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SUCCINIC ACID: A BIO-BASED BUILDING BLOCK FOR SUCCINATE POLYESTER POLYOLS IN MODIFIED THERMOPLASTIC URETHANES USING A CAST MOLDING URETHANE PRE-POLYMER PROCESS

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bioamber[™]

ABSTRACT

Bio-based Succinic Acid (Bio-based SA) has emerged as one of the new bio-based chemicals. BioAmber's highly efficient yeast based fermentation process produces a high quality polymerization grade succinic acid (C₄H₆O₄) and does so in an efficient process that reduces the CO₂ emissions and saves energy compared to analogous petrochemical based organic acids such as succinic acid (p-BA) or adipic acid (AA). As a platform chemical, BioAmber's bio-based succinic acid can react with glycols to make succinate polyester polyols (SA-PEPs) useful in polyurethane (PU) chemistry. These polyols are comparable to adipic acid based polyester polyols (AA-PEPs) however, polyester based polyurethanes made using succinate polyester polyols tend to exhibit excellent strength and elongation profiles along with excellent solvent resistance compared to adipates and can generate PU with greater than 60% renewable carbon. In this study, we will present recent findings comparing polyurethanes made with different SA polyester polyols and will describe the impact of the SA-PEP composition on viscosity, hydrolysis rate and TPU end physical properties. We will conclude by discussing how these properties can influence the performance window of these urethanes in elastomer applications. Bio-based SA and SA-PEPs provides formulation flexibility to polyurethanes and can enable thermoplastic urethane with differentiated properties and renewable carbon content, thus enabling what BioAmber believes to be a valuable tool for bringing sustainability and performance to the PU tool box.

INTRODUCTION

Bio-based building blocks for urethanes have been used for decades. Bio-based glycerin, sucrose and sorbitol have been used as initiators for polyether polyols. Whereas bio-based polyester polyols for urethanes have used building blocks mostly consisting of natural oil polyols, fatty acid dimers and diacids such as sebacic acid (C₁₀-dicid). However, recent advances in fermentation by BioAmber Inc. and others are making C₄ succinic acid readily available as a key building block for polyester polyols in urethanes and other ester resin applications. Moreover, with the completion of BioAmber's 30,000T capacity manufacturing facility in Sarnia Ontario, BioAmber has the largest plant for bio-based succinic acid, with commercial capacity and a robust supply chain, to enable the use of bio-based succinic acid as a key new chemical in the formulation of urethanes that provide a unique combination of performance and sustainability.

In the last few years, BioAmber has published several application papers on the use and performance of bio-based succinic acid and SA-PEPs in a variety of applications.² In fact, the performance benefits of succinate polyols in urethanes have been further substantiated by several commercial announcements³ in diverse applications areas such as polyurethanes for synthetic leather, thermoplastic elastomers, PU coatings, bio-based succinic acid ester lubricants and PC emollients. Figures 1 and 2 summarizes some of the main technology and application areas where bio-based succinate esters are being adopted and key performance attributes associated with the succinates in these different urethane application areas. In this paper, we will highlight some recent advances of succinate polyester polyols in thermoplastic elastomers made by a cast polyurethane (CPU) process.

FIGURE 1: Bio-based Succinate Polyester Polyols



TPU AND CPU ELASTOMERS

VALUE PROPOSITION

- Wear and chemical resistance
- Tear Strength
- Stiffness



PU COATINGS

VALUE PROPOSITION

- Good Hardness and Flexibility
- Excellent abrasion and solvent resistance
- Bio-content



PU LEATHER

VALUE PROPOSITION

- Softer
- Abrasion Resistant
- Tear Strength
- Better resistance to solvents
- Gloss resistance, after wear



ADHESIVES

VALUE PROPOSITION

- Solvents or PUD adhesives
- Solvent resistance
- Bio-content



Bio-Succinic Acid shortens the Polyesters Polyol chain, increases modulus, hardness, solvent resistance without losing elongation.

FIGURE 2: Application and Value Proposition for Bio-based Succinate Polyester Polyols in Polyurethanes

BIO-SA™ BASED SUCCINIC ACID IN POLYESTER POLYOLS FOR URETHANES



APPLICATIONS



SYNTHETIC LEATHER



WOOD COATINGS



FOOTWEAR



TEXTILE COATINGS



ELASTOMERS/ PLASTICS



ADVANTAGES OF BIO-SA™ POLYESTER POLYOLS IN PU

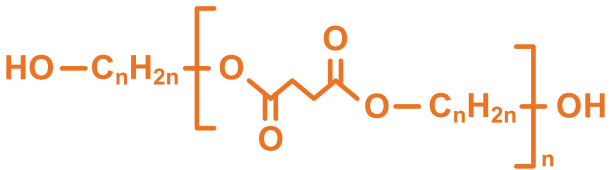
- Greater than 60% new carbon content with
- Improved solvent and oil resistance
- Excellent mechanical properties
- Strong and flexible
- Tear and abrasion resistance
- Broad resiliency range

EXPERIMENTAL SUMMARY

The series of succinate and adipate polyester polyols (SA-PEPs and AA-PEPs) were prepared using typical a commercial process. The polyol hydroxyl numbers were controlled to 56 ± 3 mg-KOH/g polyol corresponding to polyols with an approximate molecular weight of 2,000 g/mol. The abbreviations for the glycols used in this study are defined as MPD = 2- methyl 1,3 propane diol, BDO = 1,4 butane diol, HDO = 1,6 hexane diol, PDO = biobased 1,3 propane diol (Susterra™ from Dupont Tate & Lyle bioproducts). Table 1 summarizes key polyol properties. The molded thermoplastic polyurethanes were made using a cast polyurethane process where the desired polyol was pre-reacted with 4,4'-MDI to produce an NCO terminated pre-polymer with about 6wt% NCO end groups. The NCO prepolymer was reacted further with 1,4 butane diol as the chain extender, transferred to a sheet mold and were cured at 100 °C for 2 hrs followed by a 4 hr post cure also at 100 °C. In order to minimize the influence of residual catalyst in this study, it should be noted that no additional isocyanate catalyst was used for reaction between the polyol and the isocyanate to for the NCO prepolymer or the final polyurethane. The cured sheets were allowed to condition for about 1 week at room temperature and were then die cut into desired parts for testing. The PU control samples were based on AA-BDO (2,000 g/mol) and polytetramethylene glycol (PTMEG, poly THF) and were obtained from commercially available sources of cast polyurethanes using a commercial production process. The final dimension of the sheets were approximately 30.5 cm² x 2 mm. The mechanical property testing was conducted using previously published methods and testing facilities compliant with ASTM test methods for mechanical property evaluations.⁶⁻⁸ Taber abrasion testing was conducted in accordance with ASTM D4060-10. An H22 abrasive wheel and 500g weight was used and the results were recorded as milligram weight loss (mg). Additional details about the test methods, testing facilities and data are available from the primary author.^{1a}

Average number of repeat units and ester count:

The average number of repeat units, n of the polyester polyols were calculated from the generalized chemical structure 1 using Equation 1 and are shown in Table 1.

STRUCTURE 1:	EQUATION 1:
	$n = (MwP - MwG) / MwRu$

Where n is the number of repeat units for a polyol to have a molecular weight of MwP , MwG is the glycol molecular weight and $MwRU$ = molecular weight of the repeat unit. It should be noted if the target polyol consist of mixed glycols or mixed acids or both that the value of MwG and $MwRU$ are simply the numerical averages of the molar content of the glycols and acids. Thus, for a mixed glycol system based on 50 mole% of PDO (78 g/mol) and 50% of BDO, 90g/mol, the value of MwG is 83 g/mol). The number of esters in the polyol is $2n$ and gives an indication of the ester density of the polyol and in the subsequent polyurethane. The number of esters in the polyol is a useful numerical indicator of the possible hydrolytic and chemical resistance of the polyurethane made with this polyol. However, it should be emphasized this is only an indication since many factors impact the hydrolytic stability of the PU including isocyanate type used in the PU, crystallinity, branching, and the incorporation of other polar groups in the polyol such as ethers.

TABLE 1: Key Characterization Data for Polyester Polyols described in this Study

Polyol Abbreviation	SA-MPD	SA-MPD/BDO	SA-HDO/BDO	AA-HDO/BDO	SA-PDO	AA-PDO	AA-BDO	PTMEG
diol Type (glycol ratio 50% mole)	2-methyl 1,3-propane diol	2-methyl 1,3-propane diol and 1,4 butane diol	hexane diol and 1,4 butane diol	hexane diol and 1,4 butane diol	bio-based 1,3 Propane diol	bio-based 1,3 Propane diol	1,4 butane diol	polytetramethylene oxide
OH# (mg-KOH/g polyol)	55	55	56	54	55	53	56	NR
Average number of repeat units, n , for 2000 g/mol	11.1	11.1	10.2	8.6	12.2	10.3	9.6	NR
Polyol Viscosity (cps, 60°C)	5100	3100	2360	1400	6500	2800	1800	NR
Prepolymer Viscosity (cps, 100°C)	1760	1800	1620	1300	2160	1640	590	1420
wt%-NCO prepolymer	6.1	5.93	6.0	6.0	6.1	6.1	6.1	6.6
Tm Polyol (peak, °C)	ND	45	56	30-36	ND	35	65	NR
Tg Polyol (onset °C)	-37	-43	-54	-69	-38	-61	ND	NR
Tg Polyol (mid point °C)	35	41	52	60	37	59	ND	NR
Calculated New Carbon Content (NCC)	50%	50%	45%	0	100%	33%	0	0

ND = not detected by DSC; NR = not reported by supplier; PDO = biobased 1,3 propane diol (Susterra™ from Dupont Tate & Lyle bioproducts).

DETERMINATION OF POLYMER SOLVENT ABSORPTION

Solvents and polymers were used as received. Polymer samples 2 mm thick were cut to approximately 20x20 mm pieces and dried to constant weight under vacuum. The cured polyurethanes were weighed by means of a Mettler AE200 balance to four decimal places. The polymer samples were then submerged in the appropriate solvent at room temperature or elevated temperature in closed glass jars. The samples were removed periodically from the solvents, dried with a paper towel, weighed, and then placed back in the solvent jar. The samples were run in duplicate and averages of weight changes were reported. A control specimen was maintained to determine if significant swell occurred due to atmospheric moisture, (which it did not). However using this specimen it was possible to measure the density of the polyurethanes. These values were recorded and are shown in Table 3.

DETERMINATION OF GLASS TEMPERATURE (Tg) AND MELTING POINTS (Tm)

Tg and Tm values for the PEP and CPU samples were determined by use of Toledo DSC 1 Star System Differential Scanning Calorimetry using a temperature ramp rate of 10° C per minute. The samples were heated from 30° C to 220° C cooled to -60° C and heated at 10° C /min to 220° C. The Tg and Tm values are reported from the transition detected using the second heat. The Tg values are reported as the mid-point of the transitions. The melting point range values are reported as the onset and peak melt values of the endotherm.

DETERMINATION OF BIO-BASED CARBON CONTENT

Reported content of bio-based carbon was determined by C-14 analysis per ASTM 6866 and was conducted by a certified analytical testing facility. When the bio-based carbon content was calculated, the bio-based carbon was calculated as a fraction of total carbon count in the molecule. For example, to estimate the bio-based carbon content for the polyol based on adipic acid and bio-based 1,3 propane diol (AA-PDO), the number of bio-based carbons (3 for PDO) is divided by the total number of carbons (3/9 = 33.3%).

RESULTS AND DISCUSSION

SA-POLYOL CHARACTERIZATION

The main physical properties of the different polyester polyols (PEPs) used to make the thermoplastic polyurethanes are shown in Table 1. The PEPs were prepared using standard polyol reaction equipment and conditions and no significant differences in the reaction rates for the syntheses of the polyols were noted. However, when comparing the structure-property relationship between succinate polyester polyols (SAPEPs) and adipate polyester polyols (AA-PEPs) the shorter 4 carbon chain decreases the number of atoms between the ester groups, reduces the degree of freedom for bond rotation and therefore increase the glass transition temperature (T_g) and polyol viscosity (η), see Figures 3 and 4. As reported previously, the structure of the glycol also influences the polyol properties.^{2b} The property trends suggest that as the average length of the glycol increases the T_g and the viscosity decreases. Generally we have noted that if the sum of the carbons of the SAglycol combination is an even number then the polyol is likely to be a solid at room temperature whereas, if the SA-glycol combination contains an odd number of carbons, then the polyols are likely to be a liquid or a soft wax at room temperature (25 °C).^{2b} Thus, the tendency for SA-PEPs to have higher viscosities can be off-set by the use of a long chain, branched or odd-numbered glycol.

FIGURE 3: Glass Transition Temperatures (T_g °C) for SA-Polyester Polyols (SA-PEP) and AA-Polyester Polyols

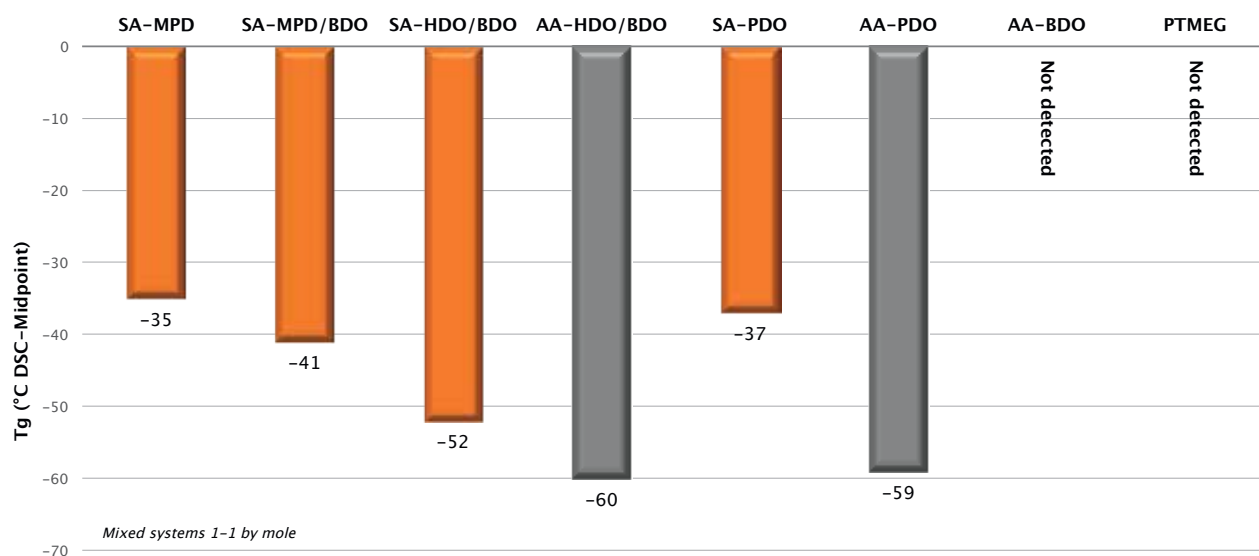
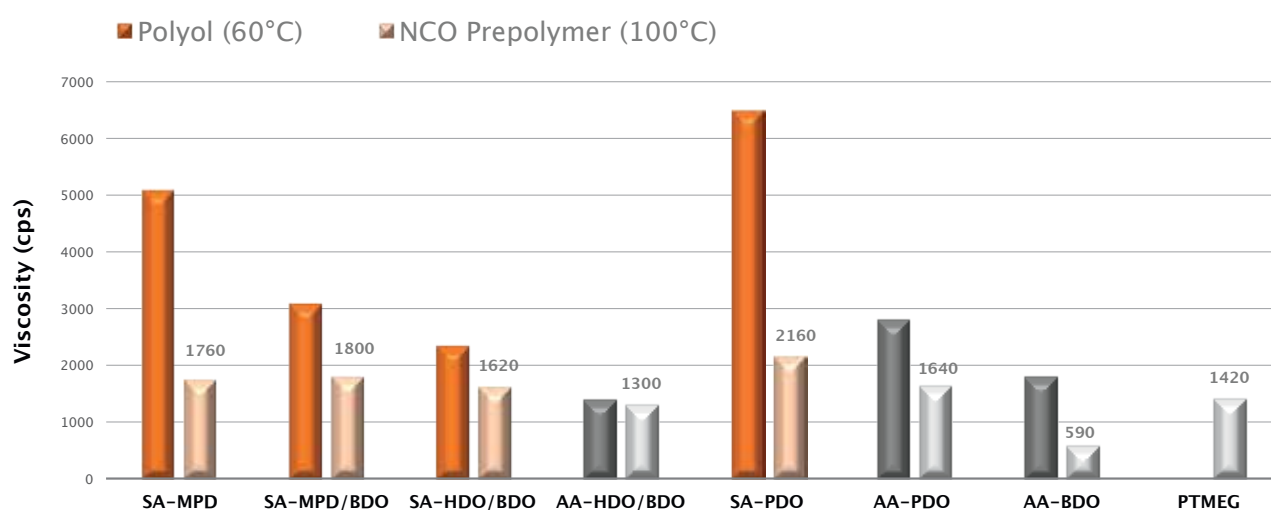


FIGURE 4: Brookfield Viscosity of Polyester Polyols and NCO Prepolymers (see Scheme 1, Structures 2 and 3)



It is noteworthy, that polyols based on glycol combinations with SA-BDO/X containing least 50 mol% of BDO solidify at room temperature even if X is a branched glycol or one with an odd number of carbons. Thus, SABDO/X with 2-MPD, 3-MPD and PDO are solids at room temperature, whereas for SA-BDO/DEG, no melting endotherm was detected. These observations are highlighted in Table 2 for a series of copolyester polyols with the general chemical structure 2, where R = 50 mole% BDO.

STRUCTURE 2

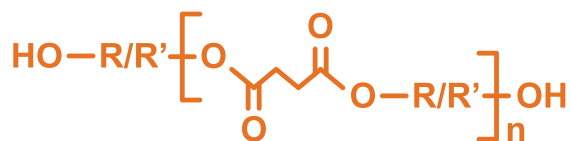


TABLE 2: Glass and melting temperature matrix for succinate polyester polyols (SA-PEP) with mixed glycols based on a 1-1 mole ratio.*

	EG	PDO	BDO	HDO	NPG	DEG	2-MPD	3-MPD
EG	-12 ~80	-28	-34 48-60			-22		
PDO	-28	-38 36-40	-44 36-56	-48	-31	-45		-47
BDO	-34 48-60	-44 36-56	ND 104-110	-54 48-52	-30 45-52	-47	-42 35-45	-57 30
HDO		-48	-54 48-52	ND 44-48	-42	-42		
NPG		-31	-30 45-52	-42		-50		
DEG	-22	-45	-47		-50	-28		-53
2-MPD			-42 35-45				-34	
3-MPD		-47	-57 30			-53		-57

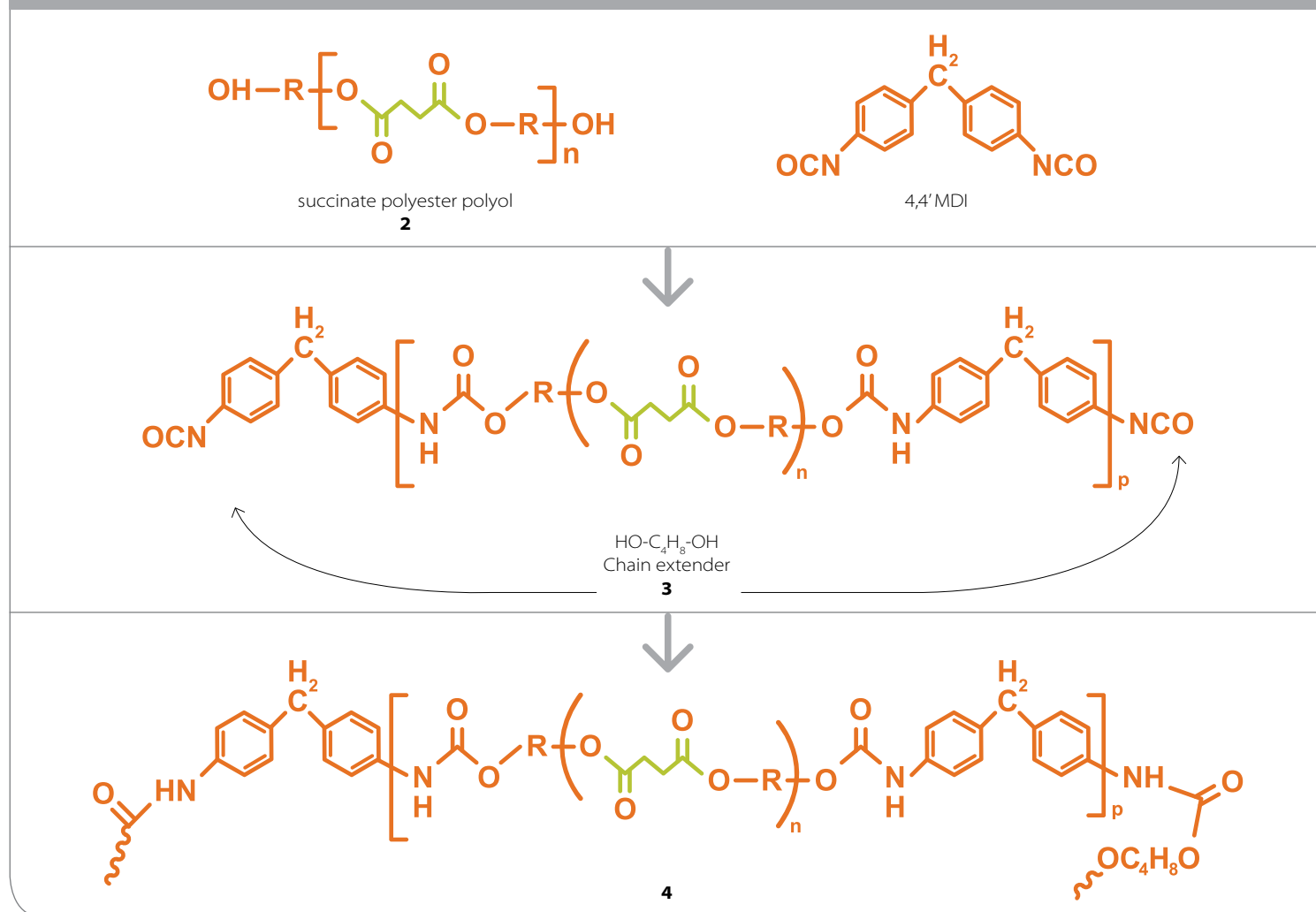
(*) Tg, top value of the cell and Tm lower value of the cell. Thermal transition data based on polyols with ~1000g/mol. Some values also cited from References 6 and 7.

NCO-PREPOLYMER AND CPU PREPARATION AND CHARACTERIZATION

As shown in Scheme 1, the polyurethane thermoplastic systems used in this study were readily synthesized by the reaction of the bio-based succinate polyester polyols (2) with 4,4'-methylene diphenyl diisocyanate (MDI) to form the isocyanate terminated polyester urethane pre-polymer 3, containing about 6 wt% NCO end groups. The NCO prepolymer 3 was then mixed at about 80-100 °C with BDO as the chain extender and cast into a mold and cured at 100 °C for 60 minutes followed by a 4 hr post cure at this temperature to form the final molded CPU 4. The viscosity values of the NCO pre-polymer 3, are also shown in Figure 4 and allow for comparison to the polyester polyols 2. As noted, the NCO prepolymer viscosity values are similar to each other regardless of the nature of the polyol 2 ranging from about 2100 cps for SA-PDO to about 1600 cps for SA-HDO/BDO. Although still slightly higher than the corresponding adipates prepolymer systems, they are in a very usable processing viscosity range.

The preparation of the thermoplastic urethanes by the pre-polymer method differs from the "TPU one shot-method" described in References 6-8. Unlike the TPU one-shot method, the prepolymer reaction technique used here enables the formation of a well-defined polyester soft block in the PU microstructure. As shown in Scheme 1, only the PEP can react with the isocyanate in the initial stage to form the NCO pre-polymer intermediate 3. By contrast, in the TPU one shot process, the PEP, BDO chain extender and the MDI are mixed together and can form polyester soft-blocks which contain **both** the BDO chain extender and the polyester polyol in its microstructure. It is important to point out this process difference since the preparations methods could result in polymers with different microstructure and that it is reasonable to anticipate these processing differences could influence the end physical properties of the polyurethane.⁹

SCHEME 1: Preparation of Succinate NCO Prepolymers and Cast Thermoplastic Polyurethanes made with BDO Chain Extender



The work-life and gel times associated with the conversion of the prepolymer 3 to the thermoplastic urethane 4 were essentially unchanged by the nature of the polyol, see Table 3. The PU systems were compared to typical industrial bench mark systems based on AA-BDO and PTMEG and the characterization properties of the cured PU sheets are shown in Table 3. All the polyurethanes exhibited a similar hardness range of about 80-85 Shore A. There were some differentiated property trends noted in these systems and a few of these trends will be highlighted in the following sections.

MECHANICAL, THERMAL AND CHEMICAL PROPERTIES

The mechanical properties of the polyurethanes were tested using standard ASTM techniques as out lined in previous publications⁶⁻⁸. Table 3 summarizes these data, some of which are highlighted in Figures 5-9. The cast thermoplastic polyurethanes studied here exhibited excellent mechanical properties compared to the control polymers listed in Tables 1 and 3. Representative stress-strain curves from tensile testing data are graphed in Figure 5 and the actual tensile and strain values are shown in Table 3 and graphed in Figure 6. One interesting feature of the SA-PEP systems is that the polyurethanes exhibit very good break tensile/elongation profiles. Often the break stress/strain values tend to trend in opposite directions (meaning higher break stress typically comes with lower elongation). However as exemplified, especially by the PU based on SA-HDO/BDO and SA-PDO and shown in Figure 6, these systems had higher or similar tensile break values and higher elongations than the corresponding AA based systems.

FIGURE 5: Representative Stress-Strain Curves for the Initial Mechanical Properties of the Thermoplastic Polyurethanes used in this Study

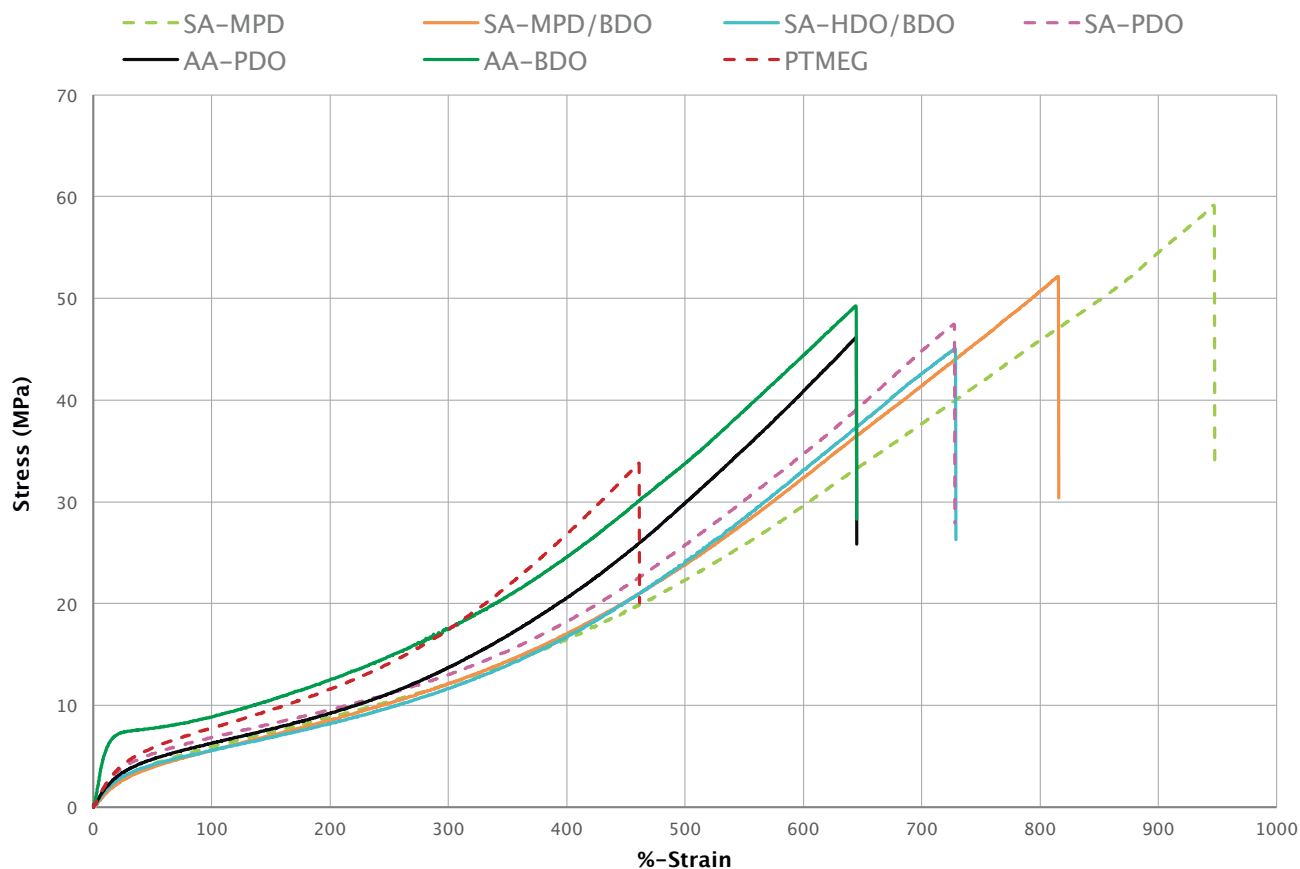
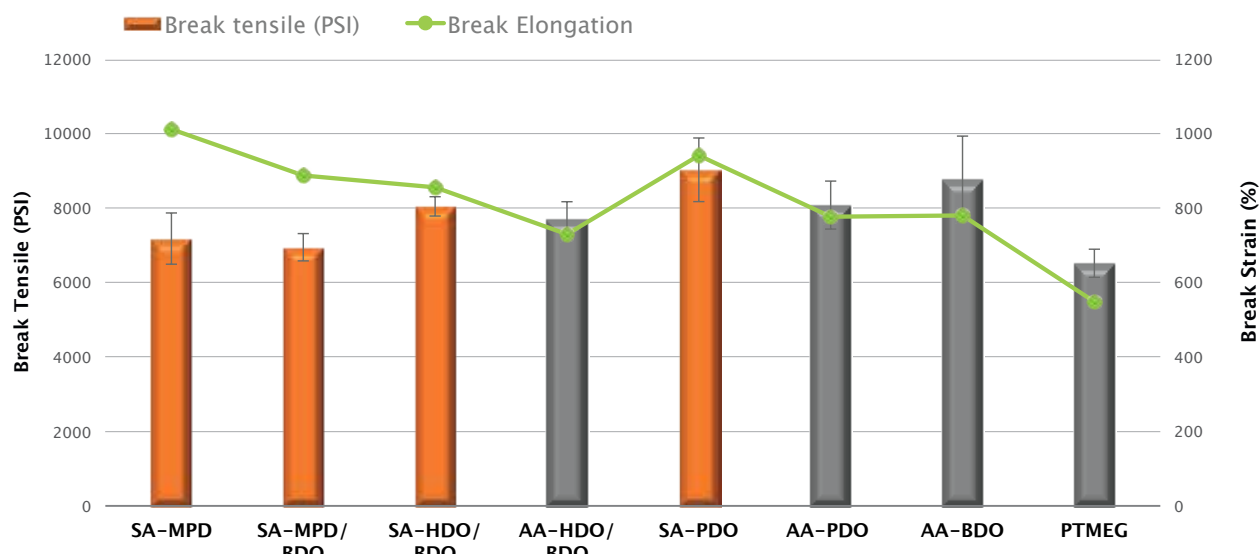


TABLE 3: Key Characterization Data for NCO and CPU polymers used in this study

Polyol Abbreviation in CPU	SA-MPD	SA-MPD/BDO	SA-HDO/BDO	AA-HDO/BDO	SA-PDO	AA-PDO	AA-BDO	PTMEG
diol Type	2-methyl 1,3-propane diol	50 mol% 2-methyl 1,3-propane diol and 1,4 butane diol	50 mol% hexane diol and 1,4 butane diol	50 mol% hexane diol and 1,4 butane diol	bio-based 1,3 Propane diol	bio-based 1,3 Propane diol	1,4 butane biol	poly tetramethylene oxide
Prepolymer-Processing Information work life @ 100° (min)	13	14	14	13	16	20	14	11
CPU Soft Segment Tg onset (°C)	-12	-18	-37	-42	-20	-39	-41	-40
CPU Soft Segment Tg (°C)	-8	-13	-33	-39	-20	-38	-37	-34
CPU Hard Segment Tm (°C)	162/168	159/165	168	170	170	170	166	166
Bio-based Carbon in CPU (C14 by ASTM D6866)	29	29	26	0	63	21-estimated	0	0
Tensile Properties at RT (before aging)								
Tear strength, kN/m (ASTM D624)	41 ±1.8	72 ±2.1	89 ±2.4	91 ±1.5	92 ±1.4	95 ±2.2	127 ±4.4	90 ±1.2
Tensile Strength at break at RT, psi (ASTM D412)	7172 ±693	6944 ±368	8040 ±260	7710 ±460	9017 ±850	8070 ±640	8780 ±1148	6510 ±380
Tensile Strength at 50%, psi	512 ±8	525 ±10	683 ±14	712 ±25	667 ±5	707 ±10	1078 ±39	864 ±11
Tensile Strength at 100%, psi	704 ±11	725 ±10	900 ±17	923 ±34	879 ±6	934 ±11	1226 ±33	1142 ±14
Tensile Strength at 300%, psi	1403 ±23	1503 ±19	1795 ±24	1971 ±84	1702 ±21	1967 ±23	2529 ±55	2566 ±33
Break Strain (%)	1011 ±57	887 ±22	855 ±25	730 ±26	940 ±50	777 ±38	780 ±70	548 ±24
Hardness (Shore A)	85	85	85	86	87	86	89	87
Density (g/cm ³)	1.21	1.24	1.2	1.18	1.25	1.18	1.18	1.09
Taber Abrasion ASTM D4060-10 (H22 Wheel, 500g, weight loss (mg loss after 5000 cycles)	6	10	<2	<2	<2	<2	<2	<2
Bashore Rebound (%)	10	16	38	55	27	50	50	48
Hydrolysis Resistance (7 days, 70°C 95% RH)								
Tensile Strength at 100%, psi	646 ±17	640 ±25	682 ±19	742 ±26	753 ±50	783 ±21	828 ±349	915 ±27
Tensile Strength at 300%, psi	1317 ±34	1392 ±7	1377 ±43	1568 ±48	1410 ±30	1603 ±44	1860 ±17	2170 ±74
Tensile Strength Break	6360 ±630	6692 ±506	5069 ±259	5416 ±431	6038 ±238	5147 ±190	6435 ±225	4966 ±413
Tensile Retention after Hydrolysis (%)								
100% Strain	75%	78%	82%	82%	77%	80%	67%	80%
300% Strain	74%	78%	79%	78%	76%	80%	75%	84%
at Break	82%	89%	78%	82%	88%	77%	90%	97%

FIGURE 6: Tensile and Elongation at Break values of Polyurethanes (*)



(*) standard deviation based on the average of 5 measurements

POLYURETHANE SOLVENT ABSORPTION BEHAVIOR

The solvent resistance of polyurethanes based on SA-PEPs continues to exceed those of urethanes based on adipates polyester or PTMEG systems. Table 4 summarizes the weight percent solvent absorption of the polyurethanes room temperature.

TABLE 4: 7 Day Solvent Weight Absorption (%)

Polyol in PU	SA-MPD	SA-MPD/BDO	SA-HDO/BDO	AA-HDO/BDO	SA-PDO	AA-PDO	AA-BDO	PTMEG
Solvent	Wt% Solvent Swell after 7 days							
Water	1.3	1.5	1.2	1	1.6	1.3	1.1	1.7
5% NH₄OH	2.3	2.7	1.2	1	2	1.4	1	1.8
Ethanol	14	13.2	12.7	14.4	9.8	13	10.8	27.4
MEK	114 ¹⁰	84 ¹⁰	73.9	75.1	59.5	68.4	73.5	69.3
Toluene	39	35	47.5	55.4	22.4	41	47.3	56
Ethyl Acetate	83	68	64.3	63.2	48.6	58.6	60.4	56.1
IRM 903 (63°C)	0.5	0.3	2.1	4.4	0.5	2.2	3.2	9.7

Generally, the SA-HDO/BDO and SA/PDO exhibit an excellent combination of mechanical strength, abrasion, tear and solvent resistance properties. Most remarkable is the extremely low oil pick up of the PU based on SA-PEPs.¹⁰

DSC ANALYSES OF POLYURETHANES

The T_g and T_m values of the polyurethanes were determined by DSC as described in the Experimental Section. A typical DSC trace is shown in Figure 7 for polyurethanes made with SAPDO and compared to AA-PDO. The thermal transitions detected by DSC were consistent with a phase-separated thermoplastic elastomer. A glass transition temperature associated with the thermal motion of the polyester polyol soft block and a melting transition associated with the urethane hard block linkage were detected. As anticipated and shown in Figure 8, the polyurethanes made with SA polyester soft block have a higher T_g than the analogous AA-PEPs. However, by using a polyol with a mixed glycol such as SA-BDO/HDO it is possible to lower the T_g to less than -30° C. As a general rule, as the number of carbons between the ester groups increases the T_g decreases and if pendent alkyl groups are added the T_g will tend to increase relative to an all linear system. This behavior is exemplified by comparing the T_g values detected for the polyurethanes made with SA-MPD, SA-MPD/BDO and SA-HDO/BDO. The T_g of the polyester soft block decreases from about -8° to -13° to -33° C. The thermal transition associated with the urethane MDI hard block is not significantly influenced by the phase separated polyester segment and therefore all the polyurethanes exhibit similar melting endotherms at approximately 165° C. These T_m values are summarized in Table 3.

THERMOPLASTIC POLYURETHANES BASED ON SA-PDO

It is interesting to compare the stress-strain behavior of urethanes made with the “branched glycol,” 2-methyl-1,3-propane diol (2-MPD) compared to SA-PDO. In these cases each polyol has 3 carbons between the ester linkages (the SA-BDO/2-MPD has on average 3.5 carbons between ester groups). All the polyols are low melting solids or liquids at room temperature (see Table 1). As is known for polyethylene and polypropylene of similar melt indices, the pendent methyl group in 2-MPD, like the pendent methyl group in polypropylene decreases the end physical properties. However this structural group also reduces the low strain tensile values of the polymer (often inaccurately called modulus at 50% and 100% strain). Lower tensile values are a feature commonly sought after for softer polyurethane coatings and for polyurethanes used in synthetic leather since these values give an initial indication of softness and flexibility. As shown in Table 5, the polyurethanes based on SA-MPD have the lowest tensile values at 50% and 100% strain of the series and are even lower than the PTMEG system used in this studied. However, the polyurethane made with SA-PDO have the next lowest stress values at low strain, yet this polyurethane also exhibited improved solvent, tear and abrasion resistance and low temperature transitions than these branched polyols. Moreover, the polyurethanes based on SAPDO compared very well to the similar polyurethane made with AA-PDO. This suggest the SA-PDO system could bridge a performance hurdle by generating PU systems that are “softer” and or more flexible with improved solvent resistance and containing 63% bio-based carbon content.

TABLE 3: Key Characterization Data for NCO and CPU polymers used in this study

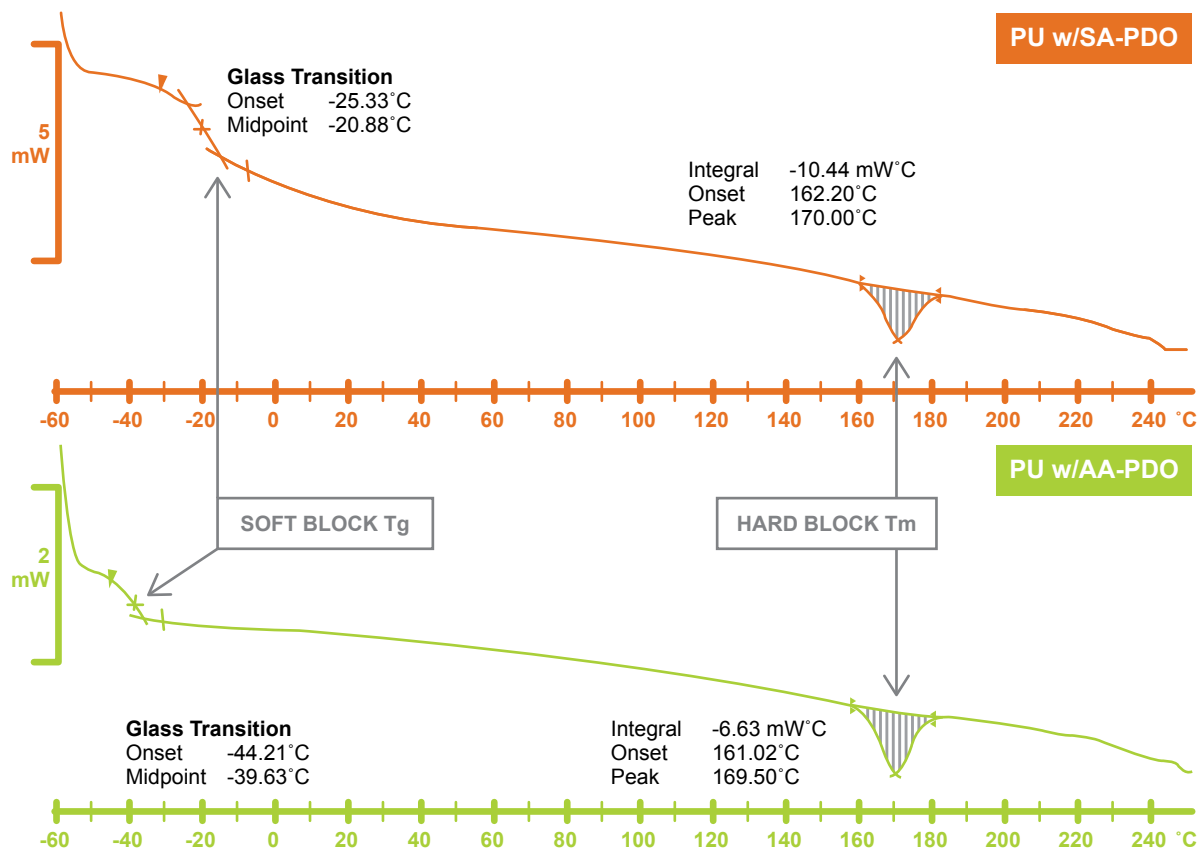


FIGURE 8: Soft block Glass Transition Temperatures for Polyurethanes

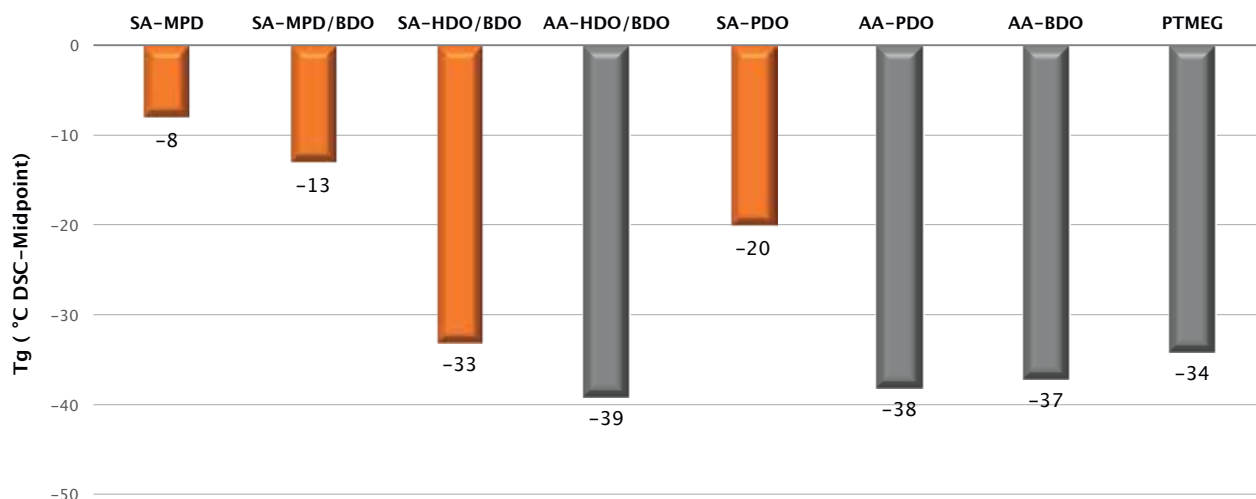


TABLE 5: Property Summary of SA-PEPs with Pendent Methyl Groups Compared to SA-PDO

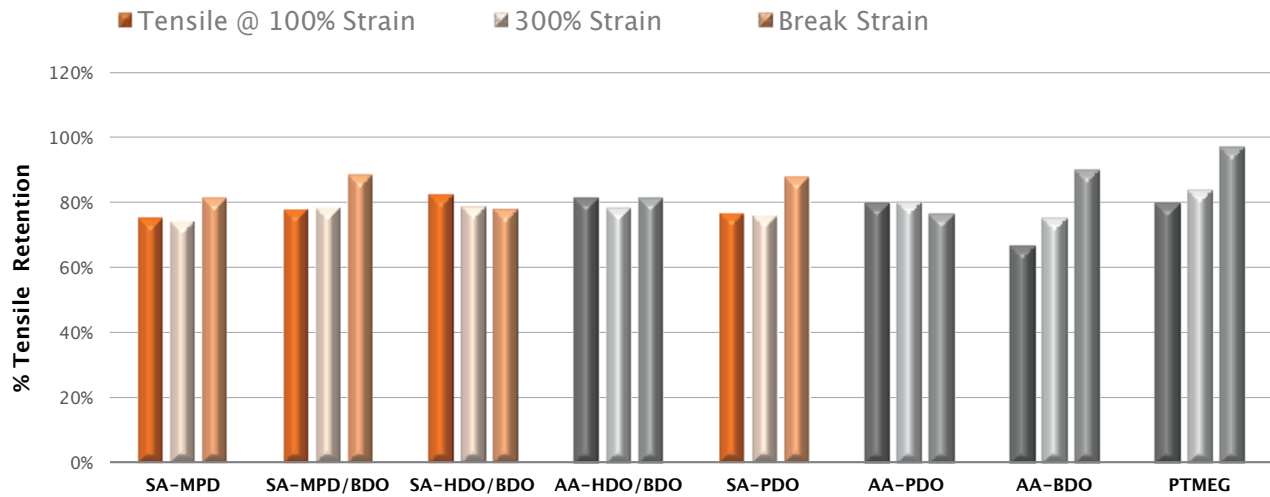
PU	SA-MPD	SA-MPD/BDO	SA-PDO	AA-PDO	PTMEG
Bio carbon content (ASTM D6866)	29	29	63	20*	0
Tg-mid-point (°C)	-8	-13	-20	-40	-34
T@50% Strain (MPa)	3.5	3.6	4.6	4.8	5.9
T@100% Strain (MPa)	4.9	5.0	6.0	6.4	7.9
Tear Resistance die C (kN/m)	41	72	92	95	90
Taber Abrasion (mg weight loss)	6	10	<2	<2	<2
Break Stress (MPa)	49.5	47.9	62.2	55.6	44.9
Break Strain (%)	1011	890	940	777	550
7 day Ethanol Swell (%)	14	13	10	13	27
7 day Toluene Swell (%)	39	35	22	41	56
7 day Oil Swell at 63°C (%)	0.5	0.3	0.5	2.2	10

*Calculated bio-based carbon content based on 33% bio content in AA-PDO and at 66% polyol content

HYDROLYSIS RESISTANCE

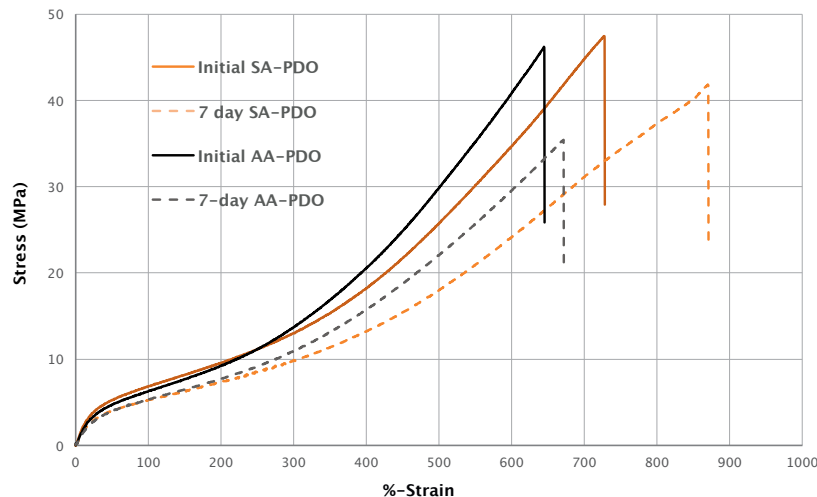
The hydrolytic degradation of polyurethanes made with polyesters is likely to occur via the hydrolysis of the aliphatic ester followed by chain scission, loss of molecular weight and subsequent reduction of polymer chain entanglements. Thus, by mechanical property testing and measuring the change in the tensile stress properties before and after exposure to hydrolysis conditions, it should be possible to determine if there is significant hydrolysis of the ester linkages in a polyester polyurethane. The hydrolysis resistance of the polyurethanes made with these polyols were evaluated by exposure of the test specimen to 70° C, 95% relative humidity for 7 days. The change in tensile values were compared to the initial properties and are shown graphically in Figure 9. In addition, to comparing the change in the break tensile values, it is also useful to compare the lower strain tensile values at 100% and 300% strain since the standard deviation of these tensile values are much smaller than the break values, and if significant molecular weight reduction of the polymer network occurred it would also be detected at these low strain tensile value. As shown in Table 3 and Figures 9 and 10, no significant difference in the mechanical properties of these polyurethanes were noted.¹¹ In these unstabilized polyurethane systems, we noted that changes in the physical properties of the SA based polyurethanes were very similar to AA based polyurethanes made under similar conditions.

FIGURE 9: Percent Retention of Original Tensile Properties after Exposure to Humidity (7 day, 70° C, 95% RH)



In Figure 10, representative stress-strain curves for the polyurethanes made with SA-PDO and AA-PDO are compared. The change in the mechanical properties appears similar to plasticization of a polymer network rather than significant molecular weight degradation. The before and after stress-strain curves show a drop in the tensile values at a given strain, **without** a significant loss of the elongation. This is not to claim that hydrolysis of the SA or AA polyurethane systems is not occurring and these systems are somehow exempt from the thermodynamics of esters, but rather the SA and AA systems prepared by this method exhibit similar behavior under these test conditions. Furthermore the formulation and processing conditions influence the polymer network and therefore the physical properties including hydrolysis resistance. As is known, urethane coatings made from PUDs tend to have poorer hydrolysis resistance than solvent borne PU coatings since the dispersing acid used to make the PUD increases the hydrophilicity of the polymer and hence increases the water-polymer interactions and thus reduces its hydrolytic resistance.⁵ Ultimately, the hydrolytic stability of the polyurethanes (or other resin systems) needs to be evaluated in a manner consistent with the intended applications and many factors influence this critical property including the use of stabilizers, processing conditions and even the geometry of the final part.

FIGURE 10: Representative stress-strain curves of polyurethanes made with SA-PDO and AA-PDO



CONCLUSIONS

Bio-based succinic acid is becoming a chemical building block that provides performance and sustainability in the urethane industry. As we continue to develop familiarity with the succinate systems more and more opportunities become available and result in commercial adoption for bio-based polyurethanes. In this study we have demonstrated that bio-based succinate polyester polyols are a viable alternative to petroleum based polyester polyols and bring value in performance and sustainability to the urethane tool box and that they are useful in a variety of applications. These thermoplastic polyurethane data exemplifies the formulation flexibility of biobased succinic acid and its utility as a key building block in polyester polyols for polyurethanes. The succinate based aliphatic polyols enable greatly improved solvent resistance and in many cases one can gain this benefit without loss of other key properties such as strength, tear resistance and even in some cases hydrolysis resistance. The primary trade-offs of the SA polyols in the preparation of bio-based polyurethanes are higher viscosity (which is still in a very useful range), higher glass transition temperatures and rebound. However as noted in this study, the selection of the glycol and acid SA/AA mixtures can allow modification of these properties too.



Dr. William (Bill) D. Coggio is the Global Applications and Technology Support Manager for BioAmber. He earned his Ph.D. in chemistry from The Pennsylvania State University under the direction of Prof. Harry Allcock. Previously he was the Global Applications Development Lead for Silicone Elastomers with Cabot Corporation and was a Senior Research Scientist for 21 years with 3M Company in St. Paul, MN. He holds more than 25 issued US patents, has 12 peer reviewed journal publications and has given numerous professional seminars and lectures.

BioAmber is a sustainable chemicals company that has a proprietary biotechnology technology platform to convert renewable feedstocks into renewable chemicals for use in a wide variety of everyday products including plastics, resins, food additives and personal care products. See www.bio-amber.com for more information.

Polyurethane Specialties Co (PSC) is a manufacturer of polyesters, solution polymerized urethanes, prepolymers and curatives for the castable urethane market and specialty polymers. It has served the marketplace for over 50 years.

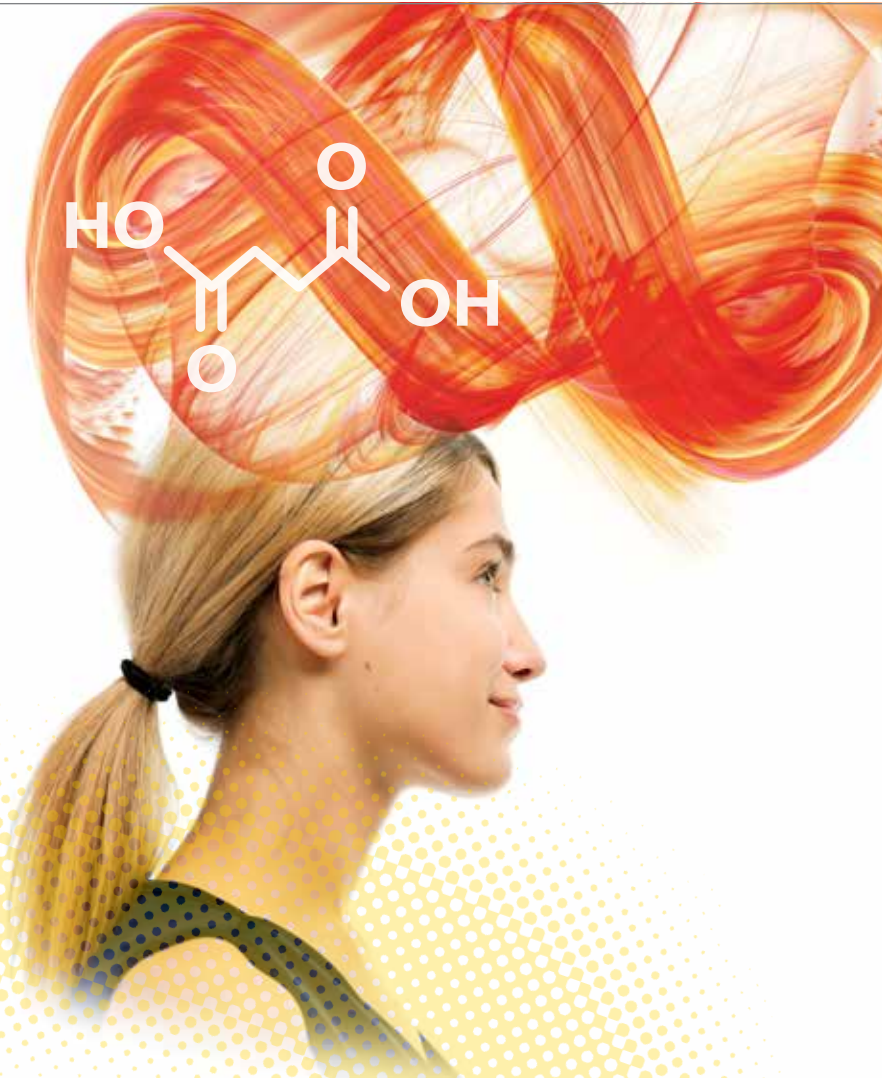
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REFERENCES

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- On April 24, 2015, Bayer Material Science announced BioAmber as a supplier for their new IMPRANIL™ Eco product line for BioBased urethanes. On June 23, 2015, Flokser Group announced the introduction of Sertex® Synthetic Leather utilizing BioAmber's bio-based succinic acid and Susterra™ 1,3-propane diol for DuPont Tate and Lyle to produce a bio-based synthetic leather with about 70% biobased content and excellent performance properties. For other press releases see www.bioamber.com-newsroom.
- The stress-strain data in Table 3 are average values and reported by Troy Polymer Inc. and the reported standard deviations are considered accurate. The graphed stress-strain curves in Figures 5 and 10 are from a single data set selected by the author from one of the 5 repeats that was considered closest to the average values listed in Table 3. However the values in the Table 3 should be considered more accurate and should be used for comparative analysis of the values between the different polyurethanes.
- Coggio, W.D., **Succinic Acid; A Bio-based Building Block for Higher Performance Polyurethanes Dispersion for Coatings**. Presented at the Waterborne Coatings Conference, New Orleans, LA February 10, 2015. In this study, thin PU films based on SA and AA PEP and made with H12-MDI were cast from a PUD and cured. The mechanical properties were evaluated after exposure to 60° C, 95% humidity and for 3, 7, 19 days. Our data indicated the PU based films based on these systems showed substantial degradation after 7 days and were fully decomposed after 19 days. But again the SA and AA systems exhibited very similar behavior under these test conditions
- Miller, R.; Janssen, R.; Theunissen, L.; **Evaluating the Properties of Performance of Susterra® 1,3 Propanediol and Biosuccinium™ Sustainable Succinic Acid in TPU Applications**. Center for Polyurethane Industry (CPI) Conference Atlanta, GA Sept 2012.
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- BioAmber is not making any recommendation or endorsements of one preparation method over the other, but feel it is necessary to highlight these differences as they could be a source of difference between values reported here and those from other sources such as References 6-8.
- Although the urethanes made with SA-MPD and SA-MDP/BDO polyols exhibited higher relative solvent swell compared to others in this series. As presented in TPE Summit Conference, Vienna Austria, Dec 4 2014, comparative polyurethanes made with AA-MDP and AA-MDP/BDO had 7 day solvent swell values in MEK: 125%, 78%, Ethyl acetate: 94%, 68%, Toluene: 62%, 50%, IRM 903: 2.0%, 2.4% respectively. These swell data again show that SA polyols tend to improve the solvent resistance compared to similar adipate based systems.
- In a companion study presented at the **UTECH-NA Sustainable Automotive Conference**, June 3, 2015, Charlotte, NC, hydrolysis data were presented on similar systems tested at 65° C, 95% RH for 15 days. The mechanical property retention data for polyurethanes made with adipates and succinates was essentially the same as shown in Figures 8 and 9 and seemed more consistent with plasticization and not degradation.



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