

Susterra® Propanediol – Evaluating the Structure-Property Relationship in CASE Applications

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ABSTRACT

Susterra® propanediol (PDO), a 100% bio-based diol, has been successfully evaluated in a variety of polyurethane applications such as coatings, adhesives, sealants, and elastomers (CASE) as well as microcellular elastomers. PDO adipate polyols perform similarly to 1,4-butanediol (BDO) adipate polyols, and can be formulated into polyurethane systems without extensive re-work. MDI-based TPU's were synthesized and evaluated using a prepolymer method to achieve a hardness ranging from 67 Shore A to 95 Shore A using a 2000 mw PDO adipate based polyester polyol. For reference, TPU's based on BDO adipate polyester polyol were also prepared. Physical and dynamic properties, and solvent resistance were measured. 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

In polyurethane applications, recent activity has successfully demonstrated the use of PDO as an alternative replacement for BDO as polyester building block or chain extender in the production of cast elastomers^{1,2,3} and microcellular elastomers^{4,5}. As with conventional MDI and TDI prepolymers, Susterra® adipates can be reacted with isocyanates to form NCO-prepolymers with comparable properties and performance. Uses in downstream markets include high performance elastomers and footwear.

PDO-based polyurethanes have structural differences that offer unique mechanical properties in the final product. Some highlighted improvements included flexibility and toughness, compression set and rebound, extended pot-life, and transparency as a result of less crystallinity. We believe it is the “odd-even” effect that illustrates how the PDO-based soft block and PDO-based hard block enable unique and new urethane applications (Figure 1). Different explanations have been proposed to explain this effect, including crystal packing, hydrogen bonding, dipole moments, and molecular symmetry^{6,7,8}. A more detailed explanation can be found in the CPI Polyurethanes 2010 Technical Conference Proceedings.³

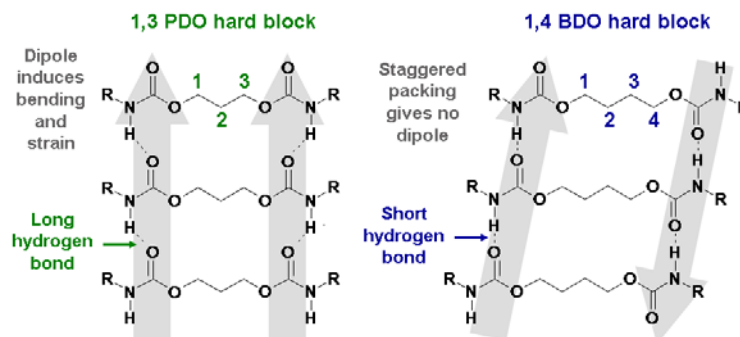


Figure 1: Schematic representation of the crystal packing of PDO and BDO based polyurethane hard blocks

This paper reports PDO-based polyurethanes having structural differences that offer unique mechanical properties of the final polyurethane product. MDI-based TPU's were synthesized using a prepolymer method to achieve a hardness ranging from 67 Shore A to 95 Shore A. As reference, BDO-based polyurethanes were prepared. The physical and dynamic properties and solvent resistance 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. The melting point of the PDO adipate is 20°C lower than the BDO adipate. Viscosities at 60°C are reported in Table 1.

Designation	Identification	Supplier
Poly S2000 PAR	Propanediol Adipate, MW 2000 OH#: 53.7 mg KOH/g Acid #: 0.6 mgKOH/g Visc.@60°C: 1398 cPs Mp: 46°C	ITWC, Inc. (Malcolm, IA)
Poly S2000 BA	Butylene Adipate, MW 2000 OH#: 55.9 mg KOH/g Acid #: 0.26 mg KOH/g Visc.@60°C: 1300 cPs Mp: 65°C	
Susterra® propanediol	1,3 Propanediol	DuPont Tate & Lyle
1, 4 Butanediol	1,4 Butanediol	Alfa Aesar
Dabco T-12	Dibutyltin dilaurate	Air Products
Mondur MB	Diphenylmethane 4,4'-diisocyanate (Fused) NCO% = 33.7	Bayer AG

Preparation of NCO-prepolymers:

The NCO-prepolymers based on 1,3-PDO adipate polyester polyol of 2000 MW and BDO adipate polyester polyol of 2000 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 at 70° - 80°C for 120 minutes in the case of BDO prepolymer and 105 minutes in the case of PDO-prepolymer. The NCO% of the prepolymers was checked periodically during synthesis. Afterwards, the prepolymer was 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 30°C and 50°C with a Rheometer.

Preparation of polyurethane elastomers:

TPUs were prepared by reacting 4,4'-MDI polyester prepolymer 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 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 30 and 50°C via Rheometrics.

Elastomers – The following properties were measured on 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

Polyester Polyols

GPC analysis was carried out on the polyester polyols, Figures 2 and 3. Polydispersity index of both PDO and BDO polyol were similar to the typical values for polyester polyols. This indicated that the molecular weight distribution of the PDO adipate was similar to the BDO adipate. It is well known that molecular weight distribution has an impact on properties of TPUs. Hence, in this study the properties of TPUs should relate mainly to the chemical structure of polyols.

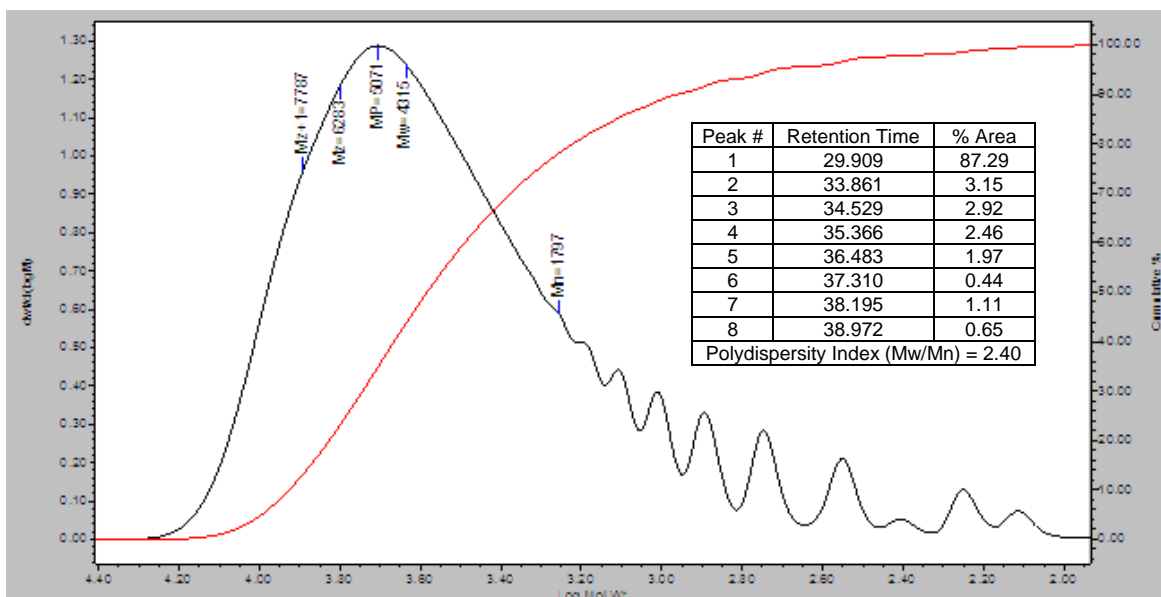


Figure 2. GPC chromatogram of Poly S2000 PAR (PDO adipate 2000Mw)

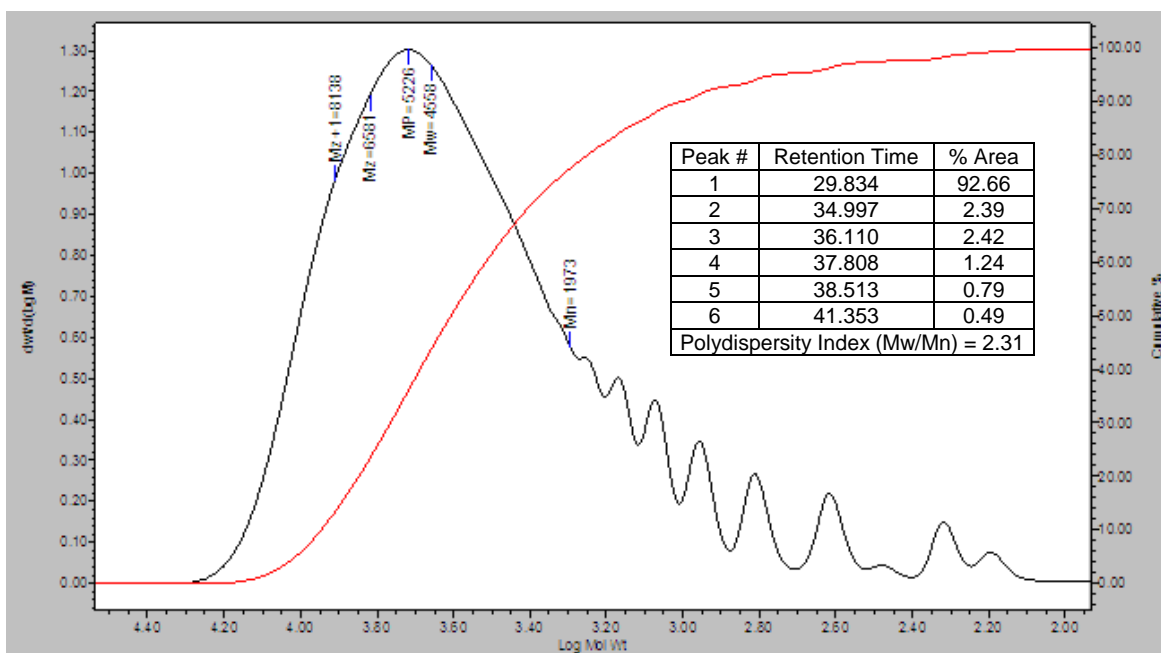


Figure 3. GPC chromatogram of Poly S2000 BA (BDO adipate 2000MW)

NCO-Urethane Prepolymer

The formulation of NCO-prepolymers that are based on 4, 4'-MDI and polyester polyols, PDO adipate and BDO adipate are shown in Table 2. The final NCO% of both prepolymers was identical to theoretical values. Both prepolymers have high viscosities at 30°C, which it to be expected; both polyester polyols are solid at RT. The viscosities of PDO and BDO polyester polyols were almost identical at 50°C at 6500 and 6000 Pa.s, respectively (Table 2).

<i>Table 2. Formulation of NCO-prepolymers</i>		
Prepolymer Formulation (pbw)	BDO	PDO
Mondur MB	332.3	332.3
Poly S 2000BA	1304.7	-
Poly S 2000PAR	-	1358.1
NCO/OH Ratio	2.05/1	2.05/1
Reaction temperature and time		
Time of Polyol Addition	85 min.	75 min.
Time of Reaction	120 min.	105 min.
Temperature (°C)	70-80°C	70-80°C
Properties of prepolymer		
NCO% Theoretical / Measured	3.31 / 3.32	3.23 / 3.23
Consistency at RT	Waxy Solid	Thick Paste
Viscosity at 30°C,Pa.s	119000	94000
Viscosity at 50°C,Pa.s	6000	6500

Polyurethane Elastomer Formulation

Thermoplastic polyurethane elastomers were prepared by the prepolymer method at a 1.02 isocyanate index and hard segment concentration of 22-23%, using the same protocol. Formulations and curing conditions are shown in Table 3. A small amount of gelling catalyst was added to polyurethane system to facilitate polymerization. The gelling of PDO prepolymer was slower than the BDO prepolymer.

<i>Table 3. Formulations and Curing Conditions</i>		
Type of Elastomer	BDO Elastomer	PDO Elastomer
Formulation, pbw		
NCO-Prepolymer MDI/BDO 2000	80	-
NCO-Prepolymer MDI/PDO 2000	-	80
BDO	2.8	-
PDO	-	2.3
Dabco T12 Catalyst	0.0066%	0.0063%
Isocyanate Index	1.02	1.02
Hard segment concentration, %	23.0	21.9
Curing Conditions		
Temperature of NCO-prepolymer, °C	90	90
Temperature of 1,4-Butane Diol/1,3-PDO, °C	RT	RT
Mixing via speed mixer, sec	30-60	30-60
Gel Time	8 min.	12 min.
Curing time and temperature	2 hours @ 120°C	2 hours @ 120°C
Post-curing time and temperature	16 hours @ 100°C	16 hours @ 100°C

Polyurethane Elastomer Properties

Physical and mechanical properties are shown in Tables 4-7 and Figures 4-7.

The hardness of both PDO and BDO elastomers were identical at 67 Shore A. The tensile strength of both elastomers was very similar at approximately 4000 psi. However, the elongation at break of the PDO elastomer was somewhat higher. The tensile modulus at 100%, 200% and 400% were lower for the PDO elastomer, which correlates well with higher elasticity. (Table 4)

The tear strength of the PDO elastomers was higher, which could be explained by a higher concentration of polar ester groups in the PDO elastomer. (Table 4)

The abrasion resistance of both elastomers, as measured by the weight loss in the Taber Abrader test, was very good. The compression set at 70°C for both elastomers was about 8%, which is also very good. (Table 4)

The resilience as measured by bayshore rebound was in the range of 50%, although slightly higher for the BDO elastomer. However, PDO elastomers exhibited significantly lower hysteresis in both the 1st and the 10th cycle (Table 4). The lower hysteresis indicates that material absorbs less energy and is more resilient when stretched. Figure 4 shows the PDO elastomer has higher heat resistance and approximately 40% less deformation. This is an opportunity for parts to be engineered with a narrower specification range for use in applications where material is exposed to dynamic forces (less “dynamic creep”).

Type of Elastomer	BDO Elastomer	PDO Elastomer
Properties		
Hardness, Shore A (ASTM D2240)	67	67
Density, g/cm ³	1.18	1.20
Tensile Strength, psi (ASTM D412)	4026	3954
Elongation at break, %	689	837
Tensile Stress at 100% elongation	420	364
Tensile Stress at 200% elongation	548	520
Tensile Stress at 400% elongation	1227	971
Resilience, % (ASTM D2632)	55	48
Hysteresis, up to 250% elongation, %		
• 1 st loop	57	35
• 10 th loop	30	12
Compression Set, % (ASTM D395)	8.2	8.1
Tear Strength, lbf/in (ASTM D6246)	380	457
Coefficient of thermal expansion, (in/in-°F)		
• From -75°C up to Tg	4.49×10 ⁻⁵	4.28×10 ⁻⁵
• From Tg to 0°C	1.39×10 ⁻⁴	1.39×10 ⁻⁴
Glass transition temperature, °C		
• DMA	-28	-26
• TMA	-41	-38
• DSC	-35	-31
Abrasion resistance, weight loss:		
mg/2000 cycles	4	7.0
mg/1000 cycles	2	3.5

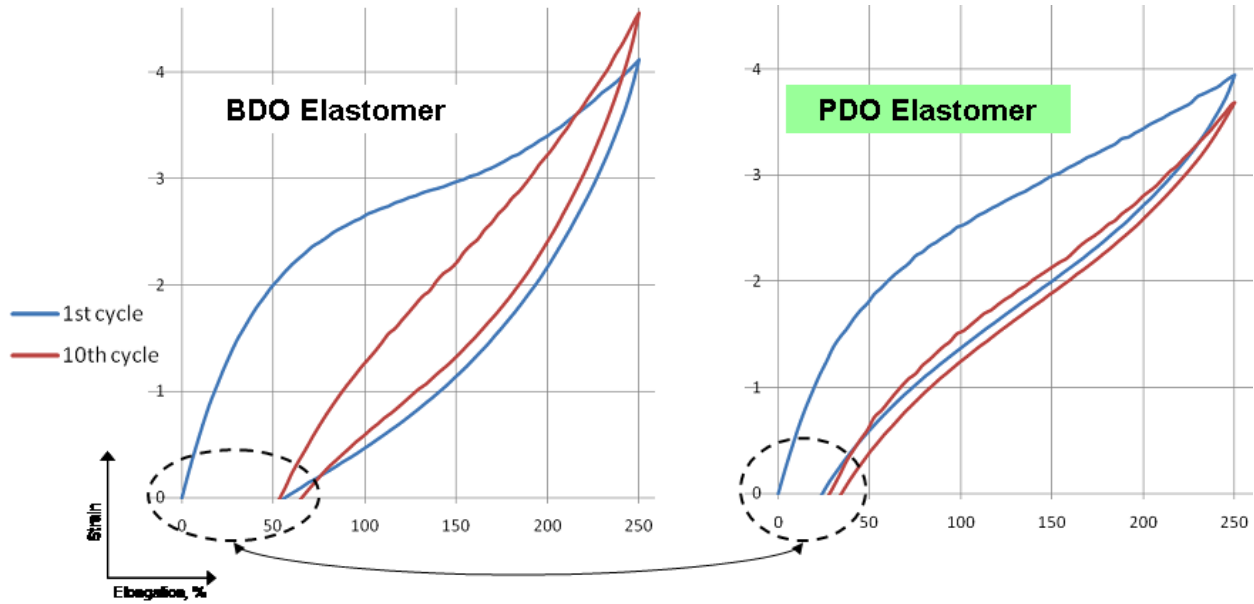


Figure 4. Hysteresis graph of TPU prepared via pre-polymer method from BDO adipate polyol of 2000MW (Tables 2 and 3)

Ross Flexing test was performed per ASTM D1052. The PDO elastomer significantly outperformed the BDO elastomer. The PDO elastomer showed no cut growth after 89,000 cycles and only a 20% growth after 250K cycles. The BDO elastomer exhibited 500% cut growth after 89,000 cycles (Table 5). These results are in good agreement with lower hysteresis of PDO elastomers as measured by Instron tester. Good dynamic properties as indicated by the Ross Flexing results are significant advantage for PDO elastomers and are important in many applications where material is exposed to dynamic forces.

Table 5. Cut growth using Ross Flexing Apparatus per ASTM D 1052

Sample ID:	Th. (in.)	Cycles to original cut					OR Cut length at 250K (in.)
		100% Growth	200% Growth	300% Growth	400% Growth	500% Growth	
BDO Elastomer	0.236	30,000	52,000	64,000	77,000	89,000	(test stopped at 500% growth)
PDO Elastomer	0.242	N/A	N/A	N/A	N/A	N/A	0.12

The Glass Transition Temperatures (Tg's) measured as maximum of the loss modulus (G'') in DMA graphs of BDO and PDO elastomers are very similar, -28°C and -26°C, as well as Tan Delta maximum, -18°C and -17°C, respectively (Figure 5).

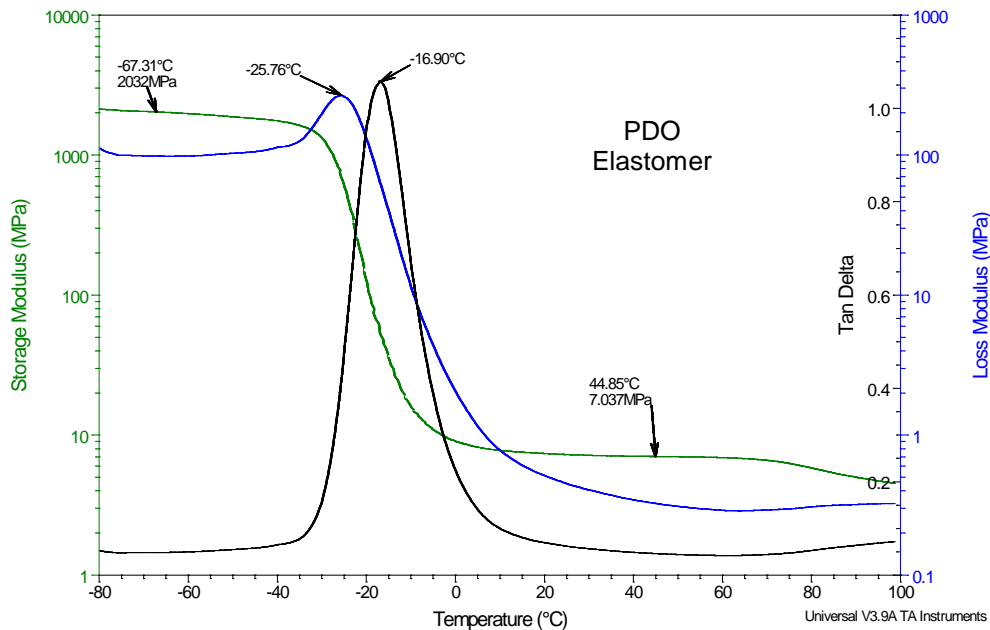
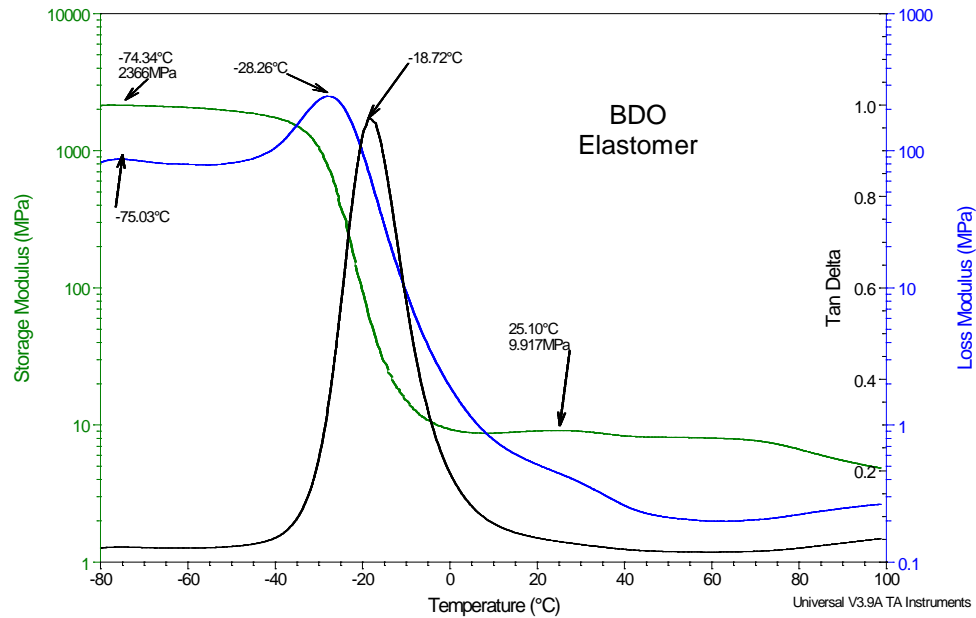


Figure 5. DMA graph of BDO and PDO Elastomers

The glass transition temperature of both elastomers as measured by TMA and DSC (Table 4) are slightly lower in temperature compared to the PDO elastomer. All three methods used to measure glass transition temperature indicate that same trend.

Coefficient of thermal expansion, as measured by TMA, was very similar for both elastomers (Table 4). The ratio of Coefficient of thermal expansion measured above and below T_g is between 3 and 4 which is a typical for elastomeric materials.

There is another transition in DSC graphs, at 45°C for BDO-elastomers and 52°C for PDO-elastomers that could be associated with melting of crystalline phase of polyols. There is a weak transition at about 90-100°C that could be associated with hydrogen bonding dissociation (Figure 6). There is continuous decline in DSC curve being more visible starting at about 150°C and higher temperatures. This could be associated with melting of the hard segment. However, the measurement of melt index would give much better insight into melting properties of those TPUs.

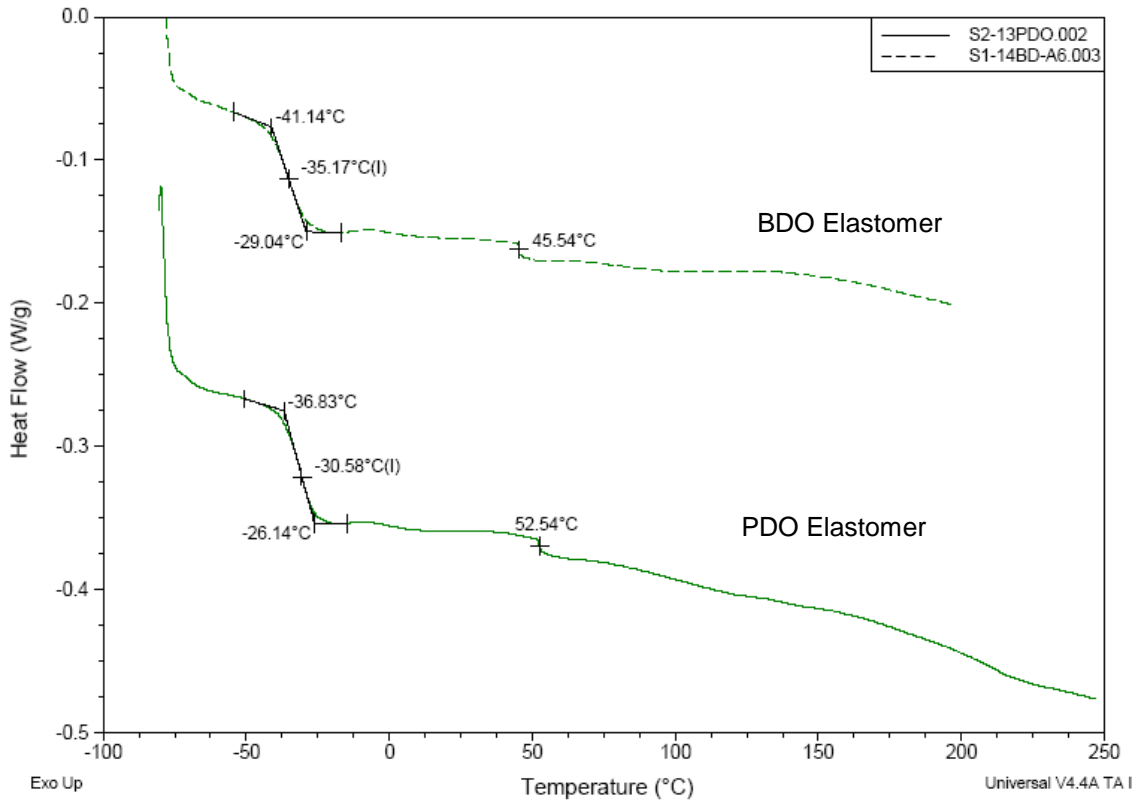


Figure 6. DSC graphs of elastomers

Heat resistance of elastomers was measured as retention of tensile modulus at 50° and 70°C relative to those at room temperature (Table 6, Figure 6). There was good retention at 200% strain – above 90% at 50°C, and 70% at 70°C. The PDO elastomer has shown signs of higher heat resistance across temperature and strain.

<i>Table 6. Tensile properties of elastomers at elevated 50 & 70 °C</i>						
Elastomer Type	BDO Elastomer			PDO Elastomer		
	RT	50°C	70°C	RT	50°C	70°C
200% Modulus	548	505	387	520	495	381
% Retention	-	92%	71%	-	95%	73%
300% Modulus	788	625	480	708	600	450
% Retention	-	79%	61%	-	85%	63%
400% Modulus	1227	820	606	971	734	545
% Retention	-	67%	49%	-	75%	56%

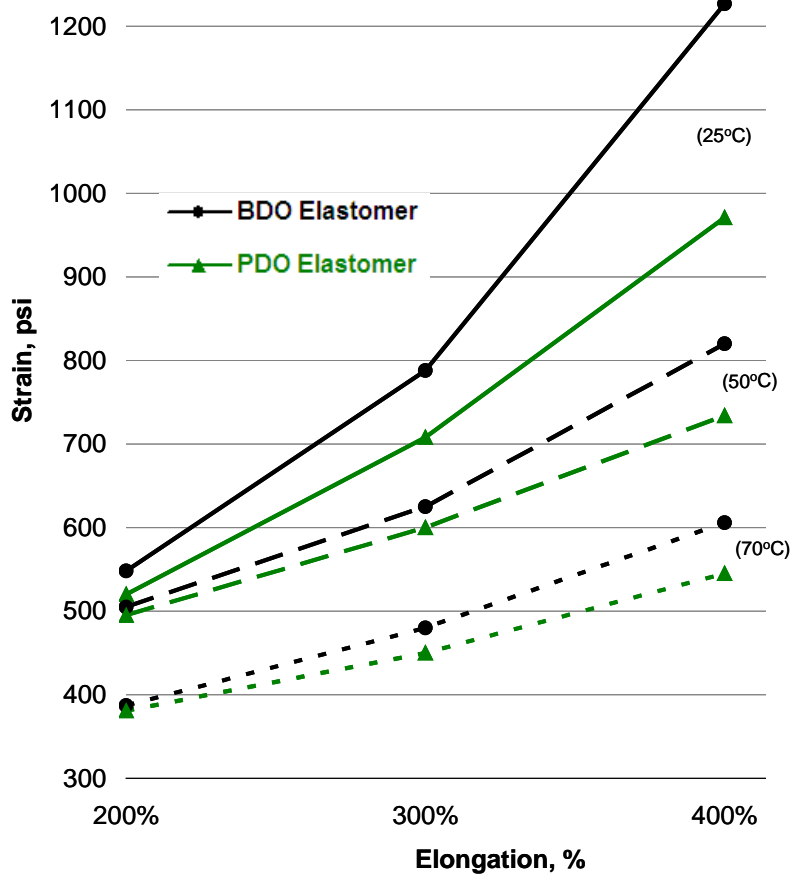


Figure 7. Tensile properties of PDO and BDO elastomers at different temperatures

The solvent resistance of elastomers in various solvents, including water is shown in Table 7. The PDO elastomer showed less weight and volume change in organic solvents, and was comparable for all others. However, the PDO elastomer also exhibited signs of cracking in the 3N HCl.

Table 7. Solvent resistance of PDO and BDO elastomers

	24 Hour Change				7 Day Change				Appearance Day 7	
	wt, %		vol, %		wt, %		vol, %		BDO	PDO
	BDO	PDO	BDO	PDO	BDO	PDO	BDO	PDO		
3N HCL	1	1	-3	0	0	-4	1	-7	Hazy	Hazy/ Cracked
3N KOH	1	1	5	2	-1	-3	2	-1	Hazy	Hazy
Mineral Oil	0	0	3	-2	0	0	1	-7	Clear	Clear
3% H ₂ O ₂	1	1	4	0	1	1	3	7	Clear	Clear
Acetone	135	105	94	80	134	107	92	77	Yellow, Hazy	Swelled, Haziness (less over time)
Toluene	62	50	76	79	60	51	71	69	Clear	Clear
IPA	10	8	12	16	14	12	19	16	Clear	Clear
DI Water	1	1	-1	7	1	1	1	2	Clear	Clear

CONCLUSION

Susterra® 1,3-propanediol based polyurethanes have structural differences that offer unique mechanical properties in the final elastomers. Potential use for these unique properties exists for applications requiring softness with better elasticity and tear strength. A particular opportunity is for parts to be engineered with a narrower specification range for use in applications where material is exposed to dynamic forces (e.g., urethane coated nip rollers). Lower crystallinity may be an advantage for applications that require transparent parts.

ACKNOWLEDGEMENT

The authors would like to thank Aisa Sendjarevic and Vahid Sendjarevic, Troy Polymers, Inc., for their dedication to this project and the ultimate preparation, syntheses and analyses.

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