

Dynamic Properties of High-Load Wheels Based on Cerenol[®] Polyol

ROBERT CZEISZPERGER, STEVE SENEKER

*Anderson Development Company
1415 E. Michigan Street
Adrian, MI 49221*

WILLIAM BARTELS, DENISE KENNEY

*Caster Concepts
16000 E. Michigan Avenue
Albion, MI 49224*

ABSTRACT

Cerenol[®] polyols are derived from 1,3-propanediol which is a bio-based monomer and would therefore be considered a 100% renewable resource polyol. The 1,3-propanediol is produced from corn sugar using a metabolic engineering process. Cerenol[®] polyols are polytrimethylene ether glycol (PTriMEG) and are produced using the same basic technology as polytetramethylene ether glycol (PTMEG).

In this paper, we compare the processability and physical/mechanical properties of TDI/MBOCA cured elastomers based on PTriMEG and PTMEG polyols. We produced high-load wheels based on these elastomers and measured the dynamic performance using a dynamometer. The dynamometer results showed that the dynamic performance of elastomers based on PTriMEG[®] polyol are comparable to those based on PTMEG.

INTRODUCTION

Cerenol[®] polyol is manufactured from 1,3-propanediol monomer. The 1,3-propanediol monomer (Bio-PDO[™]) is produced from a bio-based process which utilizes corn as a feedstock. This makes Bio-PDO[™] a 100% renewable resource monomer. So Cerenol polyol, which is derived from Bio-PDO[™], is a 100% renewable resource product as well [1]. The production of Bio-PDO monomer begins with the harvesting, drying and wet milling of corn where the sugar-rich starch is extracted. A patented microorganism is then added to the corn sugar which converts it into 1,3-propanediol or Bio-PDO[™] monomer. The microorganism is then deactivated and removed from the mixture along with the unreacted sugar, salts and water. The resulting mixture is refined to give pure 1,3-propanediol. This industrial biotechnology monomer can be used to create a new family of renewable resource products that offer high-performance properties in a wide range of end-use applications.

One of those high-performance products resulting from the biotechnology-based 1,3-propanediol is Cerenol[®] polyol. Cerenol[®] polyol is produced by the polymerization of 1,3-propanediol to form polytrimethylene ether glycol (PTriMEG). It uses the same general reaction process as is used to produce the high-performance polyol, polytetramethylene ether glycol (PTMEG). PTriMEG has the same general structure as PTMEG except for one less methylene group between the ether oxygens as shown in Figure 1. Since PTriMEG has a similar structure to PTMEG, it should have similar utility in end-use applications such as personal care, functional fluids, performance coatings and high-performance elastomers [2-5]. In this paper, we compare PTriMEG with PTMEG in high-performance elastomers. In particular, we evaluated the processability and physical/mechanical properties of toluene diisocyanate (TDI) prepolymers based on PTriMEG and PTMEG polyols cured with methylene bis-(ortho-chloroaniline) [MBOCA]. Both conventional and low-free TDI prepolymers were evaluated and compared. Additionally, we produced high-load wheels based on these elastomers and evaluated their dynamic performance on a dynamometer.

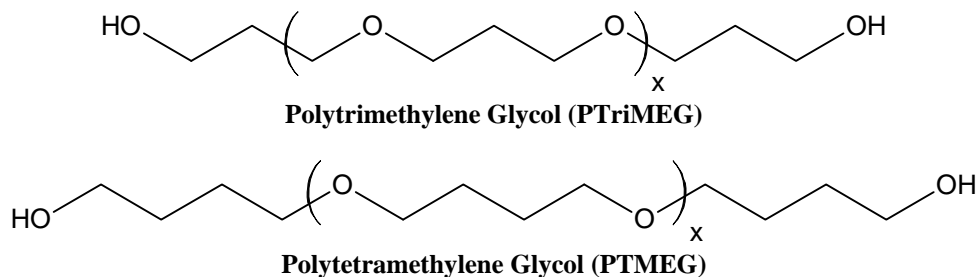


Figure 1

EXPERIMENTAL

Materials:

Isocyanate: 2,4-Toluene Diisocyanate (TDI-100); 80:20 2,4-:2,6-Toluene Diisocyanate (TDI-80)
 Polyols: Cerenol[®] H650, H1000 and H2000
 PTMEG-250, PTMEG-650, PTMEG-1000 and PTMEG-2000
 Curative: methylene bis-(ortho-chloroaniline) (MBOCA)

Prepolymer Preparation:

The toluene diisocyanate was charged to the reaction flask followed by the polyol (PTriMEG or PTMEG). The reaction mixture was acidified with 10 to 20 ppm of phosphoric acid to prevent unwanted isocyanate side reactions. This reaction mixture was stirred and heated to 80°C until the percent isocyanate content (% NCO) was slightly below the theoretical value. The %NCO was determined using ASTM D 2572-80 where the isocyanate prepolymer is reacted with an excess of dibutyl amine and then back titrated with standard hydrochloric acid. The prepolymer viscosity was determined using a Brookfield DV-II Pro Viscometer.

Cast Elastomer Preparation:

The TDI prepolymers were heated and degassed at 80°C (176°F). They were then cured with MBOCA at a 0.95 stoichiometry or NCO/OH of 1.05. The solution was stirred thoroughly by hand or with a StateMix Vortex mixer and then poured into steel molds preheated to 100°C (212°F). The potlife was determined as the time required for the solution to become no longer pourable and the demold time was measured as the time where the elastomer could be demolded without being deformed or damaged (good “green strength”). After the elastomers were demolded, they were post cured at 100°C (212°F) for approximately 16 hours.

Physical/Mechanical Property Testing:

The elastomers were conditioned at ambient temperature for at least two weeks prior to physical/mechanical property testing. We performed the following tests using specified ASTM methods as shown in Table 1.

Table 1 – Tests and ASTM Methods

<i>Test</i>	<i>ASTM Designation</i>
Shore Hardness	D2240
Tensile Properties	D412
Die C Tear Strength	D624
Split Tear Strength	D1938
Compression Set	D395, Method B
Bashore Rebound	D2632

High-Load Wheel Casting:

The polyurethane elastomer solution was poured onto cast iron cores which had been grit-blasted, cleaned with solvent, coated with an adhesive and preheated to 250°F. The preheated core at 250°F was placed in the preheated mold at 212°F and the elastomer solution was cast and cured at 212°F. The demolded wheels were postcured for 16 hours at 212°F. The finished wheels were eight inches in diameter, two inches wide and the tread thickness was 0.38 inches. The wheels were conditioned at least one month prior to dynamometer testing.

Dynamometer Testing:

The dynamometer used for this study was developed by Caster Concepts and is called the Dynamic Wheel Endurance Tester (DWET). The DWET is a fully computerized and automated wheel testing platform capable of simulating realistic use conditions in order to measure, analyze and verify the performance of industrial casters or high-load wheels [6]. For this study, the wheel was initially subjected to an 800 pound load at six miles per hour. The load was increased by 200 pounds every two hours until the wheel failed. Failure occurred by two modes: 1) urethane tread melting or 2) debonding of the urethane tread from the metal hub. During the test, an infrared thermometer measured the temperature on the urethane tread at the point where it was bonded with the metal hub. A picture of the dynamometer is shown in Figure 2.



Figure 2: Caster Concepts' Dynamic Wheel Endurance Tester

RESULTS AND DISCUSSION

Comparison of PTriMEG Polyol with PTMEG

A comparison of the typical properties of PTriMEG polyols with PTMEG are shown in Table 2. PTriMEG polyols are available in the same molecular weights as PTMEG of 650, 1000 and 2000. The viscosities of the PTriMEG polyols are equivalent to PTMEG at a 650 molecular weight, but have significantly lower viscosities as the molecular weights increase to 2000. Lower polyol viscosity could translate to a lower prepolymer viscosity.

Unsaturation is a measure of the monol content of the polyol. PTriMEG polyols have unsaturations from 0.010 meq/gm at 650 MW up to 0.015 meq/gm at 2000 MW. PTMEG polyols do not have any significant unsaturation or monol content. Monol will act as a chain terminator in a polymerization reaction resulting in a lower polymer molecular weight and potentially lower physical/mechanical properties.

When producing aromatic isocyanate prepolymers it is important that the overall reaction mixture is slightly acidic. If the reaction mixture is alkaline or basic it will cause isocyanate side reactions which will form crosslinks and could gel the prepolymer. PTriMEG polyols have some alkalinity, so it is important that the reaction mixture be acidified with something like phosphoric acid or benzoyl chloride. Even though PTMEG polyols are neutral, it is recommended that they be acidified as well.

Table 2: Typical Properties of PTriMEG and PTMEG Polyols

Molecular Weight	650		1000		2000	
	H650	PTMEG-650	H1000	PTMEG-1000	H2000	PTMEG-2000
Polyol Type						
Viscosity, cps @ 40 C	150	150	230	270	840	1250
Unsaturation, meq/gm	0.010	<0.001	0.013	<0.001	0.015	<0.001
Alkalinity Number, meqOH/kg x 30	0.4	-0.4	0.8	-0.4	1.1	-0.6

Comparison of TDI Prepolymers based on PTriMEG and PTMEG Polyols

Our objective was to design conventional and low-free TDI prepolymers based on PTriMEG that would result in elastomers with physical/mechanical properties comparable to those based on PTMEG. Table 3 shows the resulting TDI prepolymers based on PTriMEG and PTMEG which when cured with MBOCA would give Shore hardnesses of 83A, 95A and 73D.

Table 3: TDI Prepolymer Properties based on PTriMEG and PTMEG Polyols

Hardness	83 Shore A		95 Shore A		73 Shore D	
	PTriMEG	PTMEG	PTriMEG	PTMEG	PTriMEG	PTMEG
Polyol Type						
% NCO Content	3.3	3.2	6.2	6.2	9.1	8.5
Viscosity @ 70 C, cps	1340	2600	420	650	670	950
Viscosity @ 100 C, cps	530	800	140	200	170	230

The results in Table 3 showed that the % NCO required to achieve a given hardness was similar for both PTriMEG and PTMEG at hardnesses of 83A and 95A. However, a higher % NCO was required to obtain a 73D hardness with PTriMEG polyol compared to the PTMEG (9.1 vs 8.5). The viscosity results show that the prepolymers based on PTriMEG have significantly lower viscosities than those based on PTMEG. In particular, the PTriMEG based prepolymer at a 3.3% NCO had nearly half the viscosity of its PTMEG counterpart. This may be due in part to the lower viscosity of the PTriMEG H2000 versus PTMEG-2000 since these were the primary molecular weight polyols used in the lowest %NCO prepolymers.

In Table 4, we show the property comparison of low-free TDI prepolymers which would give a 95A hardness if cured with MBOCA. The results show the same trends as the “conventional” TDI prepolymers. The % NCO to obtain a 95 Shore A hardness is comparable for both PTriMEG and PTMEG and the PTriMEG based prepolymer had a significantly lower viscosity.

Table 4: Low Free TDI Prepolymer Properties

Hardness	95 Shore A	
	PTriMEG	PTMEG
Polyol Type		
% NCO Content	6.35	6.20
Viscosity @ 70 C, cps	365	450
Viscosity @ 100 C, cps	120	180

Elastomer Comparison of TDI Prepolymers based on PTriMEG and PTMEG Cured with MBOCA

The conventional TDI prepolymers based on PTriMEG and PTMEG were cured with MBOCA resulting in elastomers with Shore hardnesses of about 83A, 95A and 73D. A summary of the processability and the physical/mechanical properties is given in Table 5.

We evaluated the processability by determining the pot life and demold time of the elastomer systems. The pot life of the PTriMEG based systems were comparable to those based on PTMEG. The PTriMEG based systems took longer to achieve good green strength as shown by the longer demold times. This may be due to the fact that PTriMEG polyol contains a small amount of monol which could reduce the polymer molecular weight build over time.

An overview of the physical/mechanical properties shows that the elastomers based on PTriMEG were comparable to those based on PTMEG. The largest differences were in the stress/strain or tensile properties. The PTriMEG elastomers consistently had lower tensile strengths but higher elongations at break. This is the type of trend reported when comparing elastomers based on polypropylene glycol (PPG) to those based on PTMEG [7]. The explanation is that PTMEG elastomers have a tendency to stress crystallize when elongated which lowers the percent elongation but increases the tensile strength. Elastomers based on PPG cannot stress crystallize due to the methyl groups sticking out along the backbone, therefore they have higher elongations, but lower tensile strengths. We believe that the PTriMEG backbone may have less of a tendency to stress crystallize than the PTMEG backbone resulting in a higher elongation and lower tensile strength. If one considers the “toughness” of an elastomer as the area under the stress/strain curve, then the elastomers based on PTriMEG are just as tough or tougher than those based on PTMEG as shown by the energy at break in Table 5. A comparison of the stress/strain curves are shown in Figures 3, 4 and 5. The tear strengths and compression sets of the elastomers were similar. The Bashore rebound of the 95A and 73D elastomers were comparable, however the softer 83A elastomer had a lower rebound with the PTriMEG backbone. We believe the lower rebound may be due to the small amount of monol content which would have a tendency to absorb energy.

Table 5: TDI/MBOCA Cured Elastomer Comparison: Processability and Physical/Mechanical Properties

Hardness	83 Shore A		95 Shore A		73 Shore D	
	PTriMEG	PTMEG	PTriMEG	PTMEG	PTriMEG	PTMEG
Polyol Type						
NCO Content, %	3.3	3.2	6.2	6.2	9.1	8.5
Renewable Content, %	76	0	62	0	42	0
Pot Life, minutes	5.0	5.0	6.0	5.0	2.0	2.75
Demold Time, minutes	40	30	25	20	15	10
Hardness, Shore	82A	83A	96A	95A	72D	73D
Elongation, %	810	500	440	350	310	220
Tensile Strength, psi	4500	4900	6800	7400	7070	7830
100% Modulus, psi	680	810	1920	2130	4520	5310
300% Modulus, psi	1040	1500	3100	5300	6460	-----
Energy to Break, in*lbf	234	158	232	232	331	258
Die C Tear Strength, pli	380	340	490	480	1110	1100
Split Tear Strength, pli	85	60	140	145	285	280
Compression Set, % 22 hrs @ 70 C	29	28	32	30	n.d.	n.d.
Bashore Rebound, %	59	64	48	46	n.d.	58

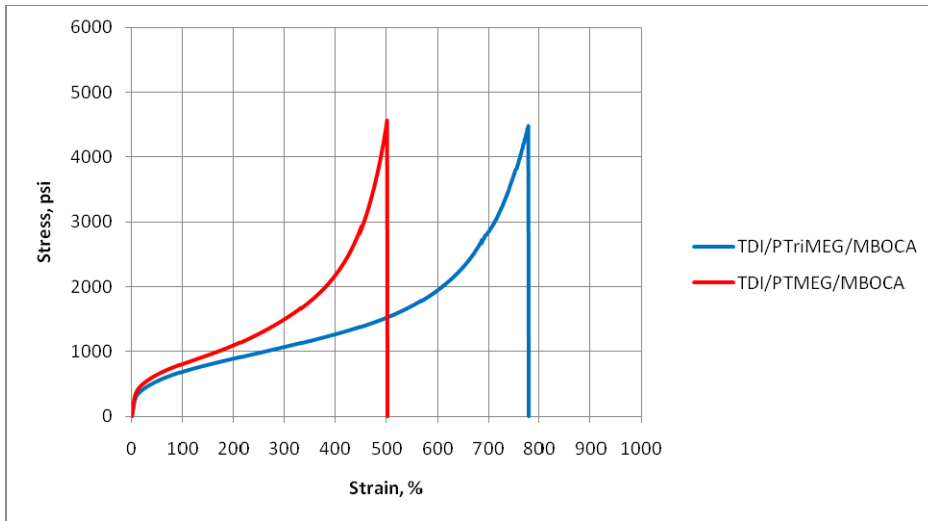


Figure 3: Stress/Strain Curves – 83A TDI Elastomers

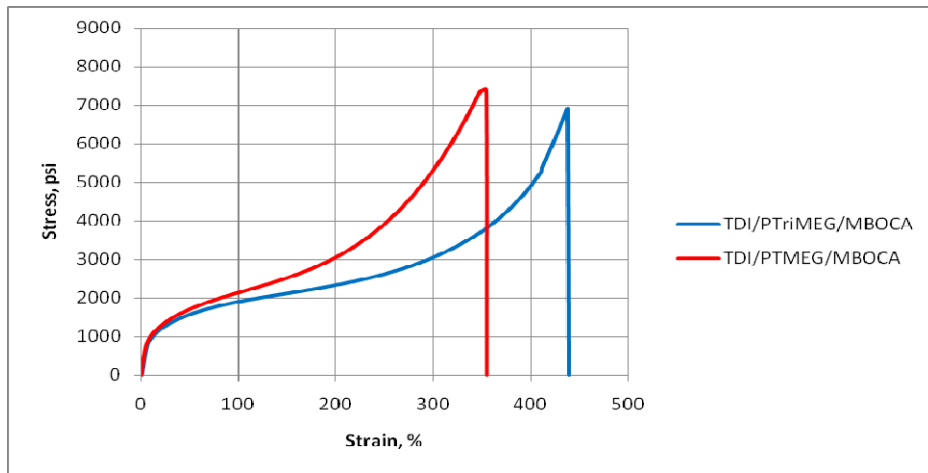


Figure 4: Stress/Strain Curves – 95A TDI Elastomers

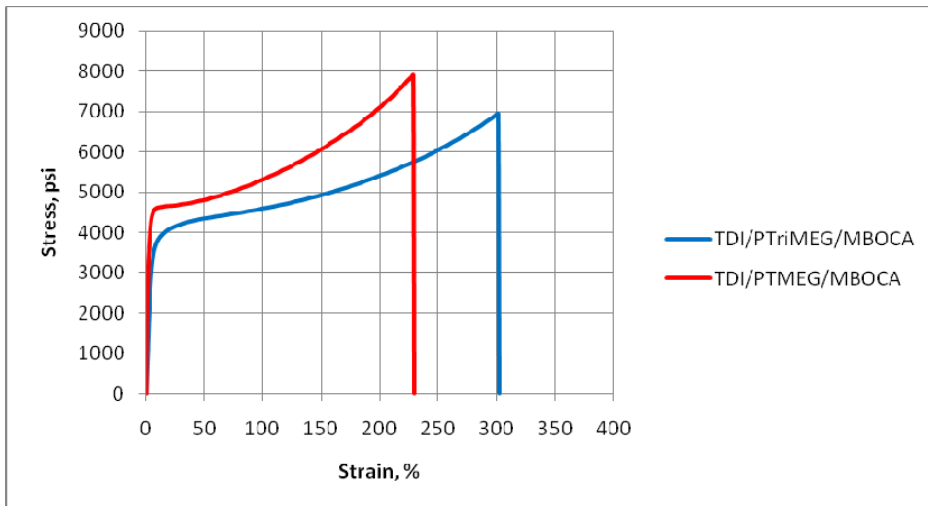


Figure 5: Stress/Strain Curves – 73D TDI Elastomers

The low-free TDI prepolymers cured with MBOCA resulted in elastomers with a hardness of about 95 Shore A. The processability and physical/mechanical properties of these elastomers are shown in Table 6. As expected, the elastomers based on the low-free TDI prepolymers showed the same processability trends as the conventional TDI prepolymers with comparable pot lives and longer demold time of the PTriMEG based elastomer. In regards to physical/mechanical properties, the PTriMEG elastomer once again had a lower tensile strength and higher elongation at break than the PTMEG elastomer. The toughness of the PTriMEG and PTMEG elastomers are comparable as shown by the area under the stress/strain curves in Figure 6 which is the energy to break in Table 6.

Table 6: Low Free TDI/MBOCA Cured Elastomer Comparison

Hardness	95 Shore A	
	PTriMEG	PTMEG
Polyol Type		
NCO Content, %	6.1	6.2
Renewable Content, %	62	0
Pot Life, minutes	6.5	5.5
Demold Time, minutes	25	20
Hardness, Shore	96A	95A
Elongation, %	400	320
Tensile Strength, psi	6360	7560
100% Modulus, psi	2180	2440
300% Modulus, psi	3500	6400
Energy to Break, in*lbF	236	223
Die C Tear Strength, pli	490	550
Split Tear Strength, pli	130	130
Compression Set, % 22 hrs @ 70 C	31	32
Bashore Rebound, %	47	48

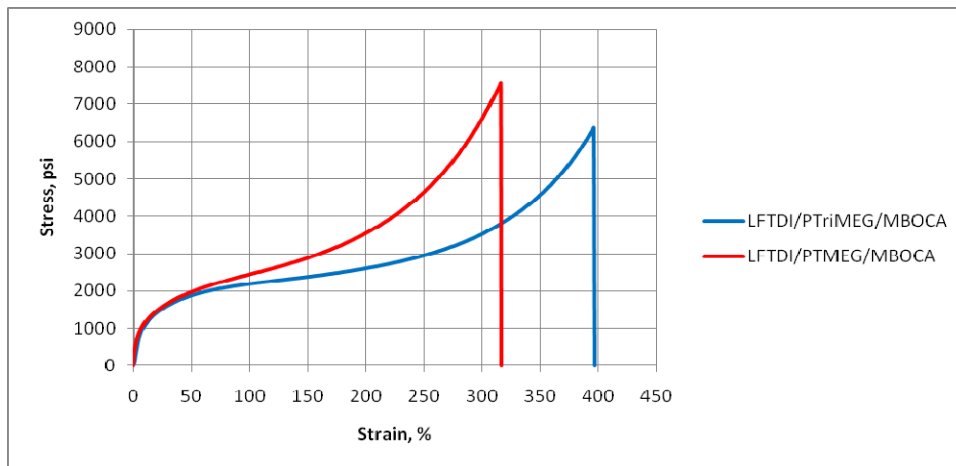


Figure 6: Stress/Strain Curves – 95A Low-Free TDI Elastomers

In summary, we found that the processability and physical/mechanical properties of elastomers based on PTriMEG were comparable to those based on the high-performance polyether polyol, PTMEG. PTriMEG is a high-performance polyol that has a 100% renewable content resulting in elastomers with renewable contents of 42 to 76 weight percent as shown in Tables 5 and 6.

Dynamometer Testing of Elastomers based on PTriMEG and PTMEG

One of the high-performance applications for PTMEG elastomers is as a tread for high-load or caster wheels. So we evaluated the dynamic performance of elastomers based on PTriMEG versus PTMEG by casting high-load wheels and testing them on a dynamometer.

We used conventional and low-free TDI prepolymers based on PTriMEG and PTMEG using MBOCA to give 95 Shore A elastomers which is a typical hardness for high-load wheels. We cast two 8" x 2" wheels of each type and conditioned them at ambient temperature for at least one month prior to testing. The dynamic performance was determined using Caster Concepts' dynamometer which is called a Dynamic Wheel Endurance Tester. The wheels were subjected to an initial load of 800 pounds and then the load was increased by 200 pounds every two hours until wheel failure.

We used conventional TDI prepolymers based on PTriMEG and PTMEG cured with MBOCA. Elastomers based on low-free TDI prepolymers were used as well. There was a total of four formulations. We cast and evaluated two wheels of each formulation for a total of eight wheels. The polyurethanes based on conventional TDI prepolymers are identified as TDI/PTriMEG/MBOCA and TDI/PTMEG/MBOCA and those based on low-free TDI prepolymers are identified as LFTDI/PTriMEG/MBOCA and LFTDI/PTMEG/MBOCA.

The temperature of the tread at the point where it is in contact with the metal hub was recorded during the test as shown in Figures 7 and 8. With each increase in the load, the tread temperature would increase initially and then level out. The load would continue to increase as would the temperature until the wheel failed. The wheel would fail by either the urethane tread getting so hot that it melted or the urethane tread would debond or delaminate from the metal hub or a combination there of.

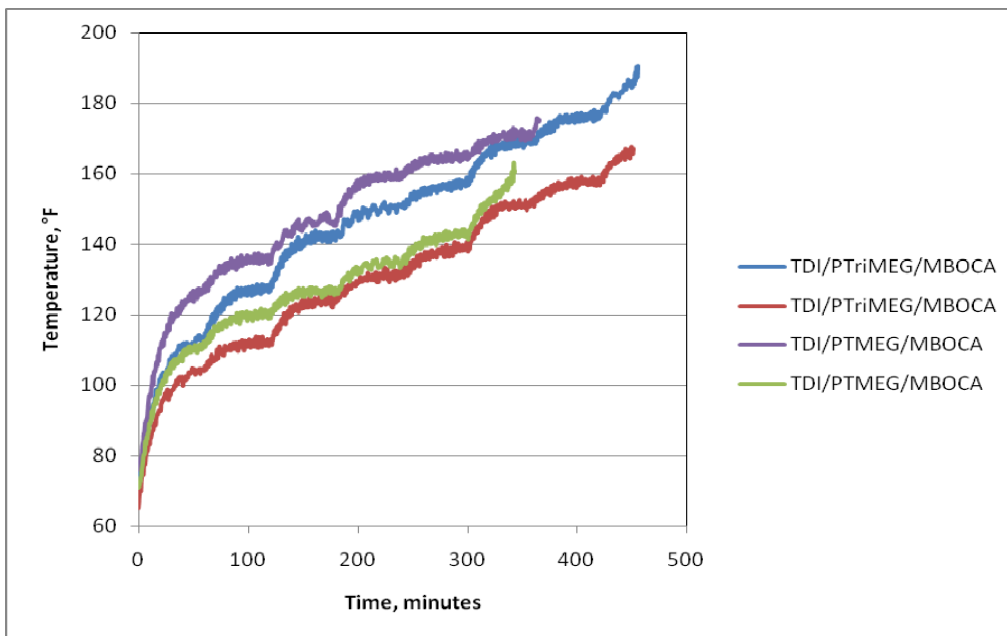


Figure 7: Tread Temperature vs Time for TDI Elastomers

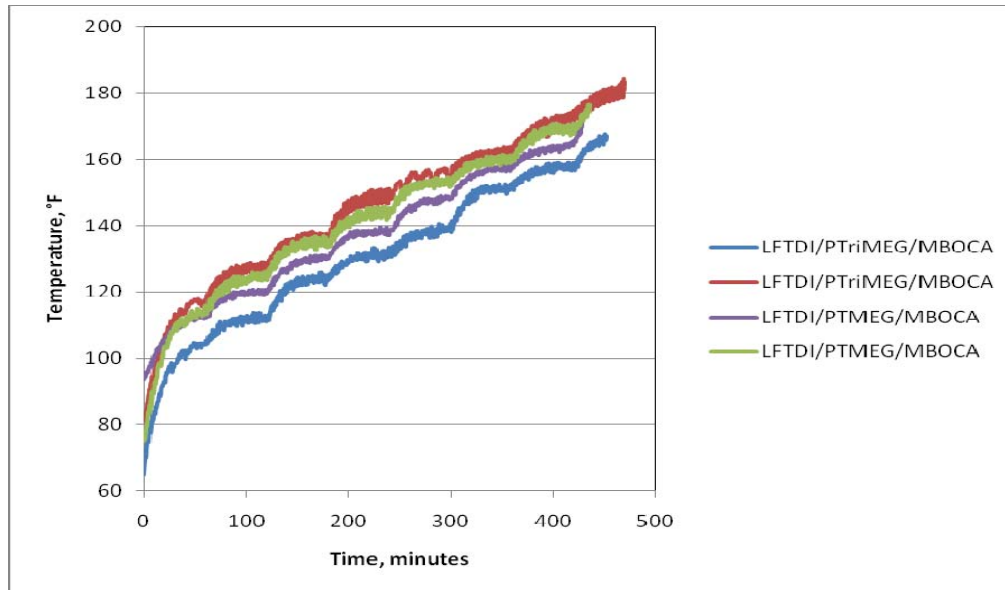


Figure 8: Tread Temperature vs Time for Low-Free TDI Elastomers

A summary of the high-load wheel failure results is shown in Table 7. The results showed that the load at failure was about 200 lbs higher for the elastomers based on PTriMEG than those based on PTMEG (2200 vs 2000 lbs). Overall, the elastomers based on low-free TDI prepolymers performed better than those based on conventional TDI prepolymer counterparts, as the load at failure was 200 lbs higher. The LFTDI/PTriMEG/MBOCA wheel performed best with a load at failure of 2400 lbs. The primary failure mode for all the wheels was bond failure or delamination from the metal hub. One wheel showed signs of polymer melting which was the wheel that ran at the highest temperature.

The temperatures at failure ranged from 160 to 190 F. The wheel to wheel temperature difference was higher for the conventional TDI elastomer treads. This temperature difference is typical when running only two wheels of each formulation. We would need to perform some more repetitive tests to determine a more accurate average failure temperature.

Table 7: Dynamometer Results for 95A High-Load Wheels

Polyurethane Type	Failure Temperature (°F)	Load at Failure (lbs)	Failure Mode
TDI/PTriMEG/MBOCA	190	2200	Bond/Polymer
	170	2200	Bond
TDI/PTMEG/MBOCA	175	2000	Bond
	160	1800	Bond
LFTDI/PTriMEG/MBOCA	170	2400	Bond
	180	2400	Bond
LFTDI/PTMEG/MBOCA	170	2200	Bond
	175	2200	Bond

CONCLUSIONS

We found that the processability of high-performance elastomers based on TDI prepolymers cured with MBOCA using PTriMEG and PTMEG were comparable. The pot lives or pour times were equivalent. The PTriMEG elastomers had slightly longer demold times. We believe this may be due to the monol content of the PTriMEG. Surprisingly, the TDI prepolymers based on PTriMEG had significantly lower viscosities.

The physical/mechanical properties of the elastomer were comparable as well. The Die C tear, split tear and compression sets were equivalent. The stress/strain curves showed that the PTriMEG elastomer had lower tensile strengths but higher elongations indicating that they may stress crystallize less than those based on PTMEG. The overall toughness of the elastomers were equivalent as shown by the area under the stress/strain curve. The Bashore rebound of the PTriMEG elastomers was slightly lower which may be due to the monol content.

The dynamometer testing showed that the wheels based on the PTriMEG elastomers had slightly better dynamic performance than those based on PTMEG since the load to failure was 200 lbs higher. The elastomers based on low-free TDI prepolymers performed better than those based on the conventional TDI prepolymers by 200 lbs load.

Overall, PTriMEG was very comparable to PTMEG in high-performance TDI/MBOCA cured elastomers. PTriMEG can truly be considered a high-performance polyether polyol with the added benefit of having a 100% renewable resource content. The renewable resource contents of the resulting elastomers were in the 40 to 80 weight percent range depending on the hardness.

REFERENCES

1. U.S. Patents 6,977,291, 7,074,969 and 7,323,539 assigned to E.I. du Pont de Nemours and Company.
2. U.S. Patent 6,852,823 assigned to E.I. du Pont de Nemours and Company.
3. U.S. Patents 6,875,514, 7,169,475 and 7,268,182 assigned to E.I. du Pont de Nemours and Company.
4. Sunkara, H.B., "DuPont™ Cerenol™: A Novel Renewably Sourced Ingredient for Polyurethanes" a technical conference paper presented at the UTECH Europe 2009 Conference, March 31-April 2, 2009.
5. Sunkara, H.B. and Demarest, C., "DuPont™ Cerenol® Polyol: A Novel Renewably Sourced Ingredient for Polyurethanes" a technical conference paper presented at the CPI Polyurethanes 2010 in Houston, TX, October 11-13, 2010.
6. Lee, Elmer, "Dynamic Wheel Endurance Tester", Caster Concepts, Inc., 2007.
<http://www.casterconcepts.com/media/Dynamic%20Wheel%20Endurance%20Tester.pdf>
7. Seneker, S.D., Barksby, N. and Lawrey, B.D., "New Ultra-Low Monol Polyols with Unique High-Performance Characteristics", a technical conference paper presented at the SPI Polyurethanes 1996 in Las Vegas, NV, October 1996.

Cerenol® is registered trademark of E.I. du Pont de Nemours and Company.

Bio-PDO™ is a registered trademark of the DuPont Tate & Lyle Bio Products Company, LLC.

BIOGRAPHIES

ANDERSON DEVELOPMENT COMPANY

Robert Czeiszperger

Robert Czeiszperger is currently a Senior Chemist in the Polyurethane Elastomers Group at Anderson Development Company. He has Bachelor's degrees in Chemistry and Mathematics from Siena Heights University and earned a Master's degree in Polymer and Coatings Technology from Eastern Michigan University in 2003. He has been working at Anderson Development Company since 1998.

Steve Seneker

Steve Seneker is a Senior Scientist in the Polyurethane Elastomers Group at Anderson Development Company. He received his B.A. Degree in Chemistry from Point Loma Nazarene College. He received his Ph.D. in Chemistry with an emphasis on Polymers and Coatings from North Dakota State University. After graduation in 1986, he joined Mobay Corporation (currently Bayer Material Science). In 1993, he joined

ARCO Chemical/Lyondell Chemical. He has been working at Anderson Development Company since 2000.

CASTER CONCEPTS, INC.

William Bartels

William Bartels is currently a third year junior at Kettering University, pursuing a degree in mechanical engineering. He has been an intern at Caster Concepts for over two years and has been the primary operator of their dynamometer.

Denise Kenney

Denise Kenney is currently a Polymer Engineer at Reaction Industries, LLC, a subsidiary of Caster Concepts, Inc. She earned her Bachelor's degree in Materials Science and Engineering from Michigan State University in 2006. Later that year, she joined Reaction Industries, LLC.