

Expanding the Structure-Property Relationship of Susterra® 1,3-Propanediol in Elastomers

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ABSTRACT

In this paper we have prepared a series of PDO-based elastomers with the focus on expanding the structure-property relationship of 1,3 Propanediol (PDO) as a building block in TPU soft segments and hard segments. Several MDI-based TPU's were prepared using the prepolymer method to achieve a hard segment concentration ranging from 20% to 37%, and to evaluate the performance of 1000 and 2500 Mw PDO adipate polyester polyols. The physical and dynamic properties of these materials will be discussed. The combined use of Susterra® in a polyester polyol and chain extender can produce a final polyurethane product containing up to 33 wt% bio-based content.

INTRODUCTION

Susterra® 1,3-propanediol (PDO), a 100% bio-based diol, continues to be used successfully as a building block in a variety of polyurethane applications globally. The successful evaluation of PDO as an alternative to 1,4-butanediol (BDO) has been reported at CPI Technical Conferences, PMA Technical Conference and literature.^{1,2,3,4,5,6,7} At the 2011 Conference we reported the evaluation of PDO-based thermoplastic polyurethanes with structural differences that offered unique physical and dynamic properties, including improved strength, flexibility and transparency. Those differences were attributed to the “odd-even” effect that illustrates how the PDO-based soft block and PDO-based hard block enable unique and new urethane applications⁶. A detailed explanation can be found in conference proceedings^{3,6} and literature.^{8,9,10}

This paper attempts to expand this subject by reporting the use of alternate molecular weight polyester polyols based on PDO adipates, and their resulting elastomers with varying hard segment concentrations. MDI-based TPU's were synthesized using a prepolymer method to achieve a hard segment concentration ranging from 20% to 37%.

As reference, BDO-based polyurethanes were prepared. The physical and dynamic properties were measured.

EXPERIMENTAL

Materials

The raw materials used in this study are shown in Table 1. Prior to preparation of prepolymers, polyols and BDO were dried for 24 hours at 75 -80°C under vacuum of 1-3 mm Hg and continuous mixing by magnetic stirrer. The water content after drying was checked by Karl Fisher Titrator. The water content of PDO was low and no further drying was necessary.

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).

Both the PDO and BDO polyol is a solid at room temperature. Viscosities at 60°C are reported in Table 1.

Table 1. Materials		
Designation	Identification	Supplier
Poly S2500 PAR (PDOAA 2500)	Propanediol Adipate, MW 2500 OH#: 47 mg KOH/g, Acid #: 0.7 mgKOH/g Visc.@60°C: 1941 cPs	BASF (Formerly ITWC, Inc.)
Poly S2500 BA (BDOAA 2500)	Butylene Adipate, MW 2500 OH#: 47 mg KOH/g, Acid #: 0.7 mgKOH/g Visc.@60°C: 1893 cPs	
Poly S1000 PAR (PDOAA 1000)	Propanediol Adipate, MW 1000 OH#: 110.6 mg KOH/g, Acid #: 0.3 mgKOH/g Visc.@60°C: 341 cPs	
Poly S1000 BA (BDOAA 1000)	Butylene Adipate, MW 1000 OH#: 114.6 mg KOH/g, Acid #: 0.3 mg KOH/g Visc.@60°C: 323 cPs	
Susterra® propanediol	1,3 Propanediol	DuPont Tate & Lyle
1, 4 Butanediol	1,4 Butanediol	Alfa Aesar
Mondur M	Diphenylmethane 4,4'-diisocyanate (Flaked) NCO% = 33.6	Bayer AG

Preparation of NCO-prepolymers:

The NCO-prepolymers and quazi-prepolymers based on 1,3-PDO adipate polyester polyol of 2500 MW and BDO adipate polyester polyol of 2500 MW were prepared utilizing laboratory procedure for prepolymer preparation, 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 was continued under heating. Afterwards, the prepolymer was degassed and transferred into glass jars and sealed under dry nitrogen. Formulations of NCO-prepolymers and processing conditions are shown in Table 2.

The NCO% of prepolymers was checked after 24 hours. NCO% of the NCO-prepolymers was measured according to ASTM D5155 and viscosities at 70°C with a Rheometer.

Preparation of polyurethane elastomers:

TPUs were prepared by reacting 4,4'-MDI polyester prepolymer (or quazi-prepolymers) with a chain extender at an isocyanate index of 1.02. TPUs 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 100°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 15-40 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 ten days at RT prior to testing.

Testing

Polyols – GPC analysis was performed on the polyester polyols.

NCO-Prepolymers – NCO% was measured according to ASTM D 5155, viscosity at 70°C via Rheometrics.

Elastomers – The following properties were measured on the Shore A 67, 83 and 90 elastomers

- Hardness, ASTM D-2240, Shore A
- Tensile properties (Tensile Strength, Tensile Modulus and Elongation%), ASTM D 412
- Tear Strength, Dye C, ASTM D 624
- Abrasion Resistance, ASTM D 1044 (H22 wheels, weight load 500g, 2000 cycles)
- Compression set, at 70°C, ASTM D 395
- Resilience, % (Bayshore rebound), ASTM D2632
- Hysteresis, in tensile mode; the 1st and the 10th cycle from zero to 250% strain. The absolute and relative area of absorbed energy was calculated
- Thermo-mechanical analysis, TMA (TMA Q 400, TA Instruments)
- Dynamic mechanical analysis, DMA, in bending mode (DMA 2980, TA instruments)
- Differential scanning calorimetry, DSC (DSC Q 10, TA Instruments)
- Heat resistance of elastomers: modulus of elasticity (200%, 300% and 400% elongation) at 50 and 70°C was measured by using heat chamber attached to Instron tester.
- Solvent resistance (including water resistance) of elastomers: 3 elastomer specimens (10 x 40 x 2mm) (cut from the sheet) were weighed together and immersed in solvent at room temperature. The samples were taken out after 1 day and 7 days of immersion. Their weight and dimension were measured.
- Resistance to flexing was measured as cut growth using Ross Flexing Apparatus per ASTM D 1052.

RESULTS & DISCUSSION

Six polyurethane elastomers based on 4,4'-MDI, and 1000 Mw or 2500 Mw polyester polyols based on PDO adipate (PDOAA) or BDO adipate (BDOAA) were prepared (Table 2).

Designation	1000 Mw Adipate	2500 Mw Adipate	Chain extender	% Hard Segment
BDOAA 1000	BDO		BDO	37%
PDOAA 1000	PDO		PDO	37%
BDOAA 2500		BDO	BDO	20%
PDOAA 2500		PDO	PDO	20%
BDOAA 2500		BDO	BDO	30%
PDOAA 2500		PDO	PDO	30%

NCO-Prepolymer / Quasi-Prepolymer Formulations

Formulations of NCO-prepolymers and quazi-prepolymers are shown in Table 3. All prepolymers and quazi-prepolymers were solid at room temperature. The viscosity of prepolymers based on polyester polyols of 2500 MW was significantly higher at 70°C than that of prepolymers based on 1000 MW polyols. The NCO% of the prepolymers was very close to the theoretical (calculated) values.

<i>Table 3. Formulation and properties of NCO-prepolymers</i>						
Designation	BDOAA 1000 (2:1)	PDOAA 1000 (2:1)	BDOAA 2500 (2:1)	PDOAA 2500 (2:1)	BDOAA 2500 (3:1)	PDOAA 2500 (3:1)
NCO/OH Ratio	2:1	2:1	2:1	2:1	3:1	3:1
<i>Formulation, pbw</i>						
Mondur M	439.5	517.6	231.3	257.0	275.7	417.7
BDOAA 1000	836.4	-	-	-	-	-
PDOAA 1000	-	1014.5	-	-	-	-
BDOAA 2500	-	-	1058.49	-	800.0	-
PDOAA 2500	-	-	-	1176.14	-	1176.1
<i>Reaction temp & time</i>						
Polyol Addition, min	7 min	33 min	21 min	9 min	20 min	30 min
Reaction Temp (°C)	64-79	64-77	68-85	66-80	71-87	68-81
Reaction Time	145 min	145 min	140 min	135 min	145 min	145 min
Degass Time	40 min	40 min	40 min	45 min	40 min	40 min
<i>Properties</i>						
NCO% Theoretical	5.626	5.63	2.87	2.87	5.79	5.98
NCO% Measured	6.10	5.66	2.88	3.06	5.85	6.05
Consistency at RT	Solid	Solid	Solid	Solid	Solid	Solid
Visc. at 70°C, Pa.s	26500	21000	47000	45000	39000	40000

Polyurethane Elastomer Formulation

Thermoplastic polyurethane elastomers were prepared by using NCO-prepolymers from Table 3 at a 1.02 isocyanate index. Hard segment concentrations of 20% & 30% were prepared using 2500 Mw samples, and 37% hard segment sample was prepared using 1000 Mw. Formulations and curing conditions are shown in Table 4.

<i>Table 4. Formulations and curing conditions of elastomers</i>						
Type of Elastomer	BDOAA 1000	PDOAA 1000	BDOAA 2500	PDOAA 2500	BDOAA 2500	PDOAA 2500
Hard Segment, %	37%	37%	20%	20%	30%	30%
Formulation, pbw						
NCO-Prepolymer						
BDOAA 1000 (2:1)	75.09	-	-	-	-	-
PDOAA 1000 (2:1)	-	76.10	-	-	-	-
BDOAA 2500 (2:1)	-	-	77.64	-	-	-
PDOAA 2500 (2:1)	-	-	-	77.88	-	-
BDOAA 2500 (3:1)	-	-	-	-	75.82	-
PDOAA 2500 (3:1)	-	-	-	-	-	75.82
1,4-Butanediol	4.91	-	2.40	-	4.26	-
1,3-Propanediol	-	3.90	-	2.11	-	4.18
Dabco T-12	-	-	-	-	-	0.004
Isocyanate Index	1.02	1.02	1.02	1.02	1.02	1.02
Curing Conditions						
Temp of NCO-prepolymer, °C	100	100	120	120	100	120
Temp of diol, °C	100	100	80	80	80	80
Mixing, sec	15s	45 s	25s	25s	30s	40 s
Gel Time	40s	180s	60s	60s	100s	120s
Curing time & temp	2 hours @ 120°C					
Post-curing time & temp	20 hours @ 110°C					

Polyurethane Elastomer Properties

BDOAA 2500 vs. PDOAA 2500, 20% Hard Segment

Physical and mechanical properties are shown in Tables 5-8 and Figures 1-6. Overall the PDOAA 2500 elastomer at 20% hard segment appeared to have a more desirable combination of properties compared to the BDOAA 2500 elastomer at 20% hard segment.

The PDO elastomer exhibited a significantly lower hardness (Shore A63) than the BDO elastomer (Shore A81). However, the PDO elastomer had a significantly higher resilience and lower hysteresis compared to the BDO elastomer, which combine to indicate the PDO elastomer exhibits better dynamic properties (Table 5, Figure 1 & 2).

Tensile strength and elongation at break for both elastomers was similar (Table 5, Figure 3 and 4). However, the BDO elastomer did exhibit a yield at low strain (20 % strain).

The abrasion resistance of the PDO elastomer was significantly better, and the compression set was lower.

The tear strength of the PDO elastomers was slightly lower, which could be explained by a lower concentration of polar ester groups in the PDO elastomer.

<i>Table 5. Physical properties of elastomers (2500Mw, 20% hard segment)</i>		
Type of Elastomer	BDOAA 2500	PDOAA 2500
Hard Segment, %	20%	20%
Properties		
Hardness, Shore A (ASTM D2240)	81	63
Resilience, % (ASTM D2632)	27	53
Tensile Strength at break, psi (ASTM D412)	4028	4508
Tensile Strength at yield, psi (ASTM D412)	540	-
Elongation at break,%	721	748
Elongation at yield,%	20	-
Tensile Stress at 100% elongation	557	434
Tensile Stress at 200% elongation	777	641
Tensile Stress at 300% elongation	1130	874
Tensile Stress at 400% elongation	1566	1244
Tear Strength, lbf/in (ASTM D6246)	1520	1354
Compression Set Ca, % (Based on original)	14	11
Compression Set Cb, % (Based on deflection)	54	45
Abrasion resistance, wt. loss, mg/2000 cycles	89	6
Hysteresis, up to 250% elongation, %		
• 1 st loop	80	37
• 10 th loop	40	14
Coefficient of thermal expansion, (µm/m°C)		
• From -75°C up to Tg	56.8	67.7
• From Tg to 0°C	255	244
Glass transition temperature, °C		
• DMA		
• TMA	-22.5	-35.9
• DSC	-37	-37

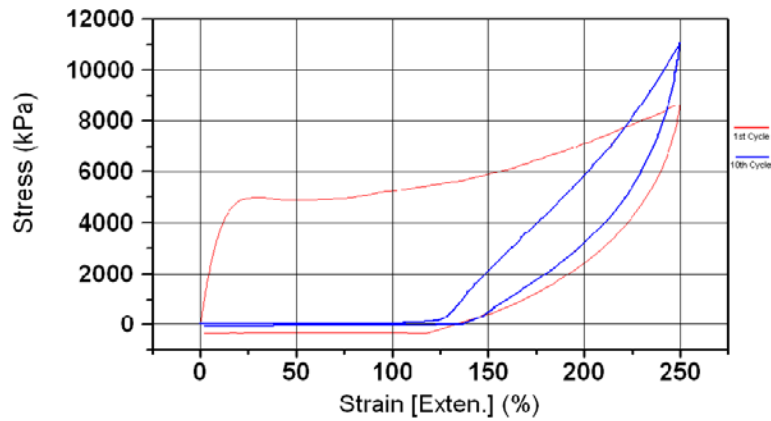


Figure 1. 1st and 10th cycle hysteresis graph of BDOAA elastomers (2500Mw, 20% hard segment)

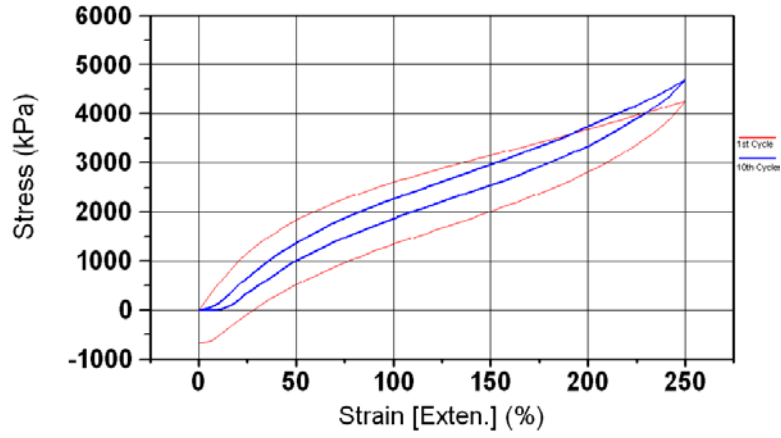


Figure 2. 1st and 10th cycle hysteresis graph of PDOAA elastomers (2500Mw, 20% hard segment)

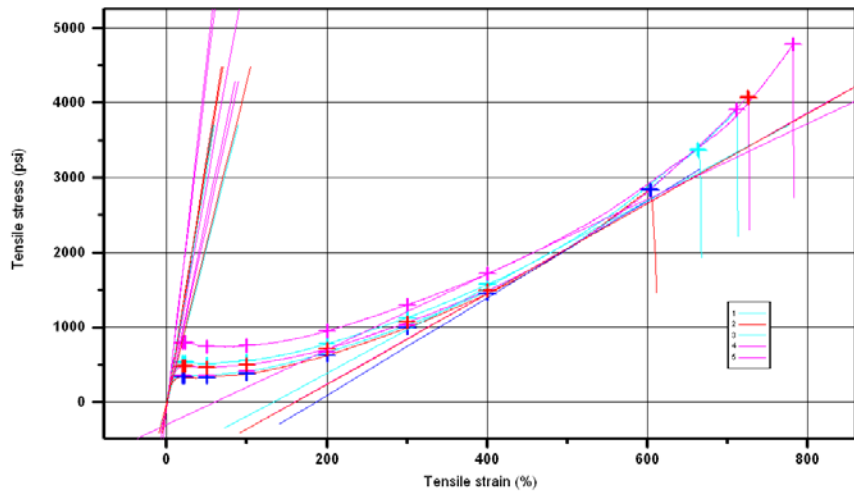


Figure 3. Stress-Strain curve of BDO elastomers at room temperature (2500Mw, 20% hard segment)

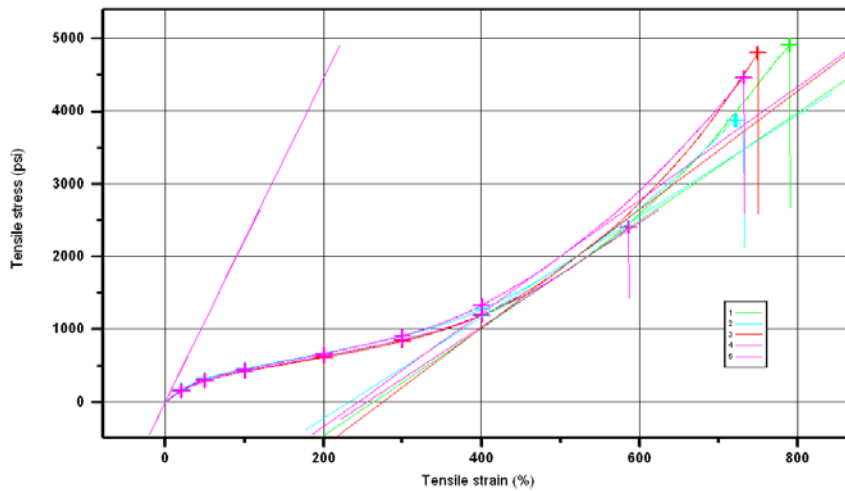


Figure 4. Stress-Strain curve of PDO elastomers at room temperature (2500Mw, 20% hard segment)

The PDO elastomer had higher heat resistance across temperature and strain, as measured by retention of tensile properties at 50° and 70°C relative to those at room temperature (Table 6).

Type of Elastomer	BDOAA		PDOAA	
	50°C	70°C	50°C	70°C
100% elongation	56%	50%	81%	69%
200% elongation	51%	44%	72%	62%
300% elongation	48%	39%	68%	58%
400% elongation	54%	38%	62%	52%

Ross Flexing test was performed per ASTM D1052. The PDO elastomer performed slightly better than the BDO elastomer (Table 7).

Table 7. Cut growth using Ross Flexing Apparatus per ASTM D 1052

Sample ID:	Th. (in.)	Cycles to:				
		100% Growth	200% Growth	300% Growth	400% Growth	500% Growth
BDO Elastomer	0.244	8,696	16,667	28,571	39,216	44,776
PDO Elastomer	0.243	5,000	18,750	34,043	43,860	50,769

The glass transition temperature (T_g) of the PDO and BDO elastomers, as measured via DSC, was similar (Table 5, Figures 5 and 6). There is a small transition in DSC graphs at 38°C for both elastomers that could be associated with melting of crystalline phase of polyols. The PDO elastomer has a strong transition at 93°C due to hydrogen bonding dissociation (Figure 6). The continuous decline in DSC starting at about 150°C is likely associated with melting of the hard segment. However, the measurement of melt index would give much better insight into melting properties of those TPUs.

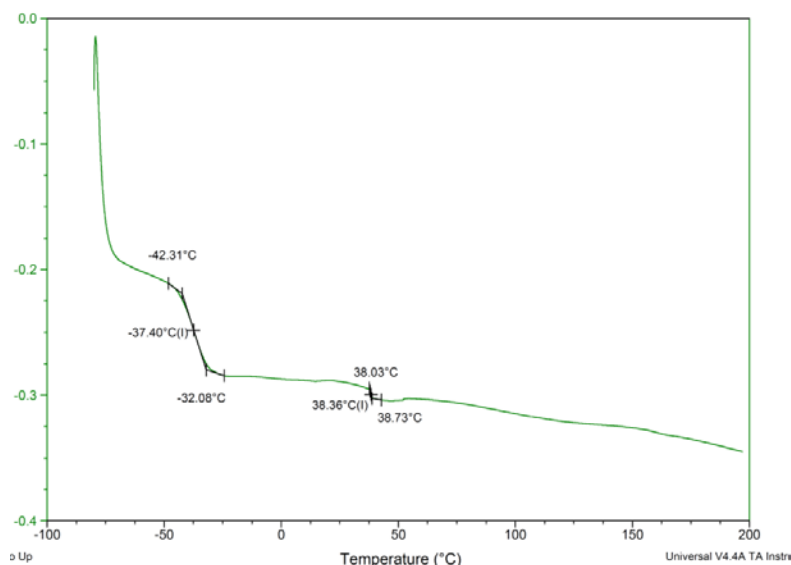


Figure 5. DSC graph of BDO elastomer (2500Mw, 20% hard segment)

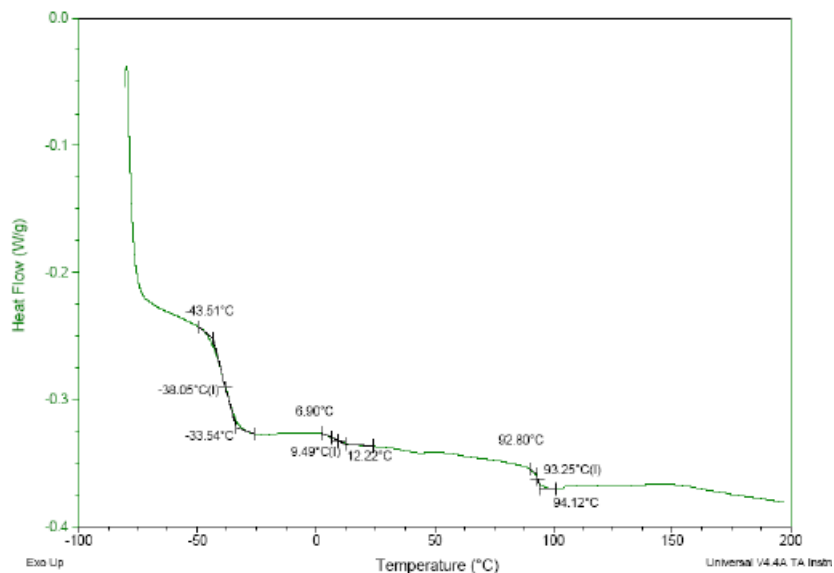


Figure 6. DSC graph of PDO elastomer (2500Mw, 20% hard segment)

The solvent resistance of elastomers in various solvents, including water is shown in Table 8. PDO elastomers appeared to be better in non-polar solvents (toluene and xylene) and comparable in polar solvents (methyl ethyl ketone and ethyl acetate). This is likely due to the more polar nature of the PDO elastomer.

Table 9. Solvent resistance of elastomers weight change, % at 20°C (2500 Mw, 20% hard segment)

Solvent	BDOAA		PDOAA	
	24 hrs	7 Days	24 hrs	7 Days
Toluene	82.79	84.34	68.63	76.44
Methyl ethyl ketone	210.72	217.20	175.19	179.47
Xylene	57.95	59.40	41.79	45.17
Ethyl acetate	122.72	123.39	130.01	129.89
Oil	1.71	1.92	1.38	1.74
Distilled Water	1.08	1.12	1.51	1.64

Polyurethane Elastomer Properties

BDOAA 2500 vs. PDOAA 2500, 30% Hard Segment

Physical and mechanical properties are shown in Table 9 and Figures 7-12. Despite the PDO elastomer having lower hardness and lower resilience, hysteresis of the PDO elastomer was significantly lower than the BDO elastomer (Table 9, Figures 7 and 8). The lower modulus of the PDO samples continues to be a trend.

The abrasion resistance of the PDO elastomer was significantly better, and the compression set was comparable. A lower concentration of polar ester groups due to an increase in hard segment concentration could explain the lower tensile strength, elongation and tear strength.

Table 9. Physical properties of elastomers (2500Mw, 30% hard segment)		
Type of Elastomer	BDOAA 2500	PDOAA 2500
Hard Segment, %	30%	30%
Properties		
Hardness, Shore A (ASTM D2240)	88	85
Resilience, % (ASTM D2632)	48	36
Tensile Strength at break, psi (ASTM D412)	5049	4389
Elongation at break,%	713	631
Tensile Stress at 100% elongation	1070	833
Tensile Stress at 200% elongation	1525	1199
Tensile Stress at 300% elongation	2012	1638
Tensile Stress at 400% elongation	2549	2261
Tear Strength, lbf/in (ASTM D6246)	1252	613
Compression Set Ca, % (Based on original)	6.3	6.8
Compression Set Cb, % (Based on deflection)	24.2	26.9
Abrasion resistance, wt. loss, mg/2000 cycles	24.5	1.8
Hysteresis, up to 250% elongation, % <ul style="list-style-type: none"> • 1st loop • 10th loop 	77 42	37 28
Coefficient of thermal expansion, ($\mu\text{m}/\text{m}^\circ\text{C}$) <ul style="list-style-type: none"> • From -75°C up to T_g • From T_g to 0°C 	50.8 170	71.0 199
Glass transition temperature, $^\circ\text{C}$ <ul style="list-style-type: none"> • DMA • TMA • DSC 	-34.2 -42.66 -41.6	-27.6 -34.03 -34

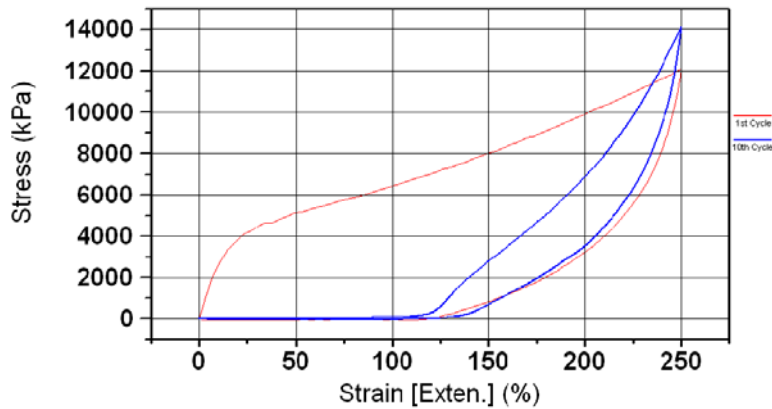


Figure 7. 1st and 10th cycle hysteresis graph of BDOAA elastomers (2500Mw, 30% hard segment)

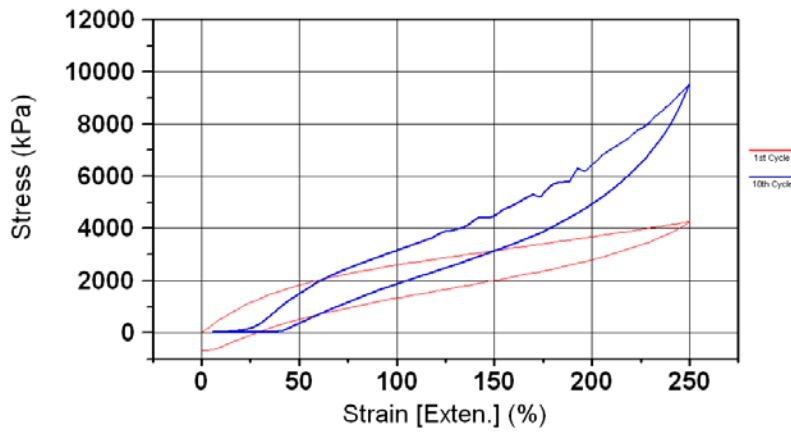


Figure 8. 1st and 10th cycle hysteresis graph of PDOAA elastomers (2500Mw, 30% hard segment)

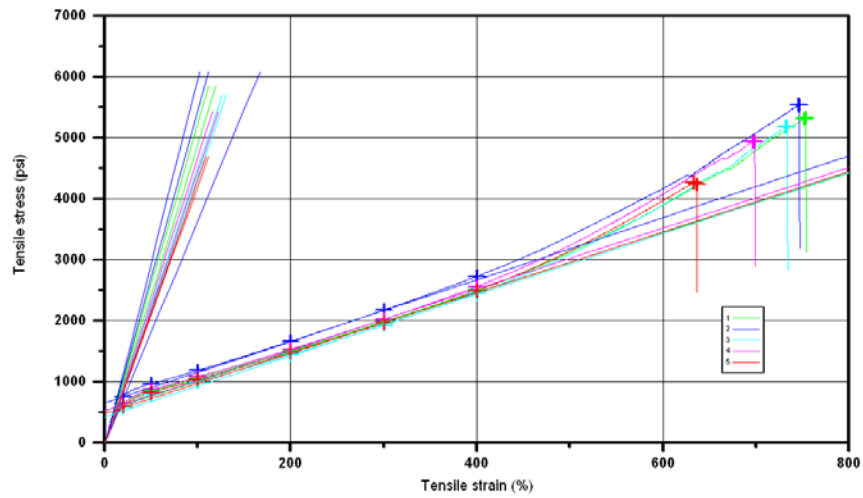


Figure 9. Stress-Strain curve of BDO elastomers at room temperature (2500Mw, 30% hard segment)

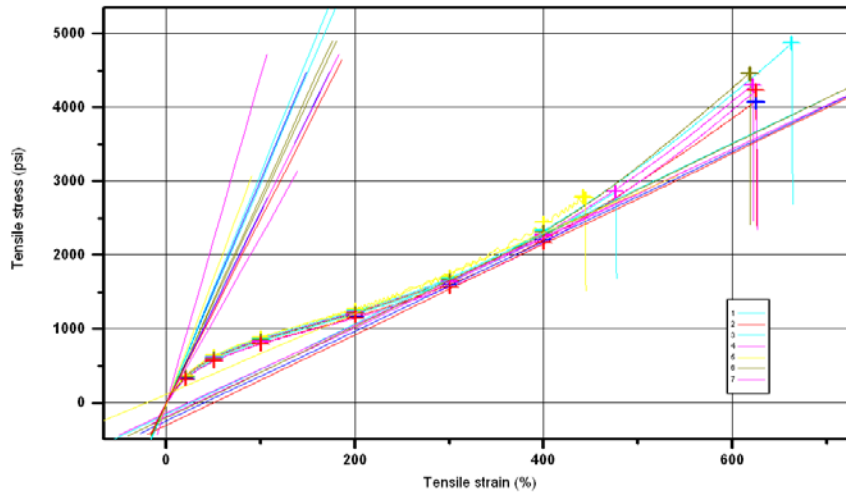


Figure 10. Stress-Strain curve of PDO elastomers at room temperature (2500Mw, 30% hard segment)

The PDO elastomer had higher heat resistance across temperature and strain, as measured by retention of tensile properties at 50° and 70°C relative to those at room temperature (Table 10).

Table 10. % Retention of tensile properties at 50°C & 70°C				
Type of Elastomer	BDOAA		PDOAA	
	50°C	70°C	50°C	70°C
100% elongation	76%	66%	94%	84%
200% elongation	70%	60%	89%	80%
300% elongation	69%	57%	88%	76%
400% elongation	69%	53%	87%	-

DSC graphs for the elastomers are shown in Figure 11 & 12. The glass transition temperature (T_g) of the BDO elastomer was lower by 7.5°C (Table 9, Figure 11 & 12). There is a significant transition in the BDO elastomer at 22°C that could be associated with melting of crystalline phase of polyols. The BDO elastomer has another strong transition at 173°C (Figure 11) likely associated with melting of the hard segment.

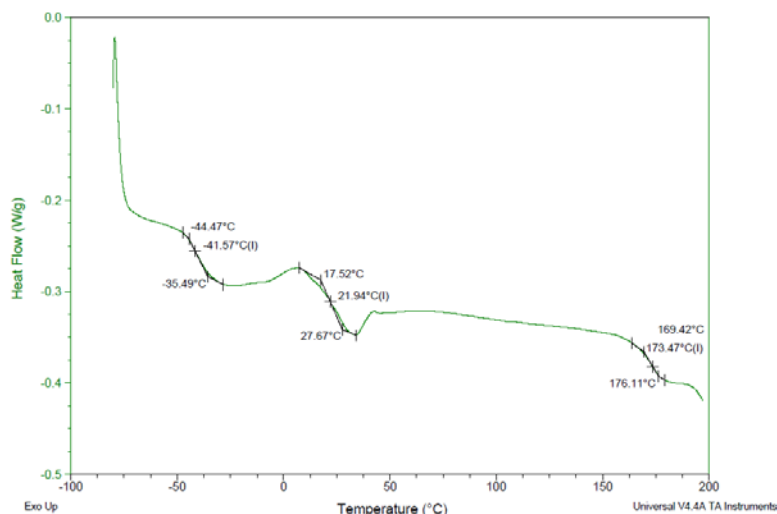


Figure 11. DSC graph of BDO elastomer (2500Mw, 30% hard segment)

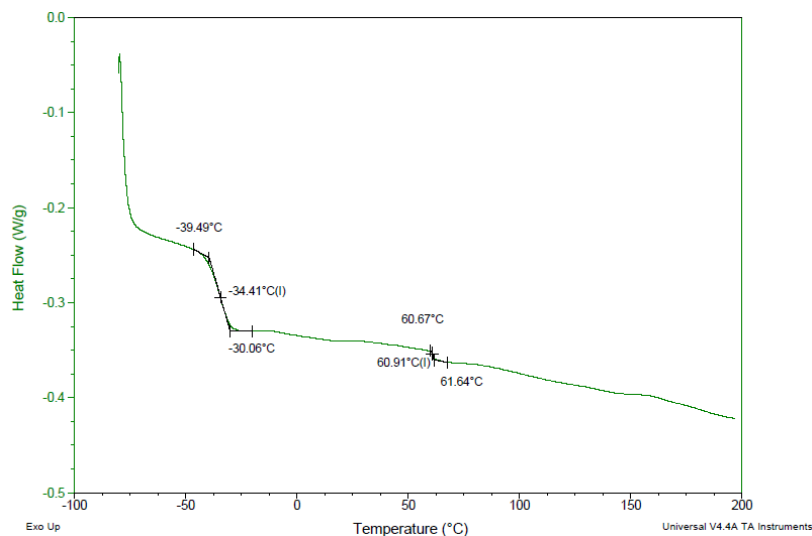


Figure 12. DSC graph of PDO elastomer (2500Mw, 30% hard segment)

The solvent resistance of elastomers in various solvents, including water is shown in Table 11. PDO elastomers appeared to be better in non-polar solvents (toluene and xylene) and comparable in polar solvents (methyl ethyl ketone and ethyl acetate). This is likely due to the more polar nature of the PDO elastomer.

<i>Table 11. Solvent resistance of elastomers weight change, % at 20°C (2500 Mw, 30% hard segment)</i>				
	BDOAA		PDOAA	
Solvent	24 hrs	7 Days	24 hrs	7 Days
Toluene	49.13	50.24	44.03	45.18
Methyl ethyl ketone	69.65	70.71	81.15	82.07
Xylene	19.07	33.16	23.25	31.92
Ethyl acetate	59.49	60.21	69.55	69.89
Oil	3.35	2.90	1.75	2.22
Distilled Water	1.09	1.02	1.68	1.55

Polyurethane Elastomer Properties

BDOAA 1000 vs. PDOAA 1000, 37% Hard Segment

Physical and mechanical properties are shown in Table 12 and Figure 13 and 14. The hardness of the PDO elastomer was lower at 88 vs. 93 for the BDO elastomer. However, all remaining physical and mechanical properties are very comparable for the PDO and BDO elastomer, most notably hysteresis and modulus.

<i>Table 12. Physical Properties of Elastomers (1000Mw, 37% Hard Segment)</i>		
Type of Elastomer	BDOAA 1000	PDOAA 1000
Hard Segment, %	37%	37%
Properties		
Hardness, Shore A (ASTM D2240)	93	88
Hardness, Shore D (ASTM D2240)	43	42
Resilience, % (ASTM D2632)	29	24
Tensile Strength at break, psi (ASTM D412)	5152	5105
Elongation at break,%	530	583
Tensile Stress at 100% elongation	1394	1223
Tensile Stress at 200% elongation	1864	1649
Tensile Stress at 300% elongation	2572	2177
Tensile Stress at 400% elongation	3612	2979
Tear Strength, lbf/in (ASTM D6246)	1520	1354
Compression Set Ca, % (Based on original)	11	8.95
Compression Set Cb, % (Based on deflection)	40.4	38.02
Abrasion resistance, wt. loss, mg/2000 cycles	2.4	0.5
Hysteresis, up to 250% elongation, %		
• 1 st loop	72	73
• 10 th loop	38	32
Coefficient of thermal expansion, (µm/m°C)		
• From -75°C up to Tg	47.9	62.8
• From Tg to 0°C	231	198
Glass transition temperature, °C		
• DMA	-15.66	-
• TMA	-25.99	-13.66
• DSC	-18.97	-14.45

Both elastomers had comparable heat resistance across temperature and strain, as measured by retention of tensile properties at 50° and 70°C relative to those at room temperature (Table 13).

Type of Elastomer	BDOAA		PDOAA	
	50°C	70°C	50°C	70°C
100% elongation	66%	56%	70%	56%
200% elongation	64%	54%	72%	56%
300% elongation	60%	48%	72%	59%
400% elongation	55%	43%	68%	55%

Neither of the elastomers performed well in dynamic testing via Ross Flexing per ASTM D1052 (Table 14). This is most likely due to higher hard segment concentration and lowered phase separation. Lower phase separation relates to heat buildup in elastomers during dynamic testing which can result in a rapid failure. Elastomers based on 2000 Mw PDO adipate and PDO chain extender at lower hard segment concentrations have performed significantly better than their BDO counterpart.

Table 14. Cut growth using Ross Flexing Apparatus per ASTM D1052

Sample ID:	Th. (in.)	Cycles to:				
		100% Growth	200% Growth	300% Growth	400% Growth	500% Growth
BDO Elastomer	0.255	1,000	6,977	9,302	10,000	12,000
PDO Elastomer	0.244	2,778	4,167	6,349	7,937	9,524

DSC graphs for the elastomers are shown in Figure 13 and 14. The glass transition temperature (T_g) of the BDO elastomer was lower by 4.5°C (Table 12, Figure 13 and 14). Both elastomers have a slight transition 46-48°C that could be associated with melting of crystalline phase of polyols. The strong transition at 162°C for both elastomers (Figure 13 and 14) is likely associated with melting of the hard segment. However, the measurement of melt index would give much better insight into melting properties of those TPUs.

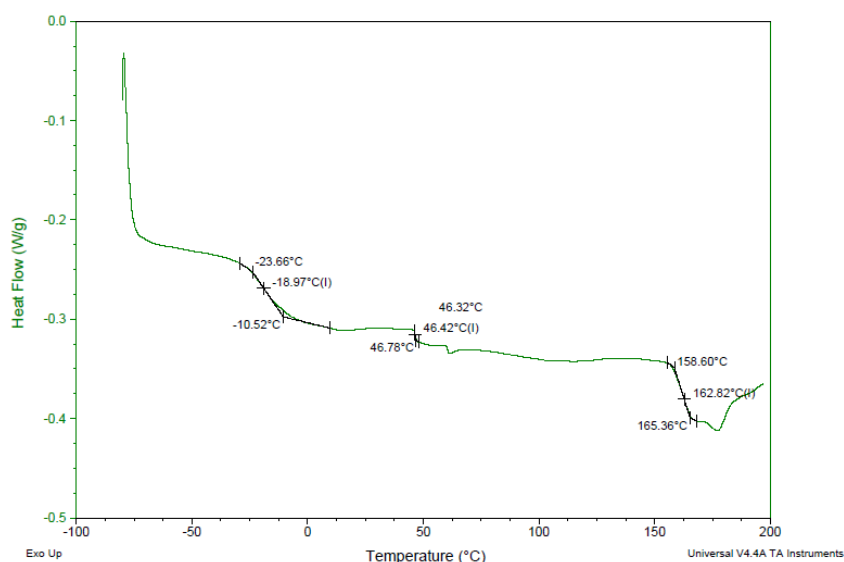


Figure 13. DSC graph of BDO elastomer (1000Mw, 37% hard segment)

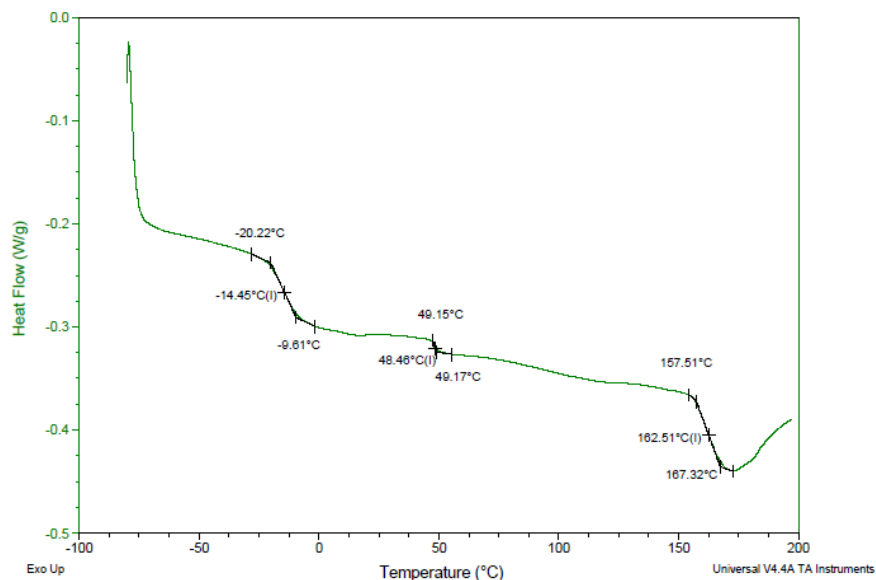


Figure 14. DSC graph of PDO elastomer (1000Mw, 37% hard segment)

The solvent resistance of elastomers in various solvents, including water is shown in Table 15. Both elastomers appeared to be comparable in non-polar solvents (toluene and xylene), while the PDO elastomer was slightly lower in polar solvents (methyl ethyl ketone and ethyl acetate).

<i>Table 15. Solvent resistance of elastomers weight change, % at 20°C (2500 Mw, 30% hard segment)</i>				
Solvent	BDOAA		PDOAA	
	24 hrs	7 Days	24 hrs	7 Days
Toluene	17.35	28.92	21.91	30.68
Methyl ethyl ketone	51.50	51.47	74.05	74.78
Xylene	8.65	21.24	9.93	20.97
Ethyl acetate	36.09	40.46	53.68	55.12
Oil	2.16	1.86	1.97	1.95
Distilled Water	0.88	1.29	1.33	1.72

CONCLUSION

The use of Susterra® 1,3 propanediol as building block for polyurethanes has been researched extensively since 2009. Several PDO elastomers based on PDO-adipate polyester polyols of different molecular weight (1000, 2000 and 2500 MW) have been shown to have structural differences that offer unique dynamic properties, and exhibited very good combination of properties that exceed standard BDO based elastomers. These include lower hysteresis and modulus, better heat resistance and abrasion resistance, and very good tensile and tear strength. Potential use for these unique properties exists in applications requiring better elasticity with softness and tear strength, as well as better transparency due to lower crystallinity.

ACKNOWLEDGEMENT

I would like to thank Aisa Sendjarevic and Vahid Sendjarevic, Troy Polymers, Inc., for their dedication to this project and the ultimate preparation, synthesis and analysis.

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