulations and curing conditions are shown in **table 5**. A gelling catalyst was added to each polyurethane system to facilitate polymerization.

4.3.2 One-shot method using PDOSA + PDO

In order to overcome the high viscosity of prepolymers, TPUs based on 4,4'-MDI and PDO as a chain extender were prepared by using one-shot. The formulations of one-shot TPUs based on PDOSA are shown in **table 6**.

4.3.3 One-shot method using PDOSA + BDO

TPUs were also prepared via one-shot method from PDOSA polyol using BDO instead PDO as a chain extender (**tab. 6**).

4.3.4 One-shot method using BDOSA + BDO

TPUs based on BDOSA 2000, 4,4'-MDI and 1,4-BD chain extended were successfully prepared by one-shot method at two different hard segment concentrations: ~24 %

and ~34 % (**tab. 6**). The reactivity of the system was very good; additional gelling catalyst was not required. By comparison, the one-shot method for PDOSA was very slow without catalyst.

4.4 Polyurethane elastomer properties

4.4.1 Quasi-prepolymer method using PDOSA + PDO

The properties of TPUs at 31 % hard segment concentration are shown in **table 7**. The tensile strength was 5,695 psi at 690 % elongation at break (**fig. 4**), which is significantly higher than those values measured for one-shot TPUs prepared at the same hard segment concentration, discussed in a later section. Hardness was relatively low, Shore A 87.

The tensile strength of the PDOSA TPU was significantly higher than that of TPUs prepared from PDOAA in a previous study at the same hard segment concentration [14]. Retention of tensile strength at 100 %, 200 %, and 300 % elongation was good and comparable to that of the TPUs prepared from PDOAA at the same hard segment concentration.

Tab. 6: Formulation and curing conditions of one-shot TPUs

Label	J	K	L	M	N	O	P
Type	PDOSA + PDO			PDOSA + BDO		BDOSA + BDO	
Hard segment / %	22	22	31	23	33	24	34
Formulation / pbw							
PDOSA 2000 (tab. 3 A)	40	-	-	77.200	-	-	-
PDOSA 2000 (tab. 3 C)	-	60	40	-	60	-	-
BDOSA 2000 (tab. 3 E)	-	-	-	-	-	50	45
Propanediol	1.0705	1.647	2.196	-	-	-	-
Dabco T-12	0.0005	0.002	-	-	-	-	-
BDO	-	-	-	3.489	5.515	2.365	4.402
Mondur M	10.104	15.535	15.536	19.300	23.593	13.380	18.673
Isocyanate index	1.02	1.02	1.02	1.02	1.02	1.02	1.02
Curing conditions							
Temp. polyol / °C	120	120	120	80	120	120	120
Temp. PDO / °C	120	120	120	-	-	-	-
Temp. BDO / °C	-	-	-	80	120	120	120
Temp. Dabco T-12 / °C	120	120	-	-	-	-	-
Temp. Mondur M / °C	80	80	80	80	80	80	80
Mixing @ 2,200 RPM / s	20 s	20 s	20 s	30 s	20 s	20 s	20 s
Gel time / s	170	100	95	390	75	105	60
Curing time & temp.	2 h @ 120 °C						
Post-curing time & temp.	20 h @ 100 °C						

Tab. 5: Formulation and curing conditions of prepolymer TPU (PDOSA + PDO)

Label	H	I
Hard segment / %	30	31
Formulation / pbw		
PDOSA prepolymer (tab. 4 F)	35.80	-
PDOSA prepolymer (tab. 4 G)	-	50
PDO	1.5487	1.944
Dabco T-12	0.0013	0.0022
Isocyanate index	1.02	1.02
Curing conditions		
Temperature of NCO-prepolymer / °C	120	120
Temperature of PDO / °C	80	80
Temperature of Dabco T-12 / °C	80	80
Mixing @ 2,200 RPM / s	20	20
Gel time / s	180	105
Curing time & temperature	2 h @ 120 °C	
Post-curing time & temperature	20 h @ 100 °C	

The hardness of the PDOSA and PDOAA TPUs (Shore A 87 and 83, respectively) is similar as well as elasticity measured as elongation at break (690 % and 681 %, respectively), and the tear strength (559 psi and 625 psi, respectively). However, the resilience of the TPU based on PDOSA was significantly lower than that of TPU based on PDOAA (20 % and 47 %, respectively). The abrasion resistance of the TPU based on PDOSA was very good, 0.2 % weight loss under the test conditions (tab. 7). FTIR confirmed there were no traces of residual isocyanate. DSC analysis indicates three transitions: at $-10.7\text{ }^{\circ}\text{C}$ (T_g), $42.5\text{ }^{\circ}\text{C}$ (melting of soft segment) and $155\text{ }^{\circ}\text{C}$ (hard segment melting) (fig. 5). The T_g as measured via DSC of this PDOSA based TPU ($-10.7\text{ }^{\circ}\text{C}$) was a higher temperature compared to the PDOAA ($-37\text{ }^{\circ}\text{C}$) and BDOAA ($-35\text{ }^{\circ}\text{C}$) based TPUs at the same hard segment concentration (tab. 7). The ratio of coefficient of thermal expansion of TPUs as measured above

and below the T_g is higher than 4 which indicates that material is an elastomer. The shape of stress-strain curve is also typical for elastomeric materials (not shown).

Solvent resistance of TPUs was very good in water and oil, as measured by weight gain in immersion test (tab. 8). Weight gain was relatively high in polar solvents (MEK and ethyl acetate) and lower in non-polar solvents (toluene and xylene).

4.4.2 One-shot method using PDOSA + PDO

TPUs prepared at isocyanate index 1.02 and 22 % hard segment concentration showed a tensile strength ranging 2,700–2,800 psi and an elongation at break around 800 % (tab. 9, fig. 6, 7). Somewhat lower tensile strength and elongation at break were obtained for one-shot TPUs based on PDOSA prepared at hard segment concentration of ~30 %.

The hardness measured on one of TPUs based on PDOSA prepared at 22 % hard segment was Shore A 64 (tab. 9). The resilience of this TPU was low, 10 %. The overall retention of stress-strain properties of TPUs prepared via one-shot method was acceptable.

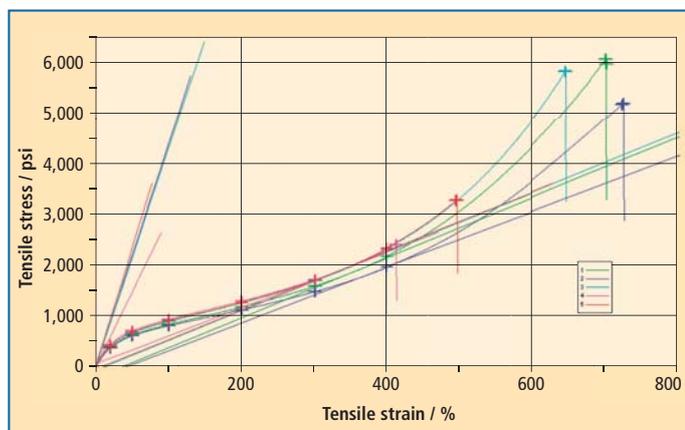
4.4.3 One-shot method using PDOSA + BDO

In order to improve resilience, TPUs were also prepared with BDO as chain extender instead of PDO. Resilience of these TPUs was somewhat higher at 25 % (tab. 9); however, the tensile strength was lower as compared to TPU based on PDO (tab. 9);

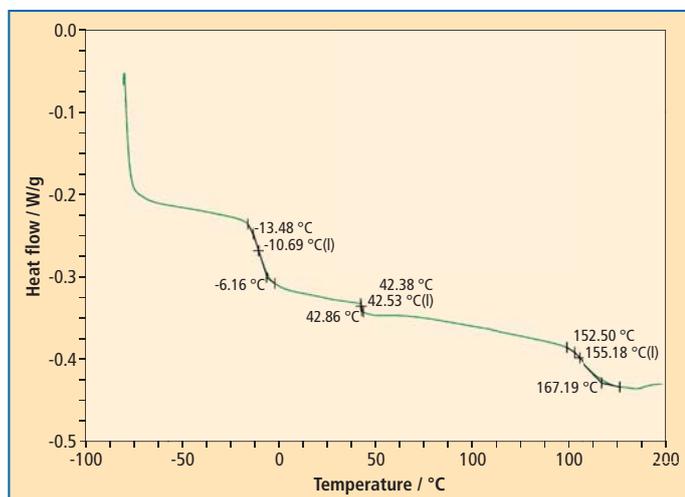
4.4.4 One-shot method using BDOSA + BDO

BDOSA TPUs exhibited very high hardness at relatively low hard segment concentrations: 55 Shore D at 24 % hard segment concentration and 57 Shore D at 34 % hard segment concentration (tab. 10). High hardness of these TPUs can be related to the high crystallinity of the soft segment. The stress-strain test results indicate that both types of elastomers exhibited yield at relatively low strain (tab. 10, figs. 8, 9), clearly indicating a thermoplastic behavior of these materials. Flexural strength and modulus were measured and shown to be very good (tab. 10). The resilience was relatively low, below 20 %. The abrasion resistance was somewhat lower than that based on PDOSA prepolymer. The retention of tensile strength at yield at 50° and $70\text{ }^{\circ}\text{C}$ is also good (tab. 10). Overall, the solvent resistance of TPUs based on BDOSA polyol is excellent which confirms earlier results by Theunissen et al. [11, 13] (tab. 11).

Others have also reported the relatively high hardness that occurs when using 2,000 g/mol BDOSA polyols for TPU. Sonnenschein et al. [9] concluded that higher percent crystallinity of BDOSA is manifest in soft segment properties when the hard segment volume is less than 40 % for 2,000 g/mol BDOSA polyols. The effect is reported to be less strong for 1,000 g/mol BDOSA poly-



◀ Fig. 4: Stress-strain properties (at RT) of PDOSA prepolymer TPU (tab. 7 I).



◀ Fig. 5: DSC of elastomer prepared via pre-polymer method from PDOSA prepolymer (tab. 7 I).

ols. Theunissen et al. [11, 13] have shown that at higher hard segment concentrations – leading to for example Shore A 93 – the resulting BDOSA TPUs are more similar to the BDOAA based TPUs (**tabs. 12, 13**) with respect to hardness and tensile properties.

Theunissen et al. [11, 13] also evaluated the effect of using a mixture of diols – in this case ethylene glycol and BDO – in the polyol (**tabs. 12, 13**). The hardness of the resulting succinate based TPU was close to the benchmark adipate TPU and the abrasion resistance was very similar. In this case tensile properties were lower probably due to the lower final hardness of EBAA TPU.

Another way to possibly break symmetry and decrease the crystallinity of BDOSA TPUs is using other types of chain extenders – such as neopentyl glycol, dipropylene glycol or a mixture of PDO and BDO.

5. Conclusion

Biosuccinium and Susterra are potential alternatives for fossil-based AA and 1,4-BDO respectively as raw material for polyester polyols and polyurethanes. This enables a potential improvement of the sustainability characteristics of polyester polyols and polyurethane materials because both materials are 100 % bio-based, renewable raw materials.

The work presented here is intended to be a reference for a first technical evaluation of use of Biosuccinium, Susterra or the combination of these materials in a straightforward standard formulation of polyester polyol and thermoplastic polyurethane. No attempt was made in any case to optimize or to improve the products, but this is of course possible and some first recommendations for optimizations are suggested.

5.1 Polyester polyols

PDOSA and BDOSA polyester polyols of 2,000 g/mol molecular weight were synthesized without any problems using a process very similar to synthesis of standard BDOAA polyester polyols. The same result was ob-

tained for PDOAA [4, 10] before. Multiple batches of each polyol exhibited OHI numbers close to theoretical values and acid numbers close to 1 mg KOH/g or lower. PDOSA polyols exhibited a typical molecular weight distribution for polyester polyols as was shown before for PDOAA as well [10]. The molecular weight distribution of BDOSA polyols could not be determined because they did not dissolve in the commonly used solvent (tetrahydrofuran) in the GPC analysis method. It is expected that the distribution is similar to the other polyols.

The main difference observed is that BDOSA polyol exhibited a higher melt temperature (~100–110 °C) compared to the other polyols, PDOSA and BDOAA having a melt temperature of 48 °C and 65 °C respectively. This also leads to a higher viscosity of the BDOSA polyol. Earlier work [11] has shown that a polyol based on Biosuccinium and a mixture of 1,4-butanediol and ethylene glycol in a 50/50 mol ratio had a melt temperature (<70 °C) similar to adipate based polyol.

5.2 Thermoplastic polyurethanes

TPUs were prepared using one-shot and prepolymer laboratory methods using 4,4'-MDI. PDOSA TPU prepared by the one-shot method was easy to process using laboratory equipment due to the low viscosity of the polyurethane system. The prepolymers based on PDOSA were viscous materials and in fact quasi-prepolymers (3/1 NCO/OH ratio) were prepared which have a lower viscosity than the straight NCO-prepolymers, due to presence of monomeric 4,4'-MDI. Processing of straight NCO-prepolymers requires higher temperature and very efficient mixing which can be achieved on industrial

▼ **Tab. 8:** Solvent resistance, mass gained / %

Toluene	21.34
Methyl ethyl ketone	62.24
Xylene	11.18
Ethyl acetate	46.57
Oil	0.32
Water	1.15

▼ **Tab. 7:** Physical properties of prepolymer method TPU

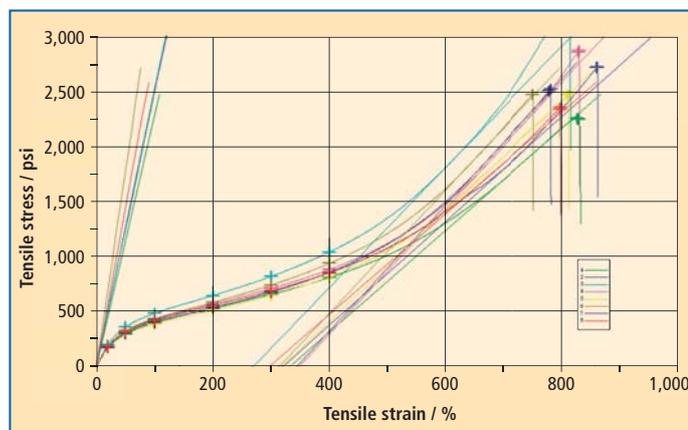
Label	I		
	PDOSA + PDO	PDOAA + PDO [14]	BDOAA + BDO [14]
Hard segment / %	31	30	30
Hardness / Shore A	87	83	83
Hardness / Shore D	37		
Tensile strength / psi:			
@ break	5,695	4,105	4,054
@ 100 % strain	842	762	668
@ 200 % strain	1,185	1,060	971
@ 300 % strain	1,590	1,404	1,383
Elongation at break / %	690	681	654
Tensile strength @ 50 °C / psi:			
@ break*	2,589*		
@ 100 % strain	792		
@ 200 % strain	1,054		
@ 300 % strain	1,379		
Tensile strength @ 70 °C / psi:			
@ break*	1,977*		
@ 100 % strain	707		
@ 200 % strain	920		
@ 300 % strain	1,118		
Elongation at break, %*:			
@ 50 °C	514*		
@ 70 °C	489*		
Toughness / psi	3,929,550		
Resilience / %	19.6	47	49
Tear strength / lbf/in	559	625	638
Abrasion, 2,000 rotations, 500 g, 60 % vac, H-22 wheels / % mass loss	0.21		
Glass transition temperature via DSC	-10.7 °C	-37 °C	-35 °C
Coefficient of thermal expansion / (µm/m)/°C			
• from -75 °C up to T _g	47.3		
• above T _g	199		
*Samples reached maximum oven height and did not break			

Label	J	K	L	M	N
Type	PDOSA + PDO			PDOSA + BDO	
Hard segment / %	22	22	31	23	33
Hardness / Shore A	64	-	-	67	-
Density / g/cm ³	1.29	-	-		
Tensile strength / psi:					
@ break	2,691	2,746	2,274	616	1,447
@ 100 % strain	394	427	735		
@ 200 % strain	526	567	983		
@ 300 % strain	662	715	1,257		
Elongation at break / %:					
@ RT	831	808	559	656	562
@ 50°C		468	406		
@ 70°C		423	402		
Tensile strength @ 50 °C / psi:					
@ break*		1,277	1,786		
@ 100 % strain		495	870		
@ 200 % strain		641	1,113		
@ 300 % strain		797	1,396		
Tensile strength @ 70 °C / psi:					
@ break*		814	1,536		
@ 100 % strain		427	799		
@ 200 % strain		536	998		
@ 300 % strain		651	1,236		
Toughness / psi	2,236,221	2,218,768	1,271,166		
Resilience / %	10	-	-	26	-

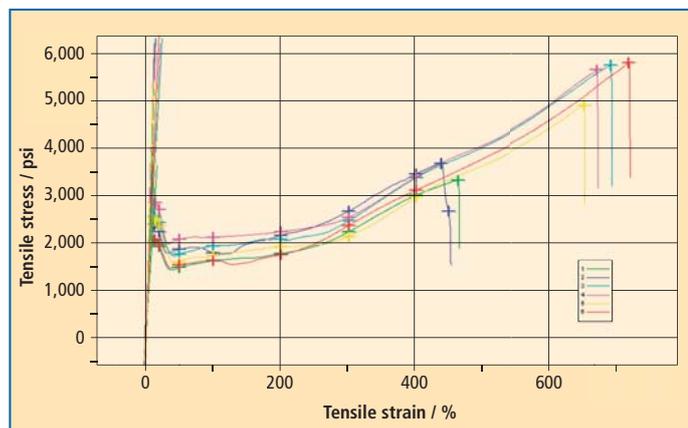
* Samples reached maximum oven height and did not break

▲ **Tab. 9:** Properties of one-shot TPU (PDOSA)

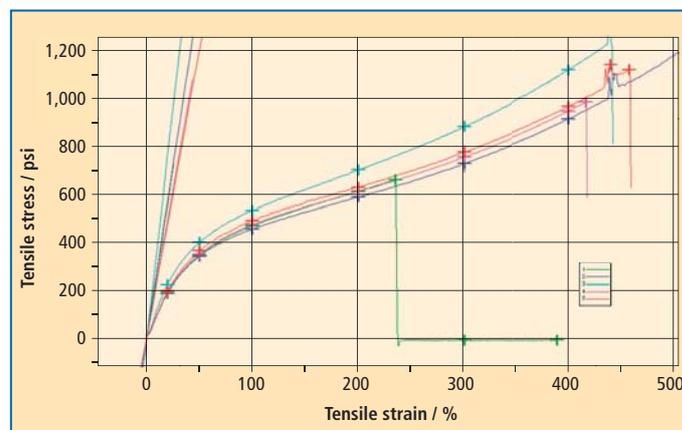
▼ **Fig. 6:** Stress-strain properties (at RT) of one-shot TPU prepared from PDOSA + PDO (tab. 9 K)



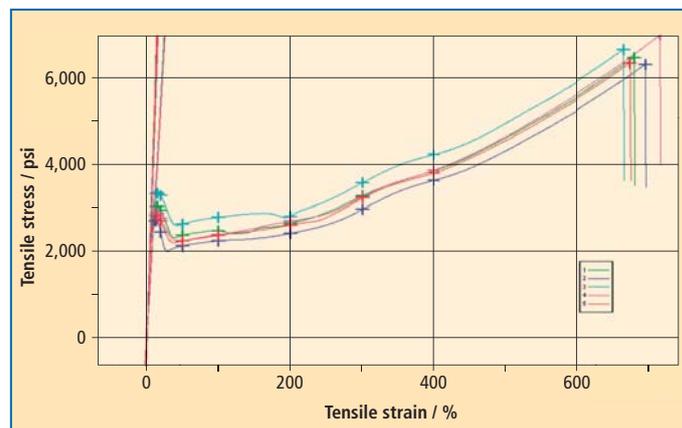
▼ **Fig. 8:** Stress-strain properties (at RT) of one-shot elastomer prepared from BDOSA and BDO as a chain extender at 23.95 % hard segment concentration (tab. 10 O)



▼ **Fig. 7:** Stress-strain properties (at 50°C) of one-shot TPU prepared from PDOSA + PDO (tab. 9 K)



▼ **Fig. 9:** Stress-strain properties (at RT) of one-shot elastomer prepared from BDOSA and BDO as a chain extender at 33.9 % hard segment concentration (tab. 10 P)



dispensing (processing) equipment. PDOSA based TPU is relatively soft and elastomeric at a 20–30 % hard segment concentration.

TPU based on the BDOSA polyol was prepared only by using one-shot method, since the viscosity of NCO-prepolymers based on BDOSA were too high to be processed with available laboratory equipment.

The prepolymer method lead to excellent strength properties that were higher than that of one-shot elastomers. The PDOSA TPU exhibits very good heat resistance, good solvent and moisture resistance and good abrasion resistance. The tensile strength of the PDOSA TPU was significantly higher than that of TPUs prepared from PDOAA in a previous study at the same hard segment concentration [14]. Retention of tensile modulus at elon-

gation was good and comparable to the benchmark BDOAA TPU at the same hard segment concentration. However, the resilience is lower than BDOAA and PDOAA TPU. Undisclosed data has shown that resilience of PDOSA based TPUs is closer to the benchmark BDOAA TPU at higher hardness grades.

Similar to the prepolymer method TPUs, the one-shot method PDOSA and BDOSA TPUs exhibited very good heat resistance, good – excellent for BDOSA TPU – solvent and moisture resistance and good abrasion properties. The resilience of these TPUs appears to be low but can be altered somewhat by selection of chain extenders.

The most prevalent differences in the properties of the bio-based one shot TPUs were found in the mechanical properties. PDOSA TPUs exhibited about 25 % lower tensile strength but similar elongation at break in comparison to the TPUs prepared via the prepolymer method at same hard segment concentration and the same isocyanate index. TPUs based on BDOSA at 20–30 % hard segment were hard plastic materials of ~55 Shore D with excellent strength properties and excellent chemical resistance. The crystalline morphology and hence the properties of the TPU based on BDOSA polyester polyols is likely controlled by high concentration of ester groups and high degree of hydrogen bonding. Other types of chain extenders – such as neopentyl glycol, dipropylene glycol or a mixture of PDO and BDO – can possibly break symmetry and decrease their crystallinity. Alternatively, copolymer polyols should be considered, using mixtures of adipic and succinic acid, or BDO and ethylene glycol. Also, lower molecular weight (e. g. 1,000 g/mol) polyester polyols are to be considered. Such polyols are expected to have lower viscosity and lower crystallinity and thus facilitate processing of TPUs.

The observed relatively high hardness behavior is in line with expectations based on previous work by Sonnenschein et al. [9] and Theunissen et al. [11, 13]. Theunissen et al. has also shown that at higher hard segment concentrations – leading to for example Shore A 93 – the resulting BDOSA TPUs

have properties similar to the adipate based TPUs (**tabs. 12, 13**). Sonnenschein et al. [9] concluded that higher percent crystallinity of BDOSA is manifest in soft segment properties when the hard segment volume is less than 40 %.

6. Acknowledgement

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7. References

- [1] G. A. DiPatri, V. Gajewski, “Green Castable Elastomers” Polyurethane Manufacturers Association 2009 Annual Meeting, April 2009, Savannah, GA, USA
- [2] S. Franyutti, J. W. DeSalvo, E. S. Miller, Jr., R. Miller, J. J. van Gorp, “Propanediol – From the Leading Edge of Biotechnology, a Renewable and Sustainable Building Block for the Urethane Industry that Delivers Performance and Versatility.” CPI Polyurethanes 2009 Technical

▼ **Tab. 10:** Properties of one-shot TPUs (BDOSA + BDO)

Label	O	P
Type	BDOSA + BDO	BDOSA + BDO
Hard segment / %	24	34
Hardness / Shore D	55	57
Density / g/cm ³	1.20	1.22
Tensile strength / psi		
@ break	5,421	6,546
@ yield	2,632	2,958
Elongation / %		
@ break	671	685
@ yield	15	15
Young's 0–1 % elasticity / psi	27,625	27,937
Young's 0–2 % elasticity / psi	45,719	45,917
Young's 0–3 % elasticity / psi	50,322	50,787
Toughness / psi	79,494	94,262
Resilience / %	15	18
Tensile strength at 50 °C / psi		
@ break	>3,441*	>4,238*
@ yield	1,382	2,201
Elongation at 50 °C / %		
@ break	>537*	>538*
@ yield	14	18
Tensile strength at 70 °C / psi		
@ break	>2,586*	>3,365*
@ yield	754	1,412
Elongation at 70 °C / %		
@ break	>537*	>534*
@ yield	15	23
Tear strength / lbf/in	975	1,441
Flexural strength / psi	3,329	3,514
Flexural modulus / psi	64,565	60,698
Abrasion, 2,000 rotations, 500 g, 60 % vac, H-22 wheels, % mass loss	5.0	2.4
Glass transition temperature		
• via DSC	-18.7 °C	-17.9 °C
• via DMA (maximum of loss modulus)	13.8 °C	11.2 °C
• via TMA	8.7 °C	5.4 °C
Coefficient of thermal expansion via TMA / $\mu\text{m}/\text{m}/^\circ\text{C}$		
• from -75 °C up to T_g	74.3	161
• above T_g	52.4	120

Conference, October, 2009, National Harbor, MD, USA

- [3] J. W. DeSalvo, R. Miller, J. J. van Gorp, "Susterra Propanediol – Susterra Propanediol – Renewability, Sustainability, and Differentiating Performance in Urethane Applications."

▼ **Tab. 11:** Solvent resistance, mass gained / %

Label	O	P
Elastomer	BDOSA + BDO	BDOSA + BDO
Hard segment / %	24	34
Toluene	3.04	3.27
Methyl ethyl ketone	13.74	12.67
Xylene	1.12	1.22
Ethyl acetate	11.73	9.70
Oil	0.55	0.66
Water	1.04	1.26

▼ **Tab. 12:** Overview of synthesized polyols (part of earlier work [11, 13])

Polyol	Mn / g/mol	Acid value / mg KOH/g	OH value / mg KOH/g	Viscosity / cPoise at 75 °C	Tm / °C
BDOAA	2,000	1.1	53.9	Solid	115
BDOSA	2,117	0.1	52.9	733	60
EBAA*	2,004	1.1	53.9	999	<70
EBSA*	2,004	1.3	56.0	579	<70

*Mixture of ethylene glycol and 1,4-butanediol in 50/50 molar ratio used in the polyol

▼ **Tab. 13:** Mechanical properties and chemical resistance of the synthesized TPUs (part of earlier work [11, 13])

Polyol	Hardness / Shore A**	Tensile test / MPa at 200, 500, 1000 %	Abrasion / mg weight loss	Toluene uptake / swell-index %	2-butanone uptake / swell-index %
BDOAA	93 A	10/15/30	0.034	16	54
BDOSA	93 A*	12/20/38	0.061	5	23
EBAA	90 A	7/10/15	0.066	11	45
EBSA	94 A	15/20/35	0.070	3	29

*Required higher processing temperature due to the higher melting point of BDOSA-polyol

**Standard formulations have been used targeting a hardness of 95 Shore A using BDO as chain extender (no optimization or improvements on the formulation have been done)

CPI Polyurethanes 2010 Technical Conference, October, 2010, Houston, TX, USA

- [4] R. Camargo, L. Cao, J. McCloud, D. Rosenvasser, "New Polyurethane Elastomers with Increased Bio-renewable Content for Footwear Applications." CPI Polyurethanes 2010 Technical Conference, October 2010, Houston, TX, USA
- [5] R. Camargo, L. Cao, J. McCloud, D. Rosenvasser, World Footwear, 2011 (Jan/Feb), 25–27
- [6] L. Born, H. Hesse, J. Crone, K. H. Wolf, Colloid and Polymer Science, 1982, 260(9), 819–828
- [7] J. Blackwell, M. R. Najarajan, T. B. Hoitink, Polymer, 1981, 22, 1534–1539
- [8] O. Bayer, Angew. Chem., A59, 257 (1947)
- [9] M. F. Sonnenschein, S. J. Guillaudeu, B. G. Landes, B. L. Wendt, "Comparison of adipate and succinate polyesters in thermoplastic polyurethanes," Polymer 51 (2010) 3685–3692
- [10] R. Miller, "Susterra Propanediol – Evaluating the Structure-Property Relationship in CASE Applications", paper, CPI Polyurethanes 2011 Technical Conference, September, 2011, Nashville, TN, USA
- [11] L. Theunissen, L. Leemans, R. J. M. Janssen, M. Smidt, "Evaluating the Properties and Performance of Biosuccinium sustainable succinic acid in Polyester Polyols for Thermoplastic Polyurethanes", paper, Utech Conference, April 2012, Maastricht, The Netherlands
- [12] M. K. Patel, A. L. Roes, B. Cok, Copernicus Institute of Sustainable Development at Utrecht University, The Netherlands. Data is pending publication.
- [13] L. Theunissen, "Biosuccinium based polyester polyols for sustainable polyurethanes", presentation, Utech Conference, April 2012, Maastricht, The Netherlands
- [14] R. Miller, "Susterra Propanediol – Evaluating the Structure-Property Relationship in CASE Applications", presentation, CPI Polyurethanes 2011 Technical Conference, September, 2011, Nashville, TN, USA

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