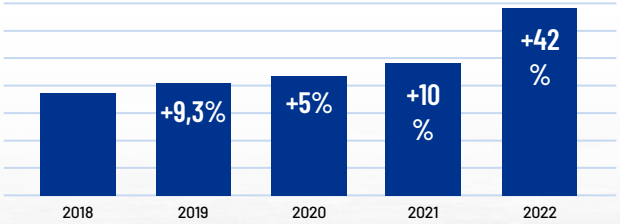
High-Performance Renewable Flexible PU Foams

Emil López Hernández
R&D Manager Engineer
Arneplant SL

FOAM EXPO
December 5, 2024

ABOUT US

SALES EVOLUTION



4
PRODUCTION CENTERS

700+
CUSTOMERS

50+
EXPORT COUNTRIES

600+
EMPLOYEES

4K+
NEWS PRODUCTS

250K+
PAIRS A DAY

Arneplant Spain Headquarter

Business division

FOAMS

Arneflex is a high-density open-cell polyurethane foam crafted for footwear insoles. It offers breathability, comfort, cushioning, antibacterial properties, and customizability.

FABRICS

We produce technical fabrics designed for comfort, durability, and safety. Equipped with advanced technology, our facility specializes in fabrics specifically engineered for insole manufacturing..

MICROFIBRE

Arnedry is an advanced microfiber with the look and feel of natural leather. It is 100% breathable, highly absorbent, and efficiently manages moisture for optimal comfort and dryness.

INSOLES

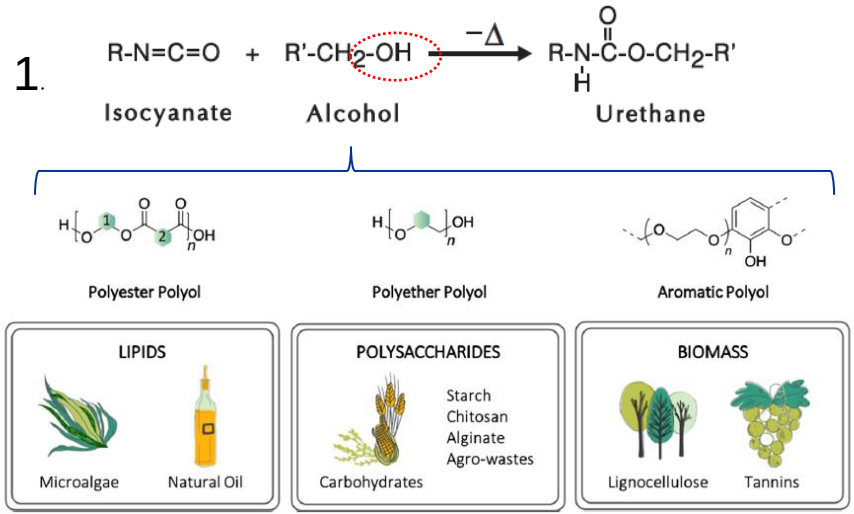
Arneplant insoles offer superior comfort, breathability, and lasting shock absorption. Designed with cutting-edge technologies and high-quality breathable materials, they ensure healthy, comfortable feet for long-term use.

High-Performance Renewable Flexible PU Foams

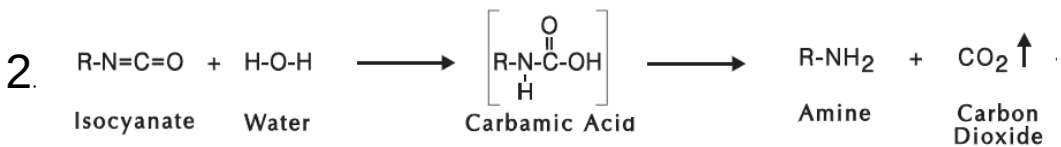
Agenda

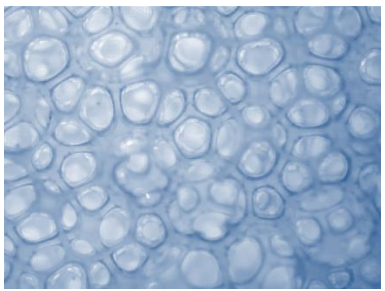
1. **Sustainable polyols overview: Flexible grades**
2. **Bio-Based Foam Properties**
   - Comparison of Mechanical Properties
   - Enhanced Formulation Strategies
   - Foam with Increased Renewable Content
3. **Summary**

Introduction

1. 

Active Hydrogen Compound	Typical Structure	Relative Reaction Rate Uncatalyzed at 25C
Primary Aliph. Amine	$R\text{-}NH_2$	100,000
Secondary Aliph. Amine	$R_2\text{-}NH$	20,000-50,000
Primary Aromatic Amine	$Ar\text{-}NH_2$	200-300
Primary Hydroxyl	$R\text{-}CH_2\text{-}OH$	100
Water	H-O-H	100
Carboxylic Acid	R-C(=O)-OH	40
Secondary Hydroxyl	R-CH(R)-OH	30
Ureas	R-NH-C(=O)-NH-R	15
Tertiary Hydroxyl	R-C(R)(R)-OH	0.5
Urethane	R-NH-C(=O)-O-R	0.3
Amide	R-C(=O)-NH_2	0.1

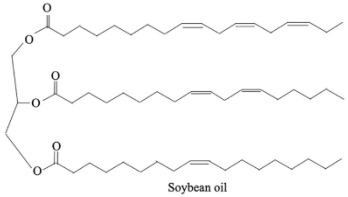
2. 



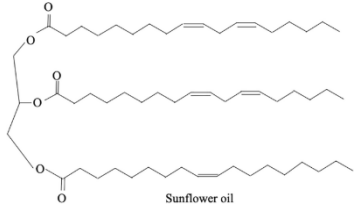
1. Ron Herrington, Kathy Hock. Dow Polyurethanes: Flexible Foams.1997.
2. From Lab to Market: Current Strategies for the Production of Biobased Polyols. Haritz Sardon et all. DOI: 10.1021/acssuschemeng.1c02361.

Natural Oil Polyols (NOPs)

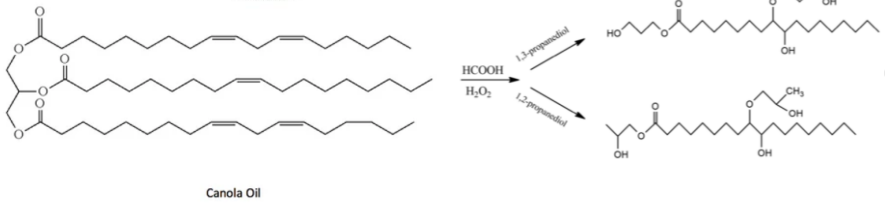
- **Soybean Oil**



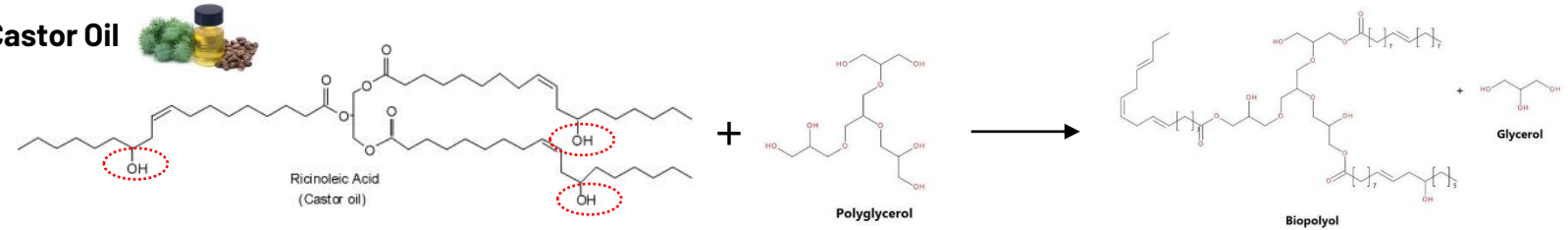
- **Sunflower oil**



- **Canola Oil**



- **Castor Oil**



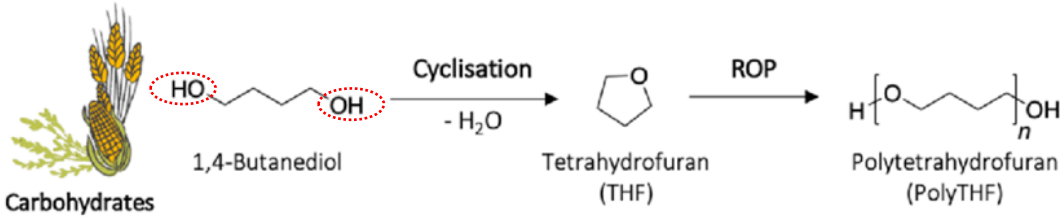
Hydrophobicity: Natural oils are inherently hydrophobic, requiring modification to increase compatibility with polyurethane systems.

Consistency: Variations in oil composition due to crop conditions can affect performance and reproducibility.

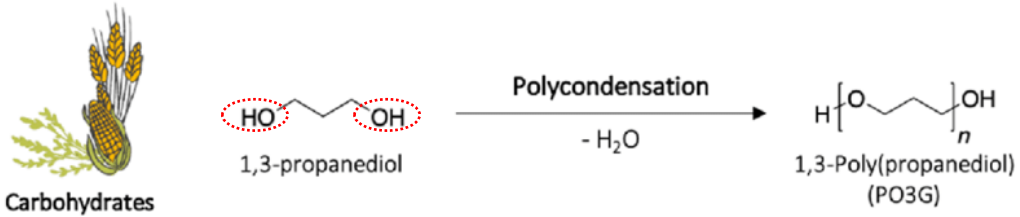
Processing Costs: Some NOPs require advanced processing to match the performance of petroleum-based polyols.

Polysaccharides

Ring Opening Polymerization of THF into poly(THF) from 1,4-Butanediol



Self-condensation of bio-based 1,3-propanediol into polyether polyols



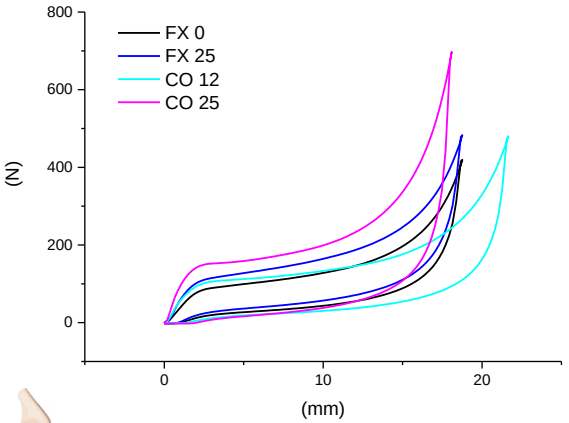
2. From Lab to Market: Current Strategies for the Production of Biobased Polyols. Haritz Sardon et all. DOI: 10.1021/acssuschemeng.1c02361.

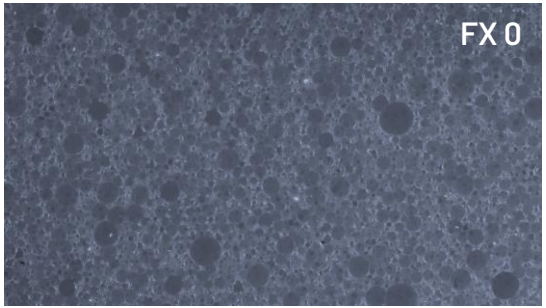
Renewable Flexible PU Foams

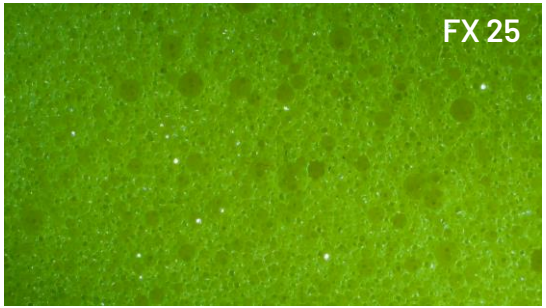
Sample ID		FX 0	FX 25	CO 12	CO 25
Solid content	(%)	25	25	25	25
Bio content	(wt%)	0	25	12	25
Based		Fossil	Starch	Castor Oil	Castor Oil
ISO index		<110>	<110>	<110>	<110>
Density	(Kg/m3)	105	98	98	108
Durometer	(Asker C)	17	18	17	22
CLD 40%	(kPa)	51,0	65,9	56,9	77,8
Cell Flow	u.a. (0 - 100)	39	36	41	34
SAG Factor		2,2	2,2	2,2	2,3
Compression set (70ºC, 50%)	(%)	3,8	3,7	4,5	4,1

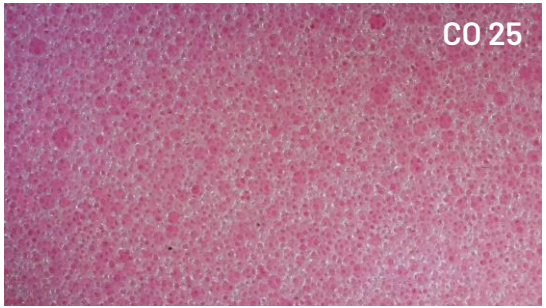
Hysteresis loss

Sample ID		FX 0	FX 25	CO 12	CO 25
Solid content	(%)	25	25	25	25
Bio content	(wt%)	0	25	12	25
Based		Fossil	Starch	Castor Oil	Castor Oil
Ball rebound	(%)	23	26	18	13
Hysteresis Loss	(%)	56	56	65	70





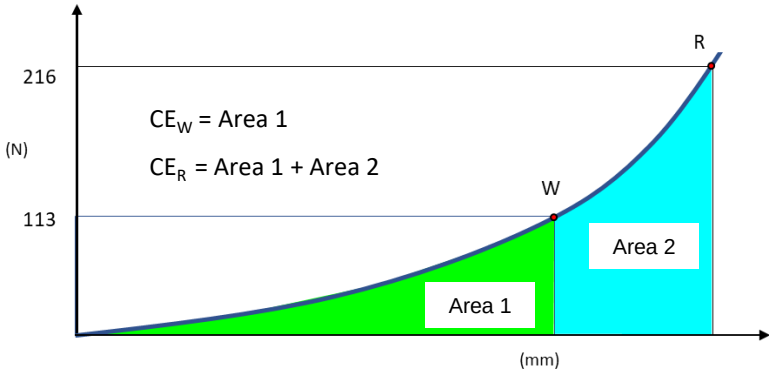




Cushion properties

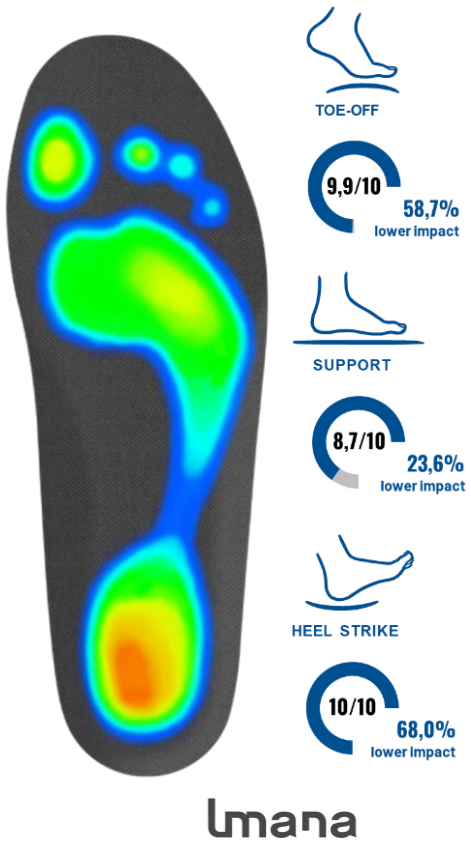
Sample ID		FX 0	FX 25	CO 12	CO 25
Solid content	(%)	25	25	25	25
Bio content	(wt%)	0	25	12	25
Based		Fossil	Starch	Castor Oil	Castor Oil
Cushion energy - walk*	(mJ)	40	44	33	35
Cushion energy - run*	(mJ)	68	74	59	62
Cushion factor - walk*		18	17	23	20
Cushion factor - run*		21	19	25	22

*INESCOP TM 4931, INESCOP TM 4932, SATRA TM 159



$$CFw = \frac{T \cdot 113}{CEw}$$

$$CFr = \frac{T \cdot 216}{CEr}$$



lmana

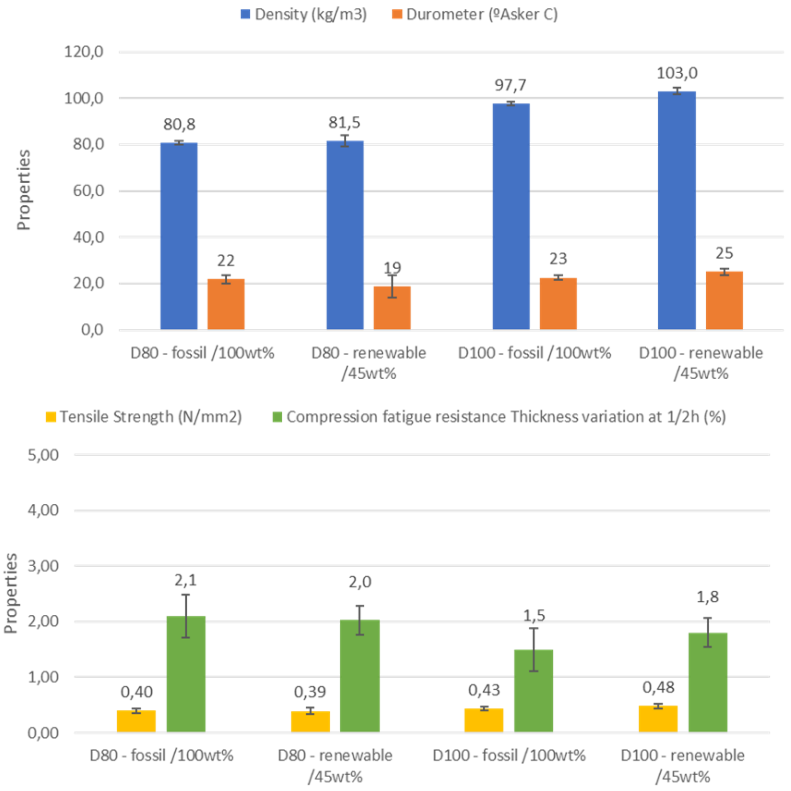
Chain extender effect

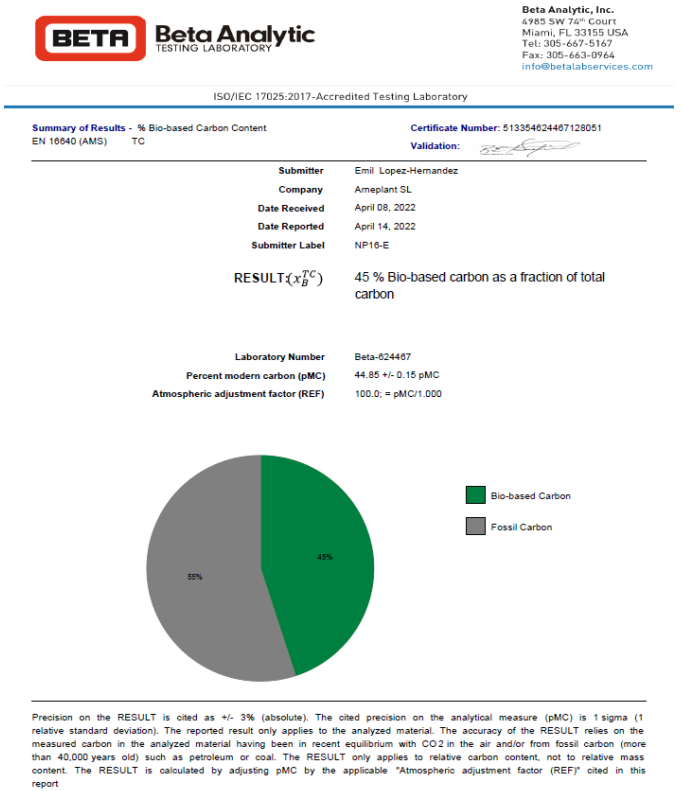
Sample ID		FY 0	FY 25 A	FY 25 B	FY 25 C
Solid content	(%)	22	22	22	22
Bio content	(wt%)	0	25	25	25
Based		Fossil	Starch	Starch	Starch
Chain extender		0	1	2	3
Density	(Kg/m3)	108	115	101	98
Durometer	(Asker C)	17	21	17	17
CLD 40%	(kPa)	49,2	69,2	67,1	50,1
Cell Flow	u.a. (0 - 100)	41	37	42	46
SAG Factor		2,3	2,1	2,2	2,6
Compression set (70ºC, 50%)	(%)	6,2	2,7	2,9	4,4
Ball rebound	(%)	27	25	22	27
Hysteresis Loss	(%)	53	59	61	55
Cushion factor - walk		18	16	17	16
Cushion factor - run		21	19	20	19

Renewable content increased

Sample ID		FZ 0	FZ 50 A	FZ 50 B
Solid content	(%)	13	13	13
Bio content	(wt%)	0	50	50
Based		Fossil	Starch	Starch
Chain extender		0	1	2
Density	(Kg/m3)	100	124	103
Durometer	(Asker C)	11	18	19
CLD 40%	(kPa)	33,5	64,0	64,8
Cell Flow	u.a. (0 - 100)	38	33	37
SAG Factor		2,2	2,4	2,2
Compression set (70ºC, 50%)	(%)	7,2	5,8	6,7
Ball rebound	(%)	23	26	23
Hysteresis Loss	(%)	60	60	62
Cushion factor - walk		29,6	20,2	22,7
Cushion factor - run		32,6	22,6	25,4

Renewable content increased





BETA Beta Analytic TESTING LABORATORY

Beta Analytic, Inc.
4985 SW 74th Court
Miami, FL 33155 USA
Tel: 305-667-5167
Fax: 305-663-0964
info@betalabservices.com

ISO/IEC 17025:2017-Accredited Testing Laboratory

Summary of Results - % Bio-based Carbon Content
EN 16640 (AMS) TC

Certificate Number: 513354624467128051
Validation:

Submitter	Emil Lopez-Hernandez
Company	Ameplant SL
Date Received	April 08, 2022
Date Reported	April 14, 2022
Submitter Label	NP16-E

RESULT: (x_B^{TC}) 45 % Bio-based carbon as a fraction of total carbon

Laboratory Number	Beta-624467
Percent modern carbon (pMC)	44.85 +/- 0.15 pMC
Atmospheric adjustment factor (REF)	100.0; = pMC/1.000

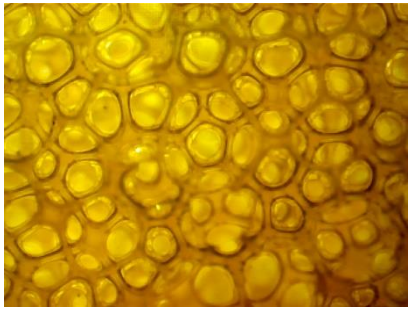
Precision on the RESULT is cited as +/- 3% (absolute). The cited precision on the analytical measure (pMC) is 1 sigma (1 relative standard deviation). The reported result only applies to the analyzed material. The accuracy of the RESULT relies on the measured carbon in the analyzed material having been in recent equilibrium with CO_2 in the air and/or from fossil carbon (more than 40,000 years old) such as petroleum or coal. The RESULT only applies to relative carbon content, not to relative mass content. The RESULT is calculated by adjusting pMC by the applicable "Atmospheric adjustment factor (REF)" cited in this report

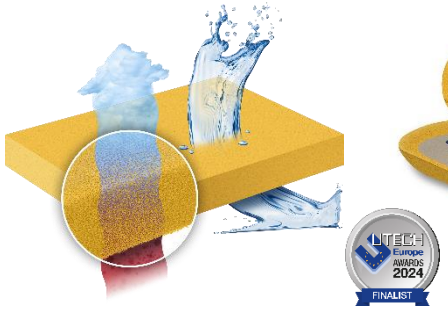
Renewable content increased

Sample ID	Density (kg/m3)	Durometer (ºAsker F)	Compression fatigue resistance* Thickness variation at 1/2h (%)	Ball rebound** (%)
D90 - fossil /100wt%	92	84	5,0	23
D90 - renewable /75wt%	95	86	6,0	36
D110 - fossil /100wt%	106	86	3,0	23
D110- renewable /70wt%	109	83	3,0	48

*Compression fatigue resistance of cellular materials (UNE 59536: 2014, method C; Sample diameter: 42mm; 13000 ciclos; Compression force: 350N)

**Determination of resilience by ball rebound (ISO 8307:2007)





Sumary

1. Flexible, renewable, and breathable **high-performance polyurethane foams with high bio-content** were successfully developed.

2. The foams demonstrated **superior properties compared to NOP-based** alternatives **and performed similarly to those made from fossil-based** raw materials.

3. Available in various grades—covering different densities, hardness levels, and bio-content—they are **versatile and suitable for a wide range of applications** in the polyurethane industry.

Reference

1. Ron Herrington, Kathy Hock. Dow Polyurethanes: Flexible Foams.1997.
2. From Lab to Market: Current Strategies for the Production of Biobased Polyols. Haritz Sardon, David Mecerreyes, Andere Basterretxea, Luc Avérous, and Coralie Jehanno ACS Sustainable Chemistry & Engineering 2021 9 (32), 10664-10677DOI: 10.1021/acssuschemeng.1c02361.
3. Sudha, G. S., Kalita, H., Mohanty, S., & Nayak, S. K. (2017). Castor oil modified by epoxidation, transesterification, and acrylation processes: Spectroscopic characteristics. International Journal of Polymer Analysis and Characterization, 22(6), 519–525. https://doi.org/10.1080/1023666X.2017.1334171
4. Gaina C, Ursache O, Gaina V, Serban AM, Asandulesa M. Novel Bio-Based Materials: From Castor Oil to Epoxy Resins for Engineering Applications. Materials (Basel). 2023 Aug 16;16(16):5649. doi: 10.3390/ma16165649. PMID: 37629941; PMCID: PMC10456403.
5. Sylwia Dworakowska, Dariusz Bogdał, Federica Zaccheria, Nicoletta Ravasio,The role of catalysis in the synthesis of polyurethane foams based on renewable raw materials,Catalysis Today,Volume 223,2014,Pages 148-156, ISSN 0920-5861. https://doi.org/10.1016/j.cattod.2013.11.05
6. Polyurethane foams from vegetable oil-based polyols: a review - Scientific Figure on ResearchGate. Available from:. https://www.researchgate.net/figure/Synthesis-of-poly-ether-ester-polyols-from-canola-oil-15_fig7_359183737.
7. McKenna, S.T., Hull, T.R. The fire toxicity of polyurethane foams. Fire Sci Rev 5, 3 (2016). https://doi.org/10.1186/s40038-016-0012-3
8. Overview of Bio-based Feedstocks. DuPont Tale & Lyle BioProducts. Susterra bio-based performances. 2020.
9. Kiany S.B. Cavalcante, Maria N.C. Penha, Karlene K.M. Mendonça, Hilton C. Louzeiro, Antonio C.S. Vasconcelos, Adeilton P. Maciel, Antonio G. de Souza, Fernando C. Silva, Optimization of transesterification of castor oil with ethanol using a central composite rotatable design (CCRD), Fuel,Volume 89, Issue 5,2010,Pages 1172-1176,ISSN 0016-2361, https://doi.org/10.1016/j.fuel.2009.10.029.
10. Hejna, Aleksander. 2018/08/28. Application of vegetable oil-based biopolyols in manufacturing of rigid polyurethane foams – short review. Journal of Polymer Science and Engineering 10.24294/jpse.v1i3.648.
11. Shrestha, M.L., Noble, I., Ionescu, M. et al. Structure Elucidation of Castor Oil Based Self-Condensed Polyols and Applications in Flexible Foams and Elastomers. J Polym Environ 32, 1717–1728 (2024). https://doi.org/10.1007/s10924-023-03060-0.


arneplant®