

Susterra® Propanediol – Renewability, Sustainability, and Differentiating Performance in Urethane Applications

JUDITH J. VAN GORP

*E. I. du Pont de Nemours and Company
Experimental Station, E302/221b
Route 141 and Henry Clay Road
Wilmington, DE, 19880-302*

JOSEPH W DESALVO, ROBERT MILLER

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

ABSTRACT

Susterra® propanediol has been successfully evaluated as a replacement for 1,4-butanediol (BDO) in polyurethane coatings, adhesives, sealants, and elastomers (CASE) as well as in thermoplastic polyurethanes (TPU). Susterra® propanediol (biologically-derived 1,3-propanediol) is a unique offering from DuPont Tate & Lyle Bio Products. Susterra® is a 100% bio-based diol that can increase the renewable content of polyurethane formulations. Polyurethane elastomers cured with Susterra® may contain up to 10% renewable content while 33% or greater content may be reached in those formulas that use Susterra® in the polyester polyol as well as the curative. Susterra® polyester polyols are similar to BDO based polyester polyols and can be formulated into polyurethanes without extensive re-work. However, they are different enough to give unique and versatile polyurethane systems. The odd-even effect tells us that the thermal transitions of Susterra® polyester polyols and polyurethanes will occur at lower temperatures, and that the crystallization half times will be longer than those of BDO adipates. It is illustrated with a few examples how these physical properties of Susterra® polyester polyol soft blocks and Susterra® hard blocks enable unique and new urethane applications. For example, Susterra® based adipates are liquid at room temperature, may improve low temperature behavior of the polyurethane part, and give transparent polyester polyol based urethane articles. We hope these examples illustrate the versatility of Susterra® in a range of performance possibilities.

INTRODUCTION

An increasing number of polyurethane manufacturers are looking to provide their customers with differentiated products that combine performance with environmental consciousness. A study of consumer purchasing habits has shown that demand for sustainable offerings remains strong despite the recent downturn in the economy. According to a recent Cone Consumer Survey (February 2009), 44% of consumers say their "green" buying habits remain unchanged despite the current economy and one-third of consumers say they are more likely to buy green today than they were previously. As a result the DuPont portfolio of renewably sourced products is seeing an increase in demand among well-known market brands.

In May 2004, DuPont and Tate & Lyle formed an equally owned joint venture – DuPont Tate & Lyle Bio Products Company, LLC – and invested \$100 million in one of the largest bio-materials processing facilities in the world at Loudon, Tennessee. Originally built to meet the global demand for the DuPont™ Sorona® polymer, a renewably sourced polytrimethylene terephthalate, PTT, the proprietary production process ferments corn sugar, a rapidly renewable feedstock, to manufacture a 100% bio-based 1,3-propanediol. This material is commercially available under the registered trade name Susterra® propanediol. The commercial success of this product has led to the recent announcement that capacity is to be expanded by 35% for start up in the second quarter 2011.

A life cycle assessment (LCA) based on design data of the cradle-to-gate production of this new material versus the production of chemically derived propanediol 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 LCA has been externally reviewed.

At the 2009 CPI conference, DuPont Tate & Lyle Bio Products presented the initial paper on the use of Susterra® propanediol as an alternative to BDO in the production of polyurethane cast elastomers. From these early tests as a curative agent in MDI prepolymers and as a co-reactant in a bio based polyester polyol, work has continued to show the expanded

opportunities for Susterra® as a raw material in polyurethanes. This paper reports that the use of Susterra® propanediol in polyester polyols at levels of up to 40 wt%, in combination with a Susterra® chain extender at levels of 3-10 wt%, makes it possible to yield a final product containing up to 33 wt% bio-based content. One example of a polyester polyol made from this bio-based PDO is that derived from adipic acid. When used as a chain extender in thermoplastic urethane formulations, Susterra® easily reacts with MDI to yield linear urethane domains. The below work compares Susterra® to four other straight chain diols: 1,2-ethanediol (EG), 1,4-butanediol (BDO), 1,5-pentanediol (PeDO), and 1,6-hexanediol (HDO).

EXPERIMENTAL

Raw Materials

Adipic acid, 1,2-ethanediol (EG), 1,4-butanediol (BDO), 1,5-pentanediol (PeDO), and 1,6-hexanediol (HDO) were sourced from Sigma Aldrich. Susterra® propanediol (1,3 propanediol, PDO) was provided by DuPont Tate & Lyle Bio Products, Loudon, TN. Diols used as chain extender were dried under reduced pressure to a water level below 500 ppm as determined by Karl Fisher titration. The butyltin tris-2ethylhexanoate catalyst used was Fascat® 4102 from Arkema. Methylene diphenyl diisocyanate (MDI) was obtained from Dow (Isonate 125M) or from Bayer (Mondur M). It was stored in an oven at 55 °C before use.

Test Methods

The acid number of adipates was determined by manual titration against 0.05 N NaOH in water using tetrahydrofuran (THF) as the solvent and 1 wt % phenolphthalein in methanol as the indicator. The OH number was measured with a method using para-toluenesulfonyl isocyanate (TSI) as described in ASTM E1899 -08. The viscosity followed from a Brookfield DVIII+ viscometer using spindle 21. The reported viscosity is obtained at a speed corresponding to a torque of 50 %. Color was determined using an UV instrument (Varian 50 conc). The yellowness index (YI) was calculated from absorbance data collected every 5 nm from 780 to 380 nm. Both the viscosity and the color were determined at 60 °C. The NCO number of prepolymers was determined by a titration method based on ASTM D5155-07. The prepolymer was reacted with excess 0.4 M dibutylamine in toluene using a 1:2 mixture of toluene and isopropanol to dissolve the sample. Excess amine was titrated with 0.5 N HCl aq. Differential Scanning Calorimetry (DSC) was performed on a Universal V4.5A TA Instrument, of model DSC Q1000 V9.8 Build 296, or on a Universal V4.2E Instrument, of model DSC Q2000 V23.5 Build 72. For the adipates a heat-cool-reheat program was followed from -90 to 200 °C at a scan speed of 10 °C/min. Transitions of the second heating run are reported. For the polyurethanes one heating run was performed from 0 to 200 °C at 5 °C/min. Transitions are indicated by the following abbreviations: glass transition temperature (T_g), melt transition (T_m), cold crystallization (T_c), all in °C, and melt enthalpy (ΔH) in J/g. Crystallization half time (t_{1/2}) experiments were run in a Perkin-Elmer DSC 7 with a maximum cool rate of 200°C/min. Half times were determined from heat flow vs time curves. The time at which the integral of a heat flow peak was half of that of the total crystallization energy was recorded as t_{1/2}. Heat flow vs time curves were obtained at a set temperature close to the main melt transition after quenching the sample in the instrument. For EG adipate and Susterra® adipate the studies were done from freezing (low side). For BDO adipate the studies were done from the melt (high side).

Preparation of polyester polyols using adipic acid and linear diols

A 4 neck, 3 liter flask was charged with a total of 2.2 kg adipic acid and diol. A slight excess of diol (1.1 -1.2 eq.) allowed for a final product with an acid number between 0.5 and 1 and an OH number of approximately 55 kg OH/ g polymer, corresponding to a number average molecular weight (M_n) of 2,000 g/mol. The amount of butyltin tris-2ethylhexanoate used was 20-30 drops. The temperature profiles were based on temperatures between 140 and 200 °C. The reaction proceeded under atmospheric nitrogen sweep for eight hours, at which point water formation had stopped, and the overhead temperature at the head of the Vigreux column had decreased. After slowly applying vacuum (about 26 mbar) and re-applying heat, the reaction proceeded for another eight to sixteen hours. Adipates were dried under reduced pressure at elevated temperature (80-100 °C) to a water level below 200 ppm as determined by Karl Fisher titration before they were converted into prepolymers.

Preparation of polyurethanes

The preparation of polyurethanes was performed in two steps. First, both BDO and Susterra® adipate were converted into prepolymers using MDI. In case of BDO adipate, the polyol (600 g) was stirred mechanically under nitrogen at 70 °C in a 1 liter, 3 neck flask. MDI was added stepwise keeping the temperature below 80 °C. The mixture was stirred for an additional

2 hours at 80 °C, and the NCO number was determined. In case of Susterra® adipate, the polyol (85 g) was stirred with a mechanical stirrer in a disposable cup. The polyol was heated to 50 °C at which point MDI was added, and the mixture reached its exotherm at 80 °C. The mixture was stirred for an additional 30 min. at 75 °C, after which the NCO number was determined. Second, the prepolymer was chain extended with diol. The diol was added to the prepolymer (100 – 200 g) in a disposable cup. No catalyst was added. After mixing vigorously by hand, the polyurethane product was poured on a metal sheet treated with mold spray (Ease Release™ 2251 from Mann Co.) and cured at 110 °C for 16 hours. The amounts of adipate and MDI used were calculated from a targeted hard block content of 25 wt%. The amount of diol followed from the prepolymer NCO number and a NCO/OH ratio of 1.03 during chain extension.

RESULTS

Polyester Polyols

The high temperature and reduced pressure condensation reaction between adipic acid and linear diol is represented in Figure 1 and the five corresponding diols are listed in Table 1.

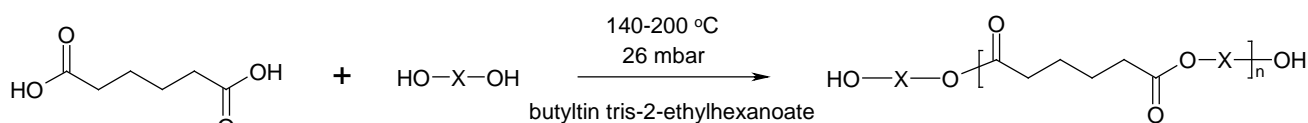


Figure 1. Preparation of the polyester polyol

Table 1: Five adipates from linear diols

Diol	- Adipate	X =
EG	1,2-ethylene-	-C2H4-
Susterra® PDO	1,3-propylene-	-C3H6-
BDO	1,4- butylene-	-C4H8-
PeDO	1,5-pentylene-	-C5H10-
HDO	1,6-hexylene-	-C6H12-

The physical properties for each polyester polyol are represented in Table 2. All materials were white to slightly yellow waxy solids. The mixed diol adipates of EG/BDO, Susterra®/BDO and EG/Susterra® were prepared by the same procedure described earlier, using a 1:1 molar ratio of two different diols. Both the EG/BDO and Susterra®/BDO adipates were obtained as white waxy solids. EG/Susterra® adipate was obtained as a clear liquid.

Table 2: Analysis of the polyester polyols

Diol	Unit	EG	Susterra®	BDO	PeDO	HDO	EG/BDO	Susterra®/BDO	EG/Susterra®
#C atoms		C2	C3	C4	C5	C6	C2/C4	C3/C4	C2/C3
M _n	[g/mol]	2114	2029	2110	2188	1961	1986	1809	1999
OH number	[mg KOH/ g]	52.8	55.3	53.2	51.3	57.3	56.5	62.0	56.1
Acid number		0.53	0.36	0.61	1.24	0.26	0.79	0.57	0.67
Viscosity	[cP]	1334	1471	1482	1316	1100	1394	1190	1321
Color	YI	1.0	4.7	7.2	10.6	ND*	5.7	1.65	0.04

* ND = not determined. Sample solidified in cuvette.

Polyurethanes

Polyurethanes were prepared in a two step procedure as shown in Figure 2. First, the adipate was converted into a prepolymer using MDI as the diisocyanate. Both Susterra® adipate¹ and BDO adipate were converted into prepolymer.

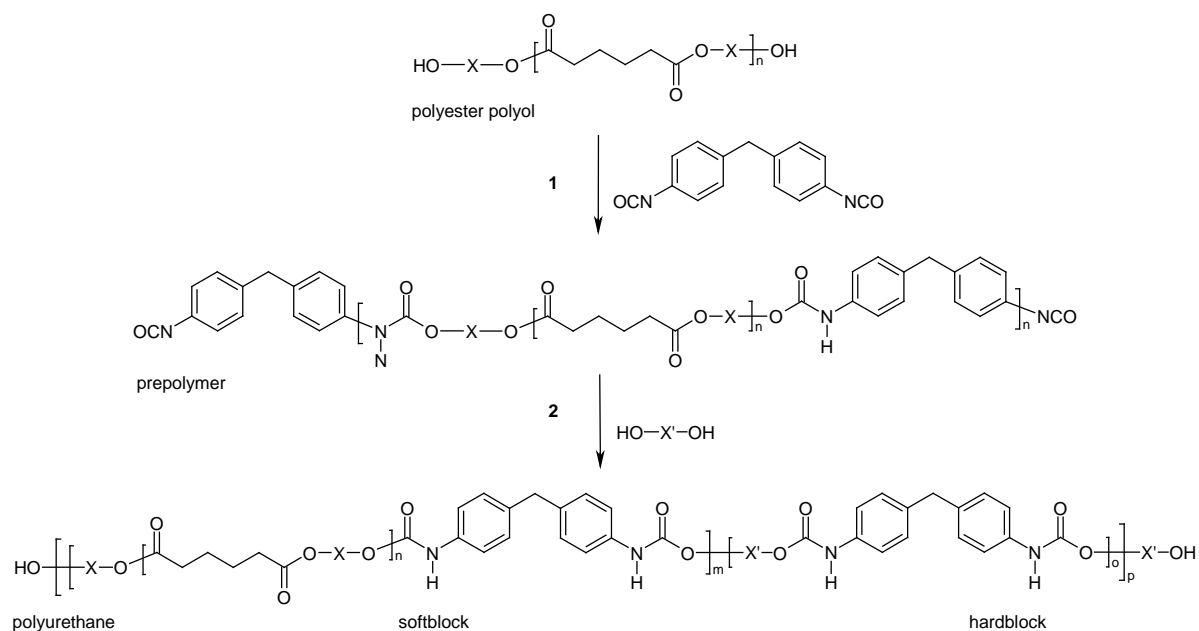


Figure 2: Preparation of the polyurethanes

Next, the prepolymers were chain extended with one of the five different diols EG, Susterra®, BDO PeDO, and HDO. The NCO/OH ratio during chain extension was kept between 1.02 and 1.1 (Table 3). The final products were cured at 110 °C. The hard block content of all samples was approximately 25 wt%.

Table 3: Analysis of the polyurethanes

Chain Extender	NCO number of prepolymer [wt%]	Prepolymer/ diol ratio in chain extension [wt%]	Hard block in TPU product [wt%]
BDO adipate – MDI prepolymer			
EG	4.05	1.021	24.0
Susterra®	4.03	1.028	24.5
BDO	4.03	1.017	25.0
PeDO	4.05	1.245	24.8
HDO	4.05	1.068	25.8
Susterra® adipate – MDI prepolymer			
EG	4.39	1.076	24.5
Susterra®	4.05	1.085	24.2
BDO	4.64	1.069	26.4
PeDO	4.32	1.089	25.6
HDO	4.45	1.076	26.4

Thermal transitions of the polyester polyols

The DSC trace of a sample of Susterra® adipate that had been aged at room temperature for 2 months showed a sharp melt transition at 40.1 °C ($\Delta H = 69.7$ J/g) upon heating. Upon cooling, almost no crystallization occurred ($T_m = -21.8$ °C, $\Delta H = 0.75$ J/g). The re-heat trace shown in Figure 3 has a cold crystallization event at 2.3 °C ($\Delta H = 37.6$ J/g), followed by two melt transitions at 30.8 and 39.7 °C (ΔH total = 38.1 J/g). A glass transition temperature (T_g) was found at -59.7 °C.

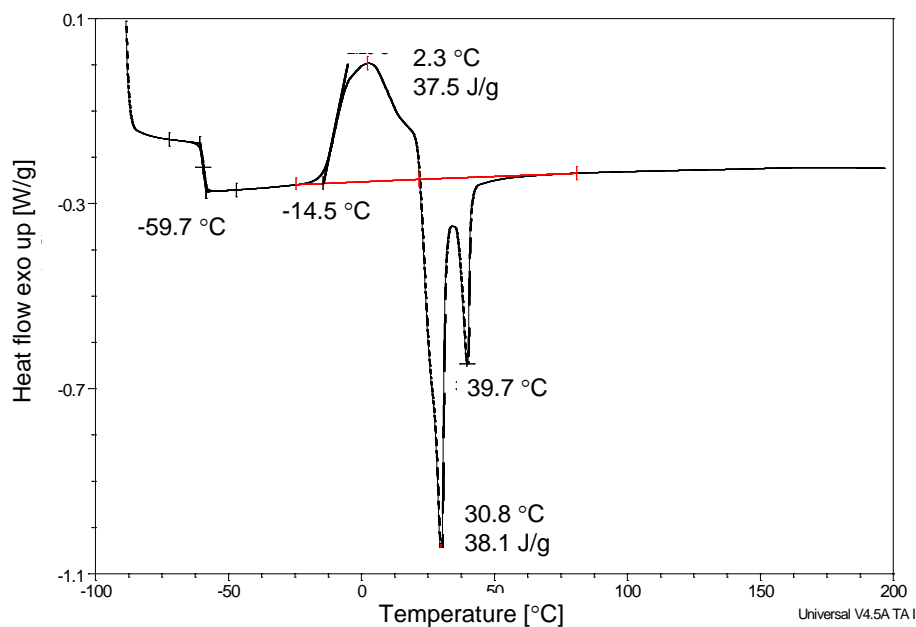


Figure 3: DSC trace of the second heating run of Susterra® adipate (10 °C/min.)

The second heating trace of Susterra® adipate was compared to that of the four other adipates. Table 4 shows the T_g of Susterra® adipate was low compared to that of the other adipates and only the T_g of PeDO was lower. Besides Susterra® adipate, EG adipate was the only other adipate showing cold crystallization. The melt transitions of Susterra® adipate occurred at relatively low temperatures and only PeDO adipate had melt transitions that were similarly low. By comparison, the melt transitions of Susterra® adipate (30 and 40 °C) occur at lower temperatures than those of EG adipate (48 °C) or BDO adipate (53 °C). The melt enthalpy (ΔH) of Susterra® adipate was only half that of the other adipates investigated.

Table 4: Thermal transitions in the second heating trace of five adipates

Diol	T_g [°C]	T_c [°C]	ΔH_{Tc} [J/g]	T_m [°C]	ΔH_{Tm} [J/g]
EG	-46.9	8.96 +31.1	56.9	48.0	59.4
Susterra®	-59.7	2.26	37.5	30.8 + 39.7	38.1
BDO	-53.7	none	none	48.0 + 53.3	76.0
PeDO	-61.8	none	none	0.66 + 31.1 + 38.6	76.3
HDO	none	none	none	51.8	96.1

The melting points of the five adipates from Table 4 are shown graphically in Figure 4 and appear to exhibit an odd even effect as shown by the dotted line. The adipates based on diols with an even number of carbons (EG:2, BDO:4, HDO:6) have slightly higher melting points than those based on diols with an odd number of carbons (Susterra®:3, PeDO:5). Except for HDO adipate², the glass transition temperature also follows a similar odd even or zig zag pattern. No pattern was observed for the melt enthalpy.

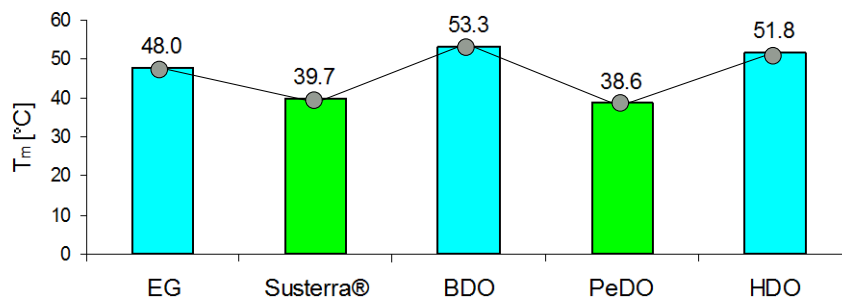


Figure 4: Melting point of the polyester polyols (10 °C/min, highest melt transition in second heating run).

Crystallization half time studies of Susterra® adipate show two polymorphs. Figure 5 shows polymorph I crystallizes quickly, and polymorph II crystallizes more slowly. At room temperature (20 °C), $t_{1/2}$ of polymorph II is 390 seconds. The minimum $t_{1/2}$ of polymorph I is 60 seconds at 5 °C.

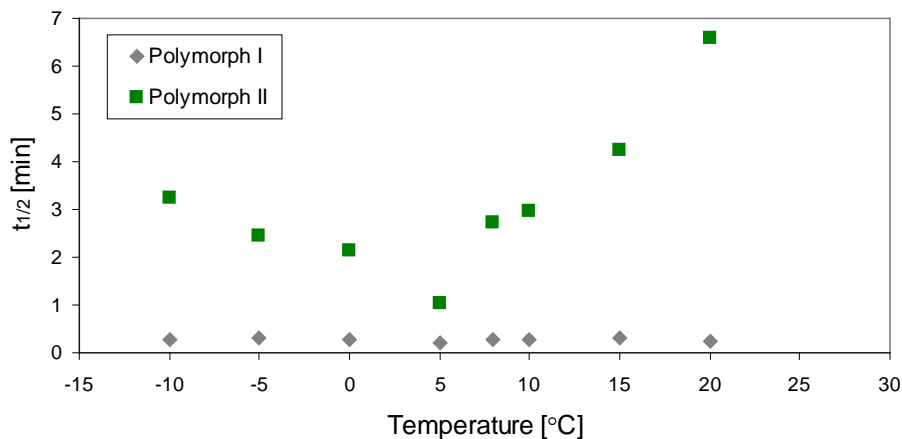


Figure 5: Crystallization half times of two Susterra® adipate polymorphs

Multiple polymorphs were also found for the EG adipate and BDO adipate. Comparison of the $t_{1/2}$ of the slower polymorph for all three adipates shows that both EG and BDO adipates crystallize faster and at higher temperatures than Susterra® adipate (Figure 6). EG adipate has its shortest $t_{1/2}$ at 19 °C (30 sec.). BDO adipate crystallizes fastest at 20 °C (45 sec.).

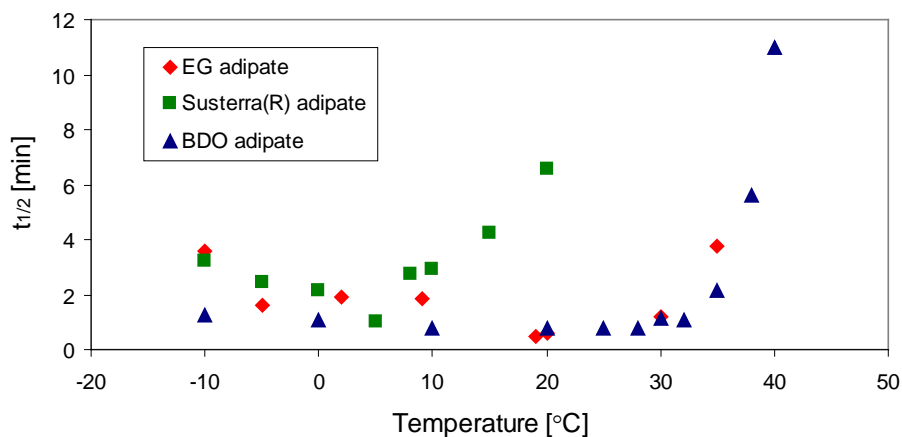


Figure 6: Crystallization half times of the slow polymorph for three adipates

Mixed diol adipates based on Susterra® were compared to the adipate based on 50 mol% EG and 50 mol% BDO in the reaction charge. The T_g of EG/Susterra® adipate was slightly lower than that of EG/BDO adipate (Figure 7a, -55.6 vs -51.5 °C). The T_g of Susterra®/BDO adipate was even lower (-63.7 °C). While the EG/BDO adipate showed a melt transition at 17.8 °C ($\Delta H = 58.4$ J/g), Susterra®/BDO adipate showed two melt transitions at slightly lower temperature (4.63 and 12.8 °C) and with slightly lower melt energy (ΔH total = 44.9 J/g) (Figure 7b). No melt transitions were found in the first heating, cooling, or second heating run for Susterra®/EG adipate.

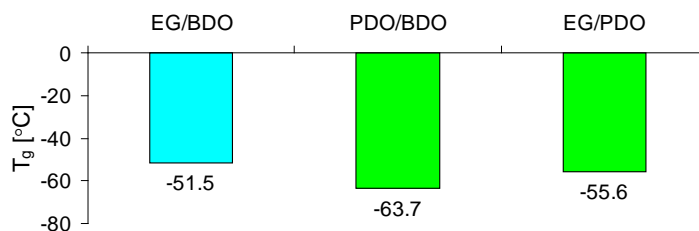


Figure 7a: Glass transition temperature of the second heating run of three mixed diol adipates

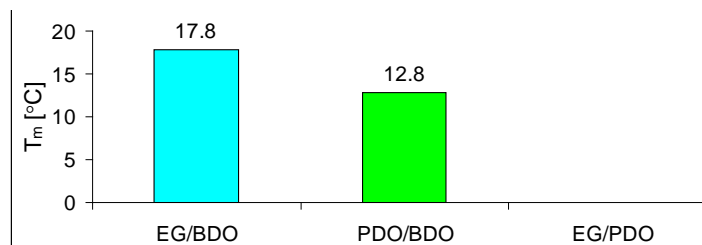


Figure 7b: Highest melt transition in DSC of the second heating run of three mixed diol adipates

Polyurethanes based on Susterra®

DSC traces of the polyurethanes show two types of melt transitions between 0 and 200 °C. The lower temperature transition is assigned to the adipate block or soft block. The transition at higher temperature corresponds to the MDI/diol block or hard block (Figure 8). Like the Susterra® adipate polyol itself, Susterra® adipate segments only crystallize slowly. The polyurethane composed of Susterra® adipate and MDI plus Susterra® chain extender shows a melt transition of low melt energy (4.7 J/g) compared to that of the BDO based polyurethane (15 J/g). The T_m of the Susterra® adipate block lies at a higher temperature than those of the BDO adipate block (65 vs 33 and 40 °C). The ΔH of the Susterra® based hard block is significantly lower than that of the BDO based hard block (1.8 and 2.8 J/g, respectively). The T_m 's of both the Susterra® hard block and BDO hard block are similar, 153 and 148 °C respectively.

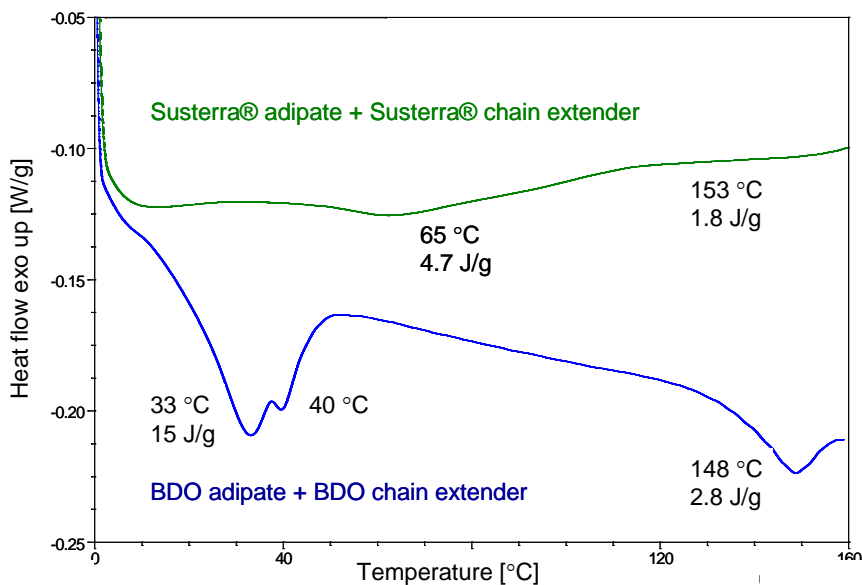


Figure 8: DSC traces (5 °C/min) of the first heating run of two polyurethanes: Susterra® adipate/MDI/Susterra® and BDO adipate/MDI/BDO.

The five different chain extenders were then compared in both the Susterra® adipate/MDI and BDO adipate/MDI polyurethane types (Table 5). The transitions were broad, and for the BDO adipate based polyurethane, multiple shoulders were observed for the soft block melt transition. The melt transition in case of PeDO was remarkably sharp (52.6 °C) with a high melt enthalpy (40 J/g). HDO as the chain extender gave three minima in the melt event. The T_m 's of neither the soft nor the hard segment show an odd even effect, but the ΔH 's of both segments do. ΔH 's of BDO adipate soft segments chain extended with a diol with an even number of carbons are lower than those chain extended with a diol with an odd number of carbons. The reverse is true for the hard segment of BDO adipate based polyurethanes.

Table 5: Thermal transitions of polyurethanes from adipate-MDI prepolymers and linear diols. Peaks that contribute most to ΔH_{Tm} are underlined.

Chain Extender	Soft block		Hard block	
	T_m [°C]	ΔH_{Tm} [J/g]	T_m [°C]	ΔH_{Tm} [J/g]
BDO adipate/MDI				
EG	28.5 + <u>41.1</u>	11	175	0.90
Susterra®	<u>36.1</u>	19	145	0.43
BDO	<u>32.8</u> + 39.5	15	148	2.8
PeDO	13.5 + <u>52.6</u> + 98.9	40	167	0.14
HDO	25.5 + <u>38.9</u> + 87.4	14	156	0.69
Susterra® adipate/MDI				
EG	62.8	3.9	178	2.9
Susterra®	65.4	4.7	153	1.8
BDO	63.5	3.8	140	3.7
PeDO	62.0	4.9	none	0
HDO	61.9	8.0	171	0.33

The Susterra® adipate segment shows low ΔH 's regardless of which chain extender is used. Also in this Susterra® adipate polyurethane case, the T_m 's of the hard segment do not follow a trend, while the ΔH 's follow an odd even trend (Figure 9). The chain extenders with the even number of carbons show relatively high ΔH 's.

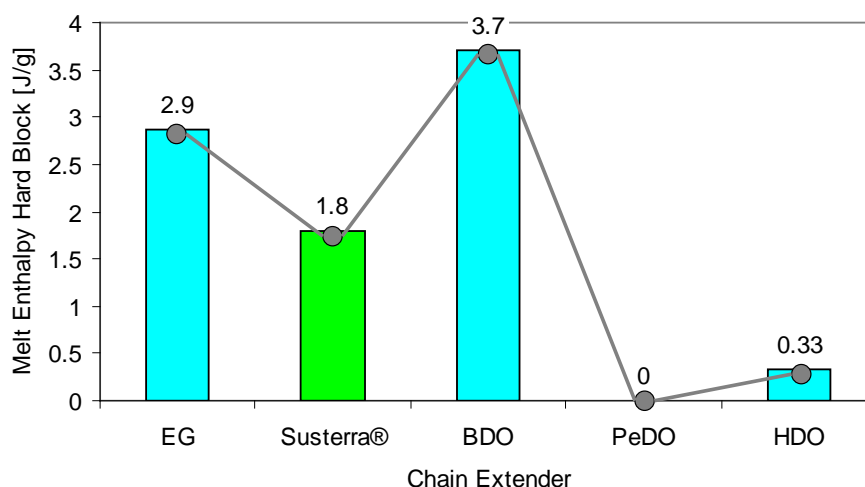


Figure 9: Melt enthalpies of the MDI/diol block in polyurethanes based on Susterra® adipate (5 °C/min, first heating run). The odd even effect is indicated by dots and connectors.

DISCUSSION

Preparation of Susterra® based polyols, prepolymers, and polyurethanes

Susterra® polyester polyols are produced just as those based on other straight chain diols such as EG, BDO, PeDO, and HDO,³ as is illustrated above for the adipates. The reactivity of ester formation of Susterra® is expected to fall in between that of EG, which is somewhat slower to react, and BDO, which reacts faster.^{4,5} While we did not perform systematic checks, a decrease in reaction time was observed with an increase in diol chain length. The synthesis of EG adipate was completed over the course of five days, while typically 3 days sufficed.

Next to Susterra® based polyols, Susterra® based prepolymers and polyurethanes are also prepared in a similar fashion as those based on other linear diols. This is illustrated by the Susterra® adipate and Susterra® chain extender combination with MDI. By comparison, Forscher et al. have found previously that the reactivity of phenyl isocyanates with 1,3-PDO is slightly higher than with BDO at 70 °C.⁶ Both the Susterra® adipate and Susterra® adipate/MDI prepolymer are commercially available,⁷ further underlining their suitability for production on commercial scale. Other straight chain diacids could also be used to prepare Susterra® polyester polyols. Renewably sourced straight chain diacids, such as succinic acid and sebacic acid are particularly of interest.^{8,9}

Thermal transitions

The thermal behavior observed with the five adipate polyols corresponds with reports in the literature.^{8,10,11,12} Umare et al. report for poly (1,3-propylene adipate) ($M_n = 6917$ g/mol) a T_g of -66.4 °C, and a T_m of 40.5 °C with a ΔH of 133 J/g.⁸ Zorba et al. find for Susterra® adipate ($M_n = 31700$ g/mol) a T_g of -57 °C, a T_c of -8 °C, and a T_m of 29 °C.¹⁰ As discussed earlier in Figure 3, we found both ~30 and ~40 °C for the T_m of Susterra® adipate, depending on sample history. Boon et al. (Shell) find the following T_m 's in the second heating run: 40 °C for PDO adipate, 52 °C for BDO adipate and 7 and 14 °C for PDO/BDO adipate.¹³ They report that PDO/BDO adipate ($OH = 45.7$ mg KOH/g) remains at ambient temperature for more than six months without solidifying. While we found PDO/BDO to become a solid within days, we did find very similar melt temperatures (Figure 7, 4.63 and 12.8 °C). Boon et al. also report system that an adipate based on PDO (53 mol%), EG (23 mol%), and BDO (23 mol%) shows no crystallization. This adipate has a reported T_g of -59 °C, in the same range as the T_g 's of our EG/Susterra® and Susterra®/BDO adipates (-57 and -64 °C, respectively).

Odd Even effect

The odd even effect observed in the straight chain polyols and urethanes in this paper is observed in different diol,¹⁴ diacid,¹⁵ poly ester, amide,¹⁶ urethane,^{17,18} and urea systems. Different explanations have been proposed to explain the effect, all based on the crystal packing of the system under investigation. Boese et al. conclude that compounds with an even number of methylene units in the alkyl spacers pack more densely than the odd analogues in homologous series of α,ω -alkanediols.¹⁴ This results in a higher melting point for the α,ω -alkanediols with an even number of methylene units. It appears that this explanation can be extrapolated to the odd even effect of the melting point of the straight chain adipates as discussed previously in Figure 4.

Born et al. (Bayer) describe model compounds for polyurethane elastomers extended with aliphatic diols. They find the characteristic fluctuation in thermal properties of the urethanes is dependent on the number of CH₂ groups in the chain extender (“even” or “odd”).¹⁸ Strain-free hydrogen bonds can form between neighboring molecules in urethanes with “even” chain extenders, while significant strains occur in urethanes containing “odd” chain extenders (Figure 10). These strains result in lack of molecular symmetry, bent molecules with curved chains, and relatively large hydrogen bond distances. Blackwell et al. explains that such contracted conformations of higher energy are necessary because an extended, all-trans conformation of the “odd” Susterra®/MDI fragment would result in the N-H groups being on the same, rather than opposite, side of the planar zigzag, inducing a net dipole moment. This is illustrated by the grey arrows in Figure 10.¹⁹ The staggered structure of BDO/MDI fragments contrasts with the unstaggered nature of Susterra®/MDI packing. This is represented by Figure 10 as well.

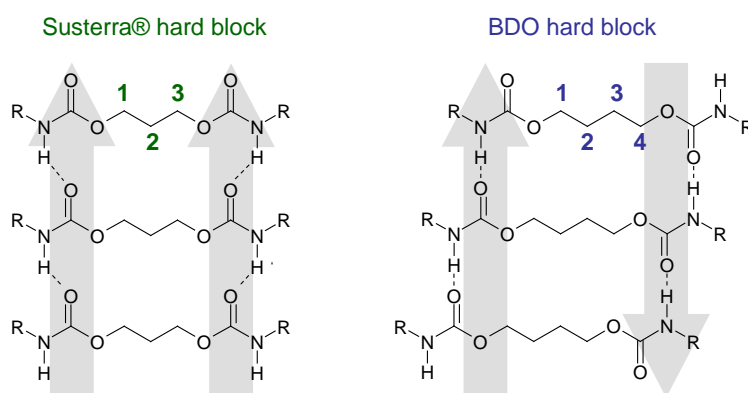


Figure 10: Schematic representation of the crystal packing of Susterra® and BDO based di-urethane fragments in polyurethane hard blocks.

Born et al. describe how the reduced stability of the physical cross linking system induces lower melt temperatures for “odd” diol based model compounds.¹⁸ This finding corresponds with the general statement by Goyert et al. that the melting point of hard segments increases with the melting points of its starting components.²⁰ α,ω -Alkanediols with an odd number of methylene units have a lower melting point.¹⁴ Camberlin et al. studied an expanded series of similar urethane model compounds up to 1,10-decanediol, and conclude there is an inverse relationship between diol length and melting point.²¹ The odd even effect in the model compounds is expected to translate to the hard segments in elastomers. The melt temperatures of the polyurethanes presented in this work do not show a pronounced odd even effect. Next to the chemical composition, the position and intensity of the DSC transitions assigned to the polyurethane hard block depend on crystal size. Crystal size can be influenced by many factors including exact percentage of hard segment, sample hardness, cure temperature, anneal temperature, and crystallization technique.²⁰ None of these were addressed in this study. Nonetheless, the reader may choose to identify an odd even effect in the melt energies of both BDO adipate based and Susterra® adipate based polyurethanes (Figure 9). The strained conformation of “odd” Susterra®/MDI and PeDO/MDI blocks will probably be of a higher energy than that for the BDO/MDI block. Therefore, the driving force for phase separation due to crystallization of the hard segments may be reduced. Crystallization of both the hard and soft block has positive, as well as, negative effects on the final properties. Each application requires its own optimum formulation and combination of crystallization properties.

Potential benefits

Mixed diol adipates based on Susterra® are formulated to be liquids at, or below, room temperature. EG/Susterra® adipate is an example of such a composition (Figure 7). Liquid adipate polyols are easier to process when they are being converted into urethanes. Some applications work best when the polyester polyol is a liquid, and these liquid Susterra® adipates should be very useful in urethane manufacture.¹³ Susterra® based adipates discussed here are strictly linear. They contain no side groups such as 1,2-propylene glycol based adipates. They are all hydrocarbons between the ester units, and contain no ether linkages such as in diethylene glycol. Therefore, good mechanical properties and good UV resistance are expected for Susterra® based straight chain polyol liquids. We also expect these polyester polyols to enable the formulation of clear or transparent polyurethanes.

Mixed diol adipates (Figure 7), as well as Susterra® based adipates (Table 4) show relatively low glass transition temperatures. While more detailed analysis of the shape of the glass transition is needed,²⁰ Susterra® based adipates are also expected to contribute to improvements in low temperature properties, such as low temperature flexibility, of the urethane part. Such flexibility is important in applications such as artificial leather used in footwear. It is also important that the artificial has a soft feel. The low melt energies of Susterra® adipate (Table 4) and Susterra®/MDI blocks (Table 5), and their long crystallization half times at room temperature (Figure 5) will contribute to this. Next to artificial leather, Susterra® has been successfully incorporated into various layers of the shoe sole as shown in Figure 11.

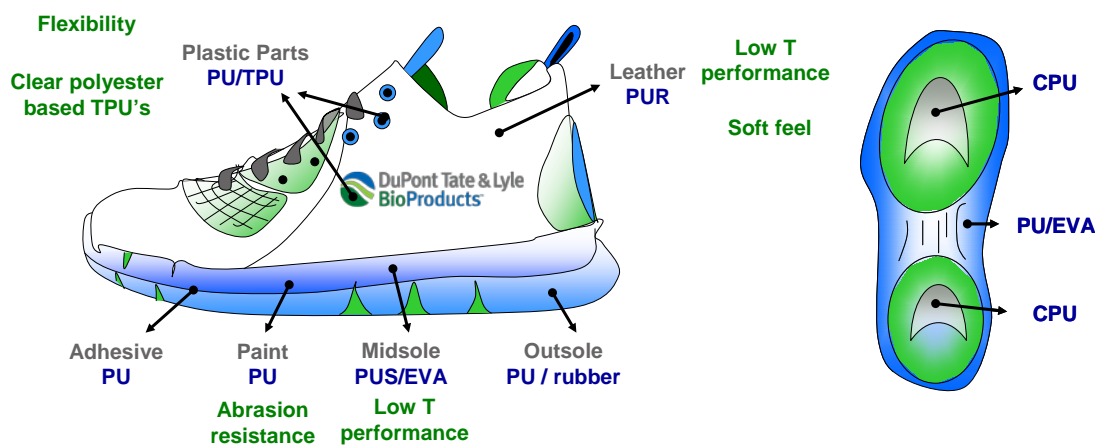


Figure 11: Envisioned application of Susterra® in the footwear industry.

Pigott et al. found in an earlier study that the the number of carbons in the straight chain diol chain extender has relatively little effect on the room temperature properties of a cast polyurethane based on EG adipate and MDI.²² However, the low crystallinity of Susterra® based polyurethanes is believed to be the basis for soft cast elastomer grades with improved abrasion resistance.⁷ Also TPU's based on MDI and BDO adipate show similar physico-mechanical properties at room temperature when chain extended with either 1,3-PDO or BDO.⁶ One exception is the coefficient of thermal expansion, which is much lower for the 1,3-PDO than for the BDO based TPU. Limited crystallinity of Susterra®/MDI hard blocks is also known to reduce solubility and increase gelation in solventborne polyurethane systems. On the other hand, mixed diol adipates based on Susterra® behave as good or better than EG/BDO adipate in such systems. Hot melt adhesives based on MDI and either 1,3-PDO adipate or poly(oxytetramethylene)glycol (PTMG) show improved tensile strength, modulus, and lap shear strength, but reduced elongation and 180° peel strength, when BDO was replaced as a chain extender by 1,3-PDO.²³ Mechanical properties of hot melt adhesives based on PDO adipate are better than those of adhesives based on PTMG.

CONCLUSION

In summary, Susterra® is a great fit for the polyurethanes industry. It offers a functional, consistent, and high purity building block that is especially suitable for use in coatings, adhesives, sealants, and (microcellular) elastomers (CASE). It can add value in thermoplastic polyurethanes, and aqueous polyurethane dispersions. Susterra® is expected to contribute to the performance of products that require low temperature stiffness, and room temperature softness, abrasion resistance or transparency. The basis of these macroscopic properties lies at the molecular level. The unique, bent crystal structure induced by Susterra® with its odd number of carbons induces relatively low glass transition temperatures, melt transitions, melt energies and crystallization speeds.

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Joseph W. DeSalvo

Joseph W. DeSalvo has worked for the past three years as Director of Marketing for DuPont Tate & Lyle Bio Products. Joseph received his B.S. in Engineering from The University of Notre Dame and his MBA from the Kelley School of Business, Indiana University. Previously to joining DuPont Tate & Lyle Joseph spent ten years in the Polyurethane Industry working for Air Products, where he held various positions throughout the United States. Joseph brings extensive knowledge and expertise to DuPont Tate & Lyle and the Polyurethane Industry.

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. Robert brings extensive knowledge and expertise to DuPont Tate & Lyle.

Judith J. van Gorp

Judith J. van Gorp has worked for the past six years as a senior research chemist at DuPont Central Research and Development in Wilmington, DE. Judith received her MSc in Chemical Engineering from the Eindhoven University of Technology in The Netherlands. Her PhD work with Prof. Bert Meijer at the same university focused on supramolecular architectures based on polyureas. Judith brings extensive knowledge and expertise to DuPont and the Polyurethane Industry.