Susterra® Propanediol – From the Leading Edge of Biotechnology, a Renewable and Sustainable Building Block for the Urethane Industry that Delivers Performance and Versatility.

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ABSTRACT

Susterra® Propanediol has been successfully evaluated as an alternative to 1,4-butanediol (BDO) in the production of polyurethane cast elastomers. Susterra® propanediol (biologically-derived 1,3-propanediol) is a unique offering from DuPont Tate & Lyle Bio Products. Susterra® is a high purity, non-regulated diol manufactured via a proprietary corn sugar fermentation process. Susterra® offers functional versatility and is an excellent short-chained diol for manufacturing prepolymers and cast elastomer products. In evaluating high performance cast elastomer polyurethane systems, the focus was on comparing the performance of polyurethanes by; 1) Substituting Susterra® for BDO as a curative in MDI based Prepolymers, and 2) Replacing 1,4 butanediol with Susterra® in the synthesis of a polypropanediol adipate polyester polyol. Formulations utilizing Susterra® as a curative could contain as much as 15% renewable content. Those products using bio-based propanediol as both a polyester polyol ingredient and as a curative were tested to show that renewable content could be as high as 50%. In some formulations, longer reactivity or pot-life was observed, allowing for catalyst optimization. Mechanical properties overall were comparable using Susterra® both as a curative, as well as a diol co-reactant in the adipate ester. In some cases, increased rebound was observed. Commercially available MDI terminated polyester prepolymers, Xthane IT22, IT33 and IT25, from ITWC Inc. were used as a basis for this study. Also TDI terminated polyester prepolymer formulations were investigated using different molecular weight adipates based on Susterra®.

BACKGROUND

Historically, polyurethane technology has relied on raw materials derived from non-renewable petroleum and natural gas feedstocks. A recent trend in urethanes has been the use of bio-based raw materials derived from renewable resources as viable alternatives for non-renewable materials. [1] While a goal OEM’s in automotive, furniture and footwear is to increase the renewable content in their products, delivering high performance foam and elastomer materials is crucial. [2][3] As a result, several suppliers of urethane intermediates have commercialized renewable natural oil polyols (NOPs) to meet each of these demands such as BASF castor oil-based Balance™, Cargill soy bean-based BiOH™ and Dow soy bean-based Renuva™. [4][5]

In May 2004, DuPont and Tate & Lyle formed an equally owned joint venture – DuPont Tate & Lyle Bio Products, LLC – to build one of the largest bio-materials processing facilities in the world in Loudon, Tennessee. Originally built to meet the global demand for DuPont™ Sorona® polymer (renewably sourced polytrimethylene terepthalate, PTT), the proprietary production process ferments corn sugar, a rapildy renewable feedstock, to manufacture Susterra® Propanediol (bio-based

1,3-propanediol). The process offers the promise of reducing dependence on petroleum and petrochemical-based feedstocks, while lowering environmental footprint.

Susterra® is a 100 percent renewably sourced monomer that can add renewable content and uncompromised performance to a variety of applications, either by itself or as an ingredient, in the production of materials that have traditionally relied on petroleum feedstocks. Examples of these applications include the new family of renewably sourced polymers DuPont™ Sorona®, for apparel and residential and commercial carpet and DuPont™ Cerenol™, high-performance polyols (polyetherdiols) ideal for soft segments in thermoplastic elastomers.

A life cycle assessment based on design data of the cradle-to-gate production of renewably sourced Susterra® versus production of chemically derived propanediol shows significant environmental benefits. Based on design data, production of Susterra® consumes up to 42 percent less energy and reduces greenhouse gas emissions by more than 56 percent versus petroleum-based propanediol. Production of Susterra® can save the energy equivalent of over 15 million gallons of gasoline per year, or enough to fuel more than 27,000 cars annually. The life cycle assessment (LCA) study was externally reviewed by Prof. Konrad Saur of Five Winds, an internationally recognized LCA expert. Susterra® is also certified as readily biodegradable based on an Organization for Economic Co-Operation and Development (OECD) Guideline Test for Biodegradation.

Coatings, Adhesives, Sealants and Elastomers

Susterra® is an excellent choice of chemical building block for CASE (Coatings, Adhesives, Sealants and Elastomers) applications. ITWC Urethane Solutions together with DuPont Tate & Lyle conducted developmental work and testing in the area of urethane cast elastomers to enable development of a line of bio-based high performance polyurethane elastomers.

The cast elastomer industry is probably one of the most versatile application segments of the CASE industry, well known for stringent high performance requirements. Application examples in the industrial mechanical, transportation, and sports and recreational segments include forklift wheels and tires, casters, pipeline cleaning pigs, motor couplers, seals, gaskets, hydro cyclones, heavy duty suspension bushings, engine mounts, footwear, skate wheels, etc. Cast elastomers are also molded into sheets, tubes and rod stock which can be cut and shaped into a wide range of parts for the industrial mechanical segment. [6][7]

The primary building blocks used in polyurethane cast elastomers are MDI (methylene diphenyl diisocyanate) and TDI (toluene diisocyanate) prepolymers cured with diols and amines. There are also niche application areas using aliphatic isocyanate prepolymers and other specialty isocyanates, like NDI, PPDI and TODI. MDI and TDI prepolymers are by far the bulk of the cast elastomer industry which can be based on PPG (polypropyleneetherglycol) or PTMEG (polytetramethyleneetherglycol) polyethers, polyester adipates and caprolactones. The choice of the polyol backbone depends on the application requirements, where key properties such as load bearing, abrasion resistance, chemical resistance, cut resistance, resilience and others determine the type of polyol backbone at specific hardness range. [8]

This paper focuses on the use of Susterra® propanediol as a curative diol compared to 1,4-butanediol, and as a co-reactant with adipic acid to make bio-based polyester polyols.

EXPERIMENTAL / RESULTS

The use of Susterra® propanediol in cast polyurethane elastomers was tested first as a curative agent comparing to 1,4 butanediol (BDO) in MDI ester prepolymers used in high performance industrial applications. It was tested as a diol co-reactant with adipic acid to produce bio based polyester polyols, which in turn were reacted with 4,4 MDI to produce a NCO terminated prepolymer. The resulting prepolymer was cured with Susterra® by itself and also separately cured with a mixture of Susterra® and Susterra® based polyester polyols, depending on the desired hardness. The resulting elastomers had a bio or renewable content from 30-55 weight % according to the carbon dating norm ASTM D6866.

Using the same Susterra® based polyester polyol, TDI prepolymers were prepared using both TDI 80/20 and TDI 100 isomers, and cured with Ethacure 300 (Dimethylthiotoluenediamine -DMTDA). The resulting elastomers had a bio content of 25-30%.

Susterra® Propanediol as Curative

Three MDI terminated polyester prepolymers (Xthane IT22, IT33 and IT25) were chosen to test and compare the Susterra® (EXT-1034) against BDO (EXT-1006). Physical property results for the resulting elastomers are summarized in Table 1.

The performance results of Susterra® (EXT-1034) in Xthane IT22 are comparable, exhibiting slightly better Die C Tear properties and an extended Pot-Life at the same catalyst level. In the case of Xthane IT33 (mix glycol adipate BDO-EG) both resilience and compression set were worse but the extended pot-life was retained. In Xthane IT25 (Susterra® based) the

Susterra® softens the elastomer by 3 points, but abrasion resistance was much better. An extended pot-life was also achieved.

Table 1. Comparison between Susterra® and BDO as Chain Extenders in Elastomers

MDI Polyester Prepolymer:	IT-22 Ethylene Adipate		IT-33 Ethylene/Butylene Adipate		IT-25 Butylene Adipate	
Chain Extender:	**1034 Susterra®**	1006 BDO	**1034 Susterra®**	1006 BDO	**1034 Susterra®**	1006 BDO
Bio-Content, wt.%	**100**		**100**		**100**	
Date Tested:	**2009**	2006	**2009**	2008	**2009**	2008
Final Bio Content, wt.% (ASTM D6866)	**5**		**6**		**6.5**	
Hardness: A scale	**86**	86	**85**	87	**90**	93
D scale						
Resilience by Vertical rebound	**40**	32	**20**	42	**46**	50
Split Tear Strength	**290**	357	**110**	175	**210**	320
Die C Tear Strength	**580**	520	**350**	500	**470**	600
Tensile Strength	**6000**	7000	**5800**	6500	**5500**	7000
Ultimate Elongation	**561**	596	**400**	540		470
100% Modulus	**850**	725	**980**	925	**1100**	1110
200% Modulus	**1350**	1070	**1650**	1200	**1750**	1680
300% Modulus	**2100**	1761	**2750**	1700	**3200**	2800
Compression Set	**23**	30	**25**	18	**21**	15
Compression Deflection						
5%	**66**	84	**76**	91	**85**	217
10%	**228**	259	**218**	291	**295**	636
15%	**407**	444	**386**	499	**530**	920
20%	**591**	642	**574**	717	**775**	
25%	**793**	840	**785**	870		
50%		883				
Taber Abrasion	**10**	14	**10**	13	**7**	20
Specific Gravity	**1.237**	1.22	**1.24**	1.22	**1.20**	1.2
Parameters						
Prepolymer Temp. F	**200**	194-212	**200**	200	**200**	194
Extender Temp. F	**110**	77-158	**110**	110	**110**	77-156
Mold Temp. F	**230**	194-248	**230**	260	**230**	221-245
Pot Life Minutes	**8**	4 to 6	**10**	35	**10**	3 to 4
Demold Time Minutes	**45**	45	**50**	60	**50**	15 to 20
Typical NCO/OH Ratio	**1.03**	1.03	**1.03**	1.05	**1.03**	1.05
Extender Equivalent Wt.	**38**	45	**38**	45	**38**	45
Ratio at % NCO						
% NCO	**6.5-6.7**	6.5-6.7	**6.9-7.2**	6.9-7.2	**8.7-9.4**	8.7-9.4

All samples catalyzed with KA1

Susterra® Propanediol as co-reactant with Adipic Acid

Susterra® was reacted with adipic acid to yield three different polyesters with molecular weights: 500, 1000 and 2000. The resulting adipates (see Table 2) then were used to make a 4,4 MDI prepolymer . Both properties and processing parameters for this prepolymer (Xthane IR95) cured with Susterra® (EXT-1034) and Susterra® based polyester polyols is shown in Table 3.

As shown in Table 3, Xthane IR95 was cured with Susterra® (EXT-1034) and the Susterra® based adipate Poly S2000PAR to high performance cast elastomers in three different hardness: 75, 85 and 95 Shore A. This hardness range covers a broad spectrum of polyurethane high performance elastomer applications. The bio or renewable content in these elastomers as tested by ASTM D6866 varied from 30 to 55 weight %.

Overall properties were comparable to standard high performance elastomers used in the industry today, and in some cases higher resilience (Bayshore Rebound) and lower Taber abrasion numbers were observed.

Table 2. Susterra® Based, Renewably Sourced Polyester Polyols

Polyester Polyol:	**Poly S2000PAR** Susterra® Adipate 2000 Mw	**Poly S1000PAR** Susterra® Adipate 1000 Mw	**Poly S500PAR** Susterra® Adipate 500 Mw
Bio Content, wt.% (ASTM D6866)	**37**	**40**	**45**
Funtionality	2	2	2
Appearance @ 25°C	Solid	Solid	Liquid
Hydroxyl Number, range	52-58 mg KOH/g	105-115 mg KOH/g	215-235 mg KOH/g
Acid Number, maximum	0.7 mg KOH/g	0.7 mg KOH/g	0.7 mg KOH/g
Water Content, maximum	0.05%	0.05%	0.05%
Color, APHA maximum	100	100	100
Viscosity @ 60°C	1200-1400 mPa.s	330-380 mpa.s	90-100 mPa.s
Speciifc Gravity @ 25°C	1.14	1.14	1.15
Bulk Density @ 25°C	9.50 lb/gal	9.50 lb/gal	9.58 lb/gal

Table 3. Comparison between Susterra® Based and BDO Based Elastomers using MDI Prepolymers

MDI Polyester Prepolymer:	**IR-95**	IT-22	**IR-95**	IT-22	IT-33	**IR-95**	IT-25	IT-321
	Susterra® Adipate	Ethylene Adipate	**Susterra® Adipate**	Ethylene Adipate	Ethylene/ Butylene Adipate	**Susterra® Adipate**	Butylene Adipate	Ethylene/ Butylene Adipate
Bio-Content, wt.%	**24**		**24**			**24**		
Chain Extender A:	**8% 1034**	1006	**20% 1034**	1006	1006	**1034**	1006	1006
	Susterra®	BDO	**Susterra®**	BDO	BDO	**Susterra®**	BDO	BDO
Bio-Content, wt.%	**100**		**100**			**100**		
Chain Extender B:	**92% Poly S2000PAR**[a]		**80% Poly S2000PAR**[a]					
Bio-Content, wt.%	**37**		**37**					
Date Tested:	**2009**	2006	**2009**	2006	2008	**2009**	2008	2008
Final Bio Content, wt.% (ASTM D6866)	**39**		**55**			**30**		
Hardness: A scale	**75**	76	**85**	86	87	**95**	93	95
D scale								
Resilience by Vertical rebound	**57**	14	**48**	32	42	**47**	50	30
Split Tear Strength	**110**	185	**180**	357	175	**252**	320	300
Die C Tear Strength	**329**	472	**425**	520	500	**487**	600	600
Tensile Strength	**5086**	7760	**5762**	7000	6500	**5307**	7000	7000
Ultimate Elongation	**512**	531	**511**	596	540	**496**	470	550
100% Modulus	**534**	246	**856**	725	925	**1440**	1110	1400
200% Modulus	**767**	789	**1204**	1070	1200	**1941**	1680	1800
300% Modulus	**1129**	1132	**1728**	1761	1700	**2682**	2800	2500
Compression Set	**21**	38	**25**	30	18	**30**	15	800
Compression Deflection								
5%	**56**	60	**245**	84	91	**219**	217	238
10%	**160**	160	**415**	259	291	**611**	636	747
15%	**274**	277	**596**	444	499		920	
20%	**393**	410	**795**	642	717			
25%	**529**	560		840	870			
50%				883				
Taber Abrasion	**8**	8	**11**	14	13	**12**	20	22
Specific Gravity	**1.205**	1.22	**1.21**	1.22	1.22	**1.216**	1.2	1.22
Parameters								
Prepolymer Temp.	**180**	170	**180**	194-212	200	**180**	194	180
Extender Temp.	**110**	75	**110**	77-158	110	**110**	77-156	140
Mold Temp.	**235**	220	**235**	194-248	260	**235**	221-245	240
Pot Life	**7**	30	**7**	4 to 6	35	**7**	3 to 4	5
Demold Time	**30**	90	**30**	45	60	**30**	15 to 20	60
Typical NCO/OH Ratio	**1.04**	1.03	**1.04**	1.03	1.05	**1.04**	1.05	1.03
Extender Equivalent Wt.	**331**	49	**165**	45	45	**38**	45	45
Ratio at % NCO								
% NCO	**9.00-9.3**	6.5-6.7	**9.00-9.3**	6.5-6.7	6.9-7.2	**9.00-9.3**	8.7-9.4	9.2-9.6

All samples catalyzed with KA1
[a] See Table 2

Lastly, Susterra® based polyester polyols were prepared with two TDI based prepolymers and cured with the aromatic diamine Ethacure 300 (Di(methylthio)toluenediamine, DMTDA). Results of the resulting elastomers compared to their equivalents (Xthane TC70S and TC87S) are shown in Table 4. The bio based elastomers exhibit better Taber abrasion, Compression set and lower Tensile strength.

Table 4. Comparison between Susterra® Based and BDO Based Elastomers using TDI Prepolymers

TDI Polyester Prepolymer:	**EXP-182798A**	TC-70S	**EXP-182799A**	TC-87S
	Susterra® Adipate	Ethylene Adipate	**Susterra® Adipate**	Ethylene Adipate
Bio-Content, wt.%	**25**		**28**	
Chain Extender:	Ethacure® 300[a] (DMTDA)		Ethacure® 300[a] (DMTDA)	
Date Tested:	**2009**	2009	**2009**	2009
Final Bio Content, wt.% (ASTM D6866)	**20**		**20**	
Hardness: A scale	**70**	68	**87**	88
D scale				
Resilience by Vertical rebound	**50**	41	**38**	34
Split Tear Strength	**133**	153	**78**	256
Die C Tear Strength	**305**	291	**260**	500
Tensile Strength	**4168**	5000	**4687**	7000
Ultimate Elongation	**677**	>800	**427**	625
100% Modulus	**477**	370	**765**	774
200% Modulus	**651**	500	**1147**	1100
300% Modulus	**821**	640	**1767**	1400
Compression Set	**22**	30	**17**	25
Compression Deflection				
5%	**19.6**	30	**66.2**	63
10%	**96**	90	**228.6**	220
15%	**165.2**	134	**387.5**	368
20%	**236.4**	190	**545.2**	520
25%	**312.6**	253	**721.9**	708
50%				
Taber Abrasion	**9**	25	**29**	40
Specific Gravity	**1.211**	1.22	**1.212**	1.25
Parameters				
Prepolymer Temp.	**170**	176	**170**	170
Extender Temp.	**110**	86	**110**	100
Mold Temp.	**230**	212	**230**	230
Pot Life	**6:56**	5	**4:28**	3 to 4
Demold Time	**20**	35	**20**	10
Typical NCO/OH Ratio	**1.05**	1.05	**1.05**	1.05
Extender Equivalent Wt.	**107**	107	**107**	107
Ratio at % NCO				
% NCO	**2.4-2.7**	2.4-2.7	**3.7-4.0**	3.7-4.0

[a] Ethacure® is a registered trademark of the Albemarle Corporation

CONCLUSIONS

Susterra® Propanediol used as curative in traditional MDI-ester prepolymers below 10% NCO content, exhibit better tear strength and abrasion resistance. It also extends Pot-Life thus allowing catalyst maximization, which usually leads to enhanced overall properties.

In the case of the Xthane IR95 prepolymer, based on Poly S2000PAR Susterra® adipate ester and cured with more Susterra® clearly demonstrates how this Bio based monomer can successfully be used to maximize the renewable content of a polyurethane cast elastomer system without compromising performance compared to currently used systems.

Interesting to note was the improved abrasion resistance and compression set when the Susterra® based polyesters were reacted with TDI and cured with Ethacure 300®. Of special interest, warranting further investigation is the 70 Shore A elastomer in high wear applications.

Further work has already begun using Susterra® based polyesters to formulate quasi prepolymers, One Shot systems, and Specialty Foams. Although the demand for green products in the Polyurethane industry has just started, Susterra® Propanediol monomer is well position as key building block, as clearly demonstrated by the work presented in this paper.

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