Susterra® Propanediol PU Applications

Performance is in our nature.

April 29, 2016

susterra®
bio-based performance

Who is DuPont Tate & Lyle?

DTL is a joint venture formed in 2004 between DuPont and Tate & Lyle to produce 1,3 propanediol (PDO) from corn starch, a sustainable & renewable resource

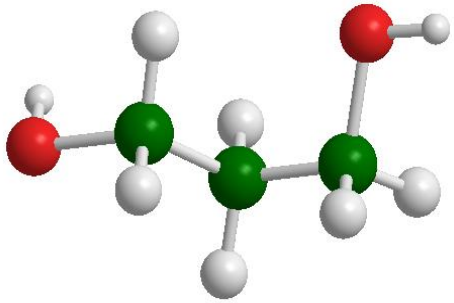
DuPont is a world leader in science and innovation across a range of disciplines, including agriculture and industrial biotechnology, chemistry, biology, materials science and manufacturing. CY2015 revenues were $35 billion.

Tate and Lyle is a global provider of renewable ingredients, solutions and services to the food, beverage and industrial customers. Revenues were $4.3 billion for Fiscal Year ending March 31, 2015.

DuPont Tate & Lyle BioProducts™

susterra® bio-based performance

Susterra® Propanediol



What is it?

- A pure, petroleum-free derived glycol
- 100% sustainably and renewably sourced
- Used in a range of applications

USDA CERTIFIED BIOBASED PRODUCT
PRODUCT 100%

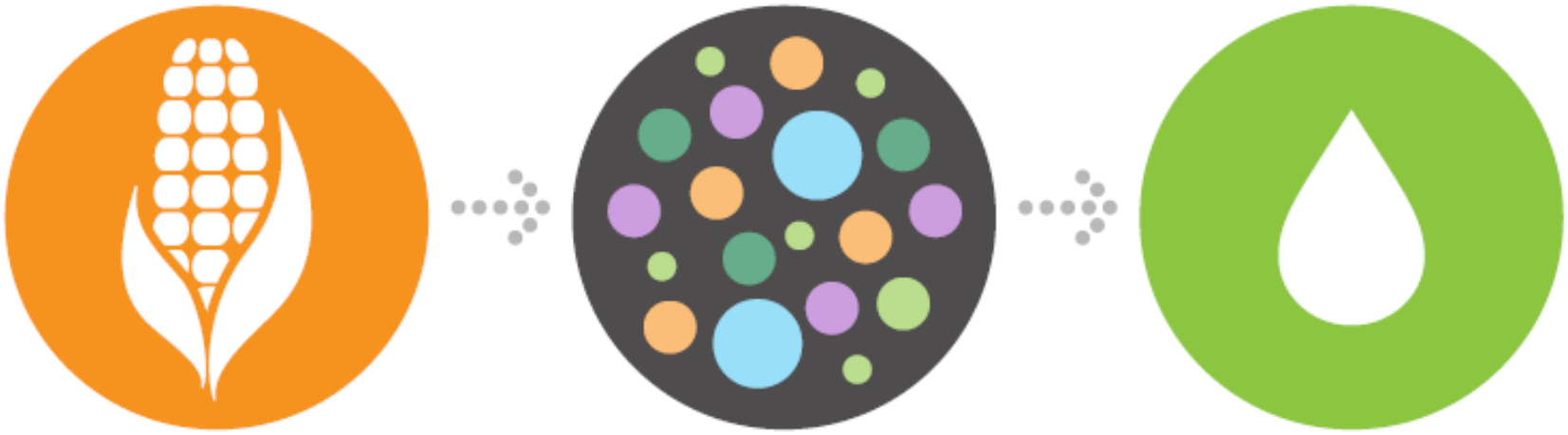
How is it made?

- Made by a fermentation process derived from glucose
- Made in the USA
- USDA 100% Certified Bio-Based Product

susterra bio-based performance

Process Technology

Renewably sourced feedstocks are harvested, fermented, and refined to manufacture Susterra® propanediol.



Harvest

Renewably sourced feedstocks are harvested, dried and then wet-milled to create a range of carbohydrate rich feedstocks such as glucose.

Fermentation

Glucose is converted into 1,3 propanediol using a patented microorganism under exact temperatures and conditions.

Refining

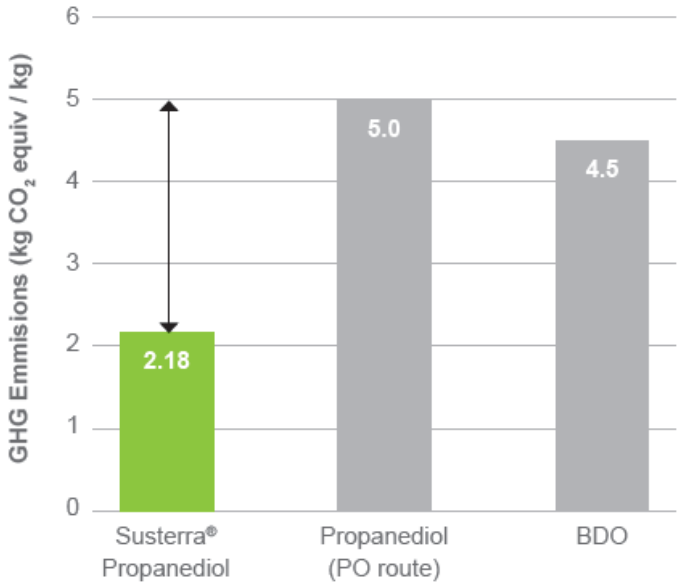
The 1,3 propanediol is refined to a final purity of 99.7% by deactivating and removing the microorganism, water, and other byproducts.

susterra
bio-based performance

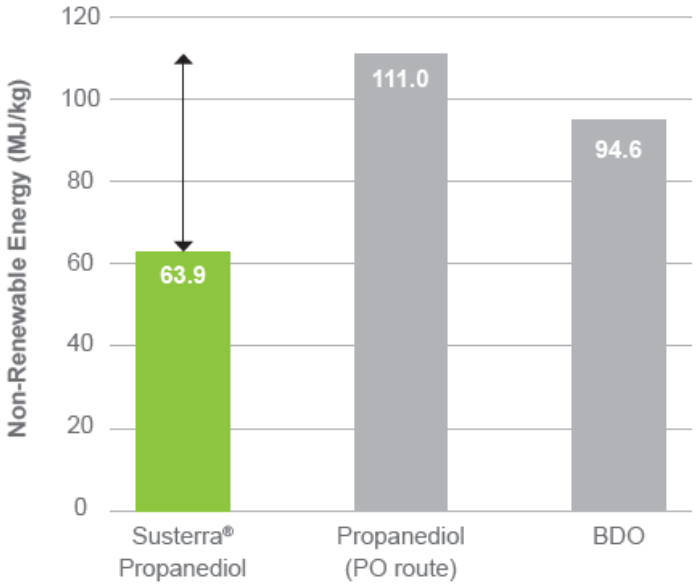
Life Cycle Analysis

Susterra® propanediol

From "cradle to gate" (extraction and production prior to delivery to the consumer), Susterra® propanediol produces 56% less greenhouse gas emissions and consumes 42% less nonrenewable energy than propylene oxide-based propanediol. Compared with butanediol (BDO), Susterra® propanediol produces 52% less greenhouse gas emissions and uses 32% less nonrenewable energy from cradle to gate.



Greenhouse Gas Emissions
56% less than Propanediol
52% less than BDO



Non-Renewable Energy Use
42% less than Propanediol
32% less than BDO

Production – Loudon, TN

Biotechnology enables a stable supply of renewably sourced 1,3 propanediol

Awards

- 2003 EPA Presidential Green Chemistry Award
- 2007 ACS Heroes of Chemistry Award
- 2009 ACS-BIOT Industrial Biotechnology Award
- 2010 State of Tennessee Governor's Award for Trade Excellence

Production

- Started November 2006
- Capacity expanded 35% in 2010
- Current Capacity = 140 million lb.

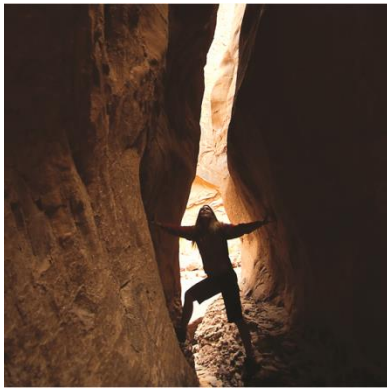
susterra bio-based performance

Key Applications

Susterra® propanediol: A high performance, bio-based building block for polyurethane applications

Footwear

- TPU elastomers
- TPU waterproof breathable films
- PU foams
- Hot melt adhesives
- PU synthetic leather



Performance Textiles

- TPU waterproof breathable films
- PU synthetic leather (i.e. accessories)

Furniture and Automotive

- TPU elastomers
- PU foam
- Hot melt adhesives
- PU synthetic leather

susterra bio-based performance

Key Applications

Susterra® propanediol: A high performance, bio-based building block for polyurethane CASE applications

Elastomers

- Cast parts
- Molded and extruded TPUs
- TPEs

Coatings

- PUD coatings
- Coatings for electronics, woods, concrete floors
- Synthetic leather skin coats

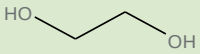
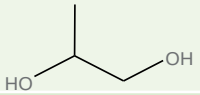
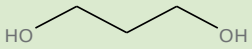
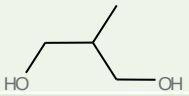
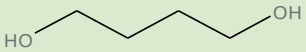
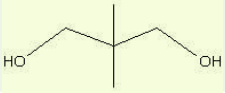
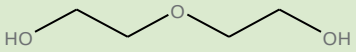
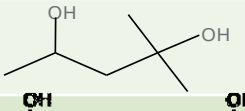
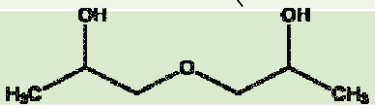
Adhesives

- Construction
- Textile (i.e. carpet backing)
- Tapes
- Solvent borne

susterra bio-based performance

Susterra® Propanediol

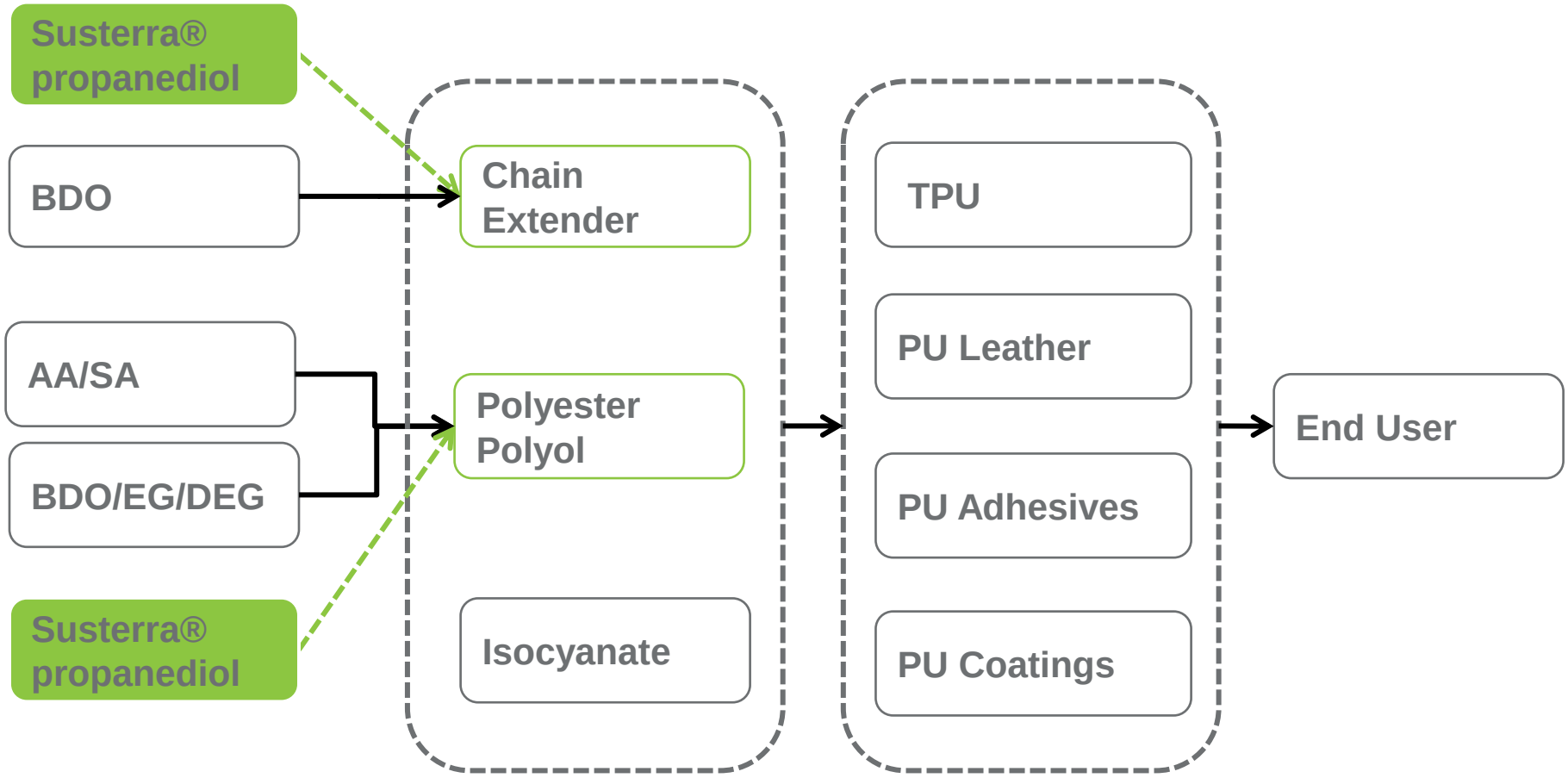
Diol comparison – chemical structure and property comparison

Common	Ingredient	CAS#	Formula	Structure	MW	BP, °C	MP, °C	Density
Ethylene Glycol	1,2-Ethanediol	107-21-1	C2H602		62.1	197.6	-12.7	1.116
Propylene Glycol	1,2-Propanediol	57-55-6	C3H802		76.1	187.3	-60	1.038
Propanediol	1,3-Propanediol	504-63-2	C3H802		76.1	214	-24	1.053
MPDiol	2-Methyl-1,3-Propanediol	2163-42-0	C4H10O2		90.1	221	-91	1.015
1,4 BDO	1,4-Butanediol	110-63-4	C4H10O2		90.1	230	16	1.017
Neopentyl Glycol	2,2-Dimethyl-1,3-Propanediol	126-30-7	C5H12O2		104.1	208	127	-~1.05
DEG	Diethylene Glycol	111-46-6	C4H10O3		106.1	245	-10	1.118
Hexylene Glycol	2-Methyl-2,4-Pentanediol	107-41-5	C6H14O2		118.2	197	-40	0.925
DPG	Dipropylene Glycol	25265-71-8	C6H14O3		134.17	231		1.023

susterra bio-based performance

Polyurethane Production

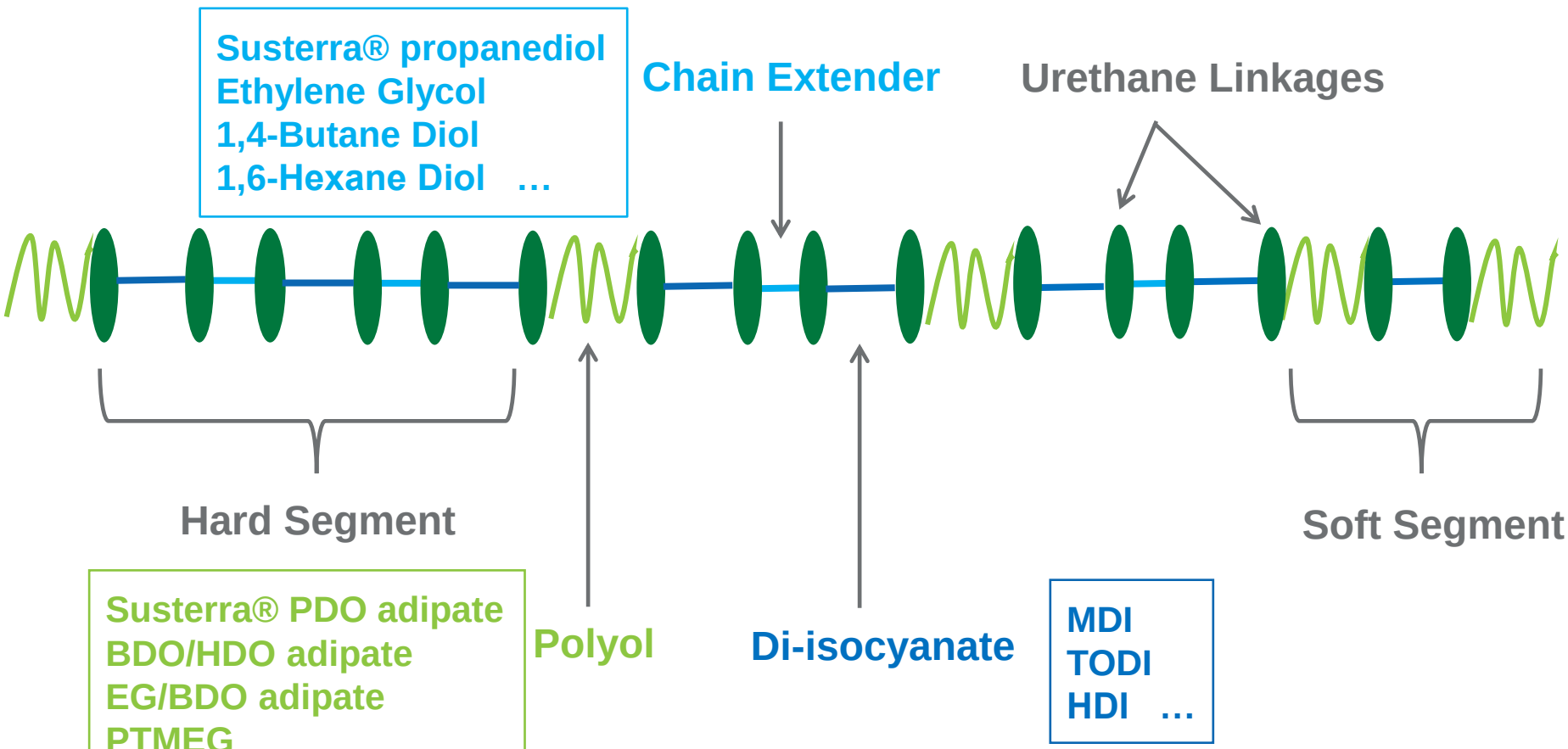
Susterra® propanediol can be used as a chain extender or polyol



susterra bio-based performance

TPU Polymer Structure

A versatile polymer chemistry



susterra bio-based performance

Susterra® Propanediol

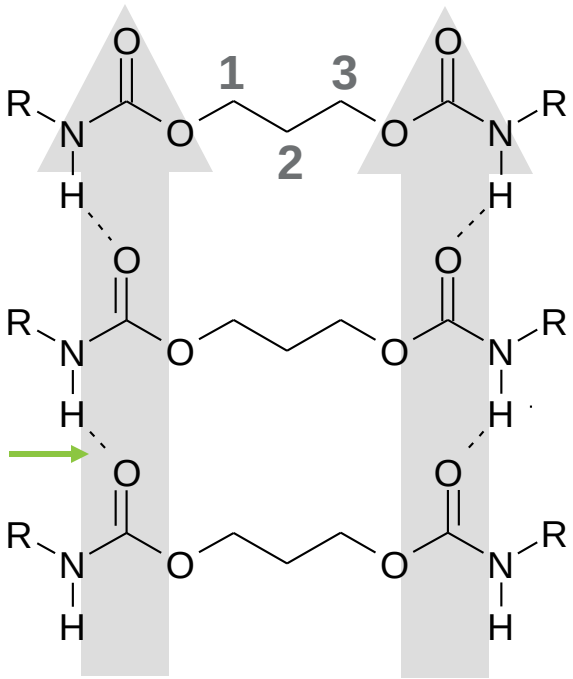
Structural Differences and the Odd-Even Effect

The odd even effect varies the packing of the hard block segments, and results in unique mechanical properties of the final product.

1,3 PDO hard block

Dipole induces bending and strain

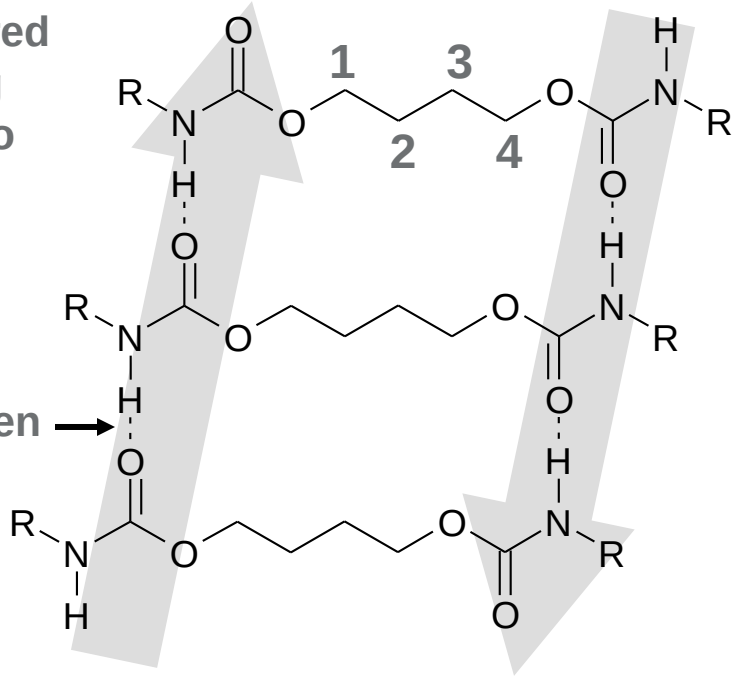
Long hydrogen bond



1,4 BDO hard block

Staggered packing gives no dipole

Short hydrogen bond



Source:
L. Born, H. Hespe, J. Crone, K.H. Wolf, Colloid and Polymer Science, 1982, 260(9), 819-828.
J. Blackwell, M.R. Najarajan, T.B. Hoitink Polymer, 1981, 22, 1534-1539.
O. Bayer, Agnew. Chem., A59, 257 (1947)

susterra bio-based performance

Susterra® Propanediol Chain Extender for TPU

susterra
bio-based performance

Susterra® Propanediol

Elastomer physical properties for polyester TPU
Chain Extender Example with AA/BDO (2000MW) polyol

TPU (One shot)	Unit	BDOAA +PDO	BDOAA +BDO
Hardness	Shore A	95	95
Tensile strength	MPA	43	46
Tear strength	KN/M	115	143
Abrasion	mm3	35	36
Elongation	%	394	370
Compression set	70°C/22hr	36	35
Rebound	%	40	35
Compression set	100°C/24hr	43	41
Melt index(200c/5kg)	g/10min	13	2

For TPUs of the same hardness where the hard segment is greater than 50% PDO as a chain extender enhances:

- **Transparency**
- **Rebound**
- **Flexibility**

susterra bio-based performance

Susterra® Propanediol

Elastomer physical properties for polyester TPU Chain Extender Example with AA/BDO/EG polyol

Polyol Chain Extender	AA/BDO/EG BDO	AA/BDO/EG PDO
Yellow Index	5.3	6.0
Hardness, Shore A	67	67
MI g/10min (190°C/5kg)	74	43
Tensile Strength (MPa)	17	20
Elongation at break (%)	770	682
100% Modulus (MPa)	2.4	3.9
200% Modulus (MPa)	5.3	7.3
300% Modulus (MPa)	6.8	9.5
Die C Tear strength (KN/m)	66	68
Compression set, 23°C (%)	45	40
Abrasion resistance (mm3)	38	39
Molding time (sec)	30	20
Tg by DSC (°C)	-38	-38
Tm by DSC (°C)	140	177

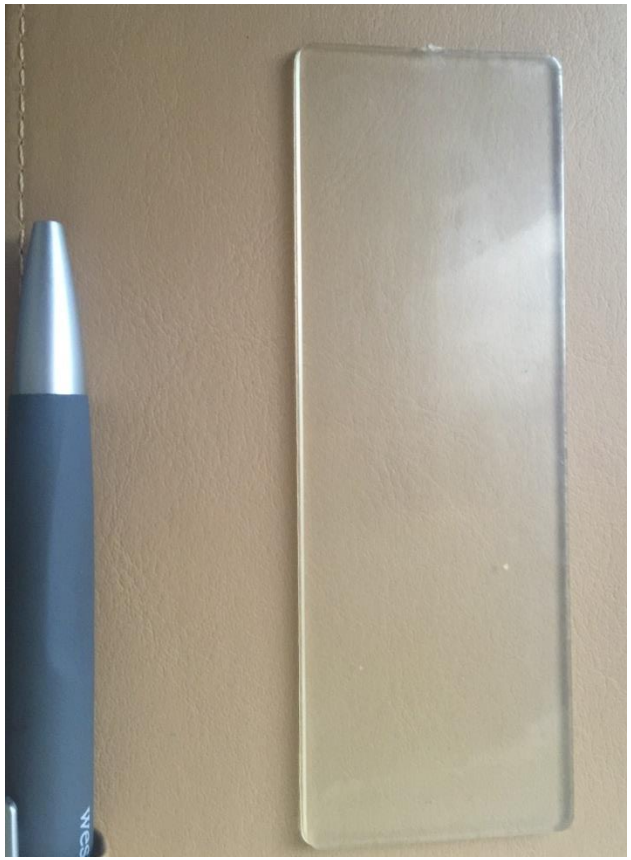
For TPUs of the same hardness where the hardness is less than 70, PDO enhances flexibility and may shorten molding times.

susterra
bio-based performance

Susterra® Propanediol

Elastomer physical properties for polyester TPU Chain Extender Example with AA/BDO/EG polyol

Polyol Chain Extender	AA/BDO/EG BDO	AA/BDO/EG PDO
Yellow Index	5.3	6.0
Hardness, Shore A	67	67
MI g/10min (190°C/5kg)	74	43
Tensile Strength (MPa)	17	20
Elongation at break (%)	770	682
100% Modulus (MPa)	2.4	3.9
200% Modulus (MPa)	5.3	7.3
300% Modulus (MPa)	6.8	9.5
Die C Tear strength (KN/m)	66	68
Compression set, 23°C (%)	45	40
Abrasion resistance (mm3)	38	39
Molding time (sec)	30	20
Tg by DSC (°C)	-38	-38
Tm by DSC (°C)	140	177

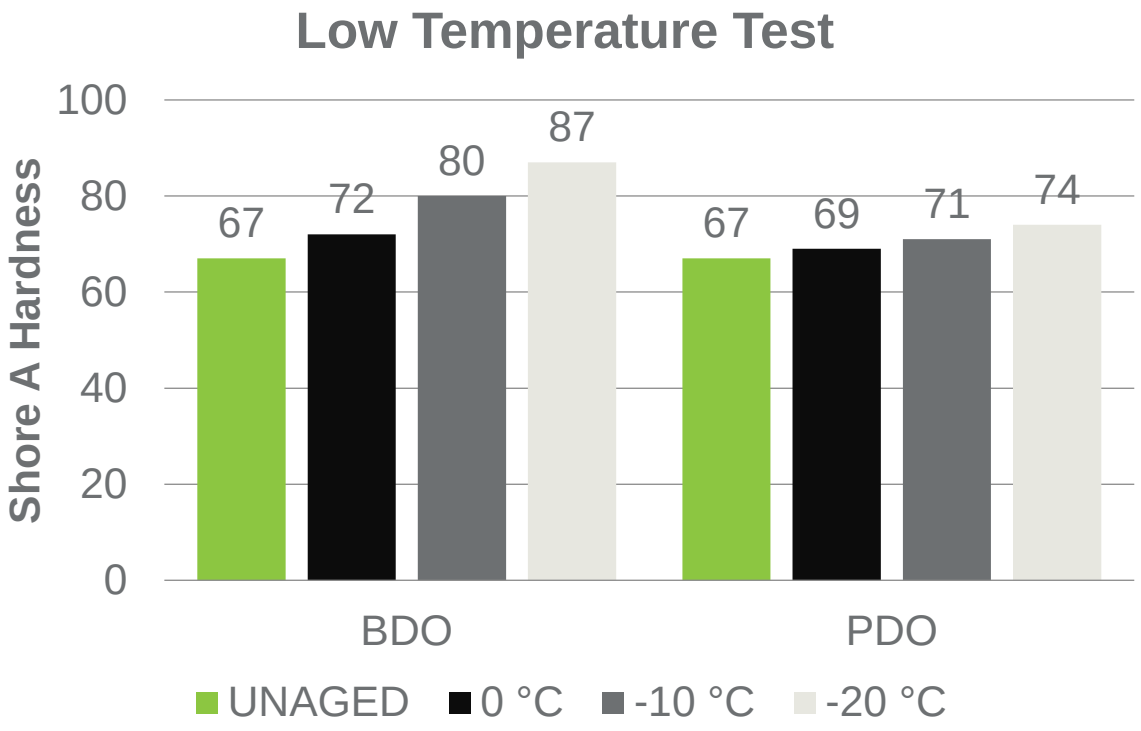


Processing Comparison
Dimensions: 120mm(L) 50mm(W) 4mm(H)

susterra
bio-based performance

Susterra® Propanediol

Elastomer physical properties for polyester TPU Chain Extender Example with AA/BDO/EG polyol

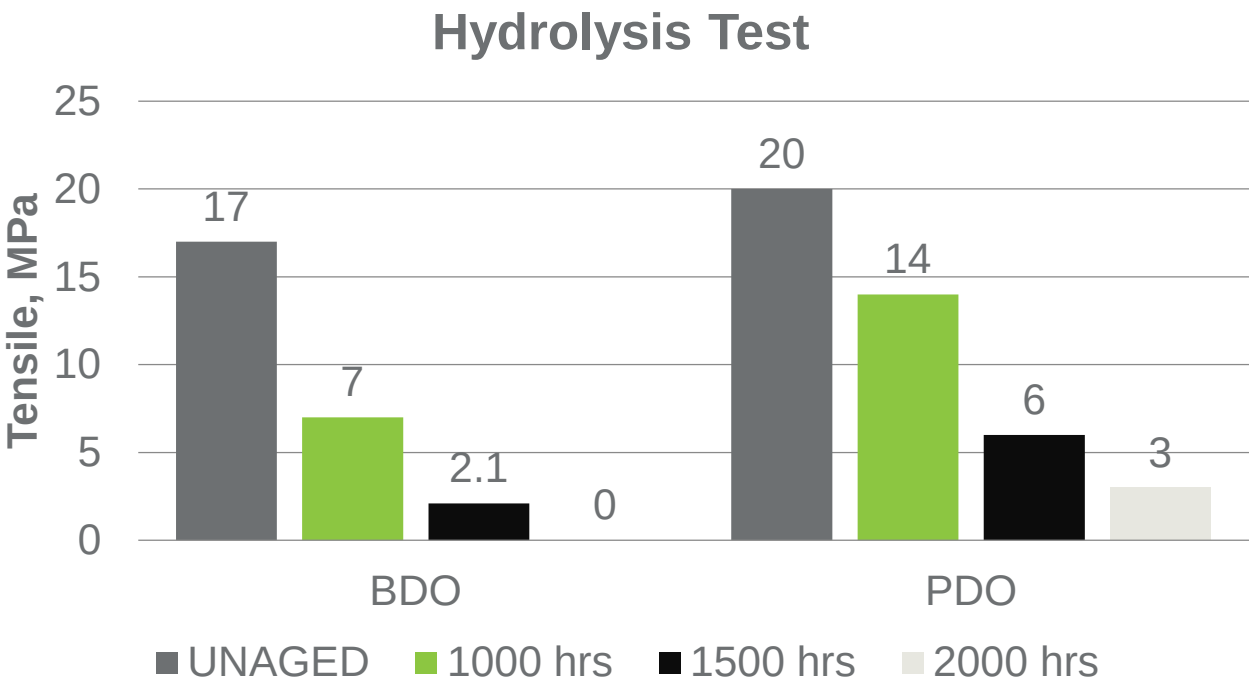


In this example when PDO is used as the chain extender the hardness of the TPU sample remains lower after exposure to low temperatures indicating improved flexibility.

susterra bio-based performance

Susterra® Propanediol

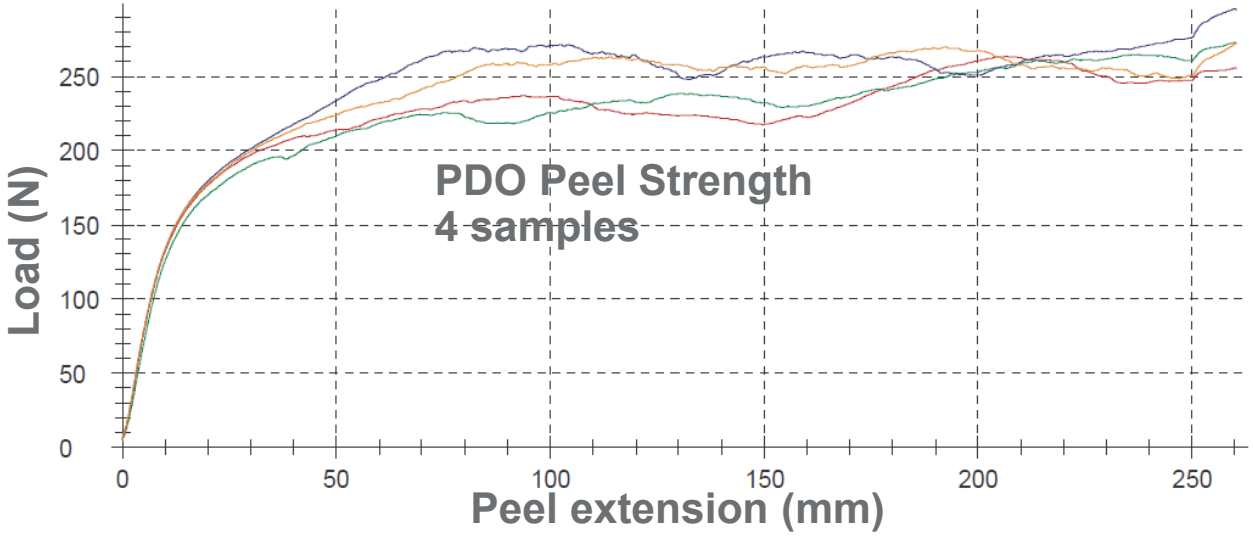
Elastomer physical properties for polyester TPU Chain Extender Example with AA/BDO/EG polyol

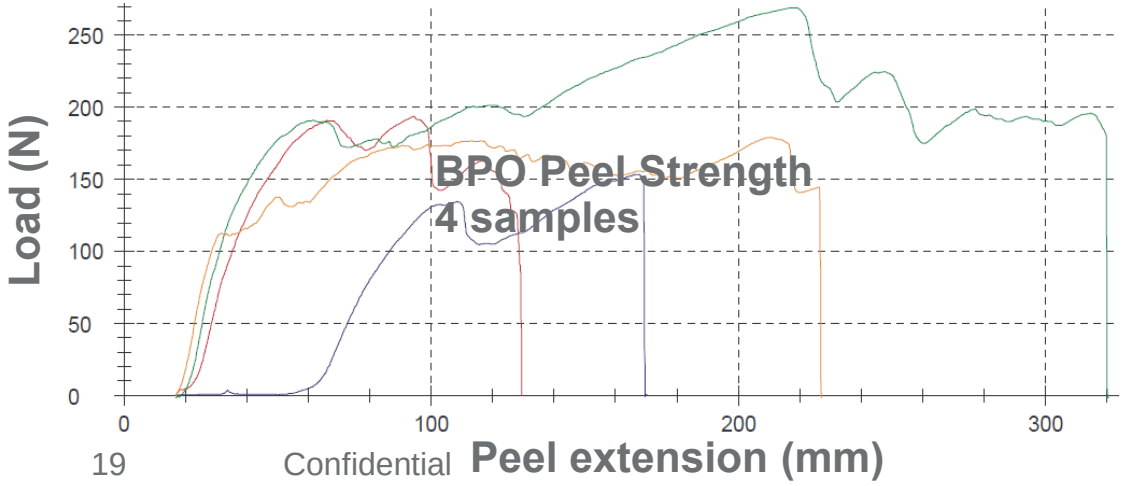


In this example when PDO is used as the chain extender the tensile properties of the TPU sample remain higher after exposure to water.

Susterra® Propanediol

Elastomer physical properties for polyester TPU Chain Extender Example with AA/BDO/EG polyol





As the hardness of the TPU decreases and PDO is used as the chain extender the Tm increases.

For TPUs of the same hardness the higher Tm will lead to better adhesion during over molding.

susterra bio-based performance

Susterra® Propandiol Polyol for TPU

Susterra® Propanediol

Elastomer physical properties for polyester TPU

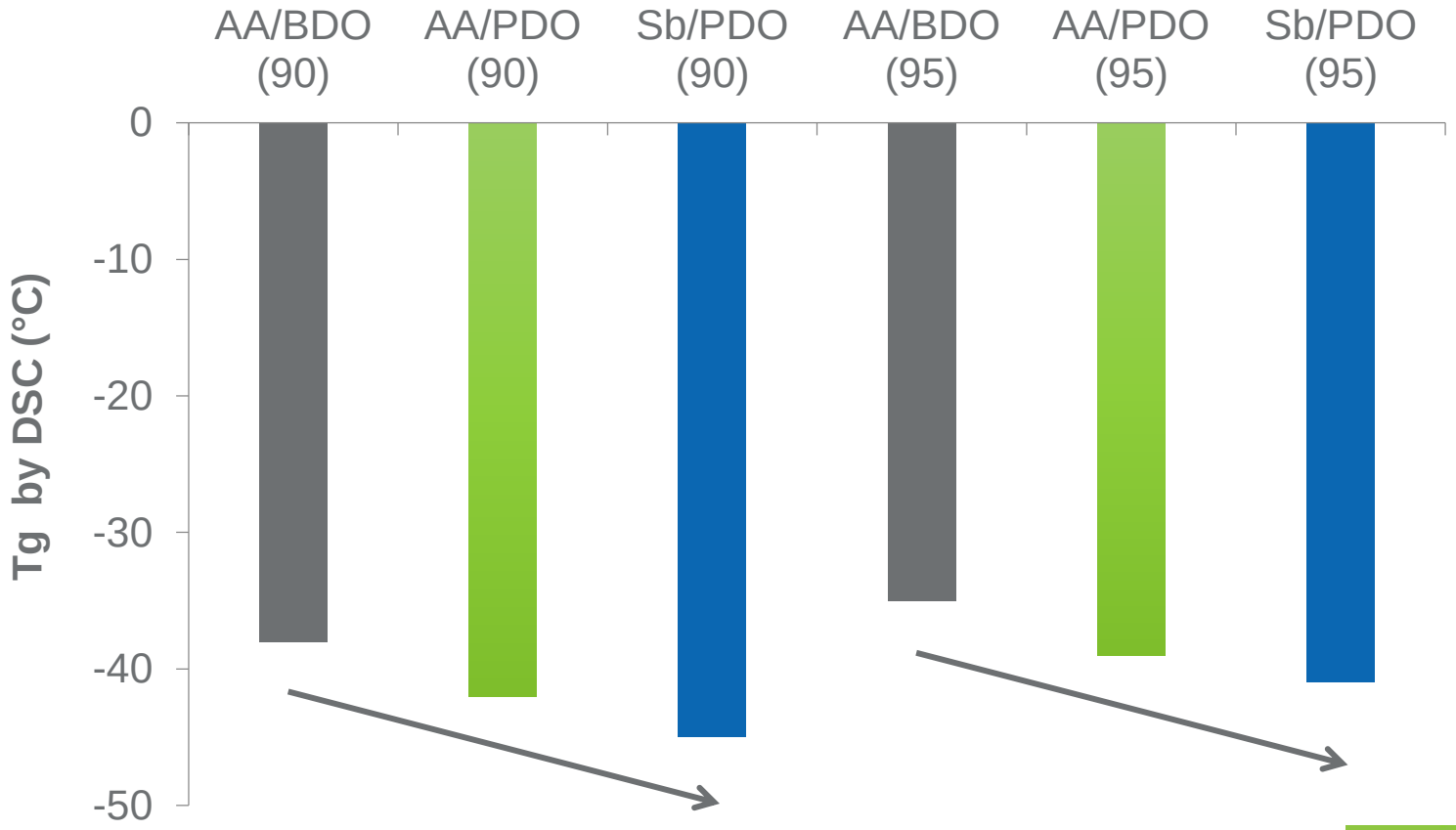
Polyol (2000Mw) Chain Extender	AA/BDO BDO	AA/PDO BDO	Sb/PDO BDO	AA/BDO BDO	AA/PDO BDO	Sb/PDO BDO
Bio content(%)	0	25	50	0	20	45
Hardness, Shore A	90	90	90	95	95	95
Tensile Strength (psi)	4691	4305	5054	4905	4691	5305
Elongation at break (%)	614	678	654	581	646	638
100% Modulus (psi)	949	1139	1068	962	967	1121
200% Modulus (psi)	1372	1516	1383	1504	1378	1596
400% Modulus (psi)	2736	2517	2910	2873	2536	2613
Die C Tear strength (lbf/in)	801	850	838	925	931	950
Compression set, 23°C (%)	25	35	20	20	30	20
Bayshore rebound (%)	43	40	49	40	38	45
Abrasion resistance	25	35	20	20	30	20
Demolding time(sec)	30	40	25	25	35	20
Tg by DSC (°C)	-38	-40	-42	-37	-42	-45

Hardness segment concentration = 40% (90A), 45% (95A) and index is 0.98

Susterra® Propanediol

Flexibility at low temperatures

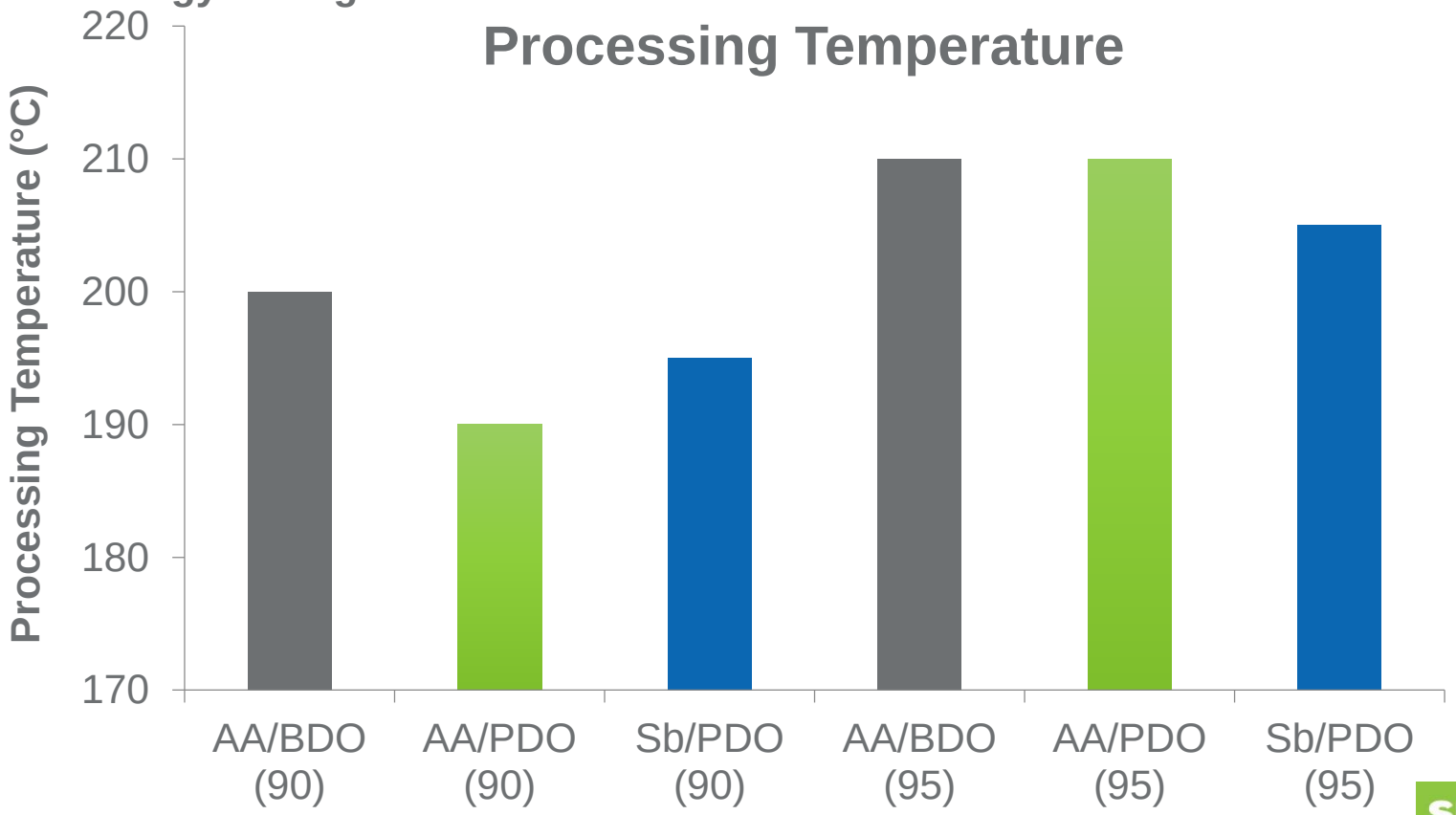
- **The glass transition temperature (Tg) of TPUs manufactured with Susterra® propanediol indicates improved flexibility at lower temperatures**



Susterra® Propanediol

Processing Comparison

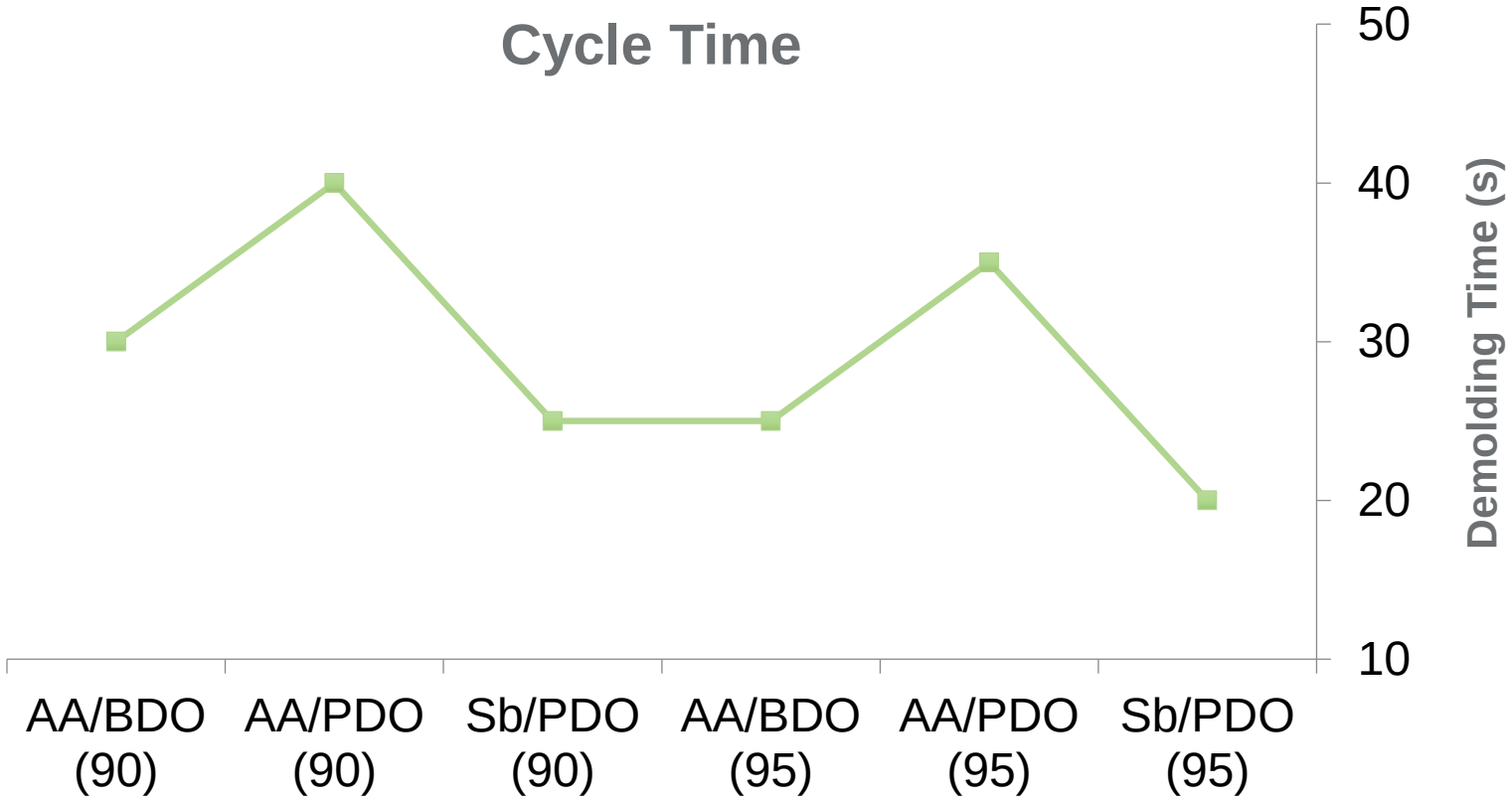
- **Susterra® propanediol and Sebasic acid TPU samples demonstrated lower processing temperatures which may lead to improved processing and energy savings for TPU manufacturers**



Susterra® Propanediol

Processing Comparison

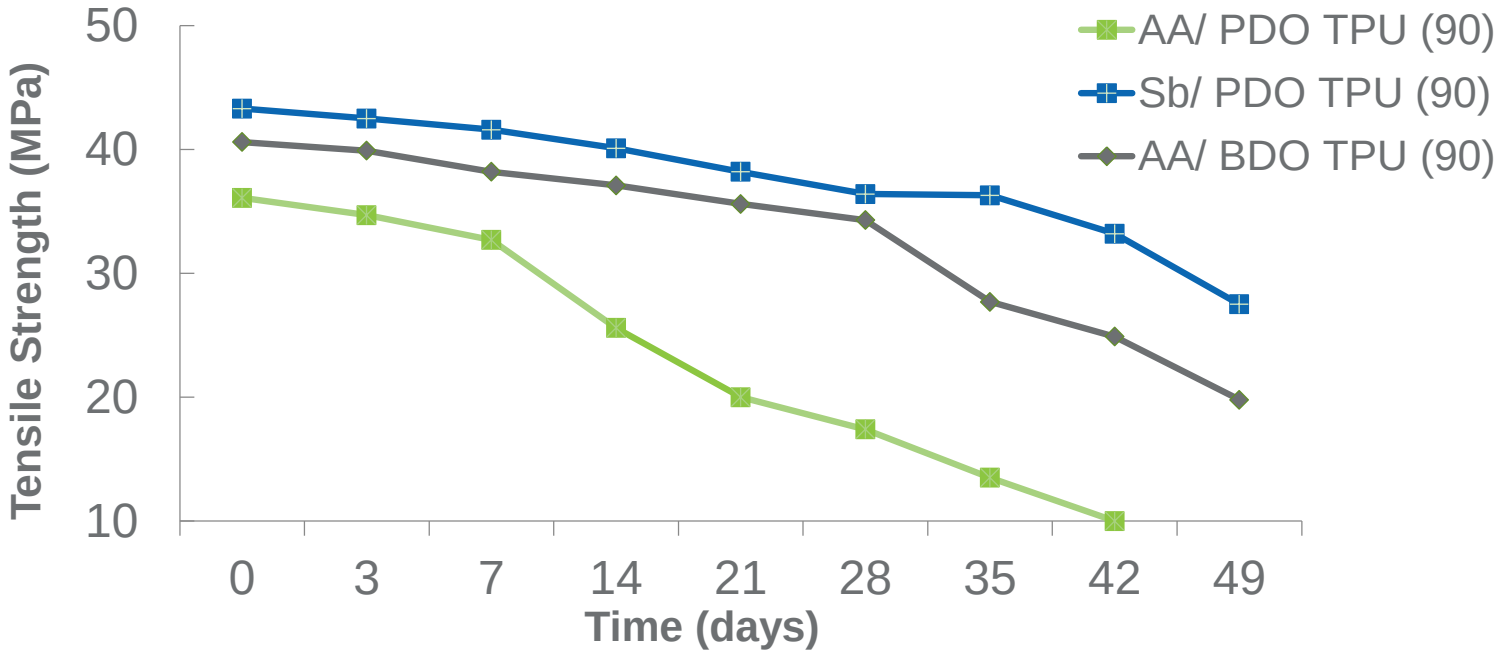
- Susterra® propanediol and Sebasic acid TPU samples demonstrated faster demolding times which may lead to cycle time improvements for TPU manufacturers



Susterra® Propanediol

Hydrolysis Comparison

- **Susterra® propanediol and Sebasic acid TPU samples showed better hydrolysis results over time compared to BDO and PDO samples combined with Adipic acid**



Susterra® Propanediol

Polyurethanes and Thermoplastic Polyurethanes

- Improved flexibility at low temperatures
- Enhanced processing with shorter demolding times
- Excellent adhesion
- Softness and transparency

Performance is in our nature.

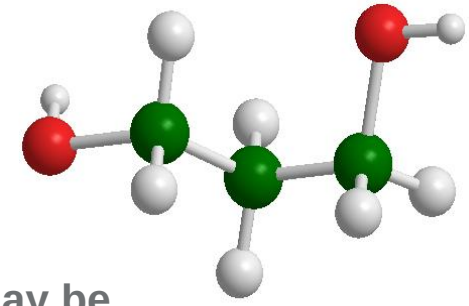
susterra
bio-based performance

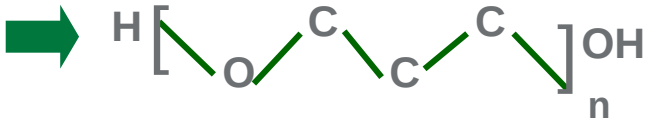
PO3G
Polymerizing Susterra® propanediol for use as a polyol

susterra
bio-based performance

PO3G

Polyurethanes and Thermoplastic Polyurethanes





Susterra® propanediol may be polymerized to form PO3G which may be used as 100% bio-based polyol.

Polytrimethylene ether polyol (PTMEPOL or PO3G)

PO3G or PTMEPOL is not a DuPont Tate & Lyle product. Third parties license a DuPont technology in order to manufacture and sell PO3G as separate entities.

For more property information on PO3G please contact Allessa or SK Chemicals

PO3G

Bio-based PO3G TPU: The customer's requirements and challenges

Customer's requirements	The challenges
• **Bio-content.** • **Mechanical performance** • **Improved performance** • **Product appearance** • **Sustainability**	• **To improve the bio-content.** • **Keep excellent mechanical performance and discover other advantages.** • **Competitive pricing** • **Promote environmental awareness and market demand**

Bio-based PO3G TPU Advantages:

- Excellent mechanical properties (Tensile Strength >35MPa)
- Excellent abrasion (Abrasion < 40mm^3)
- Low temperature flexibility (Tg < -30℃)
- Bio-content (0-60%)

Mechanical and processing properties can comparable with petroleum-based TPUs such as PTMEG

susterra bio-based performance

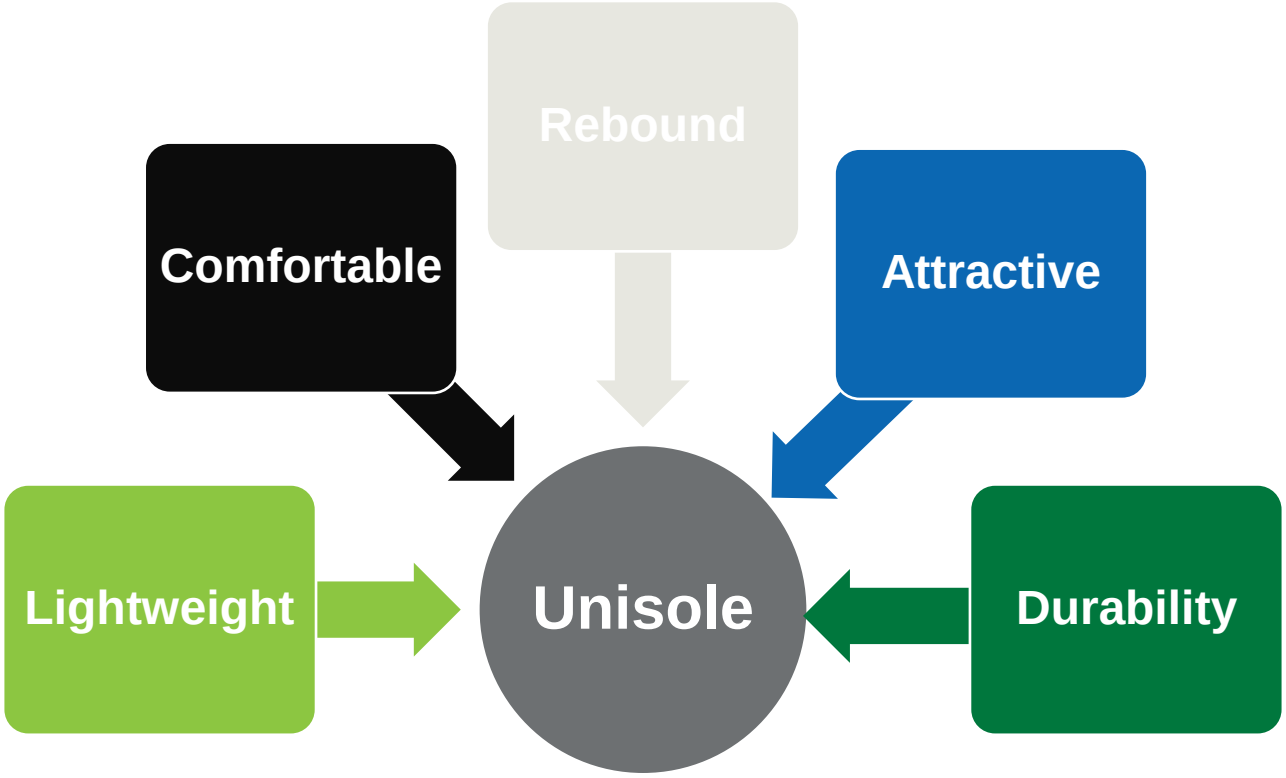
PO3G

Elastomer physical properties for PO3G polyether TPU

Polyol Chain Extender	PTMEG BDO	PO3G BDO	PTMEG BDO	PO3G BDO	PTMEG BDO	PO3G BDO
Bio content(%)	0	60	0	50	0	45
Hardness, Shore A	75	75	85	85	95	95
Tensile Strength (psi)	4126	4054	4554	4305	5391	5305
Elongation at break (%)	689	737	654	681	514	578
100% Modulus (psi)	320	387	1168	962	1449	1339
200% Modulus (psi)	648	621	1583	1475	1972	1816
400% Modulus (psi)	1327	1071	2610	2573	2836	2833
Die C Tear strength (lbf/in)	380	457	638	675	501	550
Compression set, 23°C (%)	30	35	30	32	25	30
Bayshore rebound (%)	55	58	49	53	35	38
Abrasion resistance	52	55	45	48	33	35
Demolding time	120	90	60	45	35	30
Ross flex(cycle/-20°C)	65000	70000	60000	65000	50000	55000
Tg by DSC (°C)	-45	-51	-40	-47	-38	-40

PO3G

Polyether TPUs manufactured with PO3G may offer excellent characteristics to the end user.



susterra bio-based performance

PO3G

Polyether TPUs manufactured with PO3G may offer excellent characteristics to the end user.

- Unisole combines midsole and outsole, thus requiring both good mechanical strength and softness/rebound resilience as well as low compression set

- When using conventional low VA EVA, the prepared foam with higher density (> 0.2g/cm^3) cannot provide good softness, resilience and compression set, while the foam of low density (<0.2 g/cm^3) cannot maintain sufficient mechanical strength

TPUs manufactured with PO3G based on Susterra® propanediol strike an excellent balance between mechanical strength and softness/resilience/CS at an ideal density (0.2~0.25 g/cm^3)

susterra bio-based performance

PO3G

Foam properties of unisoles manufactured with PO3G polyether TPUs

Samples	Unisole w/ TPU 1# (0.22g/cm3)	Unisole w/ TPU 2# (0.2g/cm3)	Test method
Specific Gravity (g/cm^3)	0.22	0.2	ASTM 3574
Hardness (Asker °C)	45	42	
Compression set (%)	35	40	ASTM 3574
Resilience (%)	63	61	ASTM 3574
Tensile (kg/cm^2)	28.4	26.1	ASTM D412, Die C
Elongation (%)	463	401	ASTM D412, Die C
Split Tear (180°, kg/cm)	3.5	3.2	ASTM 3574

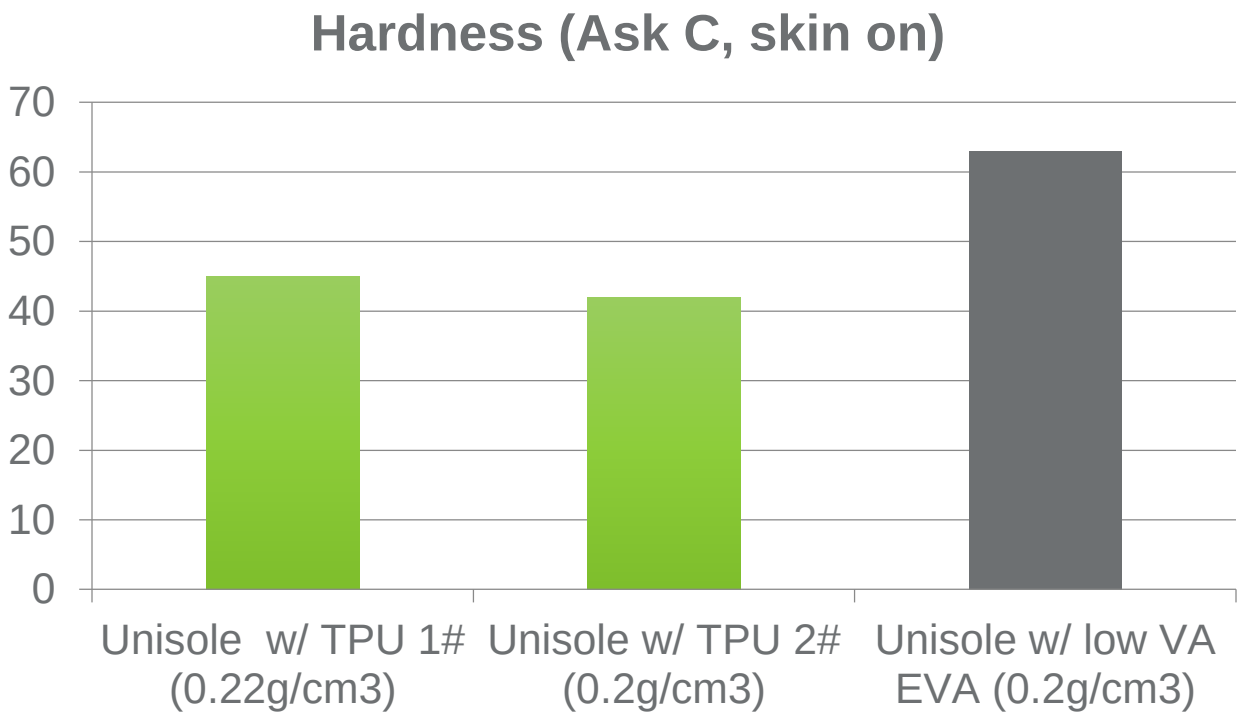
The TPUs foams manufactured with PO3G based on Susterra® propanediol preserve good mechanical strength

Note: It is recommended that anti-abrasion agents (e.g., organosilicone compound) should be used for the purpose of attributing abrasion resistance to unisole

susterra bio-based performance

PO3G

Foam properties of unisoles manufactured with PO3G polyether TPUs

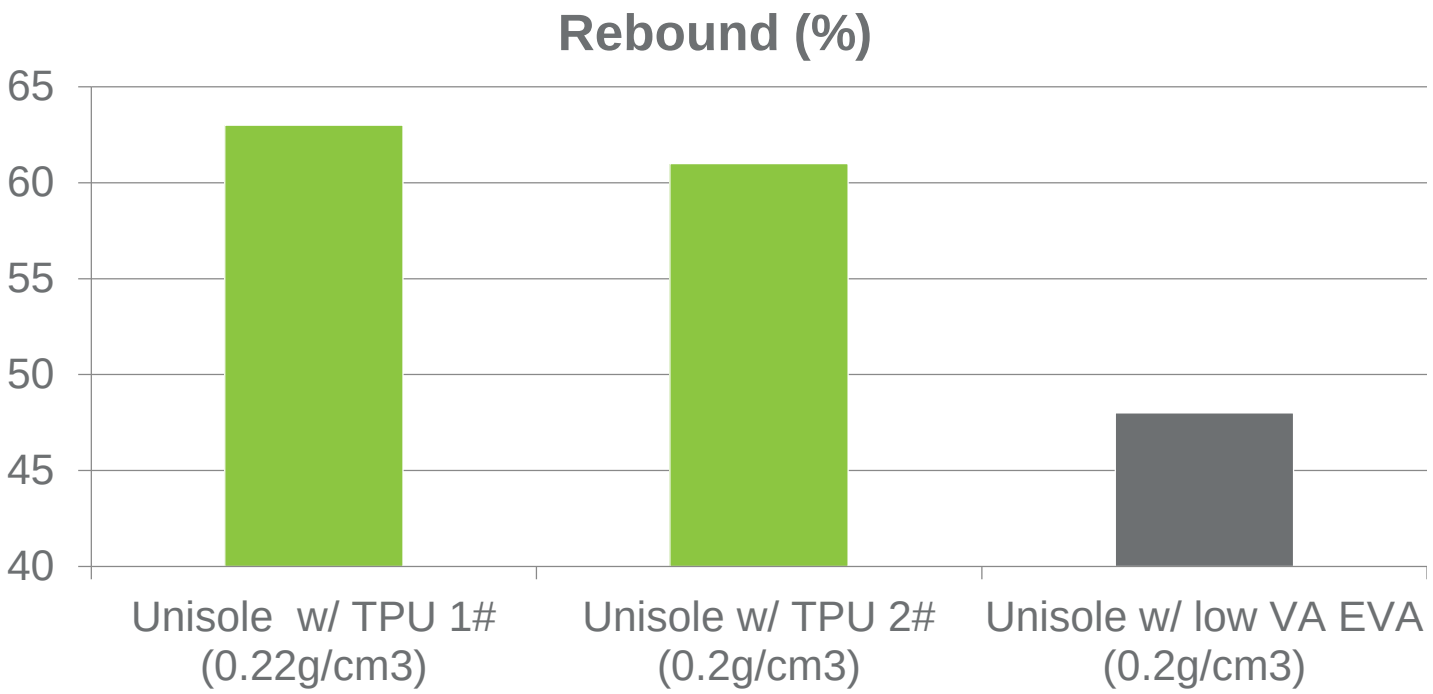


TPUs manufactured with PO3G based on Susterra® propanediol are softer compared to low VA EVA foams with the same or lower density.

susterra bio-based performance

PO3G

Foam properties of unisoles manufactured with PO3G polyether TPUs

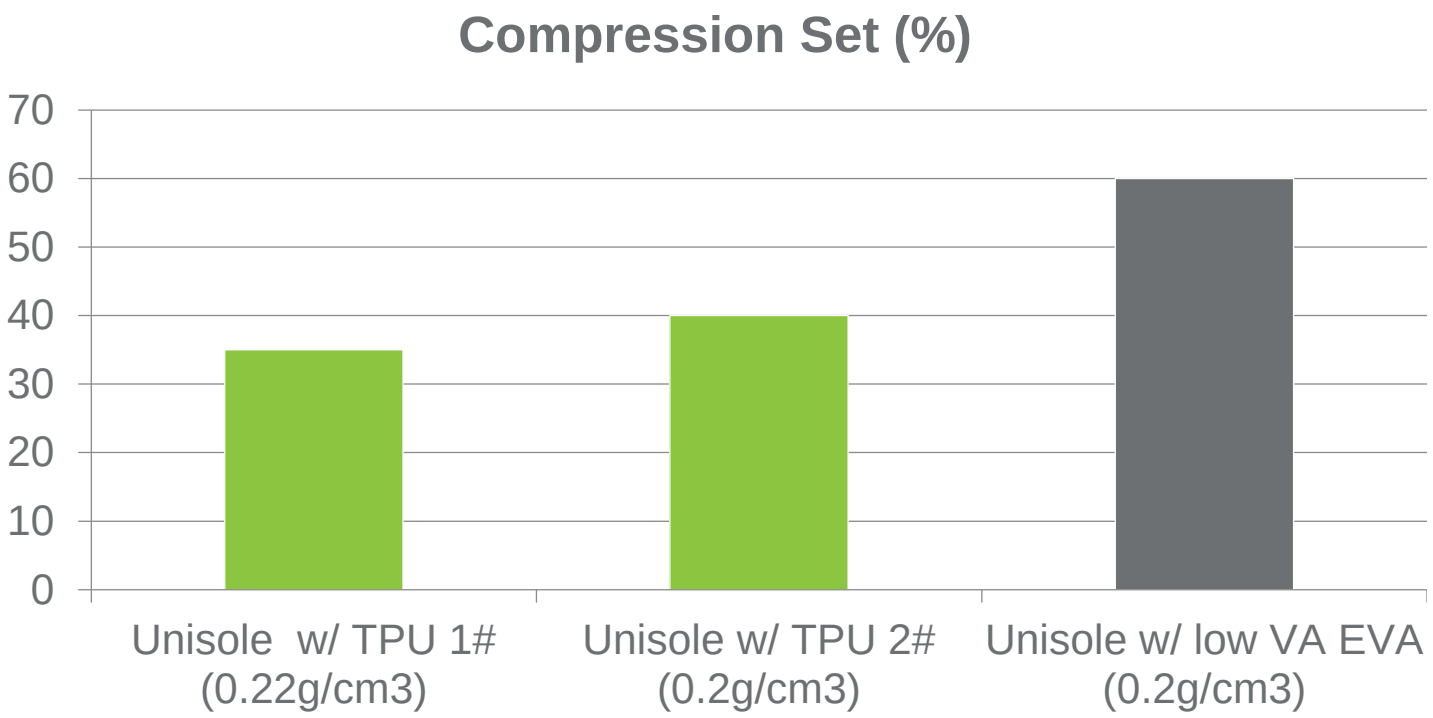


TPUs manufactured with PO3G based on Susterra® propanediol provide excellent melt strength which may ensure a finer and more stable cell structure which can lead to higher resilience.

susterra bio-based performance

PO3G

Foam properties of unisoles manufactured with PO3G polyether TPUs



The foams containing TPUs manufactured with PO3G based on Susterra® propanediol have finer and more stable cell structures leading to lower compression set

susterra bio-based performance

Susterra® Propanediol

Polyurethanes and Thermoplastic Polyurethanes

- Improved flexibility at low temperatures
- Enhanced processing with shorter demolding times
- Excellent adhesion
- Softness and transparency

Performance is in our nature.

susterra
bio-based performance

Laurie Kronenberg

Global Marketing Director

DuPont Tate & Lyle Bio Products Company, LLC.

200 Powder Mill Road

DuPont Experimental Station

Wilmington, DE 19803

302-332.0813 Mobile

302.695.8161 Office

laurel.j.kronenberg@dupont.com

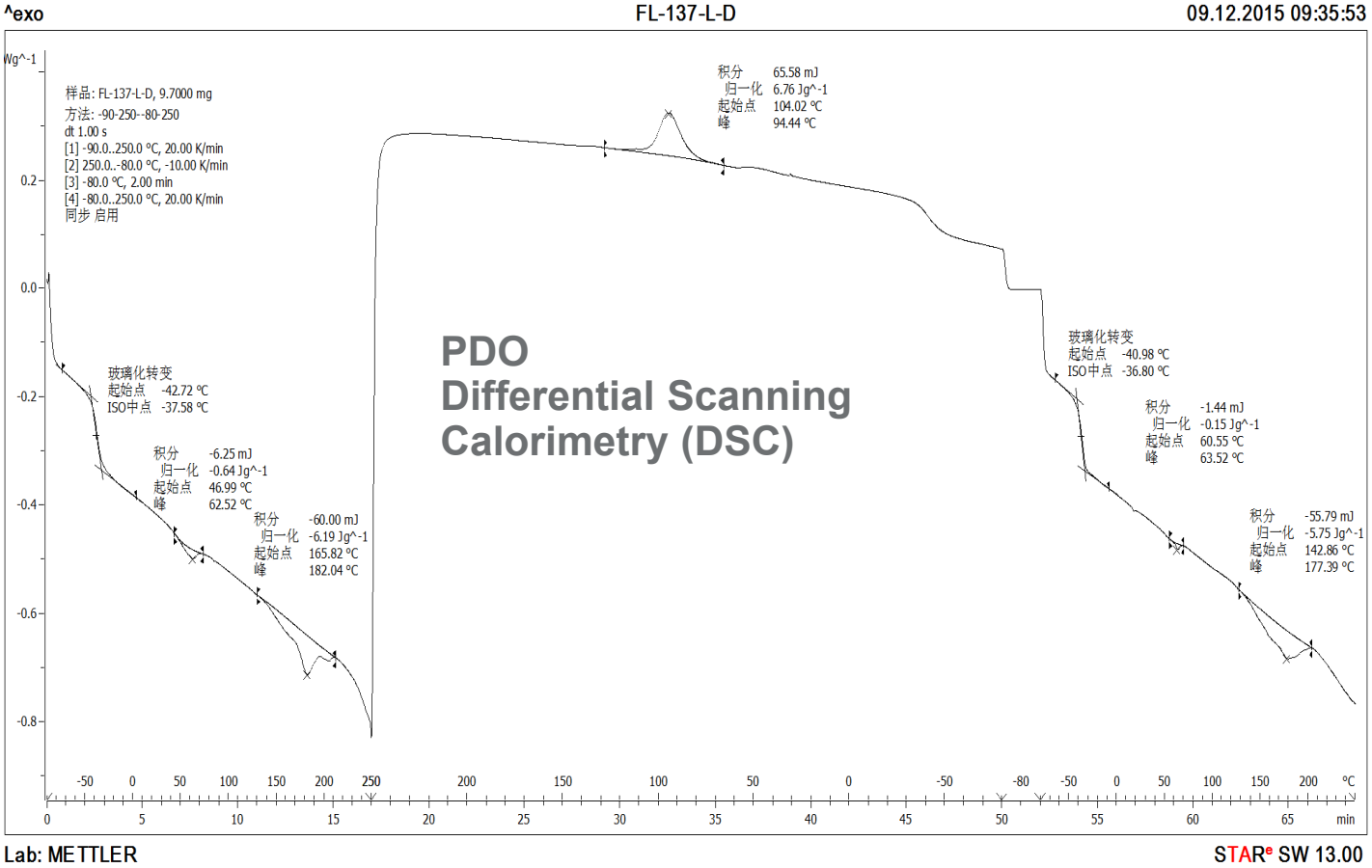
www.duponttateandlyle.com

Back-Up Slides

susterra
bio-based performance

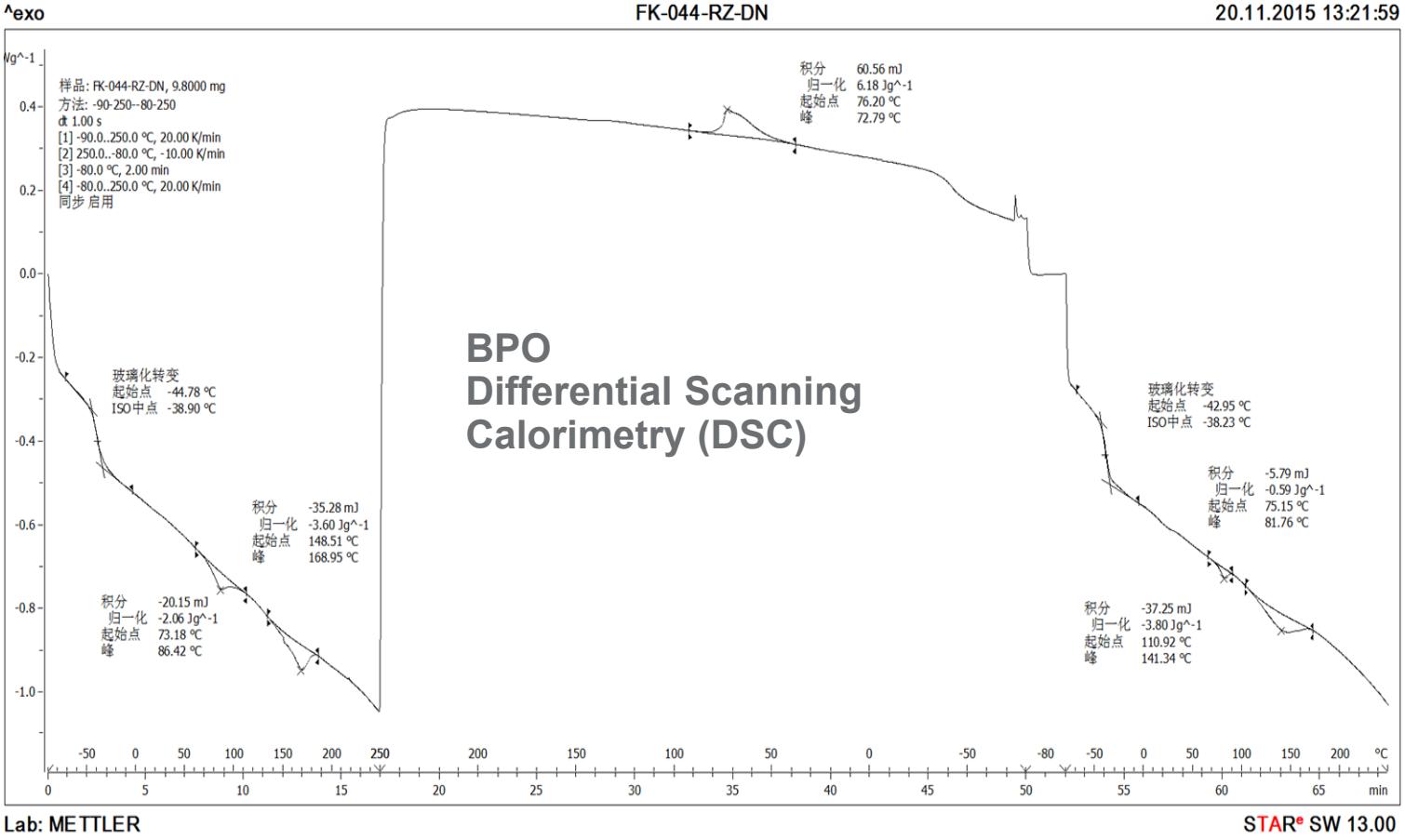
Susterra® Propanediol

Elastomer physical properties for polyester TPU Chain Extender Example with AA/BDO/EG polyol



Susterra® Propanediol

Elastomer physical properties for polyester TPU Chain Extender Example with AA/BDO/EG polyol



BPO Differential Scanning Calorimetry (DSC)