

DEVELOPMENT OF HIGH PERFORMANCE BIO-BASED POLYURETHANE SYSTEMS

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Abstract

LANXESS has developed a new line of high performance bio-based products for polyurethane cast elastomer applications. This technology enables companies to reduce emissions while helping to advance climate neutral goals.

Bio-based MDI and pPDI polyether & polyester prepolymers focus on chemical building blocks that are clearly defined to match today's elastomer properties. Processed in a similar manner to other hot cast polyurethane elastomers, these systems have reactivity profiles, demolding times, and demonstrate performance similar to petroleum-based prepolymers.

Progress has been made developing conventional bio-based MDI systems over a wide range of hardness's as well as a variety of bio-based Low Free (LF) pPDI & LF MDI systems that provide improved health & safety advantages.

LANXESS' novel bio-based technologies provide excellent performance, processing, and productivity and allow for a 20% to 30% CO₂ footprint reduction when compared to petroleum-based prepolymers.

Introduction

A major topic in the chemical industry today is sustainability. According to the EPA, to pursue sustainability is to create and maintain the conditions under which humans and nature can exist in productive harmony to support present and future generations. Industry today (especially polyurethanes) is highly dependent on fossil fuel based materials. They are more affordable, easy to obtain, and create materials that perform to the standards required of them. However, a pressure is forming to change this trend. Dependence on these fossil fuels will not lead to a future where we can exist in this productive harmony to support future generations therefore, it is important to start doing something to change this. There is an increasing realization that both industry and government need to work together to improve our future.

For LANXESS, sustainability has become one of the core tenets of our business (Lanxess Corporation, 2019). As part of this initiative, LANXESS has announced its plan to become carbon neutral by 2040. To do this, LANXESS has developed a three-pillar strategy that includes major impact projects at plants and facilities, decoupling emissions and growth and new technical innovations. To assist in this objective, it is important for us to work on developing new and sustainable products that also can match or exceed the performance of our current materials

Since a prepolymer is a reaction product of a diisocyanate with a polyol, utilizing a green polyol or diisocyanate would be one way to increase the sustainability of our systems. Looking at bio based polyols, in particular, was a particularly attractive place to begin development of these new bio based systems. Research into green polyols has been something that has been very popular for years (Demarest & Sunkara, 2010). Due to this, there are a number of green and sustainable polyols that are either currently commercial available or are being developed that can be used. In the past, factors such as price and performance have delayed the acceptance in the market. However, now with an increased push from OEMs, improved performance, and higher fossil fuel material costs, there is a growing opportunity for these type of materials. Examples of these types of materials are polypropanediol (PO3G) made from starch and polyesters that are made using sustainably sourced succinic and azelaic acid.

Experimental

Eight unique bio-based prepolymers were developed for this study. These prepolymers are shown in Table 1. The polyol and the diisocyanate are reacted together in a flask with constant temperature and under a blanket of nitrogen gas for 4-6 hours. After the reaction is finished, the NCO of the materials can be determined and the material is then casted into an elastomer and fully tested. There are two major prepolymer types that are looked at in this paper. When the polyol and diisocyanate is reacted at a set ratio, a conventional prepolymer is developed and will typically have an excess of diisocyanate greater than 1% (typically in the 5 to 10% range for MDI prepolymers). Low free prepolymers (LF) are created by removing this excess diisocyanate via a wiped film evaporator and its resulting in a free diisocyanate values are less than 0.1%.

Table 1: Sustainable Prepolymers

Type	Prepolymer	Elastomeric Hardness (Shore A or D)
Conventional	MDI/PO3G	40A
Conventional	MDI/PO3G	85A
Conventional	MDI/PO3G	95A
Conventional	MDI/PO3G	50D
LF	MDI/PO3G	55D
LF	PPDI/PO3G	97A
LF	MDI/Polyester (Azelaic)	88A
LF	MDI/Polyester (Succinic)	82D

These green prepolymers are then compared with their PTMEG based prepolymer/elastomeric counterparts. These controls will be of equivalent hardness so that the physical and dynamic properties can be compared. Table 2 indicates the typical abbreviations that will be used throughout this paper.

Table 2: Abbreviations

Shorthand	Definition
LF	Low Free Prepolymer has = <0.1% free diisocyanate
PO3G	Polypropane Diol
PTMEG	Polytetramethylene ether glycol
MDI	4,4'-Methylene diphenyl diisocyanate
PPDI	p-phenylene diisocyanate
HQEE	Hydroquinone bis(2-hydroxyethyl) ether,
1,4 BD (BDO)	1,4 Butane Diol

Viscosity data was measured by using a Brookfield RVDV-11+ pro viscometer equipped with a thermocel heating system using a #27 spindle. Reactivity measurements also taken using a Brookfield viscometer. The prepolymer is mixed with a curative at a specific temperature and then added to the viscometer set at 120°C using a spindle #27 at 10 rpm. The viscosity is measured until it reaches 20,000 cP upon which the test is completed.

These prepolymers were reacted with either 1,4 BD, HQEE, or by itself. The butane diol is added at room temperature to the prepolymer while the HQEE is heated to >100°C before addition. All of the castings were done with a 95% stoichiometric ratio and were then postcured at 120°C for 16hrs.

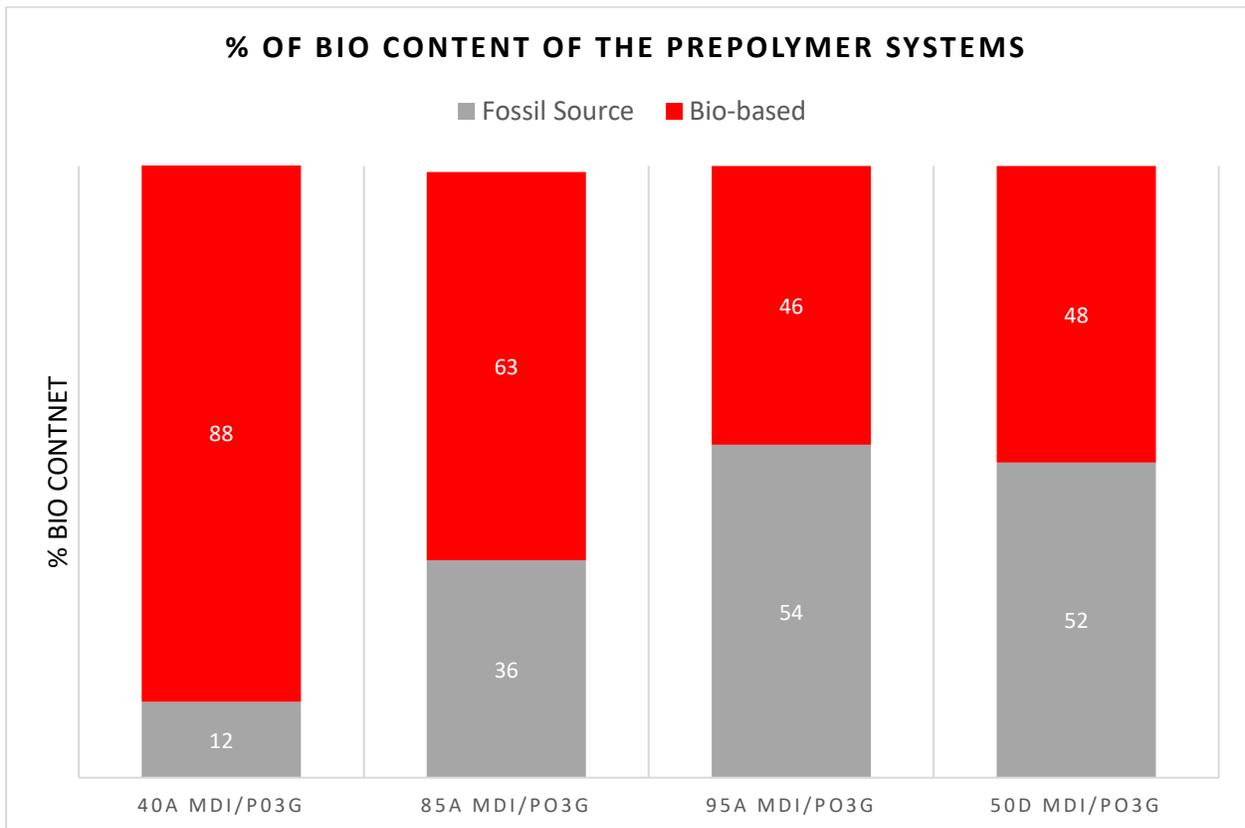
Physical samples were conditioned for at least 2 days at 72°F and 50% relative humidity. These samples were then tested following either ASTM or DIN standards. The conventional MDI samples were tested with Din procedures; 533504-S2 (tensile testing), 53515/ISO 34-1 (tear strength, nick and no nick), and 53517 Method B/ISO 815 (compression set testing). Hardness was tested with standard 53505. The LF samples meanwhile were all tested to ASTM standards, ASTM D 470 (split tear), ASTM D 412 (tensile testing), ASTM D395 method B. Hardness was measured using ASTM D 2240.

Dynamic properties were measured in torsion mode using TA Instruments ARES-G2 Rotational Rheometer with minimum transducer torque in oscillation = 0.05 $\mu\text{N}\cdot\text{m}$ and transducer torque resolution = 1 $\text{nN}\cdot\text{m}$. It is equipped with a forced convection oven (FCO) which rapidly heats and cools the sample over the temperature range of -150°C to 600°C. Rectangular test specimens were used (approximately 50 mm x 11.8 mm x 3.2 mm). Dynamic temperature step experiments were performed by heating the sample from 30°C to 180°C with 10°C step under an oscillatory strain of 4 % and oscillation frequency of 10 Hz. Samples were aged at least two weeks at ambient conditions before testing.

Results and Discussions

Using bio based polyols is a very effective way to reduce greenhouse gas emissions and to improve sustainability. Utilizing these polyols can create systems whose bio content can vary from 30% to 90% of the total material depending its NCO. Figure 1 shows the bio content of the four conventional MDI prepolymers that were evaluated in this paper. These four systems were all developed using 1,3 propanediol (PO3G) that is synthesized through biomass/starch creating a 100% green material. This increased bio-content creates systems that are more sustainable and will ultimately provide greenhouse gas and energy savings for the entire system.

Figure 1: Percentage Bio Content of the Conventional MDI Systems



Conventional MDI/PO3G

PO3G based material can be used to create prepolymers that cover a wide range of hardness. Table 3 shows the comparison between the conventional MDI/PO3G versus its PTMEG counterparts at three specific hardness values: 85A, 95A and 50D. Overall, the PO3G based elastomers had comparable elastomeric properties compared to their PTMEG counterparts. Their modulus values, compression set, and tear strength were all very similar to each other and there were no major properties can be highlighted as inferior.

Table 3: Conventional MDI Comparisons

		85A Comparison		95A Comparison		50D Comparison	
Prepolymer		MDI/PTMEG	MDI/PO3G	MDI/PTMEG	MDI/PO3G	MDI/PTMEG	MDI/PO3G
Curative		1,4 BDO	1,4 BDO	1,4 BDO	1,4 BDO	1,4 BDO	1,4 BDO
Hardness	Sh/A or D	85A	85A	95A	95A	50D	50D
100% Modulus	psi	700.5	871.6	1778.0	2120.3	2327.7	2468.4
200% Modulus	psi	1277.7	1164.6	2298.7	2691.7	3357.4	3235.6
300% Modulus	psi	1492.3	1515.5	3380.6	3524.2	4983.2	4429.2
Stress at Break	psi	6091.2	6295.7	7164.4	4822.2	7157.1	5457.4
Strain at Break	%	338	612	458	392	382	353
Tear Strength (no nick)	lbf/in	13.29	14.99	20.72	19.48	20.17	19.69
Tear Strength (with nick)	lbf/in	4.38	5.09	12.08	11.89	N/A	13.31
Rebound Resilience	%	69.8	66	58	47	47.5	46.5
Compression Set @ 70°C, 24 h	%	20.48	26.94	28.61	24.55	30.97	18.86
Compression Set @ 25°C, 72 h	%	14.8	10.31	16.65	18.81	N/A	22.07
Specific Gravity		1.08	1.12	1.13	1.17	1.15	1.18
Testing was done using DIN procedures							

This polyol can also be used as a curative. An MDI/PO3G cured by itself it produces a 40A elastomer with favorable properties as shown in Table 4. By utilizing PO3G as the curative, these systems will have a green content of about 90%.

Table 4: 40A Hardness Material

Physical Properties	Units	MDI/PO3G
Curative		PO3G
Hardness	Sh/A	40A
100% Modulus	psi	55.11
300% Modulus	psi	111.68
Stress at Break	psi	>725
Strain at Break	%	>1260
Tear Strength (w/o nick)	lbf/in	94.22
Tear Strength (w/nick)	lbf/in	10.62
Abrasion	mm ³	50
Rebound Resilience (Bayshore)	%	60
Compression Set @ 70°C, 24	%	22
Testing was done using DIN procedures		

LF pPDI/PO3G

The next step was to evaluate this material in higher performance systems. The materials listed in table 5 were developed in a reaction with pPDI, a high performance diisocyanate and made into a LF prepolymer. The PO3G based material has a lower viscosity than the PTMEG material and more importantly, is liquid at room temperature. Its PTMEG counterpart meanwhile will solidify at room temperature over time. This is a very big positive over the PTMEG material.

Table 5: LF PPDI Prepolymer Comparison

Prepolymer Properties	Units	LF PPDI/PTMEG	LF PPDI/PO3G
Nominal NCO Content	%	5.60	5.60
Viscosity @ 70°C	cP	800	600
Viscosity @ 100°C	cP	300	200
Appearance @ 23°C		Semi-Solid	Liquid

In terms of elastomeric properties, this green-based system is very similar to their PTMEG counterpart with few minor differences. Table 6, compares the LF PPDI elastomers when cured with 1,4 BDO to a hardness of 97A. The reactivity's of these systems are identical, taking ~5 minutes to reach 20,000 cP. The new green elastomer has slightly better tensile strength and elongation, similar tear strength and slightly higher compression set. Overall, these materials can be considered very similar when compared in terms of performance.

Table 6: LF PPDI Elastomer Comparison

Physical Properties	Units	LF PPDI/PTMEG	LF PPDI/PO3G
Curative		1,4 BDO	1,4 BDO
Potlife (time to 20,000 cP)	Min:sec	5:04	4:50
Hardness	Sh/A	97A	97A
100% Modulus	psi	1926	1532
300% Modulus	psi	2250	1866
Stress at Break	psi	6788	7639
Strain at Break	%	550	653
Tear Strength, Die C	lb/in	554.2	579
Split Tear	lbf/in	86.6	87.8
Trouser Tear	lbf/in	135.1	117.9
Rebound Resilience (Bayshore)	%	65	65
Compression Set @ 70°C, 22 ±2 h	%	36	42
Testing was done using ASTM procedures			

The dynamic properties are also similar. Figure 2 shows a DMA graph that was run at 4% strain. The two black lines are a comparison of its storage modulus (G') and the red line's are a comparison of the tan delta values. Tan delta is a ratio of the storage and the loss modulus and is an indication about how much heat is lost from the material as it is working. The lower the value the better. Overall, G' and tan delta followed the same trend with the PO3G elastomer had slightly higher tan delta values over the temperature span. However, the values are similar and with a value of .021 at 100°C can be considered very low.

Figure 2: LF PPDI DMA Graphs

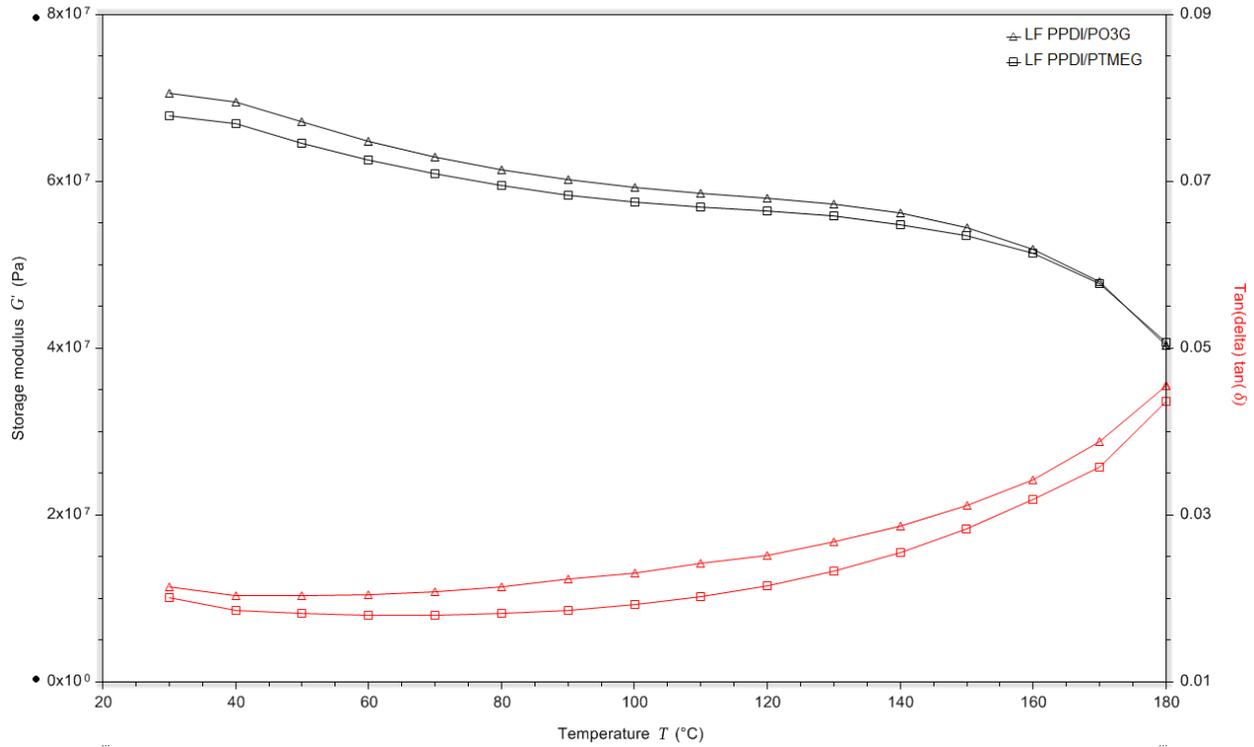


Table 7: LF PPDI DMA Comparison Data

Dynamic	Units	LF PPDI/PTMEG	LF PPDI/ PO3G
G' @ 30°C	MPa	67.88	70.56
G' @ 120°C	MPa	57.53	59.28
Tan Delta @ 30°C		.0201	.0214
Tan Delta @ 120°C		.0192	.0231

LF MDI/PO3G

In addition, a LF MDI version utilizing PO3G was also developed. Table 8 compares a LF MDI/PO3G prepolymer, with its PTMEG counterpart. Overall, the PO3G based prepolymer is again less viscous than the PTMEG material.

Table 8: LF MDI/Ether Prepolymer Comparison

Prepolymer Properties	Units	LF MDI/PTMEG	LF MDI/ PO3G
Nominal NCO Content	%	6,15	5,80
Viscosity @ 70°C	cP	1100	802,5
Viscosity @ 100°C	cP	300	220
Appearance @ 23°C		Solid	Solid

The resulting 55 Shore D PO3G based elastomer behaved very similarly to a PTMEG based material. The modulus, elongation and die C tear strength were all comparable. It has slightly lower peak stress, trouser and split tear strength, and lower compression set and higher rebound values.

Table 9: LF MDI/Ether Elastomer Comparison

Physical Properties	Units	LF MDI/PTMEG	LF MDI/ PO3G
Curative		HQEE	HQEE
Hardness	Sh/D	55±2	55±2
100% Modulus	psi	2277	2235
300% Modulus	psi	2589	2430
Stress at Break	psi	7565	5074
Strain at Break	%	456	484
Tear Strength, Die C	lbf/in	639	623
Split Tear, D470	lbf/in	120	92
Trouser Tear	lbf/in	235	142
Rebound Resilience (Bayshore)	%	35.7	52
Compression Set @ 70°C, 22 ±2 h	%	48.2	40
Testing was done using ASTM			

Figure 3 shows that these two materials are almost identical dynamically at 4% strain. The tan delta and G' curves almost overlap, with the PO3G based elastomer having slightly lower tan delta values. Tan delta values at 100°C for the PO3G is .0229 vs .0234 for the PTMEG material. Critical temperature, which is the temperature where the tan delta starts to increase, are identical at a very good 110°C.

Figure 3: LF MDI/Ether DMA Graph

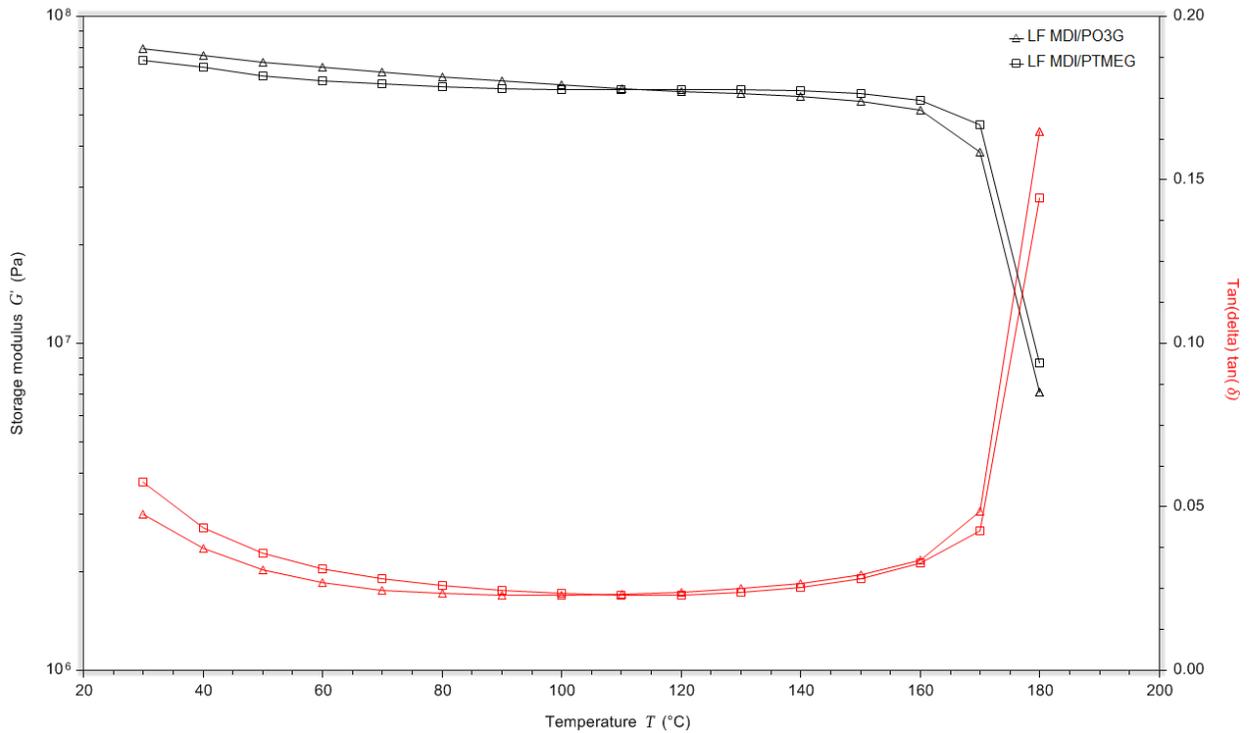


Table 10: LF MDI/Ether DMA Data

Dynamic	Units	LF MDI/PTMEG	LF MDI/ PO3G
G' @ 30°C	MPa	73.47	79.46
G' @ 120°C	MPa	59.69	61.60
Tan Delta @ 30°C		.0578	.0478
Tan Delta @ 120°C		.0234	.0229

LF MDI/ Polyesters (Green)

PO3G is not the only green polyol that is out in the market. Companies are developing a wide range of different polyols from renewable sources. Some of these sources could include wheat, starch, lignin, and even recycled materials. It is very important to keep finding new materials and evaluate their performance in our systems.

Table 11 shows two new prepolymers systems made from unique green polyesters. Sample A shows a prepolymer that is made with a polyester based on azelaic acid (a 100% green polyester) that while viscous, stays liquid at room temperature at a low NCO value. Sample B meanwhile, uses a polyester made from succinic acid (55% green polyester) with an NCO value 7.5%. This material has a higher melting point, but is less vicious then sample A.

Table 11: LF MDI/Polyester Prepolymer Data

Prepolymer Properties	Units	A	B
Prepolymer		LF MDI/Polyester	LF MDI/Polyester
Polyester Acid		Azelaic Acid	Succinic Acid
Nominal NCO Content	%	2.97	7.5
Viscosity @ 50°C	cP	18,000	N/A
Viscosity @ 70°C	cP	6,550	6,725
Viscosity @ 100°C	cP	1,840	716
Appearance @ 23°C		Liquid	Solid

When cured with HQEE, the Sample A creates an 88A elastomer with good rebound and compression set. Interestingly it also shows good reactivity providing a potlife over 5 minutes long. Typical MDI/esters would need to be catalyzed in order to react at similar rates. Sample B meanwhile also shows a good potlife of 5 minutes while at a much higher NCO value. When cured with HQEE, the Sample B material provides a product with a hardness of 82D with excellent tensile and tear strength.

Table 12: LF MDI/Polyester Elastomer Data

Physical Properties	Units	A	B
Sample		LF MDI/Polyester	LF MDI/Polyester
Polyester Backbone		Azelaic Acid	Succinic Acid
Curative		HQEE	HQEE
Potlife (time to 20,000 cP)	Min:sec	5:38	5:05
Hardness	Sh/A or D	88A	82D
100% Modulus	psi	860	N/A
300% Modulus	psi	1031	N/A
Stress at Break	psi	4347	8736
Strain at Break	%	555	14
Tear Strength, Die C	lbf/in	353	1748.2
Split Tear, D470	lbf/in	54.7	144.8
Trouser Tear	lbf/in	82.6	691.2
Rebound Resilience (Bayshore)	%	66	N/A
Compression Set @ 70°C, 22 ±2 h	%	29	N/A

Conclusions

In conclusion, LANXESS is committed to a sustainable future. Research will continue into developing new materials based on renewable chemistry, to provide the performance that is needed to succeed in today's world.

This paper illustrates a few of the possibilities to make our chemistry more sustainable without sacrificing performance. For instance, green PO3G polyols can be used to create prepolymers that

compare most favorably to PTMEG materials. These materials can be used in conventional MDI, LF pPDI and LF MDI systems and provide tensile, tear and dynamic abilities that match their PTMEG counterparts. This provides a basis that will allow the introduction of green chemistry into systems without losing any performance benefits.

Green polyester's meanwhile can be made with different bio-based acids and diols to create materials with wide range of properties that can be tailored to the specific need of the end user. These range from polyesters prepolymers that stay liquid at room temperature (such as the one based on azelaic acid) to materials to polyester materials that can achieve over 80D hardness materials (based on succinic acid).

Overall, LANXESS will continue to invest in developing new and innovative ways to become a more sustainable force in today's world.

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