

EVALUATION OF PDO-BASED POLYOLS IN CAST ELASTOMER PROTECTIVE LINERS

SEAN GAHAN

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

AISA SENDIJAREVIC

*Troy Polymers
900 E. Mandoline Avenue
Madison Heights, MI 48071 USA*

IBRAHIM SENDIJAREVIC

*Troy Polymers
900 E. Mandoline Avenue.
Madison Heights, MI 48071 USA*

MICHAEL SHEN

*DuPont Tate & Lyle Bio Products Co., LLC
Bldg. 11, 399 Keyuan Road
Shanghai, 201203, China*

ABSTRACT

Polyurethane Cast elastomer applications include protective liners for pipes for slurry transportation, coatings for mining screens, various types of caster wheels, electrical potting, electrical insulators, crack sealants, gaskets, pipeline pigs, etc. (1). Polyurethane lined steel pipes are used for transportation of abrasive slurries over vast distances and can experience a broad range of temperatures. The composition of slurries can greatly vary and can include water-based slurry from mining and drilling applications, heavy oil, salt water, petroleum, and mixtures thereof. The slurries frequently carry abrasive particles that can include sand, gravel, rocks, and other particles of varying sizes.

Polyurethane cast elastomer utilized as a pipe-lining application, as described above, is a very demanding application and thus requires a very demanding combination list of properties including physico-mechanical properties, hydrolytic and solvent resistance (a mixture of water and oil), adhesion to metal, heat resistance, and abrasion resistance.

The objective of this study was to evaluate PDO-based polyols, PDO-Sebacate 2000 polyester polyol and polytrimethylene ether glycol (PO3G) 2000 polyether polyol, which are 100% bio-based, in polyurethane cast elastomers and determine their potential in application as protective liners for steel pipe applications and/or as protective coatings in sieves for drilling application. Reference cast elastomers were also prepared using PTMG 2000, PPG 2000, and polycarbonate 2000 polyols.

Polyurethane Cast elastomers is typically a two-component (2K) systems composed of an NCO-prepolymer (or quazi-prepolymer) and a curative defined as either a di-hydroxyl chain extender or a hindered diamine chain extender. In this study, NCO-prepolymers were prepared by reaction of the polyol with TDI at 2/1 NCO/OH equivalent ratio. Subsequently, urethane/urea cast elastomers were prepared by polymerization of TDI NCO-prepolymer with a hindered diamine Ethacure 300. Cast elastomers were analyzed for physico-mechanical properties, hydrolytic, chemical, abrasion and heat resistance, and adhesive properties to determine their overall performance and suitability for these demanding applications.

In terms of overall performance, cast elastomers based on PDO-Sebacate polyols appear to be competitive candidate to cast elastomers based on PTMG polyols and polycarbonate polyols, which are both considered performance materials as internal protective coatings in pipe protection applications. Additionally, PO3G 2000 cast elastomers performed better than referent PPG 2000 cast elastomers. The properties of cast elastomers based on the blend of these two polyols improved as compared to those based on PPG 2000. PPG polyols are used as protective pipe coatings in applications requiring lower levels of protection.

INTRODUCTION

Cast polyurethane elastomers are usually two-component (2K) systems composed of an NCO-prepolymer (or quasi-prepolymer) and a curative defined as either a di-hydroxyl chain extender or a hindered diamine chain extender (1). Some of the major applications of cast elastomers includes protective liners for pipes for slurry transportation, coatings for mining screens, various types of wheels, electrical potting, electrical insulators, crack sealants, gaskets, and pipeline pigs.

PU lined steel pipe are used for transportation of abrasive slurries over vast distances and can experience a broad range of temperatures. The composition of slurries can greatly vary and can include water-based slurry from mining and drilling applications, heavy oil, salt water, petroleum, and mixtures thereof. The slurries frequently carry abrasive particles that can include sand, gravel, rocks, and other particles of varying sizes.

Polyurethane cast elastomer for pipe-lining application needs to have the following combination of properties:

- Good physico-mechanical properties
- Excellent hydrolytic and solvent resistance (a mixture of water and oil).
- Excellent adhesion to metal.
- Good heat resistance.
- Good abrasion resistance.

Most PU systems currently used in a pipe liner application are cast elastomer based on a NCO-prepolymer and a hindered diamine (e.g. Ethacure 300) as a curative. The NCO-prepolymer is based on Toluene diisocyanate (TDI) and a polyol. Polyols typically used in this demanding application environment include PTMG and polycarbonate polyols due to their high-performance qualities and contributions to the overall cast elastomer system (2). NCO-prepolymers and hindered diamines are typically applied onto interior of the pipes via a spin coating process, whereby evenly distributing the cast elastomer on the inner surface of the pipe.

PDO-Sebacate polyester polyols and PO3G polyether polyols could potentially be candidate in cast polyurethanes applications, including a protective pipe lining application. PDO-Sebacic polyols in particular had produced 2K-PUDs with a good combination of metal adhesive properties, hydrolytic resistance, corrosion protection, and solvent resistance, which in some instances outperformed 2K-PUD controls based on PTMG and polycarbonate polyols (3-5). Therefore, it is anticipated that PDO-based polyols could provide similar benefits in cast elastomer applications where wear resistance, adhesion to metal, and solvent resistance to a broad range of media constitute critical performance properties.

EXPERIMENTAL

Urethane-Urea cast elastomers based on PDO-Sebacate 2000 and PO3G 2000 polyols and reference cast elastomers based on PTMG 2000, PPG 2000 and Polycarbonate 2000 polyol were prepared and tested. NCO-prepolymers were prepared from TDI isocyanate (80/20) and following polyols:

- PDO-Sebacate 2000 polyester polyols
- PO3G 2000 polyether polyol
- PPG 2000 polyether polyol (reference)
- PTMG 2000 polyether polyol (reference)
- Polycarbonate 2000 polyol (reference)

The blend of 50:50 by weight of PPG/TDI and PO3G/TDI prepolymer was prepared as well and was used in cast elastomer preparation. Cast elastomers were prepared by polymerization of TDI NCO-prepolymers with hindered diamine Ethacure 300.

Materials

Materials used in this study are listed in Tables 1 and 2. The water content of the polyols was checked by Karl Fisher method (ASTM D-4672). If water content was higher than 0.06%, the polyol was demoiurized for 24 hours

at 75°-80°C under vacuum of 1-3 mm Hg and continuous mixing by magnetic stirrer (Table 2). Isocyanate was used as received from the suppliers. Prior to use, isocyanate content was checked by di-n-butylamine titration method (ASTM D-5155).

Preparation of NCO-prepolymers

NCO-terminated prepolymers, based on TDI 80/20 and selected polyols, were prepared at NCO/OH equivalent ratio of 2/1, according to the following procedure: calculated amount of TDI was placed in a 1-L glass reaction kettle equipped with agitation and continuous nitrogen flow. The reactor was heated via temperature-controlled heating mantle. When the temperature of isocyanate reached 70°C, polyol was added to the reactor under continuous stirring and temperature at 65-75°C. The reaction was monitored via NCO% titration. After the theoretical NCO% value was reached, the reaction was stopped by cooling to room temperature. The prepolymer was stored in a sealed glass bottle under nitrogen at room temperature.

The following properties of TDI NCO-prepolymers were measured:

- NCO%
- Viscosity at 70°C
- T_g, DSC analysis

The formulation of NCO-prepolymers and their properties are presented in Table 3.

Preparation of Cast Elastomers

Cast elastomers were prepared at NCO/NH₂ equivalent ratio 2.05 as presented in Table 4. Cast elastomers were prepared using the following procedure: calculated amount of prepolymer is weighed into a 100g cup (suited for a Speed Mixer) and heated in an oven at 80°C for one hour. Calculated amount of Ethacure 300 was added to the prepolymer and mixed by a Speed Mixer™ (FlackTek Inc.) for one minute. The resin was placed in the oven at 80°C until gel time and then dispensed into Teflon-lined molds preheated to 80°C. The mold was closed and placed in a Carver press pre-heated at 80°C, pressed to 20,000 psi, cured for one hour, and then removed. The cast elastomers were post-cured for 7 days at room temperature before testing. Cast elastomers sheets (6 x 6 inches and 3 mm thickness) and cylindrical sample “buttons” (D=1 in, H= ½ in) were prepared for testing.

Testing of Cast Elastomers

The following properties of cast elastomers were measured:

- Hardness, Shore A, ASTM D-2240
- Tensile stress-strain properties at RT, ASTM-412 (Tensile strength at break, 100% and 300% modulus, elongation at break)
- Tear resistance, Graves die C, ASTM D-624
- Resilience, Bayshore rebound, ASTM D-430
- Heat Resistance (Tensile properties at 50 and 70°C)
- Hydrolytic stability (weight change and change of stress-strain properties with exposure to 95% RH at 60°C for 5 days). The retention of tensile properties was calculated.
- Abrasion resistance, ASTM D-1044
- Oil resistance in selected hydraulic oil (weight change after three days of immersion at RT)
- Resistance in water solution at two pH values (higher than pH 7 and lower than pH 7), (weight change after three days of immersion at RT).
- Glass Transition Temperatures (T_g) via DSC.

Adhesion Properties of Cast Elastomers

The adhesion test specimens were prepared using Steel panels RS-14 (Q-Lab Corporation) of substrate. Steel panels were pre-treated with the adhesion promotor which was utilized to enhance the adhesion of cast elastomers to steel as is conventionally done in production of protective urethane liners for pipe protection.

Preparation of Adhesives

Steel panels (RS-14, 1"x4") were immersed for 30 seconds in solution of 50g Cילbond 49SF and 30g methyl ethyl ketone and then dried in a vertical position at room temperature for 1 hour. Panels were then transferred to an oven preheated at 110°C and baked for 2 hours. After cooling the panels to room temperature, NCO-prepolymer and Ethacure 300 curative were mixed at specified weight ratio via speed mixer and allowed to thicken in an oven preheated to 60°C. Resin was applied to the panels at 0.15g per 0.5" of one end of panels, and panels were clamped overlapping at 0.5". Test samples were then oven cured at 60°C for 1 hour and aged 3 days at room temperature before testing or transferring to humidity chamber for hydrolytic aging.

The adhesion properties were tested via ASTM D1002 Adhesive Lap Joint Test. The adhesion samples were also humid aged (95% RH at 60°C for 5 days) and tested after aging. The retention of adhesion properties was calculated.

Table 1. Materials			
Designation	Identification	Lot #	Supplier
Sb-PDO 2000	2000 MW PDO Sebacate polyol	199-10	DuPont Tate & Lyle Bio Products
Velvetol H2000	2000 MW PO3G Polyol	DAFA121770	Allessa GmbH
Poly-G 20-56	2000 MW PPG polyol	19DR030182	Monument Chemical
Poly(tetrahydrofuran)	2000 MW PTMG polyol	MKCG2495	Aldrich Chemistry
PLACCEL CD220	2000 MW polycarbonate polyol	DB510	Daicel (USA), Inc.
Lupranate T-80	80% 2,4-isomer and 20% 2,6-isomer of toluene diisocyanate; NCO = 48.3%		BASF
Ethacure 300	Amine Curative	4500104602	Albemarle
Cilbond 49SF	Adhesion promoter/primer	PMI-0319-2570	H. B. Fuller
2-Butanone	Methyl Ethyl Ketone; 97%	F085041	Alfa Aesar
Hydrochloric Acid; 0.1 N	Solvent testing media; Acid	4808L66	ChemPure Chemicals
Potassium Hydroxide; 0.1 N	Solvent testing media; Base	D148-07	Labchem Inc.
Vacuum Pump Oil	Solvent testing media; Oil	N/A	Mobil

Table 2. Properties of polyols			
Polyol	OH Value, mg KOH/g	Initial moisture, %	Moisture after drying, %
Sb-PDO 2000	56.7	0.0485	N/A
Velvetol H2000	56.6	0.0446	N/A
Poly-G 20-56	54.7	0.0405	N/A
PTMG 2000	55.0	0.0179	N/A
Poly-CD220	56.1	0.4053	0.0471

Table 3. Formulation and properties of TDI Prepolymers						
	Prep-PPG	Prep-PTMG	Prep-PO3G	Prep-SbPDO	Prep-PC	Prep-PPG/PO3G
Poly-G 20-56	684.01	-	-	-	-	<i>*Blend of 50% Prep-PPG and 50% Prep-PO3G</i>
Poly(tetrahydrofuran)	-	341.73	-	-	-	
Velvetol H2000	-	-	680.58	-	-	
Sb-PDO 2000	-	-	-	340.20	-	
Poly-CD220	-	-	-	-	340.83	
Lupranate T-80	115.99	58.27	119.42	59.8	59.17	
NCO %	3.58	3.48	3.45	3.55	3.52	3.52
Viscosity at 70°C, mPa·s	753	2,982	2425	6,610	47,280	1348
Transitions via DSC, °C	-53.0	-72.9, -39.4, 24.8	-64.6	-34.1, 48.5	-36.3, 42.2	-59.9

Table 4. Curing conditions in preparation of cast elastomers						
	CE-PPG	CE-PTMG	CE-PO3G	CE-PPG/PO3G	CE-SbPDO	CE-PC
Prep-PPG	55.20	-	-	27.64	-	-
Prep-PTMG	-	55.33	-	-	-	-
Prep-PO3G	-	-	55.37	27.64	-	-
Prep-SbPDO	-	-	-	-	55.24	-
Prep-PC	-	-	-	-	-	55.22
Ethacure 300	4.80	4.67	4.63	4.71	4.76	4.78
Reaction conditions						
Gel time, s	852	525	493	661	375	65
Mix time, s at 2200 rpm	60	120	90	90	90	40
Isocyanate Index	1.05					
Prepolymer pre-heat, °C	80					
Carver Press temperature, °C	80					
Approximate press pressure, psi	20,000					
Time in press, min	60					
Post cure	7 days at ambient room conditions					

RESULTS and DISCUSSION

TDI-based NCO-prepolymers

NCO-prepolymers were prepared from TDI isocyanate and following polyols:

- PDO-Sebacate 2000 polyester polyols
- PO3G 2000 polyether polyol
- PPG 2000 polyether polyol (reference)
- PTMG 2000 polyether polyol (reference)
- Polycarbonate 2000 polyol (reference)

The blend of 50:50 by weight of PPG/TDI and PO3G/TDI prepolymer was prepared as well and was used in cast elastomer preparation.

The prepolymers based on PPG 2000 and PO3G 2000 were liquid at room temperature, while those based on PTMG 2000, PDO-Sebacate 2000, and polycarbonate polyol were solid at room temperature. The viscosity of NCO-prepolymers at 70°C based on polyether polyols was lower than that based on PDO-Sebacate 2000 polyol at 6610 cps (Table 3). However, the viscosity of NCO-prepolymer based on Polycarbonate 2000 was much higher at 47,280 cps (Table 3). In general, lower viscosity of NCO-prepolymers is desirable property in cast elastomers applications.

DSC analyses indicates crystallinity of NCO-prepolymers based on PTMG polyol with melt transition at 24.8°C, PDO-Sebacate polyol with melt transition at 48.5 °C, and polycarbonate polyol with melt transition at 42.2°C (Table 3). The remaining NCO-prepolymers appear to be non-crystalline.

Cast Elastomer Performance

Cast elastomers were prepared by reaction of NCO-prepolymer with Ethacure 300 at isocyanate index of 1.05 (Table 4). Gel time (80°C) of cast elastomer resins based on polyether polyols was longer than that based on polyester PDO-Sebacate 2000 and polycarbonate polyol. Gel time in urea forming reaction can be adjusted with temperature of prepolymer, as needed. Cast elastomers were completely polymerized, after cured and post cured for seven days at RT, as indicated via FTIR analysis (Appendix A, Figures 1-6). All cast elastomers samples were transparent at room temperature.

Hardness and Resilience

Cast elastomers based on PPG 2000 exhibited lower hardness (Shore A 74.7) than those based on PTMG 2000 and PO3G 2000 (Shore A 84 and 82, respectively). The hardness of cast elastomer based on PDO-Sebacate 2000 (Shore A 86.8) and Polycarbonate 2000 (Shore A 90.8) was higher (Table 5, Figure1).

The resilience of cast elastomers based on polyether polyols was higher than of cast elastomers based on polyester and polycarbonate polyols (Table 5). It should be noted that resilience of cast elastomer based on PDO Sebacate polyol was somewhat higher than that based on polycarbonate polyol. The resilience of cast elastomers was found to correlate with their elasticity (elongation at break %) as shown in Table 5 and Figure 2.

Thermal properties

The thermal transitions of cast elastomers were measured via DSC over a temperature range from -100°C to 200°C (Table 5; Figures 3-8). The glass transition temperature was found to depend on type of polyol in cast elastomers. The glass transition temperature of cast elastomers based on polyether polyols (from -55°C to -75.9) was lower than for cast elastomers based on Polycarbonate 2000 (-34.2°C) and PDO-Sebacate 2000 (-44.1°C). DSC graph of cast elastomers based on PTMG 2000 indicate a crystalline transition at -0.15°C and cast elastomer based on PDO-Sebacate 2000 at 21.8°C.

Tensile, Tear, and Abrasion

Tensile strength of cast elastomers based on PDO-Sebacate polyol was higher than for cast elastomers based on polyether polyols, including PTMG, which is a high-performance cast elastomer (Table 5, Figures 9 &10). Tensile strength of cast elastomer based on polycarbonate polyol was notable higher at 6055 psi, but its elongation at break was substantially lower. Thereby, cast elastomers based on PDO-Sebacate, PTMG, and polycarbonate polyols exhibited comparable toughness as measured by the area under the tensile curve (Table 5). It should be noted that cast elastomers based on PO3G exhibited the highest toughness due to its very high elongation at break. Overall, cast elastomers based on PPG polyol had the lower toughness, associated with low tensile strength and elongation at break.

Perhaps a better indicator of wear performance is tensile modulus, which was highest for the cast elastomers base on polycarbonate polyols, followed by the cast elastomers based on PDO-Sebacate and PTMG polyols. Similar trend was observed in tear strength and abrasion resistance (Table 5; Figure 11 and Figure12). Abrasion resistance is very important property in many cast elastomer applications, including as protective liners for pipes for slurry transport or protective coating in sieves in drilling application. Therefore, based on abrasion resistance results, cast elastomers

based on PDO-Sebacate are comparable to those based on PTMG polyols and slightly lower in performance than polycarbonate polyol-based cast elastomers.

Tensile set of cast elastomers based on PDO-Sebacate and polycarbonate polyols were low (10% and 7.6%, respectively) which should correlate with good recovery upon stretching or resistance to shear forces. Tensile set of cast elastomers based on PTMG and PPG polyols was similar at 16.8% and 21.1%. Tensile set for cast elastomers based on PO3G 2000 was high at 66.1%.

Temperature and Hydrolytic Resistance Performance

The effect of temperature on properties of cast elastomers was evaluated via determination of change in tensile properties. Tensile properties of cast elastomers were measured at 50°C and 70°C and compared to performance at room temperature (Table 5). Mainly, the retention of tensile modulus at 100% was used as the key benchmark property. It was determined that cast elastomers based on PDO-Sebacate and PTMG polyols essentially completely retained their modulus at 50 and 70°C (Table 5). Cast elastomers based on polycarbonate polyols and PO3G experienced an approximate 10% reduction in the modulus at 70°C while those based on PPG experienced a 20% loss in modulus.

All cast elastomers performed well in hydrolytic aging test (60°C, 5 days and 95% relative humidity). Water absorption in hydrolytic aging test was the lowest for cast elastomers based on PTMG, PDO Sebacate, and polycarbonate polyols (Table 5). The weight increase was somewhat higher for cast elastomers based on PPG 2000 and PO3G 2000 polyols. The retention of tensile properties (tensile modulus at 100%) was very good with 90% or greater retentions in all cases (Table 5). However, cast elastomers based on PDO-Sebacate and polycarbonate polyols did slightly better than the rest, with essentially no change in modulus.

Solvent and Moisture Resistance

The solvent resistance of cast elastomers based on polycarbonate polyol and PDO-Sebacate polyol in non-polar hydraulic oil and alkaline and acidic aqueous solutions was very good (weight gain by immersion low), and notable better than that for cast elastomers based on PTMG and other polyether polyols (Table 6, Figures 13 &14). Good resistance of cast elastomers to both non-polar polar materials is very important in an application that includes a harsh environment such as exposure to water and chemicals found in crude-oil transport, drilling, and mining applications.

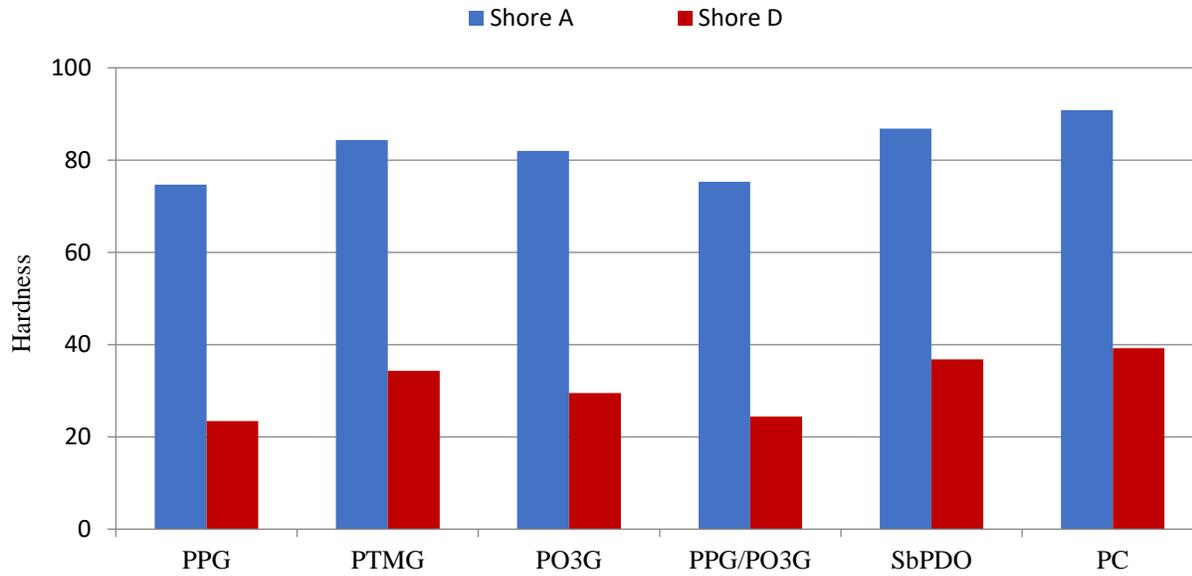
Adhesion properties

The adhesion properties of cast elastomers were evaluated using stainless steel substrate (Table 7, Figure15). Cast elastomers based on PTMG, PDO-Sebacate, and polycarbonate polyol polyols exhibited similar, very good adhesion strength which was significantly higher than for cast elastomers based on PPG and PO3G polyether polyols.

The adhesion properties of cast elastomers changed upon hydrolytic aging (60°C, 5 days, 95% relative humidity). PDO-Sebacate and polycarbonate polyol-based elastomers retained well the adhesion strength (87.8% and 92.5%, respectively), while cast elastomer based on PTMG 2000 decreased significantly (62.9%). The adhesion strength of cast elastomer based on PO3G improved significantly, which could indicate additional annealing. The adhesives based on blend PO3G2000/PPG 2000 exhibited much better retention (87.8%) of adhesion strength compared to that based on PPG 2000 (41.2%).

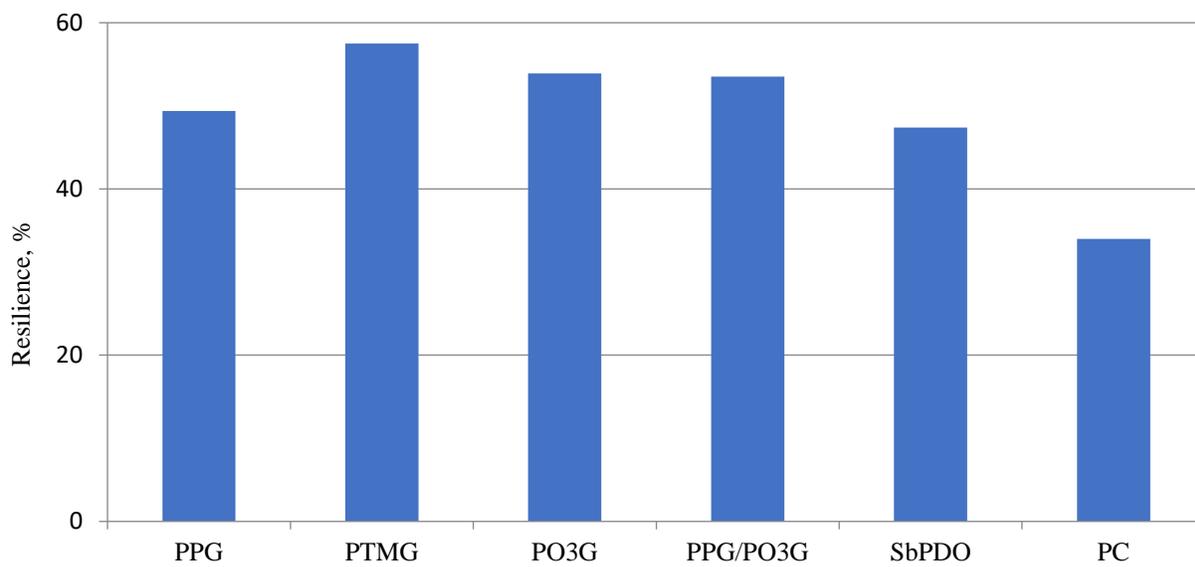
The adhesion strength is very important in cast elastomer applications such as coating inside the pipes for transport of slurries. It is also important in spray cast elastomers, such as truck bedliners. Good adhesion properties combined with good moisture as well as heat resistance are important in most cast elastomer application.

Table 5. Properties of cast elastomers						
Formulation:	CE-PPG	CE-PTMG	CE-PO3G	CE-PPG/PO3G	CE-SbPDO	CE-PC
Hardness, Shore A	74.7 ± 0.7	84.3 ± 0.7	82.0 ± 0.8	75.3 ± 0.8	86.8 ± 1.0	90.8 ± 0.6
Shore D	23.4 ± 0.7	34.3 ± 0.8	29.5 ± 0.4	24.4 ± 0.5	36.8 ± 1.0	39.2 ± 0.9
Resilience, Bayshore rebound, %	49.4 ± 3.2	57.5 ± 1.5	53.9 ± 1.1	53.5 ± 0.7	47.4 ± 1.4	34.0 ± 1.2
Tear strength, N/cm	595 ± 118	1177 ± 78	1118 ± 71	885 ± 26	1213 ± 55	1290 ± 79
Abrasion resistance, mg loss/1000 cycles	334	16	50	104	17	3
<i><u>Tensile properties at room temperature</u></i>						
Tensile strength at break, psi	649 ± 29	2937 ± 262	2533 ± 201	1195 ± 74	3685 ± 202	6095 ± 114
Tensile elongation at break, %	442 ± 23	915 ± 61	1426 ± 25	1420 ± 55	797 ± 31	557 ± 12
Tensile strength at yield, psi	-	-	-	-	-	-
Tensile elongation at yield, %	-	-	-	-	-	-
Tensile strength at 100% elongation, psi	682 ± 11	908 ± 21	764 ± 17	638 ± 17	916 ± 17	1206 ± 25
Tensile strength at 300% elongation, psi	780 ± 9	1386 ± 29	1117 ± 22	879 ± 18	1609 ± 19	2893 ± 39
Area under the curve, J	5.2 ± 0.3	28.1 ± 2.6	41.0 ± 1.9	24.6 ± 1.6	29.5 ± 1.7	32.0 ± 1.7
Modulus (Young's), MPa	10.6 ± 0.6	11.4 ± 1.6	9.4 ± 1.1	11.0 ± 2.2	8.4 ± 0.9	10.2 ± 0.2
Tensile set, %	21.1 ± 2.5	16.8 ± 4.4	66.1 ± 3.2	98.6 ± 6.6	10.0 ± 0.5	7.6 ± 0.8
<i><u>Tensile properties at 50°C</u></i>						
Tensile strength at break, psi	637 ± 28	**	**	**	**	**
Tensile elongation at break, %	292 ± 48	**	**	**	**	**
Tensile strength at 100% elongation, psi	646 ± 11	990 ± 19	777 ± 15	570 ± 10	941 ± 10	1108 ± 8
Tensile strength at 300% elongation, psi	-	1390 ± 32	1046 ± 17	715 ± 12	1388 ± 12	2043 ± 32
% strength retention at 100% elongation	94.7	109.0	101.7	89.3	102.7	91.9
<i><u>Tensile properties at 70°C</u></i>						
Tensile strength at break, psi	540 ± 6	**	**	**	**	**
Tensile elongation at break, %	225 ± 18	**	**	**	**	**
Tensile strength at 100% elongation, psi	550 ± 11	906 ± 19	705 ± 5	520 ± 7	921 ± 15	1076 ± 7
Tensile strength at 300% elongation, psi	-	1190 ± 34	900 ± 8	621 ± 8	1264 ± 19	1734 ± 20
% strength retention at 100% elongation	80.6	99.8	92.3	81.5	100.5	89.2
<i><u>Tensile properties after hydrolytic aging (5 days, 60°C, 95% RH)</u></i>						
Tensile strength at break, psi	669 ± 30	2809 ± 214	2465 ± 94	961 ± 36	3924 ± 196	5398 ± 377
Tensile elongation at break, %	355 ± 41	771 ± 39	1192 ± 58	1067 ± 106	682 ± 36	457 ± 18
Tensile strength at 100% elongation, psi	639 ± 17	861 ± 17	727 ± 11	589 ± 13	908 ± 14	1183 ± 10
Tensile strength at 300% elongation, psi	717 ± 23	1328 ± 24	1068 ± 12	813 ± 15	1622 ± 17	2894 ± 38
Area under the curve, J	3.8 ± 0.4	23.8 ± 1.9	31.8 ± 1.6	15.1 ± 0.6	27.4 ± 2.64	21.2 ± 2.2
Modulus (Young's), MPa	9.9 ± 0.4	11.2 ± 0.8	9.2 ± 0.5	9.6 ± 0.4	5.8 ± 0.4	13.2 ± 1.4
Weight change, %	0.63	0.46	0.51	0.67	0.44	0.47
Tensile set, %	15.2 ± 3.4	12.1 ± 2.3	46.3 ± 6.3	79.4 ± 12.9	6.6 ± 0.7	4.9 ± 1.6
% strength retention at 100% elongation	93.7	94.8	95.2	92.3	99.1	98.1
Transitions via DSC, °C	-53.5	-75.9, -0.2	-66.0	-59.5	-44.1, -21.1, 21.8	-34.2



Cast Elastomer Formulation

Figure 1. Hardness (Shore A and D) of Cast Elastomer prepared with various polyols



Cast Elastomer Formulation

Figure 2. Resilience of Cast Elastomers prepared with Various Polyols.

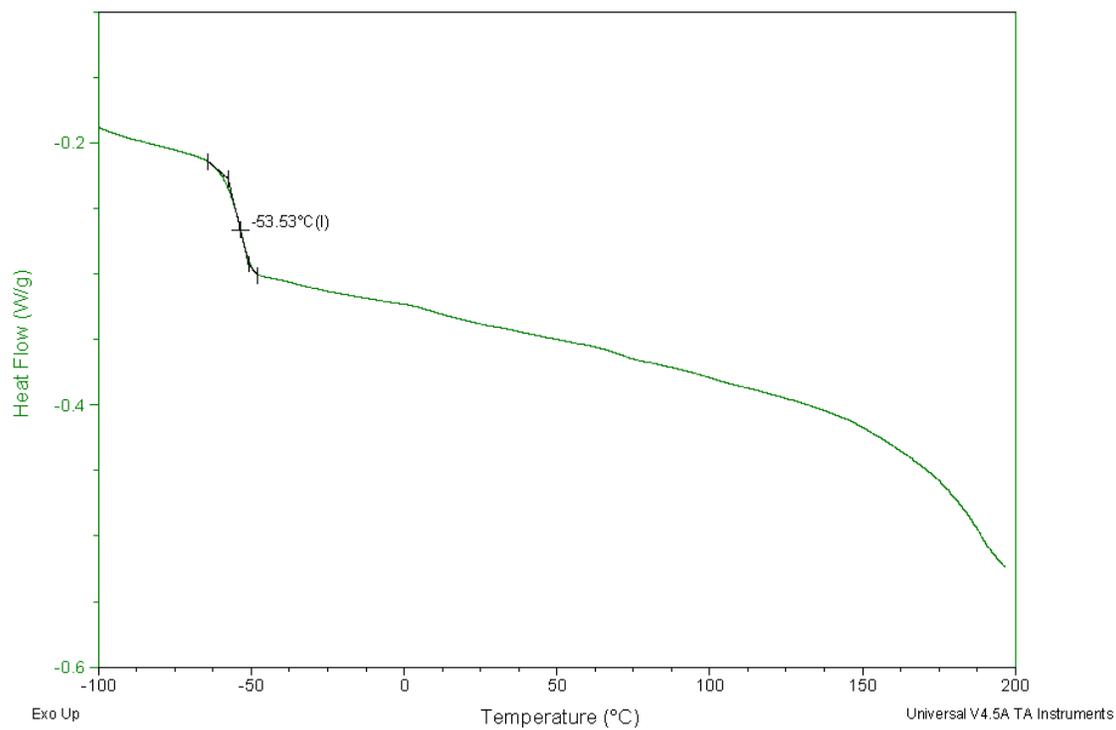


Figure 3. DSC thermal analysis of cast elastomer based on PPG 2000 polyol

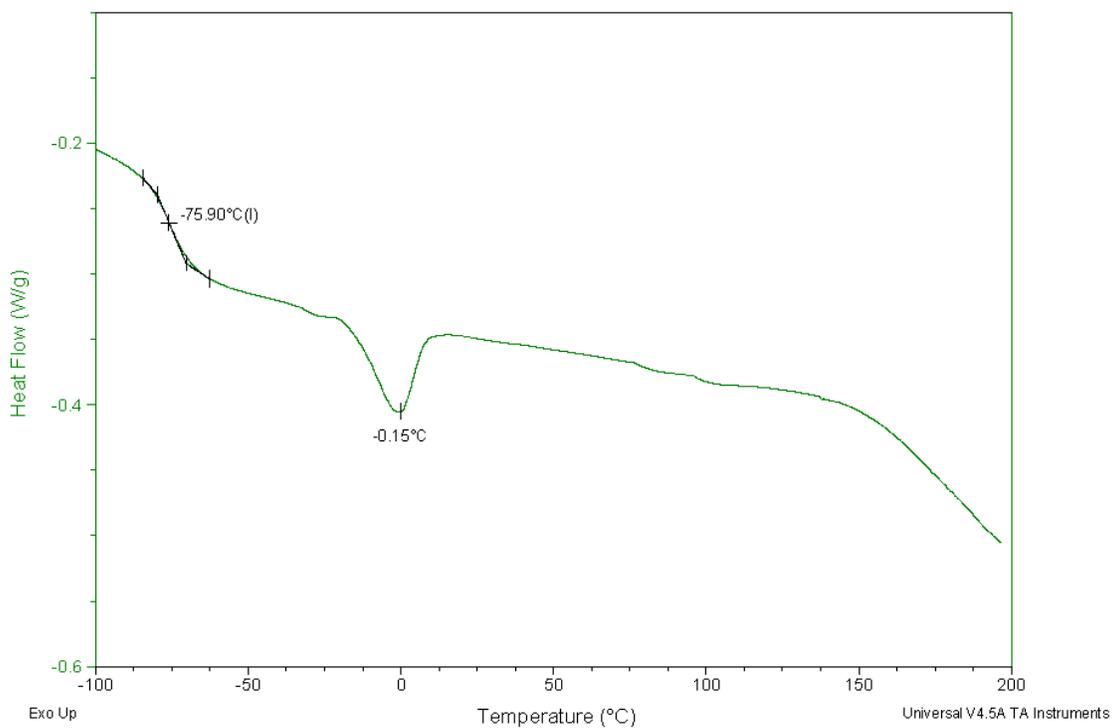


Figure 4. DSC thermal analysis of cast elastomer based on PTMG 2000 polyol

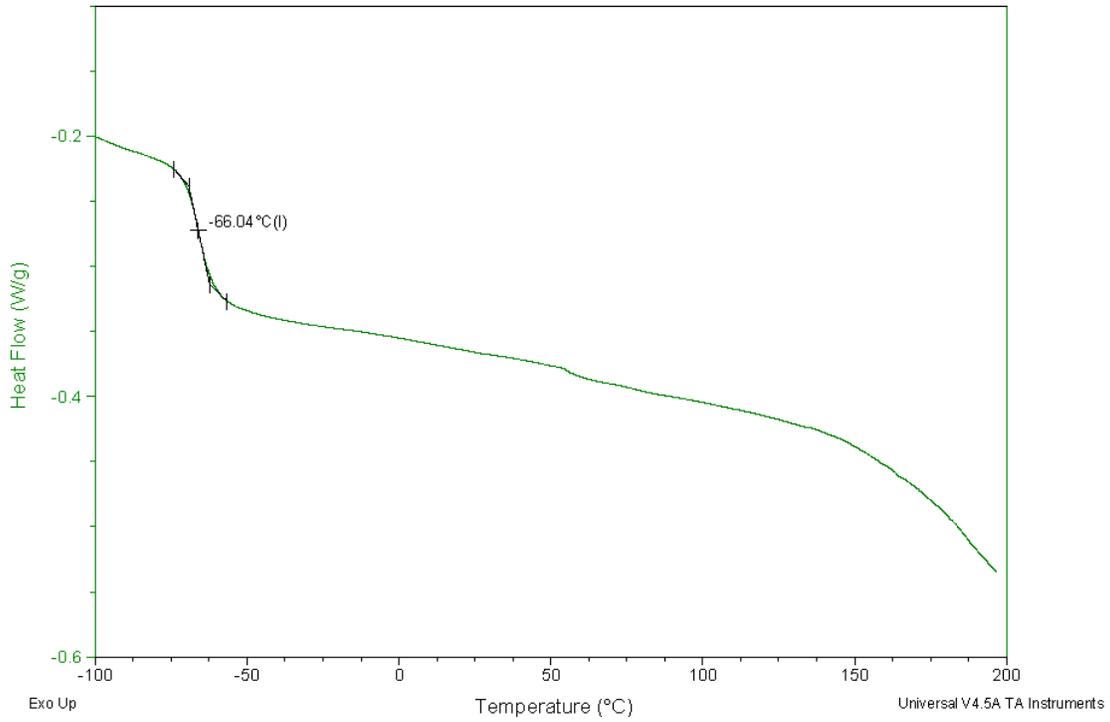


Figure 5. DSC thermal analysis of cast elastomer based on PO3G 2000 polyol

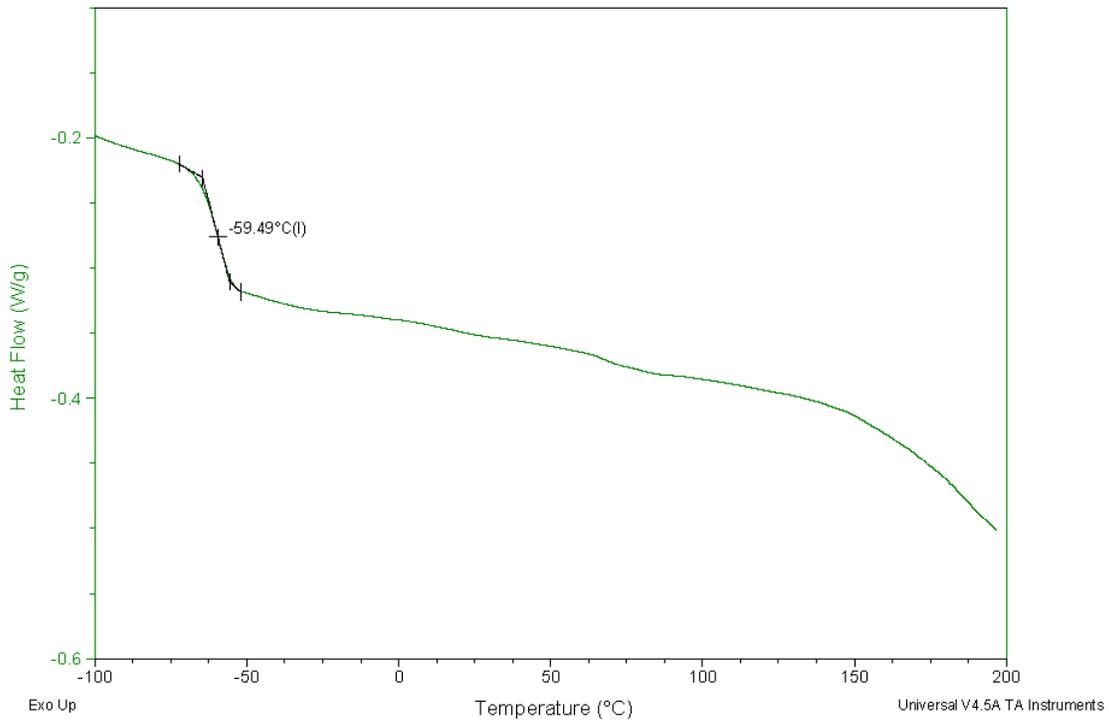


Figure 6. DSC thermal analysis of cast elastomer based on 50/50 pbw polyol blend PO3G2000/PPG2000

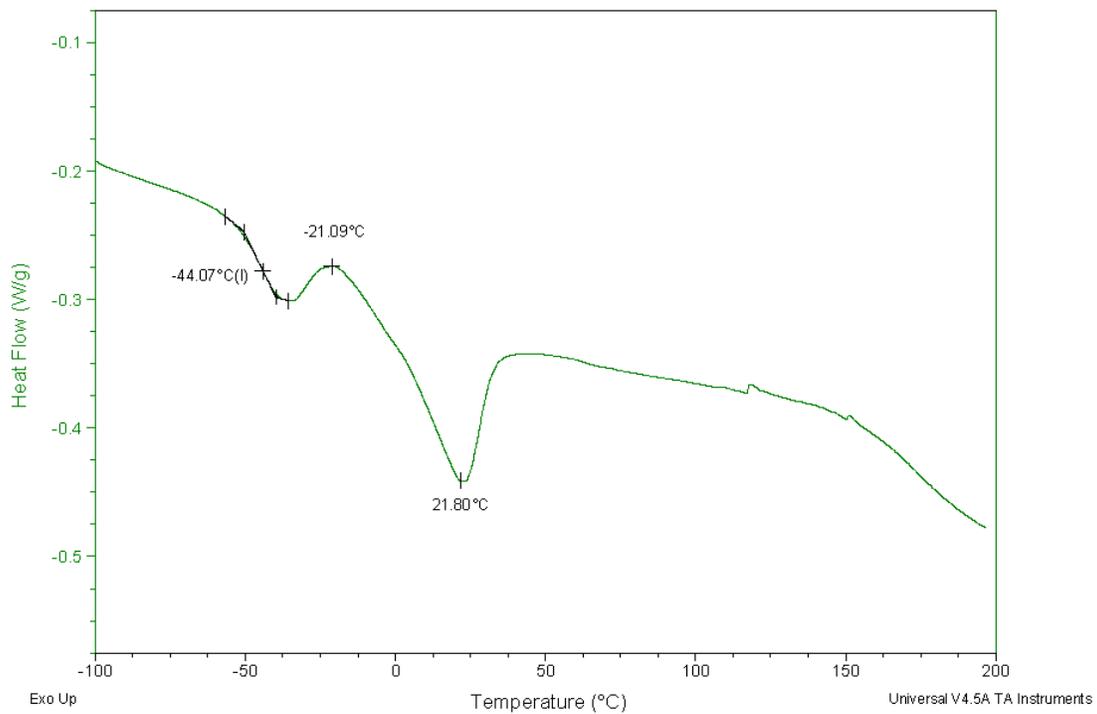


Figure 7. DSC thermal analysis of cast elastomer based on PDO-Sebacate 2000 polyol

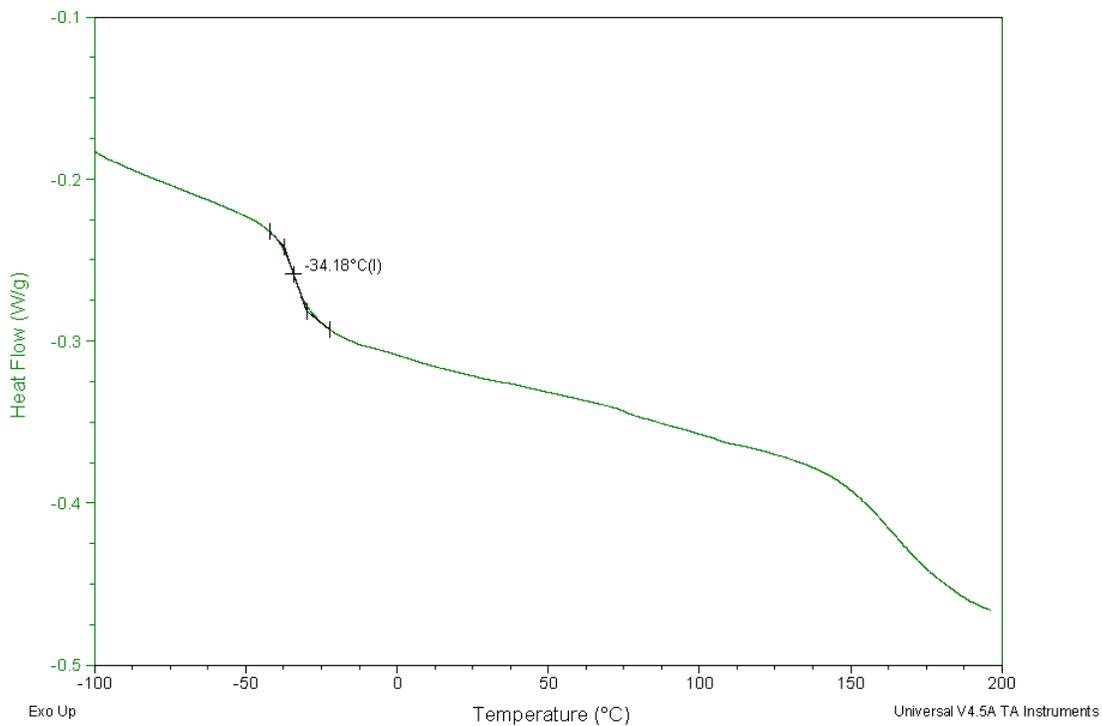


Figure 8. DSC thermal analysis of cast elastomer based on Polycarbonate 2000 polyol

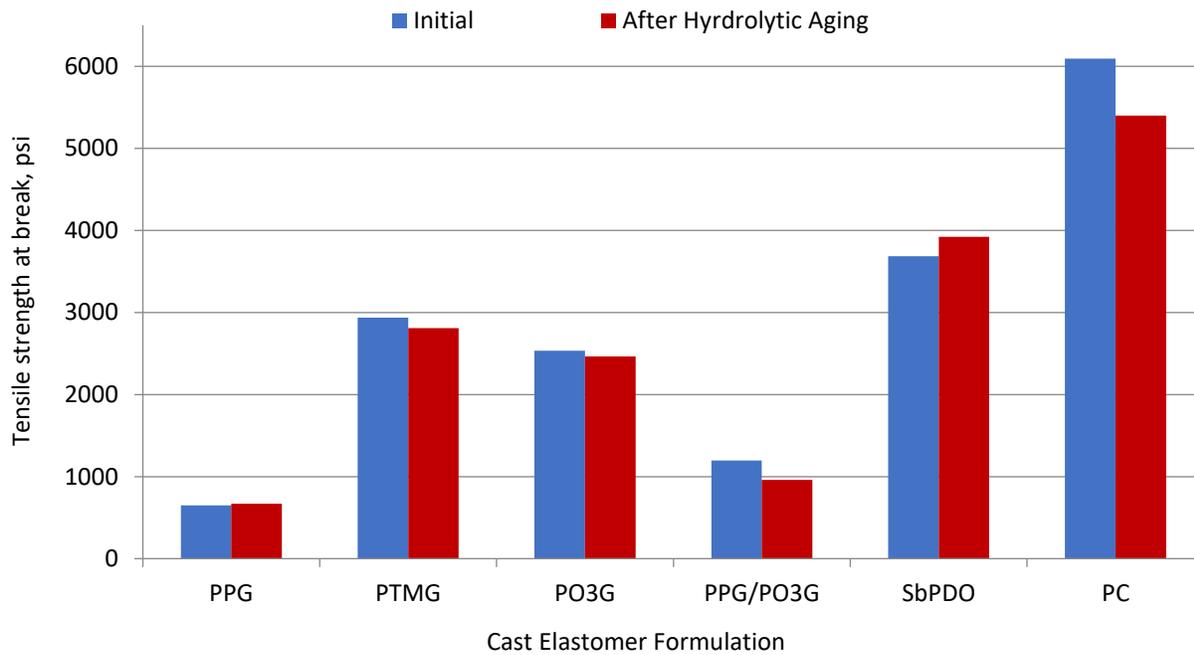


Figure 9. Tensile strength at Break of Cast Elastomers before and after Hydrolytic Aging

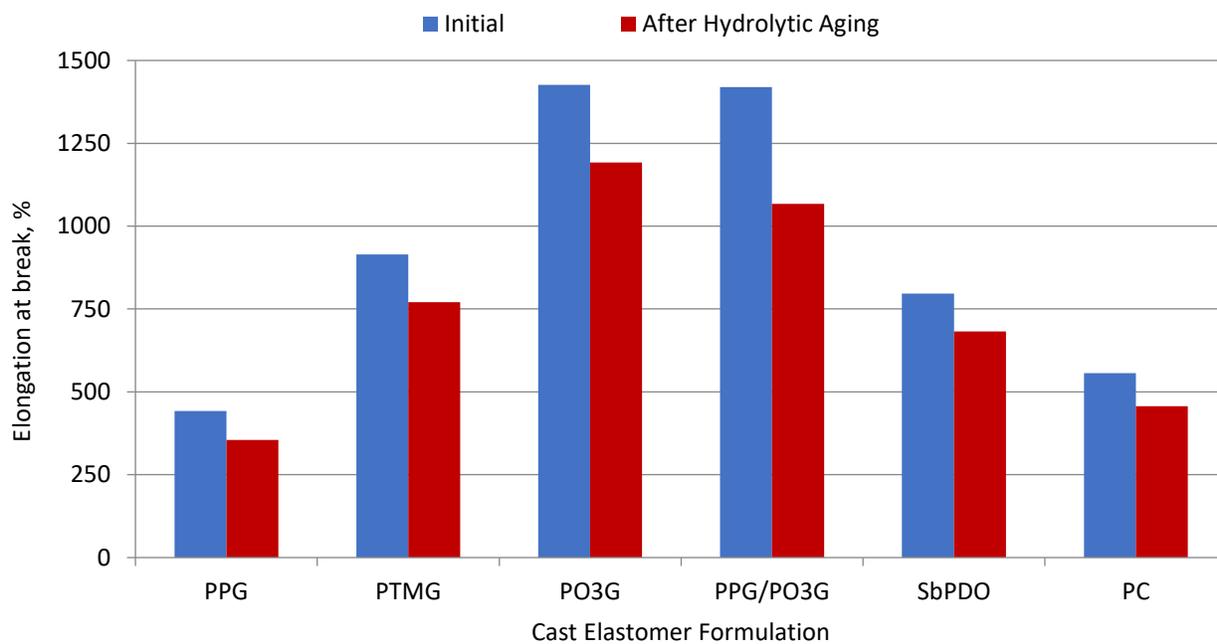


Figure 10. Elongation at Break of Cast Elastomers before and after Hydrolytic Aging.

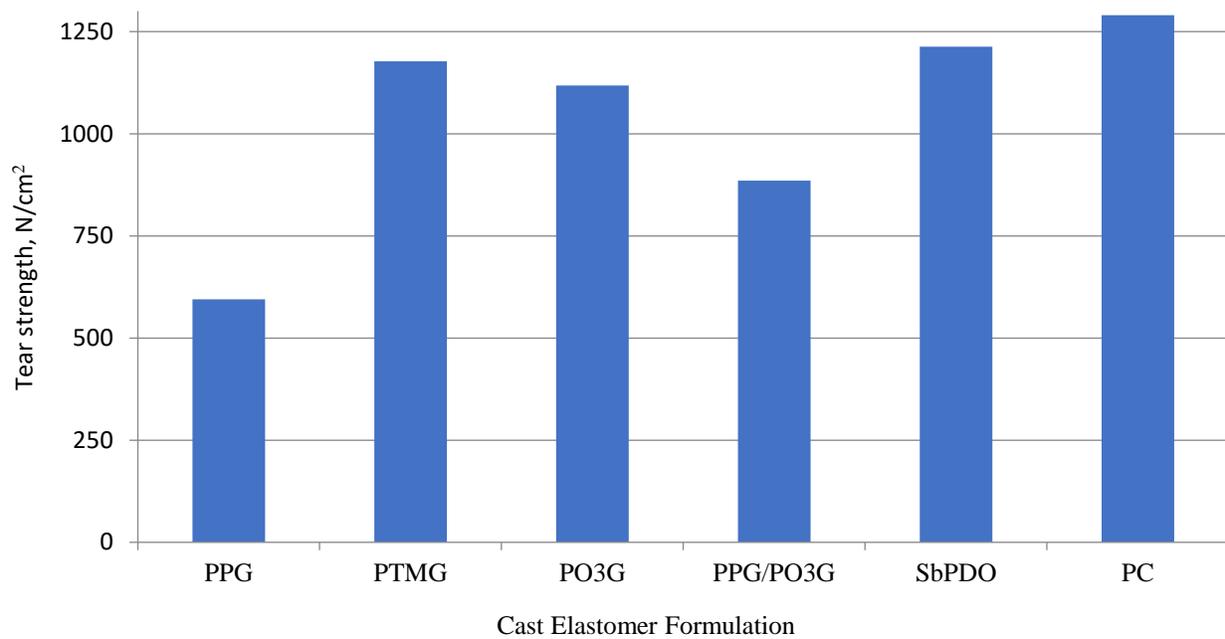


Figure 11. Tear strength of Cast Elastomer prepared with Various Polyols.

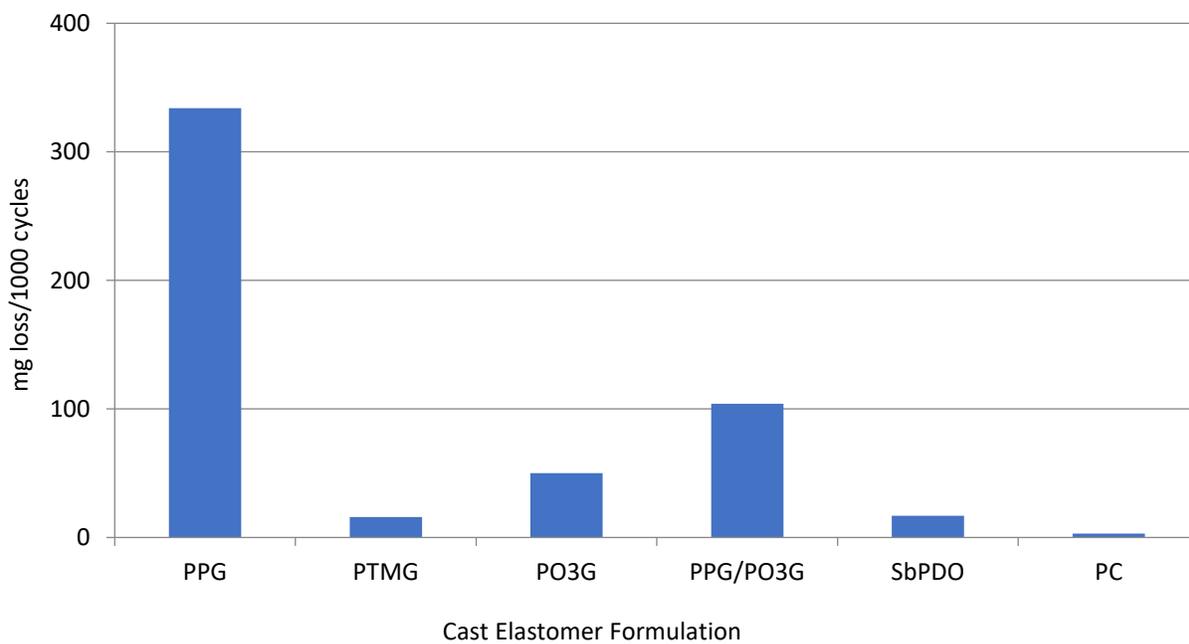


Figure 12. Abrasion resistance of Cast Elastomers prepared with Various Polyols.

Table 6. Resistance of cast elastomers in various solutions upon 3 days of immersion						
Formulation:	CE-PPG	CE-PTMG	CE-PO3G	CE-PPG/PO3G	CE-SbPDO	CE-PC
% weight change: hydraulic oil	0.82	1.47	0.11	0.43	0.14	0.11
% weight change: 0.1 N HCl	1.90	1.16	1.70	1.76	0.62	0.52
% weight change: 0.1 N KOH	2.00	1.10	1.67	1.85	0.41	0.43

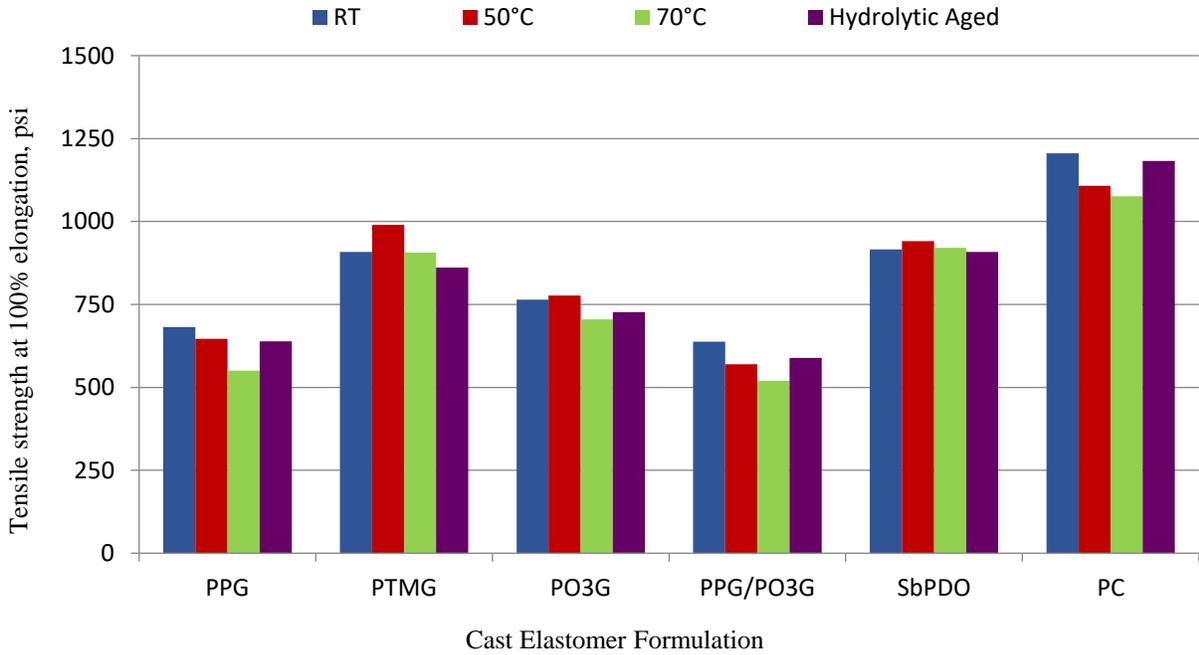


Figure 13. Tensile Modulus at 100% Elongation of Cast Elastomers under different Conditions.

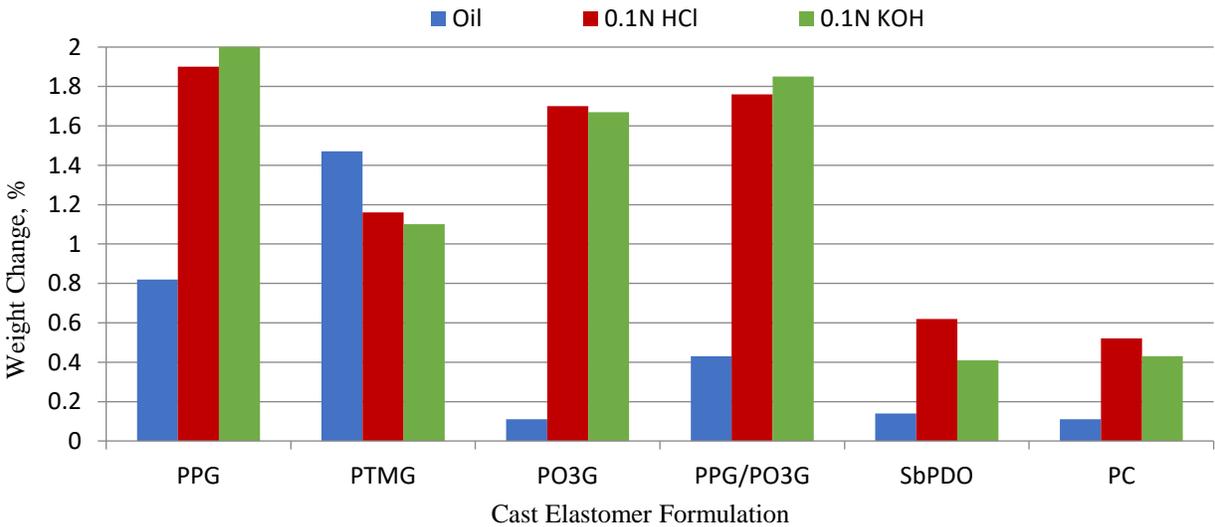


Figure 14 Resistance of Cast Elastomers by Immersion to Various Solutions.

Table 7. Adhesive properties of cast elastomers						
Substrate:	Steel					
Adhesion promotor:	Cilbond 49SF					
Amount of resin applied:	0.30 g					
Cast elastomer resin conditioning:	60°C until thick					
Curing conditions:	1 hour at 60°C and 3 days at ambient conditions					
Formulation:	CE-PPG	CE-PTMG	CE-PO3G	CE-PPG/PO3G	CE-SbPDO	CE-PC
Thickening time, s	1714	731	721	1356	367	110
<i>Initial:</i>						
Load at break, psi	442 ± 19	2092 ± 256*	1084 ± 115	720 ± 65	1921 ± 222*	2210 ± 208*
Strain at break, %	4.6 ± 0.2	15.4 ± 1.9	8.9 ± 1.0	7.0 ± 0.6	13.3 ± 1.2	14.0 ± 1.2
Area under the curve, J	0.29 ± 0.03	4.22 ± 1.13	1.48 ± 0.38	0.68 ± 0.13	3.51 ± 0.74	4.09 ± 0.78
Modulus (Young's), MPa	1044 ± 69	1023 ± 117	1103 ± 293	894 ± 99	1294 ± 195	1175 ± 117
Break type	Cohesive	Cohesive	Cohesive	Cohesive	Cohesive	Adhesive
<i>After aging 5 days, 60°C and 95% RH:</i>						
Load at break, psi	182 ± 50	1315 ± 145	1411 ± 175	638 ± 38	1686 ± 161	2044 ± 167*
Strain at break, %	2.5 ± 0.7	8.7 ± 1.1	9.7 ± 0.8	6.8 ± 1.0	10.8 ± 1.1	12.6 ± 0.8
Area under the curve, J	0.08 ± 0.05	1.67 ± 0.42	1.92 ± 0.43	0.57 ± 0.16	2.41 ± 0.59	3.18 ± 0.21
Modulus (Young's), MPa	983 ± 127	1189 ± 338	989 ± 105	811 ± 62	915 ± 152	1198 ± 320
Break type	Cohesive	Cohesive	Cohesive	Cohesive	Adhesive	Adhesive
% retention of strength	41.2	62.9	130.2	88.6	87.8	92.5

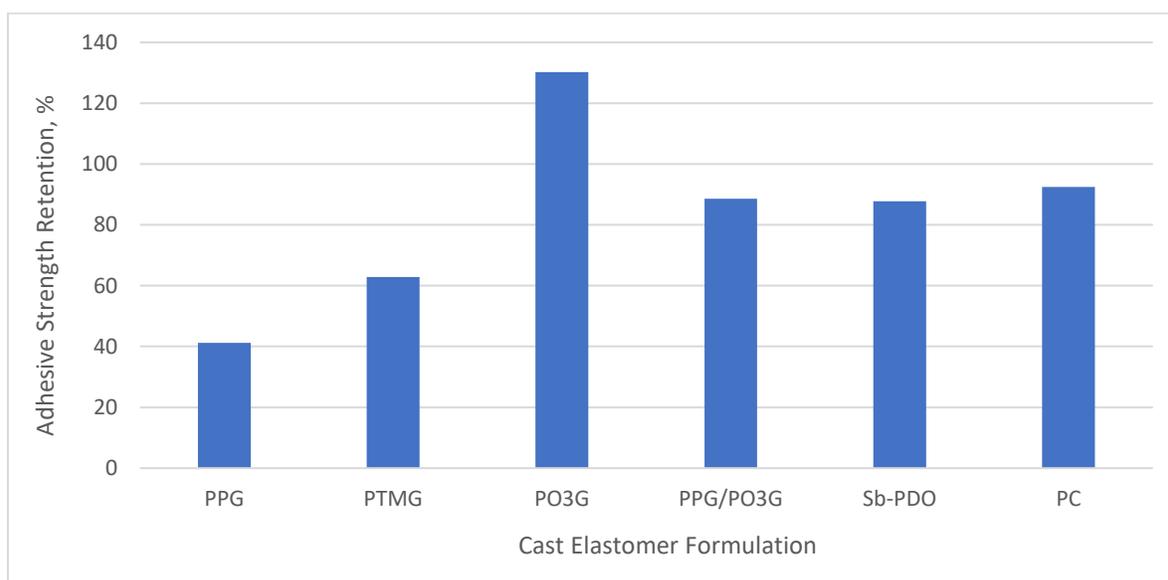


Figure 15. Retention of Adhesive Strength, Load at Break (psi), for Cast Elastomers of Various Polyols for Before & After Hydrolytic Aging.

CONCLUSIONS

Two component polyurethane cast elastomers based on 1,3-Propanediol polyester polyols (PDO Sebacate 2000), polyether polyols (Velvetol H 2000, Allessa) and a 50/50 blend of PPG 2000 polyol and PO3G 2000 were prepared via NCO-prepolymer (or quazi-prepolymer) using toluene diisocyanate (TDI, 80/20, BASF) and a hindered diamine chain extender curative (Ethacure 300, Albemarle) to evaluate their performance and commercial viability as steel pipe liners. The commercial reference PUDs were based on PPG 2000, poly(oxytetramethylene) glycol 2000 (PTMG 2000), and polycarbonate diol 2000 (PLACCEL CD220, Daicel USA, Inc.)

Overall, based on the performed analyses, it appears that cast elastomers based on PDO-Sebacate 2000 exhibit an excellent combination of tensile properties, abrasion resistance, thermal, hydrolytic, and solvent resistance as well as adhesion to metal substrate. These are desirable properties for cast elastomers intended for applications as protective coatings for pipes and coatings for sieves typically used in drilling and mining applications. In terms of overall performance, cast elastomers based on PDO-Sebacate polyol appear to be comparable or exceeding the properties of those based on PTMG and polycarbonate polyols. Cast elastomers based on PTMG polyols and polycarbonate polyols are both considered performance materials as internal protective coatings in pipe protection applications.

PO3G 2000 cast elastomers performed better than referent PPG 2000 cast elastomers. The properties of cast elastomers based on the blend of these two polyols improved as compared to those based on PPG 2000. PPG polyols are also used as protective pipe coatings when applications requiring lower levels of protection and overall performance.

ACKNOWLEDGEMENTS

DuPont Tate & Lyle Bio Products would like to thank Aisa Sendijarevic and Ibrahim Sendijarevic from Troy Polymers, Inc., for their dedication to this project and the ultimate preparation, syntheses and analyses.

REFERENCES

1. Gunter Oertel: Polyurethane Handbook, Hansen Publishers, Munich & New York, 1985
2. Case Studies/Polycarbonate diol Eternacoll, UBE
3. S.J. Hurff and M. Shen (DuPont Tate and Lyle Bio Products), I. Sendijarevic and A. Sendijarevic (Troy Polymers), "Advances in the Use of Bio-based Components in Aqueous Polyurethane Dispersions for Coating and Adhesive Applications", CPI Polyurethanes 2018 Technical Conference, October 2018, Atlanta, Georgia.
4. S. L. Gahan and M. Shen (DuPont Tate and Lyle Bio Products), I. Sendijarevic and A. Sendijarevic (Troy Polymers), "Evaluation of 1,3-Propanediol Based Polyester and Polyether Polyols in Polyurethane Water Dispersions (PUDs) for Textile Coating Applications", CPI Polyurethanes 2019 Technical Conference, October 2019, Orlando, Florida.
5. S. L. Gahan and M. Shen (DuPont Tate and Lyle Bio Products), I. Sendijarevic and A. Sendijarevic (Troy Polymers), "Evaluation of 1,3-Propanediol Based Polyester and Polyether Polyols in Polyurethane Water Dispersions (PUDs) for Direct to Metal Applications", submitted to CPI Polyurethanes Technical Conference, 2020.

APPENDIX A: FTIR SPECTRA.

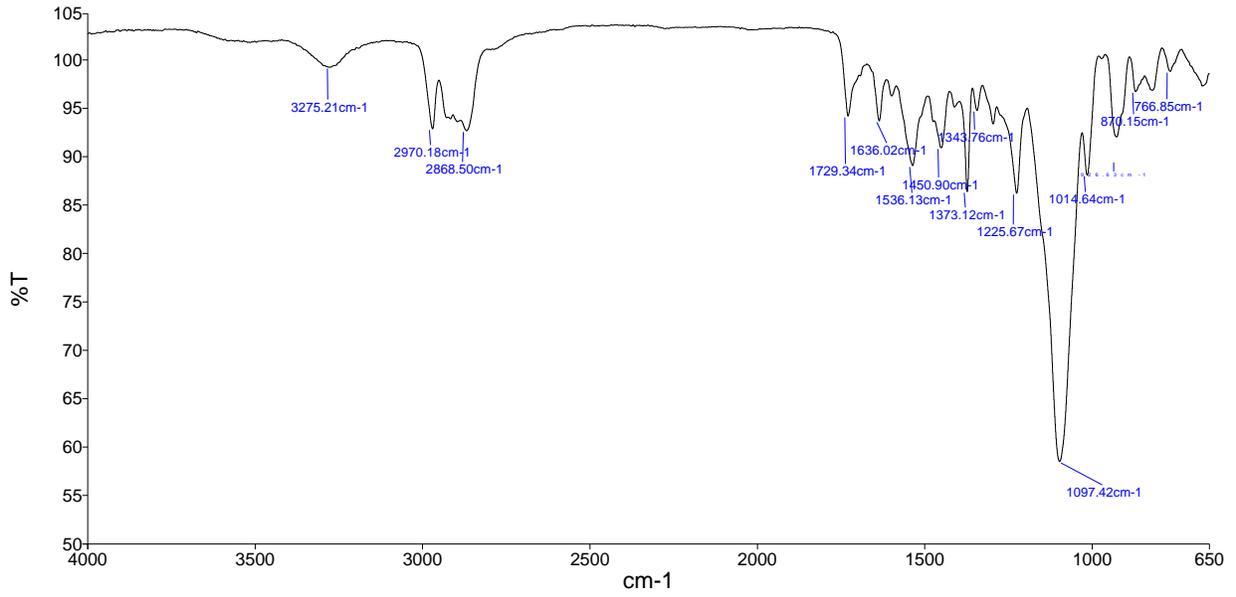


Figure 1. FTIR spectra of cast elastomer based on PPG 2000 polyol

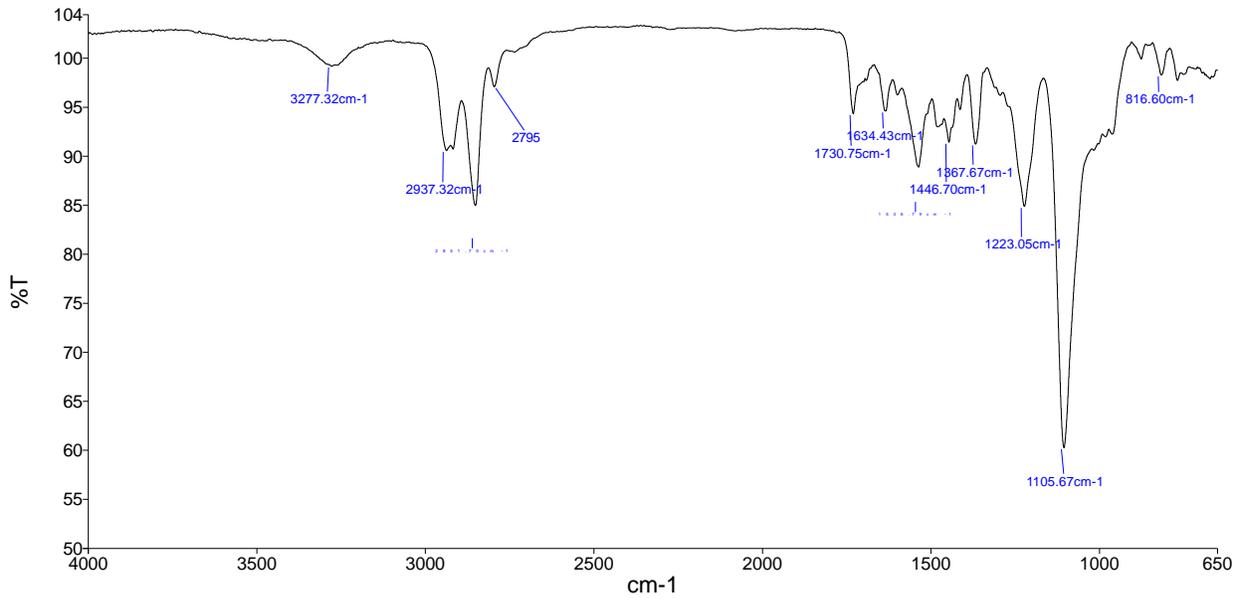


Figure 2. FTIR spectra of cast elastomer based on PTMG 2000 polyol

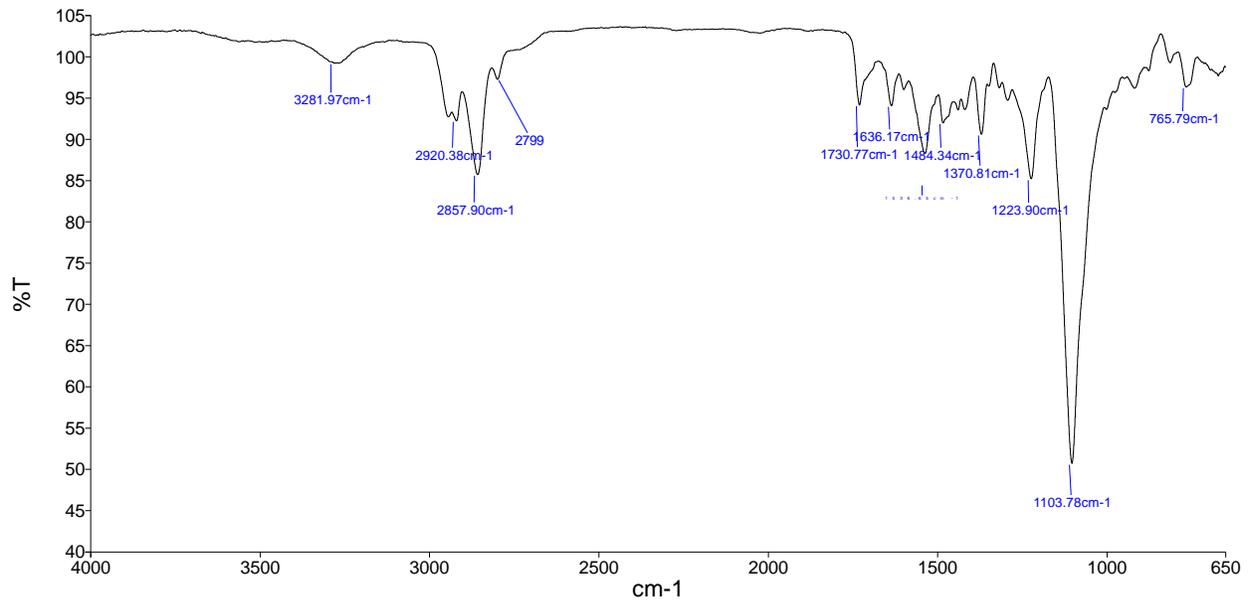


Figure 3. FTIR spectra of cast elastomer PO3G 2000 polyol

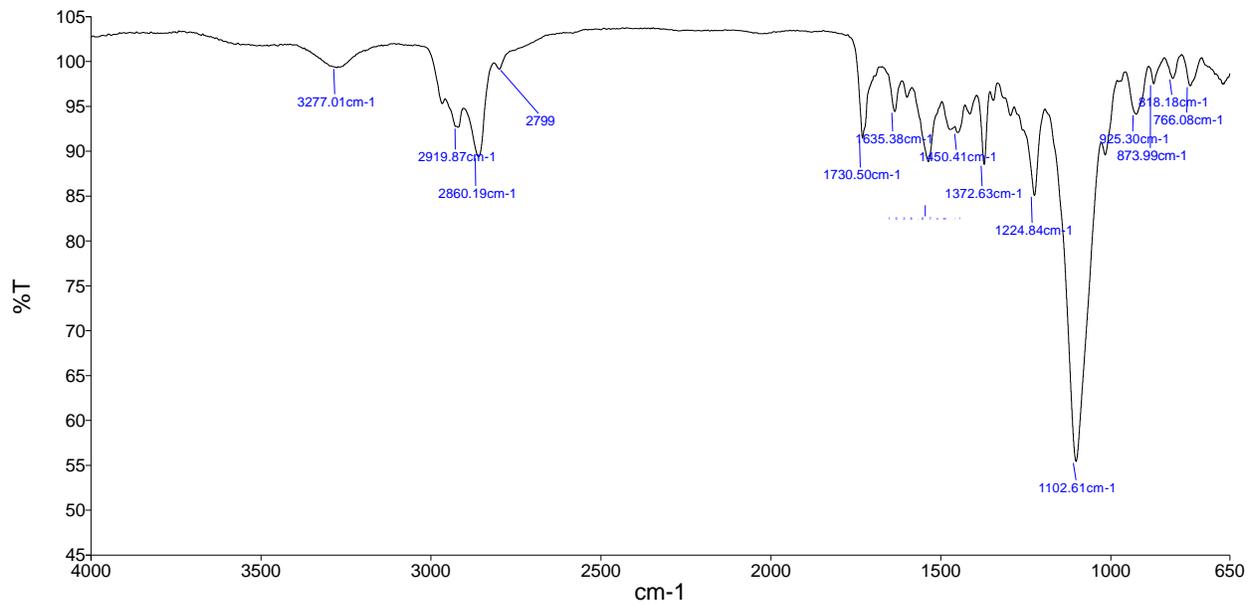


Figure 4. FTIR spectra of cast elastomer based on a blend of PPG2000/PO3G2000 (50/50 pbw)

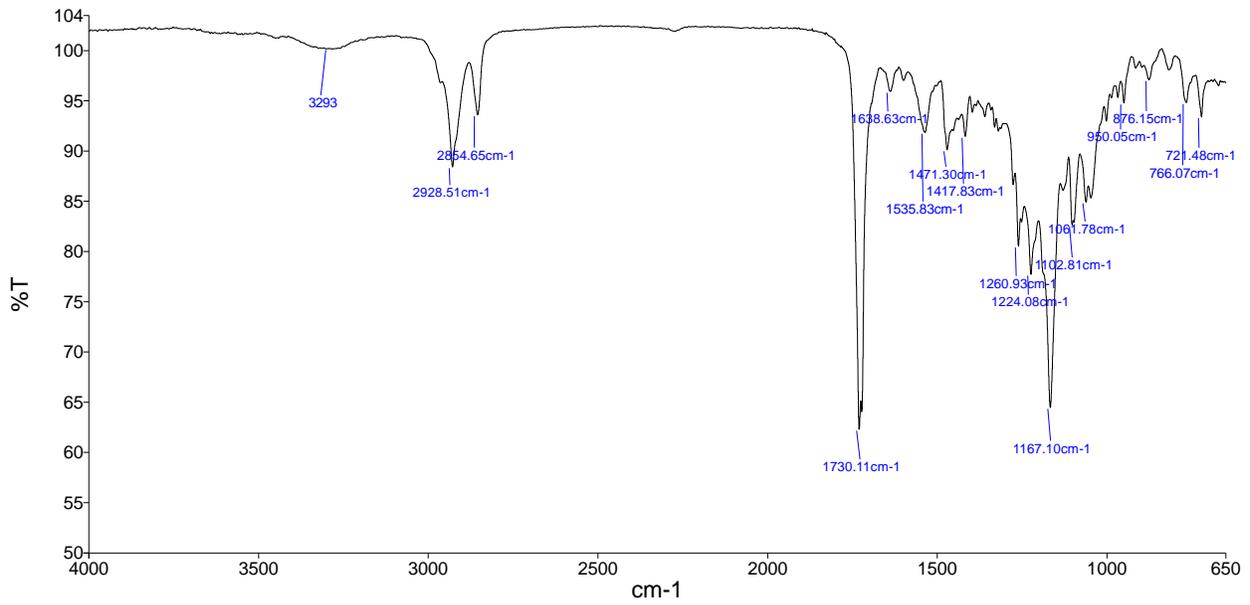


Figure 5. FTIR spectra of cast elastomer base on PDO-Sebacate 2000 polyol

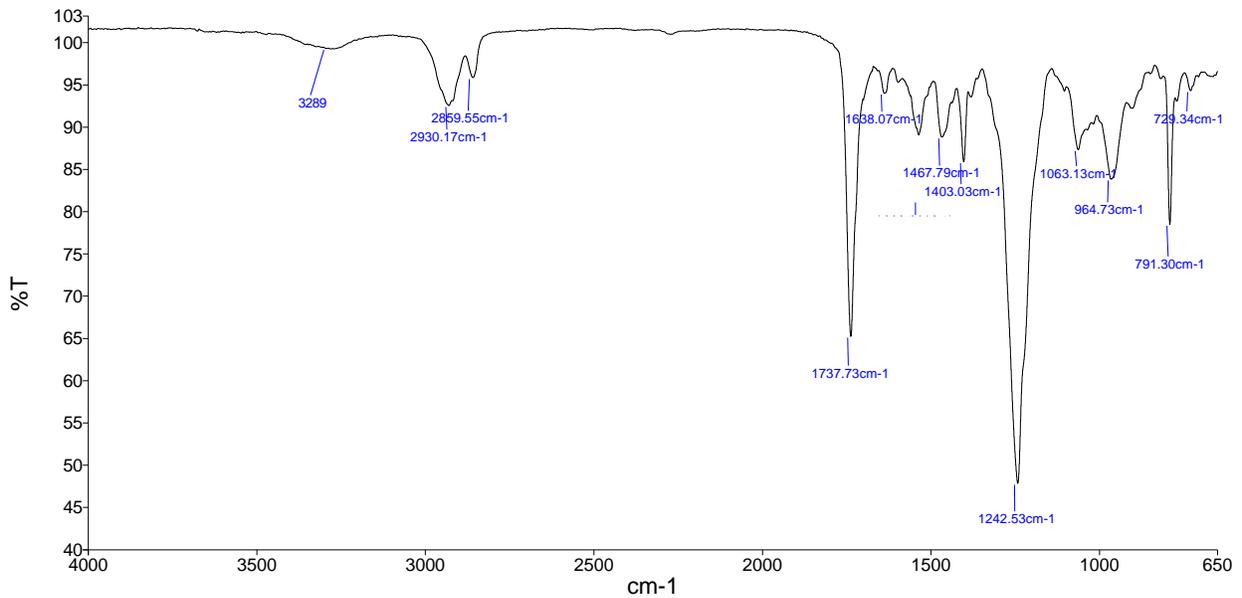


Figure 6. FTIR spectra of cast elastomer based on Polycarbonate 2000 MW polyol

BIOGRAPHIES



Sean L. Gahan

Sean is a Technical Service Manager for DuPont Tate & Lyle Bio Products Company since 2018. Sean previously worked in the coatings industry focusing on water-based wood coatings & sealants and printing inks. Sean is a graduate of Clemson University holding a Master of Science degree in Inorganic Chemistry. He is responsible for customer technical support and new business development related to the Bio-PDO™ product for all market segments and end-use applications in the Americas and EMEA.



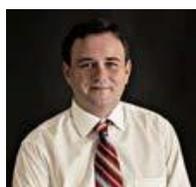
Michael T. Shen

Michael is the Technical Marketing Manager for DuPont Tate and Lyle Bio Products Company since 2013. Michael previously worked in the polyurethane industry with a focus on footwear. Michael is a graduate from the Fudan University holding a Master of Polymer Science degree. He is globally responsible for customer technical support and new business development related to the Bio-PDO™ product for all market segments and end-use applications.



Aisa Sendjarevic

Dr. Aisa Sendjarevic is a Research Director at Troy Polymers, Inc., a consulting and contract R&D laboratory specializing in polyurethanes. She has authored over 80 technical articles (papers, book chapters, and conference proceedings) and 14 US patents. She has over 30 years of research experience in isocyanate-based polymers and polyurethanes. Her research experience includes development of novel materials for medical, space, automotive, transportation and other industries. Specific interests include syntheses of isocyanate-based polymers and co-polymers of defined chemical structure and properties; morphology and structure property relationships in polyurethane elastomers, coatings and adhesives; polyurethanes based on renewable components.



Ibrahim Sendjarevic

Ibrahim Sendjarevic is Business Development Director at Troy Polymers, Inc. He is responsible for commercial development of new technologies ranging from development and marketing of sustainable raw materials to development of variety of polyurethane end-use applications. From 2009 to 2013 he served as President of InfiChem Polymers, where he led the team in implementation on novel recycling technology for production of polyols. He holds a Ph.D. in Chemical Engineering from the University of Illinois.

This paper may contain copyrighted material, the use of which may not have been specifically authorized by the copyright holder. To the extent this paper contains any such copyrighted material, the material is being used for nonprofit educational purposes reflecting a permitted “fair use” thereof as authorized under Title 17 U.S.C. Section 107. If any copyrighted material included from this paper is further used for purposes that go beyond “fair use,” the copyright holder’s permission is required.