

Evaluating the Properties and Performance of Susterra® 1,3 Propanediol and Biosuccinium™ Sustainable Succinic Acid in TPU Applications

ROBERT MILLER

*DuPont Tate & Lyle Bio Products
198 Blair Bend Drive
Loudon, TN 37774
USA*

RICHARD JANSSEN,

LAWRENCE THEUNISSEN
*Reverdia
Urmonderbaan 20H
6167 RD Geleen
The Netherlands*

ABSTRACT

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. The use of Biosuccinium™ and Susterra® makes it possible to yield a final polyester polyol and polyurethane product with a substantial renewable content (up to 100 % and 70 % respectively) and with an improved sustainability characteristic. Susterra® reduces greenhouse gas emissions by more than 56% compared to petrobased PDO; 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 biobased raw materials in a straightforward standard formulation of polyester polyol and thermoplastic polyurethane. No attempt was made to optimize or to improve the products.

PDOSA and BDOSA polyols were synthesized without any problems. Properties are within expectations of standard PDOAA type of polyols. However, the BDOSA polyol exhibited a higher melt temperature – ~100-110°C vs. 46°C and 65°C for PDOSA and BDOSA respectively – which leads to a higher viscosity and requires higher temperatures in the processing of the polyol. Reduction of the melt temperature is possible by adjusting the formulation, e.g. by using a mixture of BDO and ethylene glycol.

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 caused by the crystalline morphology of the soft block. That finding is in line with previous work by Sonnenschein et al.⁹ and Theunissen et al.^{11,13}, who also showed that at higher hard segment concentrations BDOSA TPUs have a hardness more similar to BDOAA TPUs of similar formulation.

In general the PDOSA and BDOSA TPUs exhibit very good heat and abrasion resistance. The resilience of these TPUs is low but can be altered somewhat by selection of chain extenders. Both TPUs also showed a very good solvent and moisture resistance.

This was a first evaluation of properties 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. Suggestions are

to consider the evaluation of other types of chain extenders (such as neopentyl glycol, dipropylene glycol or a mixture of PDO and BDO), use of copolymer polyols (mixtures of adipic and succinic acid, or BDO and ethylene glycol) and use of lower molecular weight (e.g. 1000 g/mol) polyester polyols.

INTRODUCTION

In the last decade a number of global megatrends have intensified the need for products made from “green materials”. First, the global upturn on sustainability is driven by the need to respect generations to come and to be careful with the resources that are available. It is leading to more efficient ways to use, reduce, re-use and recycle materials, and also to using renewable raw materials. Next, the strong growth in demand for oil due to the increasing world population dominates national and international agendas for many years already. Policy making in several parts of the worlds is focusing on securing of energy supply, now and in the future. Very recently, oil price volatility has been particularly large, and has driven many purchasing organizations to search for alternatives.

Finally, environmental concern has risen strongly in the past 10 years. The long-term maintenance of the planet’s well-being is at the forefront of the attention of governments, corporations, consumers and non-governmental organizations alike. Consumers ever more expect and demand sustainable products. Non-governmental organizations push brand owners to source responsibly and corporations have made sustainability an integral part of their strategies. Renewable materials offer a potential way of improving the sustainable characteristics of the products that are made from them.

All these megatrends have come together creating a unique situation propelling the growth of biobased chemicals.

Biosuccinium™ and Susterra®

In this paper two biobased alternatives for adipic acid (AA) and 1,4-butanediol (BDO) are investigated for their use in polyester polyols and polyurethanes. Both alternatives enable more sustainable materials with an improved environmental footprint.

Biosuccinium™ sustainable succinic acid (SA) is produced by Reverdia, a joint venture between DSM and Roquette, using a proprietary low-pH yeast process. It is a 100 % biobased and renewable diacid; biobased succinic acid being the only available biobased short chain diacid. Typically, Biosuccinium™ can be used to substitute adipic acid and is regarded as a “near drop-in” as 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 succinic acid, which will be marketed under its Biosuccinium™ brand. It will benefit from the best and most sustainable fermentation technology to produce bio-based succinic acid, 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. The proprietary production process for Susterra® ferments corn sugar, a rapidly renewable feedstock, to manufacture a 100% bio-based 1,3-propanediol. Susterra® has been shown to be an alternative replacement for 1,4-butanediol as polyester building block or chain extender in the production of cast elastomers^{1,2,3} and microcellular elastomers^{4,5}.

Intentions

The technical performance of Susterra®^{1-8,10} and Biosuccinium™^{9,11,13} in polyester polyols and polyurethanes have been evaluated (partly) already, but in this work this will be extended also to the combination of using Biosuccinium™ and Susterra™ which has not been publicly evaluated. The assessment will look at a straightforward standard formulation of polyester polyol and thermoplastic polyurethane (see table 1 for an overview). The differences in manufacturing, processing and properties of the resulting materials versus the benchmark adipic acid and 1,4-butanediol based polyesters and thermoplastic polyurethanes are to be identified. No optimization or improvements will be done at this stage, but where possible recommendations for optimizations will be given.

	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
		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

ENABLING SUSTAINABLE POLYURETHANES

Biosuccinium™ and Susterra® are made from renewable feedstocks, requiring less from the earth’s limited fossil resources, as well as deliver a reduction in greenhouse gas emissions. The combined use of Biosuccinium™ and Susterra® makes it possible to yield a final polyester polyol and polyurethane product with a renewable content of up to respectively 100 % and 70 % (including Susterra® as chain extender, table 1). The sustainability improvement potential has been evaluated for both materials by a life cycle assessment (LCA).

The externally reviewed LCA of Susterra® is based on design data of the cradle-to-gate production versus the production of chemically derived propanediol and shows significant environmental benefits. The unique manufacturing process consumes up to 42% less energy and reduces greenhouse gas emissions by more than 56%, saving the energy equivalent of over 15 million gallons of gasoline per year.

The Biosuccinium™ cradle-to-gate study was executed by the Copernicus Institute of Sustainable Development at Utrecht University, the Netherlands¹². The Biosuccinium™ process uses non-fossil raw materials, sequesters carbon dioxide (CO₂), is energy efficient and the process does not produce unnecessary by-products. Figure 1 shows the carbon footprint of Biosuccinium™. It has a large potential carbon footprint reduction - about 8 kg CO₂-equivalent per kilogram of acid - that is possible when fossil based adipic acid is “substituted” with Biosuccinium™. The adipic acid data is executed by DSM for a best in class plant with 98% N₂O abatement. DSM used SimaPro software with EcoInvent database 2.0.

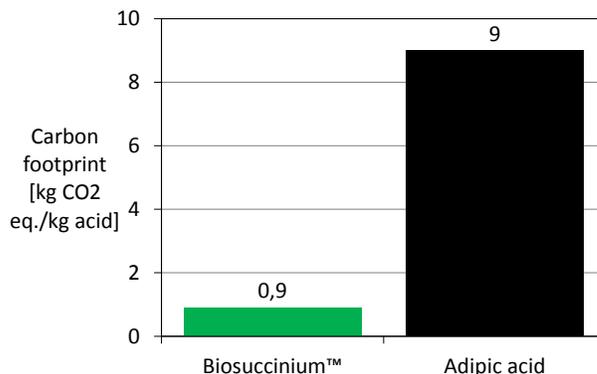


Figure 1: Reduction of the carbon footprint using Biosuccinium™ versus petrochemical adipic acid¹²².

EXPERIMENTAL

Materials

The raw materials used in this study are shown in Table 2. Polyols used in the preparation of NCO-prepolymers, quasi prepolymers and TPUs were de-moisturized for 24 hours under vacuum of 1-3 mm Hg and continuous mixing by magnetic stirrer. The temperature of the polyols during degassing was kept above melting temperature of the polyol (80°C for PDOSA 2000 and 110°C for BDOSA 2000). The PDO and BDO used were dried under vacuum of 1-3 mm Hg at 70°C and continuous mixing by magnetic stirrer. 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).

Designation	Identification
Susterra®	biobased 1,3 Propanediol
Biosuccinium™	biobased Succinic acid
1, 4 Butanediol	1,4 Butanediol
Butyltintris(2-ethylhexanoate)	Butyltintris(2-ethylhexanoate)
Dabco T-12	Dibutyltin dilaurate
Mondur M	Diphenylmethane 4,4'-diisocyanate (flaked) NCO% = 33.6
Rubinate 44	Diphenylmethane 4,4'-diisocyanate NCO% = 33.6
Water	Distilled water
Oil	Vacuum pump oil
Toluene	Toluene
Ethyl acetate	Ethyl acetate
Xylene	Xylene
Methyl ethyl ketone	Methyl ethyl ketone
Benzoyl Chloride	Benzoyl Chloride

Preparations

Polyester Polyols

The PDOSA 2000 and BDOSA 2000 polyol samples were both prepared according to the protocol described by Sonnenschein et. al⁹.

Preparation of NCO-prepolymers and NCO-quasi Prepolymers

The prepolymers and quasi-prepolymers based on PDOSA 2000 and BDOSA 2000 were prepared utilizing 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 hours.

Preparation of 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). NCO-prepolymer was preheated at 80°C, weighed into Speed Mixer cup and degassed under vacuum at 80°C for 120 minutes. The prepolymer was then heated at 90°C for 15 minutes in air circulation oven, chain extender containing catalyst (conditioned at RT) was added to the prepolymer and all components were mixed via Speed Mixer (FlackTek Inc.) for 30-60 seconds at 2200 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 hours at 120°C. Afterwards, the samples were post-cured for 16 hours at 100°C. Cylindrical “button samples” (6.5cm² 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 hours and then post-cured for 16 hours at 100°C. The TPU samples were kept in desiccators and aged for seven days at room temperature prior to testing.

Preparation of 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 isocyanates index of 1.02. TPU sheets and round bottom samples were prepared as previously described.

Testing

Polyols

- 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, (M_w, M_n & M_w/M_n)

Prepolymers

- NCO%, ASTM D 5155

Elastomers

- 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 500g, 2000 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° and 70°C was measured by using heat chamber attached to the Instron tester.
- Solvent resistance, including water: 3 elastomer specimens (10 x 40 x 2mm) (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.

RESULTS & DISCUSSION

Polyester Polyols

1,3-Propanediol Succinate Polyol (PDOSA)

Several batches of PDOSA polyols were prepared (Table 3). Molecular weight was controlled by stoichiometry. First batches were produced using Dabco T-12 as a catalyst which proved to be very reactive with the aromatic isocyanate, 4,4'-MDI. In order to decrease reactivity of the polyol, butyl tris(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.

Table 3. Formulations and Properties of PDOSA and BDOSA, Mw 2000

Type	Methods	PDOSA	PDOSA	PDOSA	BDOSA	BDOSA
Label		A	B	C	D	E
Formulation (pbw)						
Succinic acid		1000	1000	1000	1000	1000
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 ⁽¹⁾	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 @50.0°C @70.0°C	ASTM D 4878-08	5300 2680	5600 1960	4601 1360	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#	1955	1979	1968	1918	1879

⁽¹⁾ Hydroxyl Values adjusted for acidity

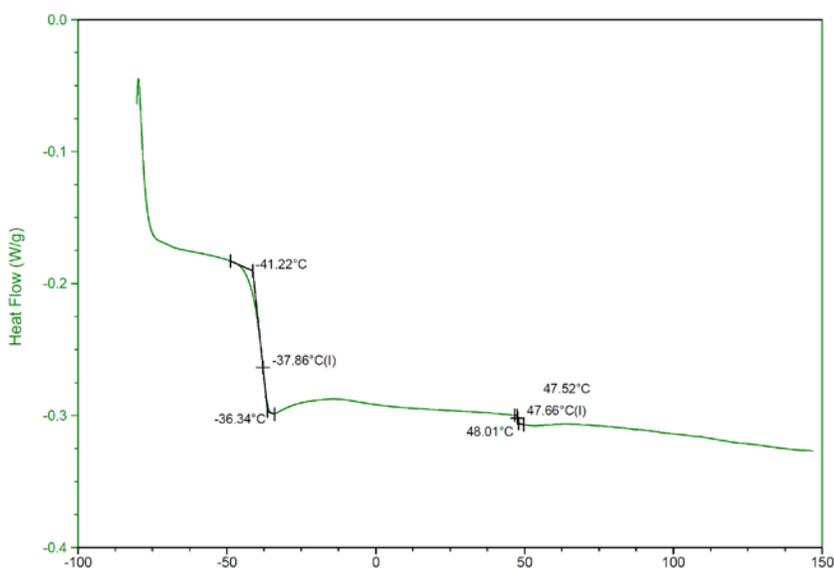


Figure 2. DSC of PDOSA polyol

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°C and 48°C, respectively (Figure 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 a 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 (Table 3). Molecular weights, calculated from hydroxyl numbers measured on each batch of polyol, were 1879 and 1918.

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°C and 108°C (Figure 3), which were almost identical to those reported by Sonnenschein et al.⁹.

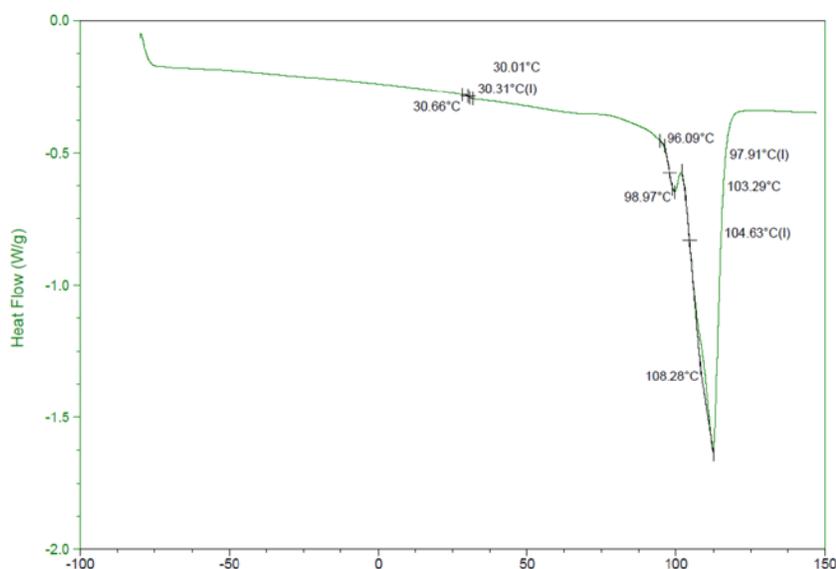


Figure 3. DSC of BDOSA polyol

NCO-Prepolymer / Quasi-Prepolymer Formulations

PDOSA + PDO

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 (Table 4). The resulting viscosity of the quasi-prepolymers was lower than the straight NCO-prepolymers, due to presence of monomeric 4,4'-MDI.

BDOSA + BDO

The viscosity of the NCO-prepolymer (NCO/OH=2/1) based on 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}. The melting temperature of BDOSA 2000 polyol is at 108°C measured via DSC (Table 3, Figure 3) which relates to the high viscosity of the prepolymers. It is not easy to measure the viscosity of a NCO-prepolymer at 120°C using a Rheometer because it will react with ambient moisture.

Label	F	G
NCO/OH Ratio	3:1	3:1
Prepolymer Formulation (pbw)		
Mondur M	81.50	196.61
PDOSA 2000 (table 3 B)	215.56	-
PDOSA 2000 (table 3 C)	-	492.11
Benzoyl chloride	5 drops	5 drops
Reaction temperature and time		
Time of Polyol Addition	21 min.	23 min.
Time of Reaction	30 min.	45 min.
Temperature (°C)	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	-	6570

Polyurethane Elastomer Formulations

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.

Label	H	I
Hard segment, %	30	31
Formulation, pbw		
PDOSA Prepolymer (table 4,F)	35.80	-
PDOSA Prepolymer (table 4,G)	-	50
PDO	1.5487	1.944
Dabco T-12	0.0013	0.0022
Isocyanate Index	1.02	1.02
Curing Conditions		
Temp of NCO-prepolymer, °C	120	120
Temp of PDO, °C	80	80
Temp of Dabco T-12, °C	80	80
Mixing @ 2200RPM, sec	20	20
Gel Time, sec	180	105
Curing time and temp	2 h @ 120°C	2 h @ 120°C
Post-curing time and temp	20 h @ 100°C	20 h @ 100°C

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.

<i>Table 6. Formulation and Curing Conditions of One-Shot TPUs</i>							
Label	J	K	L	M	N	O	P
Type	PDOSA +PDO	PDOSA +PDO	PDOSA +PDO	PDOSA +BDO	PDOSA +BDO	BDOSA +BDO	BDOSA +BDO
Hard segment, %	22	22	31	23	33	24	34
Formulation, pbw							
PDOSA 2000 (table 3 A)	40	-	-	77.200	-		
PDOSA 2000 (table 3 C)	-	60	40	-	60		
BDOSA 2000 (table 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 of polyol, °C	120	120	120	80	120	120	120
Temp of PDO, °C	120	120	120				
Temp of BDO, °C				80	120	120	120
Temp of Dabco T-12, °C	120	120	-				
Temp of Mondur M, °C	80	80	80	80	80	80	80
Mixing@2200RPM	20 sec	20 sec	20 sec	30	20	20	20
Gel Time, sec	170	100	95	390	75	105	60
Curing time and temp	2 h @ 120°C						
Post-curing time & temp	20 h @ 100°C						

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 (Table 6).

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% (Table 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.

Polyurethane Elastomer Properties

Quasi-Prepolymer Method Using PDOSA + PDO

The properties of TPUs at 31% hard segment concentration are shown in Table 7. The tensile strength was 5695 psi at 690% elongation at break (Figure 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, ShoreA 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 concentration¹⁴. Retention of tensile modulus at 100%, 200%, and 300% elongation was good and comparable to that of the TPUs prepared from PDOAA at the same hard segment concentration.

Table 7. Physical Properties of Prepolymer Method TPU			
Label	I		
Type	PDOA+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	4105	4054
@100% Strain	842	762	668
@200% Strain	1,185	1060	971
@300% Strain	1,590	1404	1383
Elongation at break, %	690	681	654
Tensile Strength @50°C, psi			
@ Break ⁽¹⁾	2,589 ⁽¹⁾		
@100% Strain	792		
@200% Strain	1,054		
@300% Strain	1,379		
Tensile Strength @70°C, psi			
@ Break ⁽¹⁾	1,977 ⁽¹⁾		
@100% Strain	707		
@200% Strain	920		
@300% Strain	1,118		
Elongation at break, % ⁽¹⁾			
@50°C	514 ⁽¹⁾		
@70°C	489 ⁽¹⁾		
Toughness, psi	3,929,550		
Resilience, %	19.6	47	49
Tear Strength, lbf/in	559	625	638
Abrasion, 2000 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, $\mu\text{m}/\text{m}^\circ\text{C}$			
From -75°C up to Tg	47.3		
Above Tg	199		

⁽¹⁾ Samples reached maximum oven height and did not break

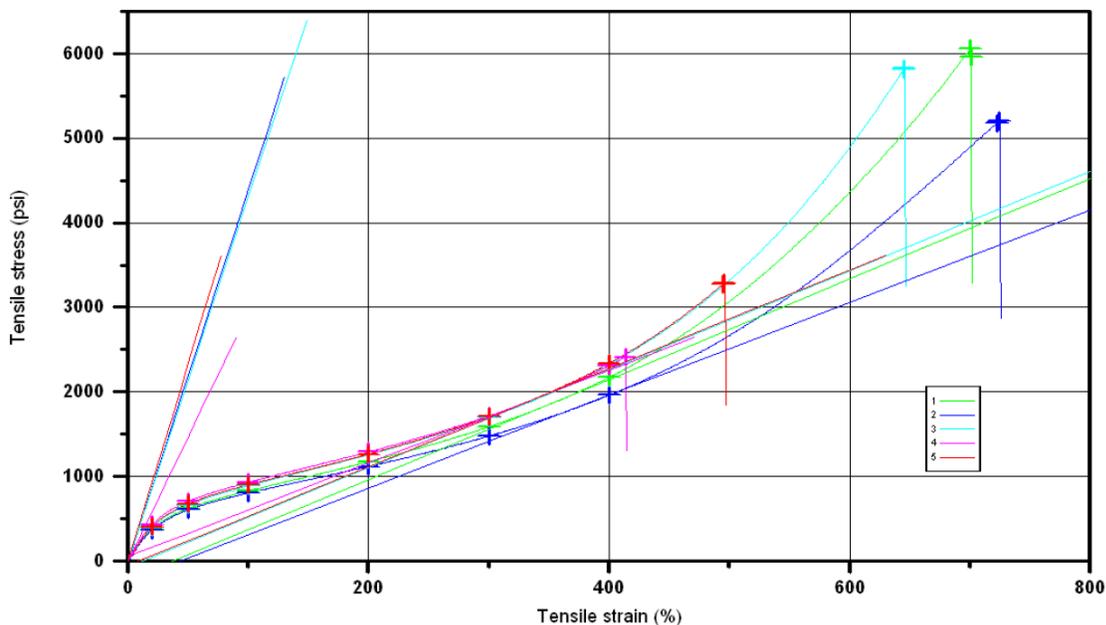


Figure 4. Stress-strain properties (at room temperature) of PDOA Pre-Polymer TPU (Table 7,I).

The hardness of the PDOSA and PDOAA TPUs (Shore A87 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 (Table 7). FTIR confirmed there were no traces of residual isocyanate. DSC analysis indicates three transitions: at -10.7°C (T_g), 42.5°C (melting of soft segment) and 155°C (hard segment melting) (Figure 5). The T_g as measured via DSC of this PDOSA based TPU (-10.7°C) was a higher temperature compared to the PDOAA (-37°C) and BDOAA (-35°C) based TPUs at the same hard segment concentration (Table 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).

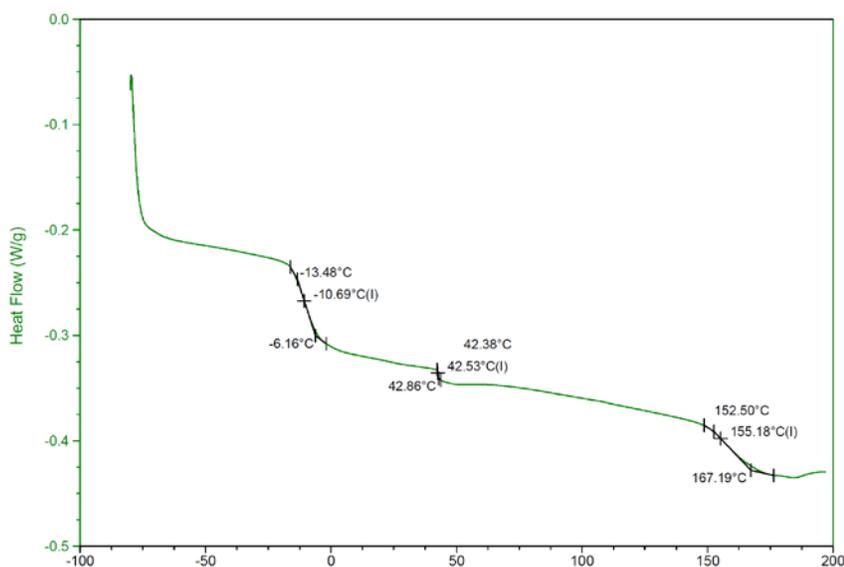


Figure 5. DSC of elastomer prepared via pre-polymer method from PDOSA Pre-Polymer (Table 7,I).

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

Solvent	Mass Gained (%)
Toluene	21.34
Methyl ethyl ketone	62.24
Xylene	11.18
Ethyl acetate	46.57
Oil	0.32
Water	1.15

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% (Table 9 and Figure 6). 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 ShoreA 64 (Table 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.

Table 9. Properties of One-Shot TPU (PDOSA)					
Label	J	K	L	M	N
Type	PDOSA +PDO	PDOSA +PDO	PDOSA +PDO	PDOSA +BDO	PDOSA +BDO
Hard Segment, %	22	22	31	23	33
Hardness, Shore A	64	-	-	67.1	-
Density, g/cm ³	1.29	-	-		
Tensile Strength, psi					
@ Break	2691	2746	2274	615.91	1447
@100% Strain	394	427	735		
@200% Strain	526	567	983		
@300% Strain	662	715	1257		
Elongation at break, %					
@ RT	831	808	559	655.94	562
@ 50°C	-	468	406		
@ 70°C	-	423	402		
Tensile Strength @50°C, psi					
@ Break*		1277	1786		
@100% Strain		495	870		
@200% Strain		641	1113		
@300% Strain		797	1396		
Tensile Strength @70°C, psi					
@ Break*		814	1536		
@100% Strain		427	799		
@200% Strain		536	998		
@300% Strain		651	1236		
Toughness, psi	2,236,221	2,218,768	1,271,166		
Resilience, %	10	-	-	25.56	-

*Samples reached maximum oven height and did not break

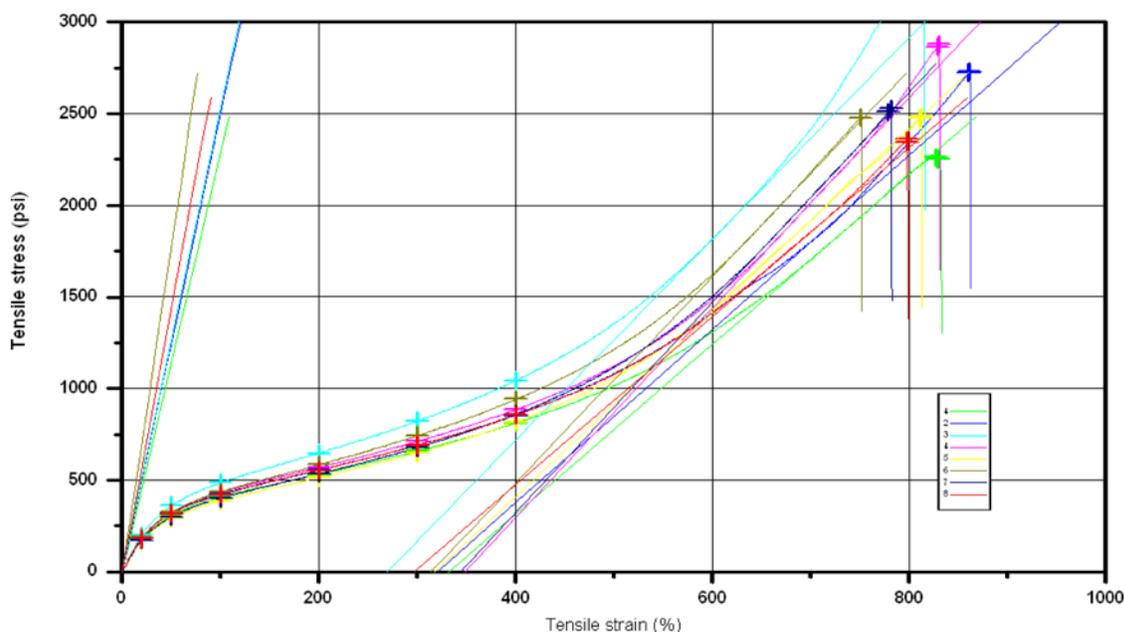


Figure 6. Stress-strain properties (room temperature) of One-Shot TPU (Table 9,K)

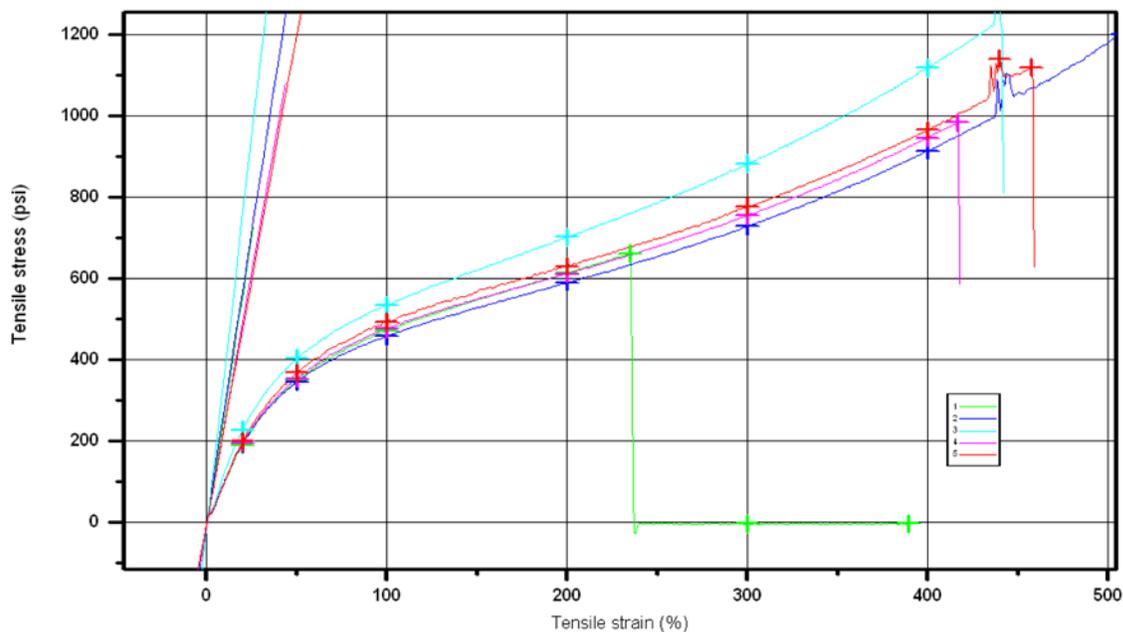


Figure 7. Stress-strain properties (at 50°C) of One-Shot TPU (Table 9,K)

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% (Table 9); however, the tensile strength was lower as compared to TPU based on PDO (Table 9).

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 (Table 10). High hardness of these TPUs can be related to the high crystallinity of the BDOSA polyol. The stress-strain test results indicate that both types of elastomers exhibited yield at relatively low strain (Table 10 and Figures 8 and 9), clearly indicating a plastic behavior of these materials. Flexural strength and modulus were measured and shown to be very good (Table 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°C is also good (Table 10). Overall, the solvent resistance of TPUs based on BDOSA polyol is excellent which confirms earlier results by Theunissen et al.^{11,13} (table 11).

Others have also reported the relatively high hardness that occurs when using 2000 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 2000 g/mol BDOSA polyols. The effect is reported to be less strong for 1000 g/mol BDOSA polyols. 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 (see tables 12 and 13) with respect to hardness and tensile properties.

<i>Table 10. Properties of One-shot TPUs (BDOSA + BDO)</i>		
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 @ Yield	5421 2632	6546 2958
Elongation, % @ Break @ Yield	671 15	685 15
Young's 0%-1% Elasticity, psi	27625	27937
Young's 0%-2% Elasticity, psi	45719	45917
Young's 0%-3% Elasticity, psi	50322	50787
Toughness, psi	79,494	94,262
Resilience, %	15	18
Tensile Strength at 50°C, psi @ Break @ Yield	>3441* 1382	>4238* 2201
Elongation at 50°C, % @ Break @ Yield	>537* 14	>538* 18
Tensile Strength at 70 °C, psi @ Break @ Yield	>2586* 754	>3365* 1412
Elongation at 70 °C, % @ Break @ Yield	>537* 15	>534* 23
Tear Strength, lbf/in	975	1441
Flexural strength, psi	3329	3514
Flexural modulus, psi	64565	60698
Abrasion, 2000 rotations, 500 g, 60%vac, H-22 wheels, % mass loss	5.0	2.4
Glass transition temperature via DSC via DMA (Maximum of loss modulus) via TMA	-18.7°C 13.8°C 8.7°C	-17.9°C 11.2°C 5.4°C
Coefficient of thermal expansion via TMA, µm/m°C From -75°C up to Tg Above Tg	74.3 161	52.4 120

*Samples reached maximum oven height and did not break

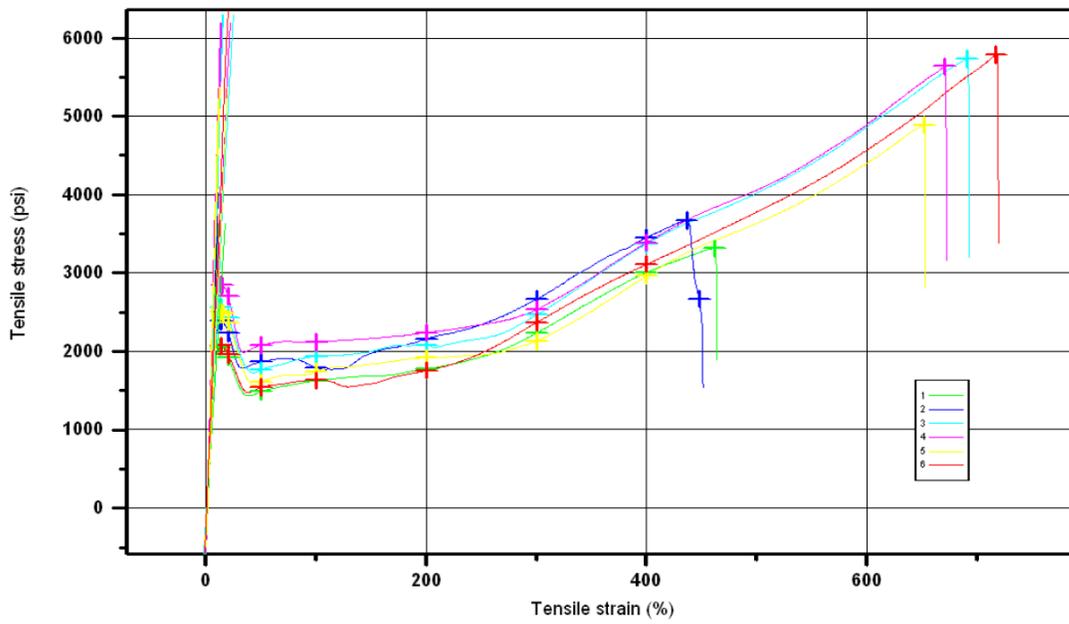


Figure 8. Stress-strain properties (measured at room temperature) of one-shot elastomer prepared from BDOSA and BDO as a chain extender at 23.95% hard segment concentration (Table 10,O)

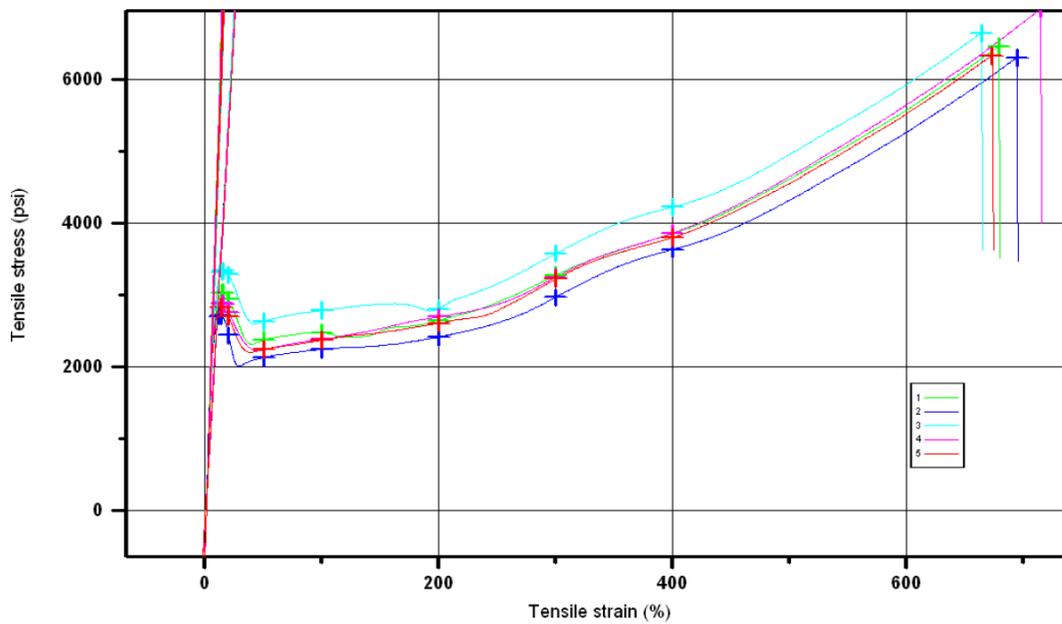


Figure 9. Stress-strain properties (measured at room temperature) of one-shot elastomer prepared from BDOSA and BDO as a chain extender at 33.90% hard segment concentration (Table 10,P)

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

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 (tables 12 and 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.

Polyol	Mn	Acid value	OH value	Viscosity	Tm
	[g/mol]	[mg KOH/g]	[mg KOH/g]	[cPoise at 75°C]	[°C]
BDOAA	2000	1.1	53.9	Solid	115
BDOSA	2117	0.1	52,9	733	60
EBAA ⁽¹⁾	2004	1.1	53,9	999	<70
EBSA ⁽¹⁾	2004	1.3	56,0	579	<70

⁽¹⁾: mixture of ethylene glycol and 1,4-butanediol in 50/50 molar ratio used in the polyol

Polyol	Hardness ⁽²⁾	Tensile test	Abrasion	Toluene uptake	2-butanone uptake
	[ShoreA]	[MPa at 200 500,1000%]	[mg weight loss]	Swell-index [%]	Swell-index [%]
BDOAA	93A	10/15/30	0,034	16	54
BDOSA	93A ⁽¹⁾	12/20/38	0,061	5	23
EBAA	90A	7/10/15	0,066	11	45
EBSA	94A	15/20/35	0,070	3	29

⁽¹⁾: required higher processing temperature due to the higher melting point of BDOSA-polyol

⁽²⁾: standard formulations have been used targeting a hardness of 95 ShoreA using BDO as chain extender (no optimization or improvements on the formulation have been done)

CONCLUSION

Biosuccinium™ and Susterra® are potential alternatives for (fossil-based) adipic acid and 1,4-butanediol 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 Biosuccinium™ and Susterra® are 100% biobased and renewable raw materials. The production of Susterra® consumes up to 42% less energy and reduces greenhouse gas emissions by more than 56% compared to fossil based 1,3-propanediol. Biosuccinium™ has a much lower carbon footprint than fossil-based adipic acid – about 8 kg of CO₂ equivalents per kg of acid – which enables it to also substantially decrease the carbon footprint of polyurethanes and products made of it.

The work presented here is intended to be a reference for a first technical evaluation of use of Biosuccinium™, Susterra® or the combination of Biosuccinium™ and Susterra® 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.

Polyester polyols

PDOSA and BDOSA polyester polyols of 2000 g/mol molecular weight were synthesized without any problems and the process is very similar to synthesis of standard BDOAA polyester polyols. The same result was obtained for PDOAA^{4,10} before. Multiple batches of each type of polyol exhibited hydroxyl numbers close to the 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 well¹⁰. 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 work¹¹ 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.

Thermoplastic polyurethanes

Manufacturing

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 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.

Properties Prepolymer Method TPUs

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 concentration¹⁴. Retention of tensile modulus at elongation 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.

Properties One-Shot method TPUs

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 biobased 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 Shore D ~55 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. 1000 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 (see table 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 %.

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Richard Janssen



Richard Janssen is New Business Development Manager for Reverdia since 2010. He has a M.Sc. in Chemical Engineering and a Ph.D. in Particle Technology both from Delft University of Technology. He joined DSM Research in 2001 and since 2007 he has worked on innovation and new business development in the DSM Innovation Center.

Robert Miller



Robert Miller has worked for the past 5 years as Technical Service Specialist for DuPont Tate & Lyle Bio Products. Robert received his B.S. in Chemistry from Ursinus College in Pennsylvania. Previously to joining DuPont Tate & Lyle Robert spent two years with DuPont Central Research and Development in Wilmington, DE.

Lawrence Theunissen



Lawrence Theunissen received a degree in Mechanical Engineering. He worked in the field of virtual product design and application engineering (CAD/CAE). He joined DSM in 2002, and since then managed application development activities for various business units in research and innovation environments. Since 2011 Lawrence works for Reverdia as Manager Application Development.