

# A Broad Evaluation of PO3G Polyols versus PTMEG in Low Free TDI-based Polyurethane Elastomers

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## ABSTRACT

Bio-based polytrimethylene ether glycol (PO3G) diols have been on the market for a number of years. They are derived from bio-based 1,3 propanediol. Previous work with conventional MDI and TDI-based elastomers has shown that the PO3G diols are as good as or better than PTMEG in many respects. This paper expands upon previous research by evaluating new compounds based on low free TDI technology which are safer than conventional MDI/TDI prepolymers. A broader range of elastomer hardness was also investigated, especially softer elastomers, which can benefit from the lower viscosity that PO3G polyols and prepolymers exhibit versus PTMEG. Mechanical properties including tensile strength, tear resistance, compression properties, abrasion resistance, and flex fatigue were evaluated with these new compounds versus PTMEG-based elastomers.

## INTRODUCTION

Incorporating “green” polyol technology into the cast polyurethane industry has had relatively low success in the last 10-15 years, especially in high performance applications. In other polyurethane segments, including foam and coatings, more penetration to the market has occurred. This is probably in part due to the types of raw materials available. In many cases, “green” polyols based on several different feedstocks (soybeans, cashew nuts, castor oil, etc.) have functionalities higher than 2.0. Functionality higher than 2.0 causes a decrease in important elastomer properties such as tear strength, elongation, and abrasion resistance, lowering the overall performance. Other applications, such as foam, can benefit from higher functionality. PO3G diols, however, do show promise in that they have been shown to create polyurethane elastomers with not only suitable physical properties, but performance comparable to PTMEG-based elastomers [1,2], which are regarded in cast polyurethane as high-performance polyether materials.

Specifically, PO3G-based elastomers have been shown to have as good or better dynamic properties in high load wheels [1], better overall toughness based on energy to break [1,2], comparable prepolymer stability [1], and lower prepolymer viscosity when compared to similar PTMEG-based materials.

Chemically, the PO3G diols have one less methylene group than in PTMEG (Figure 1). This results in diols that are less crystalline (better liquidity) and lower viscosity, which translates to easier processing for the cast urethane processor, especially for prepolymers with low %NCO (<4%) requiring high molecular weight polyols. With PTMEG, high molecular weight diols (2000-3000 Daltons) are solid at ambient temperature, whereas PO3G diols are liquid.

Former research on PO3G diols focused on conventional (not low free monomer) TDI-based and MDI-based elastomers. In this research, only low free TDI prepolymers (TDI monomer < 0.1%) were considered. They are inherently safer than conventional TDI prepolymers with a typical monomer content of up to 2% and MDI materials which have a monomer content of 10-30% on average. The prepolymers were cured with MBOCA (4,4 methylene-bis(2-ortho-chloroaniline) and previously unassessed DMTDA (3,5-Dimethylthio-2,4-(or 2,6-) toluenediamine. DMTDA is a liquid at room temperature like the PO3G-based prepolymers, providing processors with the advantage of an all liquid system. These two diamine curatives embody the majority of TDI-based cast elastomers in the market.

Hybrid prepolymers made from blends of PO3G and PTMEG were also investigated, looking for any synergistic (or negative) effects, or if the blends would give linear relationships based on the amount of PO3G added. Levels of 50% and 20% PO3G were evaluated, and they are compared with 100% PO3G and 100% PTMEG. To be clear, these hybrid

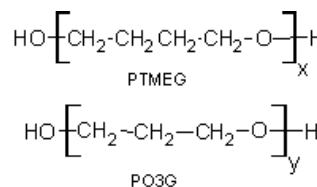


Figure 1

prepolymers were synthesized as random copolymer, not as blends of the 100% PO3G and 100% PTMEG prepolymers. They were also evaluated with MBOCA and DMTDA.

## EXPERIMENTAL

### Prepolymer Preparation

The general method of prepolymer preparation was to react an excess of TDI with the polyol(s) at 65-70°C. Once fully reacted, the materials were put through a wiped-film evaporator at high temperature and under high vacuum to remove any TDI monomer down to a level less than 0.1% by weight. The finished prepolymers had %NCO content and viscosity at 60°C measured. Table 1 is a summary of the prepolymers used, with each comparable PO3G / PTMEG side by side. In each case, the goal was to target the same %NCO and Hardness. Table 2 lists the hybrid prepolymers. A low, mid-range, and high hardness were selected for evaluation.

Prepolymer ID	A <sub>3</sub>	A <sub>4</sub>	B <sub>3</sub>	B <sub>4</sub>	C <sub>3</sub>	C <sub>4</sub>	D <sub>3</sub>	D <sub>4</sub>
Polyol MW(s)	2700	3000/2000	2000	2000	2000/1000	2000/1000	1000	1000
Appearance	Amber liquid	Waxy solid	Amber liquid	Waxy solid	Amber liquid	Light yellow liquid	Amber liquid	Light yellow liquid
%NCO	2.64	2.72	3.31	3.38	4.03	4.03	5.66	6.02
Viscosity@60°C	1821	2520	1168	1826	998	1648	651	753
Target Hardness	<85A	<85A	85A	85A	90A	90A	95A	95A

Prepolymer ID	E <sub>3</sub>	E <sub>4</sub>	F <sub>3</sub>	F <sub>4</sub>	G <sub>3</sub>	G <sub>4</sub>	H <sub>3</sub>	H <sub>4</sub>
Polyol MW(s)	1000/500	1000/650	500/1000	650/1000	500/1000	650/210	500/250	650/210
Appearance	Amber liquid	Light yellow liquid	Amber liquid	Light yellow liquid	Amber liquid	Light yellow liquid	Amber liquid	Light yellow liquid
%NCO	6.28	6.33	7.42	7.50	8.52	8.60	9.20	9.41
Viscosity@60°C	648	758	641	678	661	714	676	788
Target Hardness	50D	50D	60D	60D	70D	70D	75D	75D

A subscript 3 denotes PO3G and a subscript 4 denotes PTMEG

Prepolymer ID	B <sub>3</sub>	B <sub>34-50</sub>	B <sub>34-20</sub>	B <sub>4</sub>	E <sub>3</sub>	E <sub>34-50</sub>	E <sub>34-20</sub>	E <sub>4</sub>	G <sub>3</sub>	G <sub>34-50</sub>	G <sub>34-20</sub>	G <sub>4</sub>
% PO3G	100	50	20	0	100	50	20	0	100	50	20	0
Polyol MW(s)	2000	2000	2000	2000	1000/500	Blend	Blend	1000/650	500/1000	Blend	Blend	650/210
Appearance	Amber liquid	Viscous liquid/semi-solid	Waxy solid	Waxy solid	Amber liquid	Amber liquid	Yellow liquid	Light yellow liquid	Amber liquid	Yellow liquid	Yellow liquid	Light yellow liquid
%NCO	3.31	3.41	3.40	3.38	6.28	6.27	6.24	6.33	8.52	8.62	8.56	8.60
Viscosity@60°C	1168	1515	1796	1826	648	699	732	758	661	686	696	714
Target Hardness	85A	85A	85A	85A	50D	50D	50D	50D	70D	70D	70D	70D

A subscript 3 denotes PO3G and a subscript 4 denotes PTMEG;  
34-50 denotes 50% PO3G/50% PTMEG; 34-20 denotes 20% PO3G/80% PTMEG

### Elastomer Preparation and Testing

The elastomer samples were cast with standard practices. The prepolymer temperature was in the range of 70-85°C and the mold temperature was 100°C. MBOCA was in the range 110-120°C while the DMTDA was at ambient temperature. The elastomers were cast at an OH/NCO ratio (stoichiometry) of 0.95 and postcured for ~16-20 hours at 100°C. The cured specimens were conditioned a minimum of 14 days at 23°C/50%RH. For compression set, rotary abrasion testing, and flex fatigue, the minimum conditioning time was 28 days.

Elastomer testing was performed per the ASTM standards listed in Table 3. For the abrasion testing, method B was used with a rotating specimen and a load of 10N on the specimen. For the DeMattia flex fatigue testing, the standard frequency of 5 Hz and clamp separation of 0.75” at the closest and 3” at the farthest was used.

Property	Standard
Hardness	D2240
Tensile Properties	D412
Die C Tear	D624
Split Tear	D1938
Bashore Resilience	D2632
Compression Set	D395
Abrasion Resistance	D5963
Flex Fatigue	D813

**RESULTS and DISCUSSION: PO3G VS PTMEG**

*Prepolymer Properties*

The comparisons of PO3G and PTMEG in Table 1 show that the viscosity of PO3G prepolymers is lower in all cases, as was expected. Materials containing 2000 MW or higher diols had an average viscosity drop of 34%, while prepolymers containing 1000 MW or lower dropped 11% on average. The physical state of all the PO3G samples was liquid, even the 2700 MW-based sample. The PTMEG samples A<sub>4</sub> and B<sub>4</sub> were both waxy solids. Only PTMEG samples containing 1000 MW or lower were liquid. Another attribute to note was the color. The PO3G polyols had an amber color that translated to the prepolymer making the PO3G prepolymers darker than the PTMEG samples. The color of the final elastomers was only slightly affected since MBOCA and DMTDA have a yellowish and brownish color, respectively.

*Physical-Mechanical (Tensile/Tear) Properties*

The tensile and tear properties of PO3G versus PTMEG are comparable as can be seen in Tables 4-5. Table 4 has the properties with MBOCA and Table 5 lists the properties with DMTDA. In general, tensile strength at break was 5-10% higher on PTMEG-based samples. Due to the higher crystallinity as mentioned previously, PTMEG stress crystallizes to a higher degree than PO3G. Thus, the trend is higher tensile strength for PTMEG and increased elongation for PO3G on the order of 30-50% for 95A and softer. For harder specimens, elongation increased in the 10-30% range.

	A <sub>3</sub>	A <sub>4</sub>	B <sub>3</sub>	B <sub>4</sub>	C <sub>3</sub>	C <sub>4</sub>	D <sub>3</sub>	D <sub>4</sub>
Shore Hardness	81.5A	81.5A	85A	87A	90.5A	90.5A	96A / 46D	96A / 49D
Tensile Strength, psi	4400	4825	3340	3470	4535	4860	5355	6050
Elongation (D412), %	725	515	615	465	575	455	480	375
Die C Tear (D624), pli	335	285	385	350	430	380	480	500
Split Tear (D1938), pli	50	36	52	47	68	63	127	134
Bashore Resilience, %	65	66	63	62	58	58	52	49
Compression Set, 70°C, 22hrs.	30	19	27	20	28	23	30	30
Brittleness temp (DMA), °C	-60	-67	-58	-67	-58	-69	-56	-57
	E <sub>3</sub>	E <sub>4</sub>	F <sub>3</sub>	F <sub>4</sub>	G <sub>3</sub>	G <sub>4</sub>	H <sub>3</sub>	H <sub>4</sub>
Shore Hardness	49D	51D	59.5D	60D	68D	68D	74D	74D
Tensile Strength, psi	5920	6255	6480	7760	6915	7685	7190	7585
Elongation, %	435	340	345	320	285	255	280	225
Die C Tear, pli	515	540	685	675	860	835	1005	1080
Split Tear, pli	147	136	188	196	188	190	232	223
Bashore Resilience, %	49	52	53	52	56	59	57	58
Compression Set, 70°C, 22hrs.	35	30	33	33				
Brittleness temp (DMA), °C	-51	-58	-53	-46	-43	-39	-38	-32

A subscript 3 denotes PO3G and a subscript 4 denotes PTMEG; if a blend of MWs was used, the primary is first

In most cases, the Die C and split tear strengths for PO3G specimens were higher than PTMEG. The difference in tear strength was the highest with lower hardness elastomers and then diminished at higher hardness. DMTDA-cured specimens had higher elongations than MBOCA-cured analogs and demonstrated increased tear resistance to an even greater level, likely due to their lower hardness.

	<b>A<sub>3</sub></b>	<b>A<sub>4</sub></b>	<b>B<sub>3</sub></b>	<b>B<sub>4</sub></b>	<b>C<sub>3</sub></b>	<b>C<sub>4</sub></b>	<b>D<sub>3</sub></b>	<b>D<sub>4</sub></b>
Shore Hardness	76A	78A	82A	84A	87A	88A	95A	95A
Tensile Strength, psi	4750	4730	4075	4220	5180	5730	6200	6120
Elongation, %	870	565	745	485	650	520	535	395
Die C Tear, pli	330	305	380	355	420	390	505	480
Split Tear, pli	68	47	65	48	83	65	144	127
Bashore Resilience, %	64	66	61	62	57	60	51	50
Compression Set,70°C, 22hrs.	39	27	41	30	40	33	48	43

	<b>E<sub>3</sub></b>	<b>E<sub>4</sub></b>	<b>F<sub>3</sub></b>	<b>F<sub>4</sub></b>	<b>G<sub>3</sub></b>	<b>G<sub>4</sub></b>	<b>H<sub>3</sub></b>	<b>H<sub>4</sub></b>
Shore Hardness	50D	50D	59D	58.5D	67D	67D	71D	72.5D
Tensile Strength, psi	6845	6400	6970	7065	7260	7720	7775	8275
Elongation, %	485	375	385	330	305	300	305	285
Die C Tear, pli	535	515	660	650	885	835	1030	1060
Split Tear, pli	164	130	177	160	200	188	233	217
Bashore Resilience, %	50	51	55	52	57	56	61	63
Compression Set,70°C, 22hrs.	49	42	58	49				

**A subscript 3 denotes PO3G and a subscript 4 denotes PTMEG; if a blend of MWs was used, the primary is first**

The improvement in tear strength and increase in elongation could be explained by the small level of monol content in the PO3G polyols. Unsaturation in a polyether is a sign of the formation of monohydroxy content, or monol. PTMEG has essentially no unsaturation (<0.001meq/g) or no monol content, whereas the unsaturation content for the PO3G used in this study was ~0.023meq/g for the 2700MW and for the 2000MW, ~0.018meq/g for the 1000MW and negligible for the 500 and 250 MW. Monol content leads to lower polymer molecular weight which can affect mechanical properties [3]. It also contributes to a less “tight” polymer network in the elastomer, which is likely why a slight boost in tear properties is observed for the PO3G elastomers. Slightly lower tensile strength is likely a result of an overall lower polymer molecular weight. Monol content increases as polyol molecular weight increases, especially with 2000 MW and higher [3], which is likely why the biggest changes were in samples A<sub>3</sub> and B<sub>3</sub>.

*Compression Set / Resilience / Brittleness Temperature*

A decline in compression set of 5-9 units was seen with PO3G-based specimens, yet the results for PO3G specimens were well within acceptable limits (Tables 4-5). Monol content can lead to a reduction in properties such as compression set as well as resilience. However, there were no significant differences in resilience that could be observed, with values that were either identical or within 1-3 units between PO3G and PTMEG.

Brittleness temperatures were determined based on the MBOCA-cured specimens using dynamic mechanical analysis (DMA) via tan delta curves. Both PO3G and PTMEG had very low and similar brittle temperatures, as expected. The PTMEGs for samples A through E averaged around 10°C lower brittle points than PO3G, except for samples D<sub>3</sub> and D<sub>4</sub>, which were almost identical. For the higher hardness samples, F through H, the PO3G samples were about 5°C lower than PTMEG. In almost all applications, the PO3G brittleness temperatures would be acceptable.

*Abrasion Resistance*

The abrasion resistance of PO3G versus PTMEG is comparable. Table 6 exhibits the volume loss for samples A through E and the % change from PO3G. A positive percent change indicates an improvement in abrasion resistance for the PO3G elastomers. The volume loss for sample A<sub>3</sub> was improved versus sample A<sub>4</sub> for both the MBOCA-cured and DMTDA-

	<b>MBOCA</b>	<b>DMTDA</b>
<b>A<sub>3</sub></b>	109	80
<b>A<sub>4</sub></b>	125	87
% Change	15%	10%
<b>B<sub>3</sub></b>	114	94
<b>B<sub>4</sub></b>	102	88
% Change	-10%	-6%
<b>C<sub>3</sub></b>	107	93
<b>C<sub>4</sub></b>	97	91
% Change	-9%	-2%
<b>D<sub>3</sub></b>	89	95
<b>D<sub>4</sub></b>	92	91
% Change	3%	-4%
<b>E<sub>3</sub></b>	102	97
<b>E<sub>4</sub></b>	91	90
% Change	-11%	-8%

cured samples. Correspondingly, the split tear of  $A_3$  was much higher than  $A_4$  by a margin greater than samples B through E, and split tear is a good indicator of abrasion resistance [4]. Sample  $A_3$  had a 39% increase in split tear over  $A_4$  for the MBOCA-cured specimen and 45% increase for the DMTDA-cured specimen. This large increase in split tear translated to roughly a 10% improvement in abrasion resistance. For samples B through E, the split tear difference wasn't as great and this resulted in somewhat better abrasion resistance for PTMEG in those samples.

*Dynamic Mechanical Analysis*

Dynamic mechanical analysis was performed in a three-point bend mode on all the MBOCA-cured specimens. Figures 2, 3, and 4 (Green = PO3G, Blue = PTMEG) are overlays of samples C, D, and F which exhibited the general trends of all the samples. Overall, the storage modulus curves were very similar between PO3G and PTMEG samples. On the 95A and lower hardness elastomers, the transition of the storage modulus curve from the melting of the soft segment was usually slightly steeper for the PO3G samples and this consistently translated to a narrower and sharper tan delta peak than the PTMEG. The quicker transition corroborates the assertion that PO3G is less crystalline. Figure 4, showing the comparison of  $F_3$  to  $F_4$ , reveals that as lower molecular weight polyol is used and hard segment content is increased, the PO3G and PTMEG start to look almost the same in regards to tan delta peak shape.

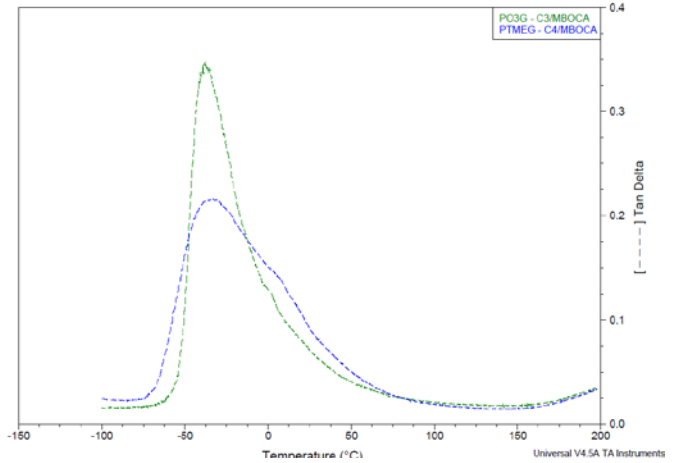


Figure 2. C3 vs. C4 (90A)

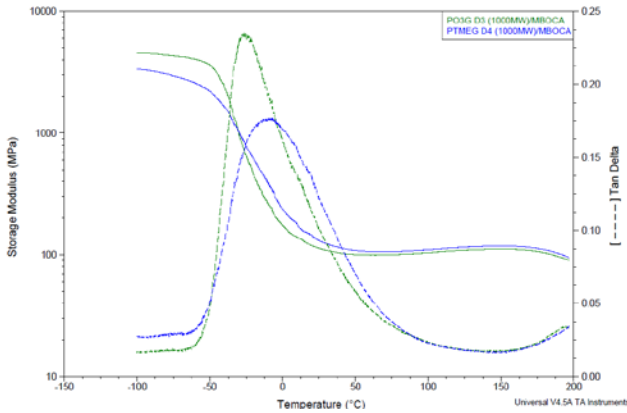


Figure 3. D3 vs. D4 (95A)

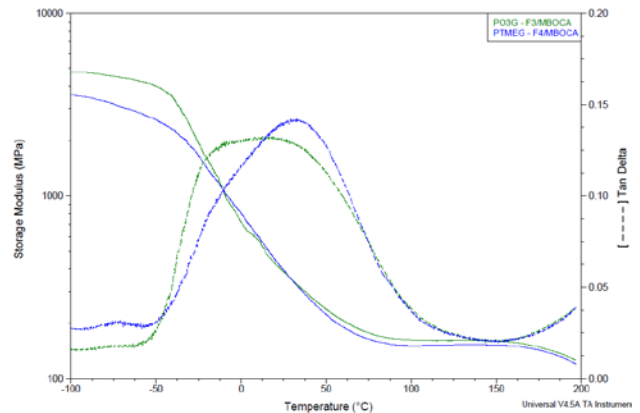


Figure 4. F3 vs. F4 (60D)

*Sub-ambient Stress-Strain Testing*

PTMEG-based elastomers are used extensively for applications requiring low temperature flexibility. It has already been demonstrated above that the brittleness point and DMA characteristics are similar between PO3G and PTMEG. Here, we look at stress-strain characteristics as the temperature is cooled from ambient to  $-30^{\circ}\text{C}$ . Figures 5-6 show samples  $B_3$  vs  $B_4$  and  $D_3$  vs  $D_4$ , which are the 2000 MW and 1000 MW-based samples, respectively. In both cases, when the specimens are cooled to  $-30^{\circ}\text{C}$ , the increase in modulus or stress is greater for the PTMEG, as shown by the greater

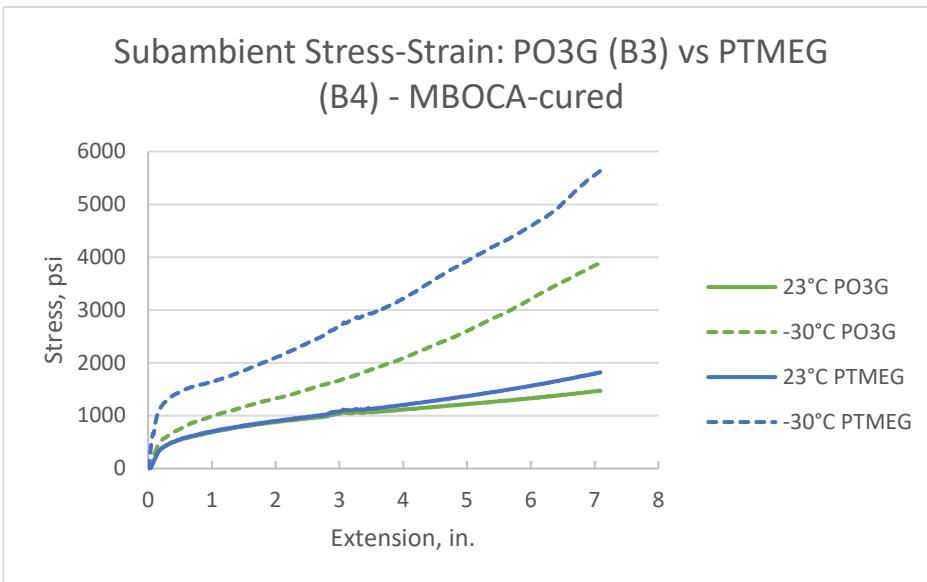


Figure 5. Subambient testing: B3 vs. B4 (2000MW)

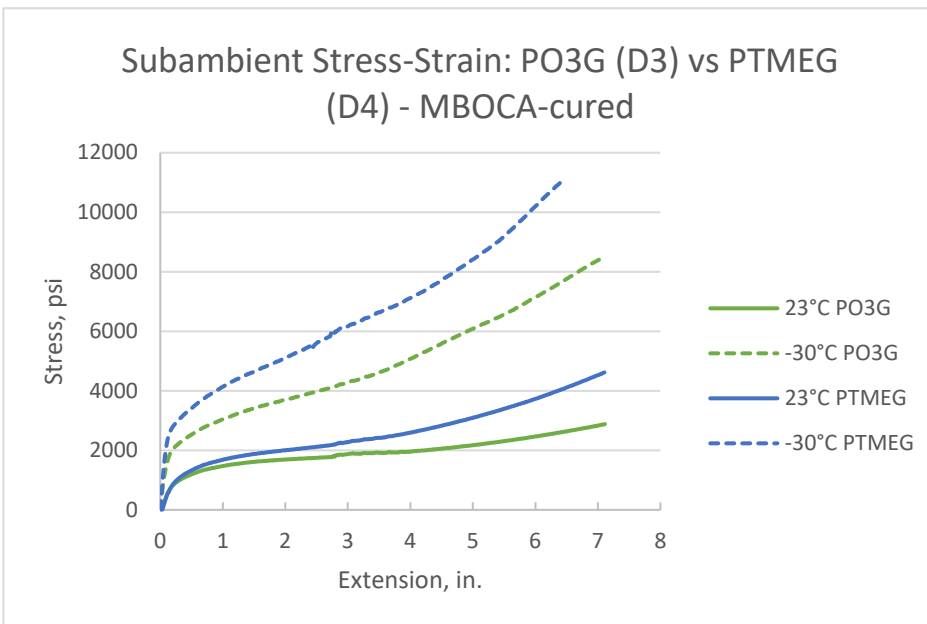


Figure 6. Subambient testing: D3 vs D4 (1000MW)

difference in stress, both at the initial linear portion (<0.25" extension) of the curve and at higher elongation values. Based on these curves it could be concluded that PO3G-based elastomers would stay more flexible in cold temperatures, down to -30°C.

*Flex Fatigue*

The Demattia flex fatigue test results were extremely intriguing. Table 7 shows the dramatic difference in the number of cycles to 50% and 100% failure for samples A<sub>3</sub>, A<sub>4</sub>, B<sub>3</sub>, and B<sub>4</sub>. As seen above, the split tear strength (a good indicator of flex fatigue resistance and tear propagation resistance) of A<sub>3</sub> and B<sub>3</sub> was higher than A<sub>4</sub> and B<sub>4</sub>. This, along with much higher elongation, created a material that is very resistant to flex fatigue as can be observed in Table 7. Once again, the monol content previously mentioned would be a major contributing factor. As stated above, the higher the molecular weight (especially at or above 2000), the more propensity for monol formation, shown by samples A<sub>3</sub> and B<sub>3</sub> that were at or above 2000. The PTMEG samples tended to tear to failure very quickly once a tear was

initiated whereas, the PO3G held on for hundreds to thousands of cycles before complete failure. The number of cycles to 50% failure was 7.2 times higher with PO3G for sample A<sub>3</sub> and 4 times higher with sample B<sub>3</sub>. The number of cycles to 100% failure was 8.5 times higher for sample A<sub>3</sub> versus A<sub>4</sub> and 4.8 times higher with sample B<sub>3</sub> versus B<sub>4</sub>. It is interesting that the flex fatigue cycles were many factors higher even though the split tear was only 1.4 times better for A<sub>3</sub> and 1.1 times better for B<sub>3</sub>.

RESULTS and DISCUSSION: HYBRID PREPOLYMERS OF PO3G/PTMEG

*Prepolymer Viscosities*

Table 2 listed the prepolymer viscosities of 100% PO3G, 50% PO3G, 20% PO3G, and 0% PO3G (100% PTMEG) for samples B, E, and G. In Figure 7,

Table 7. Demattia Flex Fatigue		
	Cycles to % Failure (tear propagation)	
	50%	100%
A <sub>3</sub>	2875	4175
A <sub>4</sub>	400	490
B <sub>3</sub>	1125	1525
B <sub>4</sub>	280	320

the viscosities are plotted versus the amount of PO3G in the prepolymer. All 3 samples are very close to linear relationships with very high R<sup>2</sup> values indicating there is no constructive or detrimental effects of blending the two backbones.

*Physical-Mechanical (Tensile/Tear) Properties Comparison*

Interesting results were observed with the tensile/tear properties of the blends (Tables 8-9). Elongation trended up as more PO3G was added to the samples, and just 20% PO3G made an impact, especially with sample B<sub>34-20</sub>. However, with Die C and split tear in several of the samples, the tear strength of the hybrid prepolymers was lower than the individual PO3G and PTMEG prepolymers suggesting a deconstructive effect of adding the two materials together. This effect can be seen in samples B and E for both MBOCA and DMTDA. The decrease was 10-20% in most cases, making it a significant effect. Evidently, a mix of the two backbones in the soft segment disrupts the morphology in a way that tear strength is lower. Due to the mix of 3 and 4 methylene groups, perhaps the network of hydrogen bonding is not as effective, or maybe the blend of the two backbones is preventing stress crystallization. However, the tensile strength and elongation results did not indicate a lack of crystallization. Sample G did not show this trend, likely due to the amount of hard segment in the elastomers taking precedence over the elastic behavior of the elastomers. As with the tensile/tear results in Tables 4-5, the harder the elastomer, the less benefit for using PO3G, except for adding renewable content.

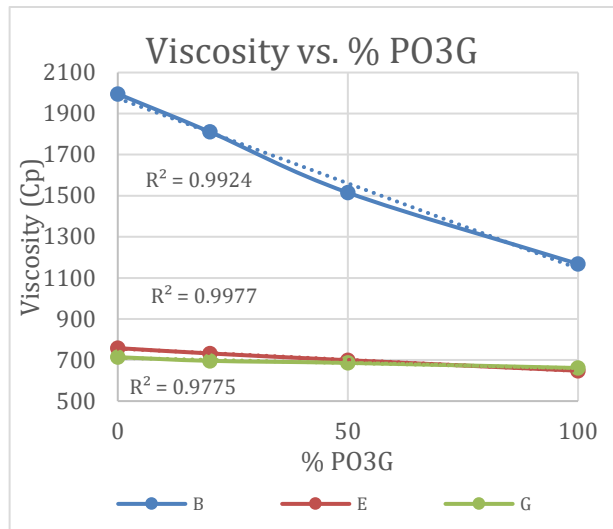


Figure 7. Hybrid Prepolymer Viscosities

	B <sub>3</sub>	B <sub>34-50</sub>	B <sub>34-20</sub>	B <sub>4</sub>	E <sub>3</sub>	E <sub>34-50</sub>	E <sub>34-20</sub>	E <sub>4</sub>	G <sub>3</sub>	G <sub>34-50</sub>	G <sub>34-20</sub>	G <sub>4</sub>
Shore Hardness	85A	87A	87A	87A	49D	51D	50D	51D	68D	68D	68D	68.5D
Tensile Strength, psi	3335	3765	3260	3470	5920	6360	6180	6255	6915	7140	7800	7685
Elongation, %	615	585	525	465	435	375	350	340	285	285	290	265
Die C Tear, pli	385	335	320	345	515	530	520	540	860	830	850	835
Split Tear, pli	52	38	42	47	147	122	128	136	188	203	199	190
Bashore Resilience, %	63	62	62	62	49	50	52	52	56	57	58	59
Compression Set, 70°C, 22hrs.	27	22	20	20	35	30	29	30	-43	-47	-41	-39
Brittleness temp (DMA), °C	-58	-65	-65	-67	-51	-57	-54	-58	-43	-47	-41	-39

	B <sub>3</sub>	B <sub>34-50</sub>	B <sub>34-20</sub>	B <sub>4</sub>	E <sub>3</sub>	E <sub>34-50</sub>	E <sub>34-20</sub>	E <sub>4</sub>	G <sub>3</sub>	G <sub>34-50</sub>	G <sub>34-20</sub>	G <sub>4</sub>
Shore Hardness	82A	83A	84A	84A	50D	49D	48D	50D	67D	68D	68D	67D
Tensile Strength, psi	4075	4120	4340	4220	6845	6725	6745	6400	7260	7405	8090	7720
Elongation, %	745	655	580	485	485	420	395	375	305	315	315	300
Die C Tear, pli	380	360	330	355	535	495	485	515	885	835	835	835
Split Tear, pli.	65	53	47	48	164	122	123	130	200	192	190	188
Bashore Resilience, %	61	63	61	62	50	49	49	51	57	52	61	56
Compression Set, 70°C, 22hrs.	39	35	30	30	49	42	40	42	-43	-47	-41	-39

### Abrasion Resistance Comparison

The deconstructive effects of PO3G/PTMEG blends were corroborated in the rotary drum abrasion testing. Table 10 has the abrasion resistance of samples B and E cured with MBOCA and DMTA at 0%, 20%, 50%, and 100% PO3G. For both B and E, the hybrid prepolymers had increased volume loss (decreased abrasion resistance). As with tear strength, the mix of these two backbones is changing the polymer network in a way that abrasion resistance is decreased.

	MBOCA	DMTDA
<b>B<sub>3</sub></b>	113.5	93.6
<b>B<sub>34-50</sub></b>	118	95.4
<b>B<sub>34-20</sub></b>	123.2	97.2
<b>B<sub>4</sub></b>	101.6	87.8
<b>E<sub>3</sub></b>	102.1	96.9
<b>E<sub>34-50</sub></b>	102.5	104.7
<b>E<sub>34-20</sub></b>	96.3	114.9
<b>E<sub>4</sub></b>	90.9	89.5

### Dynamic Mechanical Analysis

The DMA analysis of the hybrids can be seen in figures 8-10. Figures 8 and 9 show the storage modulus and tan delta overlay graphs of samples B<sub>3</sub>, B<sub>34-50</sub>, B<sub>34-20</sub>, and B<sub>4</sub>, which are the 2000 MW based samples. From the graphs it is clear that at a 50/50 blend, the storage modulus curve is close to the same as 100% PO3G. With less than 50%, the shoulder of the crystallization of the PTMEG becomes more pronounced. For the tan delta, the change is more linear as more PTMEG is added to the system, although even at 20%, the sharpness of the tan delta peak and steeper slope of the storage modulus is apparent.

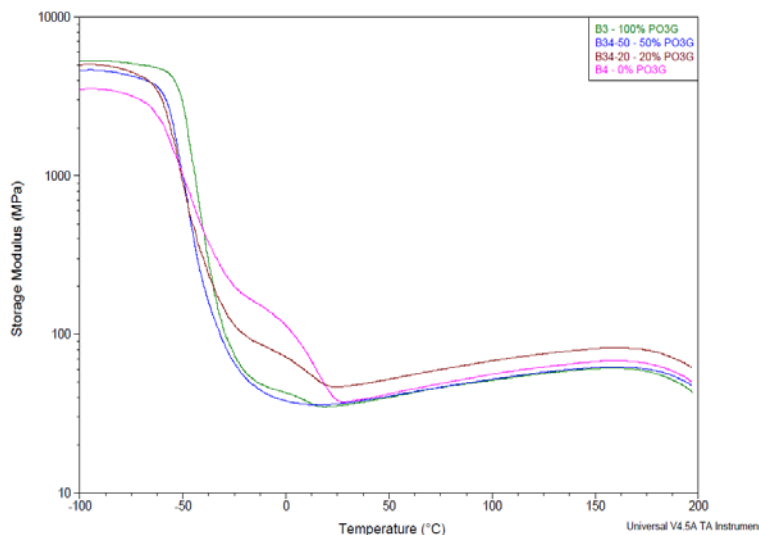


Figure 8. Storage Modulus: B<sub>3</sub> (green), B<sub>34-50</sub> (blue), B<sub>34-20</sub> (brown), B<sub>4</sub> (pink)

### CONCLUSION

PO3G is a bio-based polyol that has a similar structure to PTMEG. When comparing PO3G-based elastomers to PTMEG, most properties were found to be comparable in this study as previous studies have shown. In general, the lower crystallinity and flexibility of the PO3G backbone provides prepolymers with better liquidity and lower viscosity and creates elastomers with higher elongation and improved tear strength. The compression set of

is added to the system, although even at 20%, the sharpness of the tan delta peak and steeper slope of the storage modulus is apparent.

Figure 10 is an overlay of the storage modulus and tan delta curves for samples E<sub>3</sub>, E<sub>34-50</sub>, E<sub>34-20</sub>, and E<sub>4</sub>, which were the 50D samples. Although the tan delta peak is slightly higher and sharper and the storage modulus transition slightly steeper for E<sub>3</sub>, all 4 samples are very similar. This demonstrates again that at higher hardness and less soft segment, the differences between PO3G and PTMEG start to disappear and no clear advantage is discernable from physical/chemical/mechanical properties.

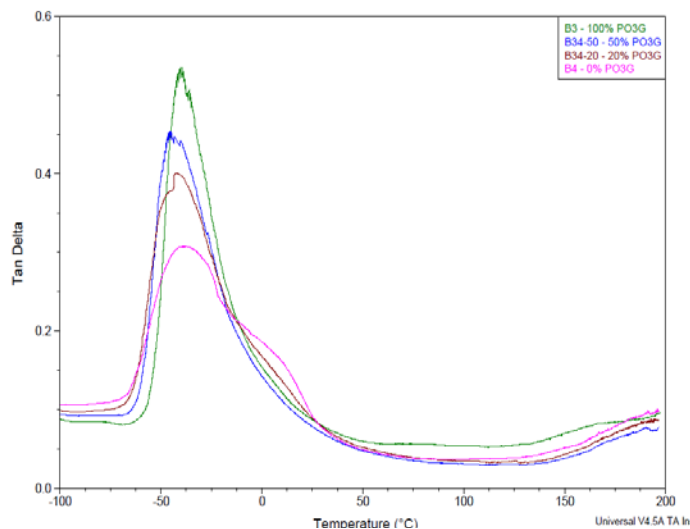


Figure 9. Tan Delta: B<sub>3</sub> (green), B<sub>34-50</sub> (blue), B<sub>34-20</sub> (brown), B<sub>4</sub> (pink)



PTMEG-based systems was slightly better than PO3G, however, the PO3G results were in the range of a good performing elastomer. Resilience was almost identical for the two backbones. The abrasion resistance was slightly improved for PTMEG, except for the softest systems tested, in which the PO3G was slightly better. The PO3G samples yielded similar DMA results with analogous storage modulus curves and tan delta curves characterized by a higher, narrower peak, indicating a quicker glass transition of the soft segment. The temperature of glass transition was only slightly lower for the PTMEG-based elastomers, but very comparable. When looking at sub-ambient stress-strain tests, the PO3G stayed more flexible at -30°C than PTMEG making PO3G a good candidate for cold temperature applications.

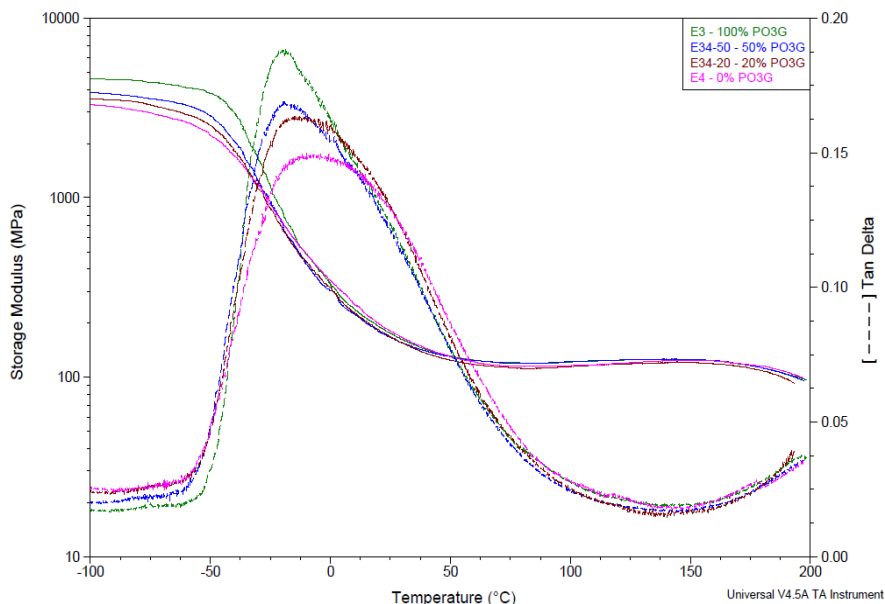


Figure 10. Storage Modulus/Tan Delta E3, E34-50, E34-20, E4

Of all the properties evaluated, the flex fatigue showed the most disparity between PO3G-based and PTMEG-based elastomers. The PO3G outlasted PTMEG by a factor of 4 to 8.5 times depending on the sample. The PO3G samples ran for thousands of cycles, while PTMEG only lasted for hundreds. As mentioned before, the monol content in the PO3G is a likely contributor of the higher tear, elongation, and flex fatigue resistance. Other properties such as tensile strength, compression set, and resilience were all adequate for a high-performance urethane elastomer. This makes the greatly increased flex fatigue a great attribute of the PO3G versus PTMEG. To prove the theory that the monol is the cause of the increase in flex fatigue resistance, an experiment could be done taking PTMEG, adding some monol content, and then measuring properties on the resulting elastomer. Future studies could also look at higher hardness (90-95A) PO3G-based elastomers to see if they have a similar increase in flex fatigue, since the amount of monol is much less for 1000 MW and lower PO3G polyols.

When blending the PO3G and PTMEG to make hybrid prepolymers, results were both expected and unexpected. Tensile and elongation properties showed the expected behavior. The tensile strength decreased while the elongation increased as PO3G was incorporated. Dynamic mechanical analysis was also straightforward. The non-synergistic, non-linear results that were observed with tear strength and abrasion resistance, however, were very unexpected for two compatible polyether backbones. At levels of 20% and 50% PO3G, both tear and abrasion were negatively impacted. As stated above, it is possible that the blend of 3 and 4 methylene polyethers in the soft segment reduced the ability to stress crystallize. The intention of the blends was for the case that processors might want to incorporate only a portion of “green” content into their parts, which could be for multiple reasons, including cost, customer resistance to change, etc. However, based on the results of these studies, it would be better to use all PO3G and go 100% “green”.

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## BIOGRAPHIES



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