Synthesis of Bio-Based Polyols: Developing Sustainable Polymers for Automotive Industry

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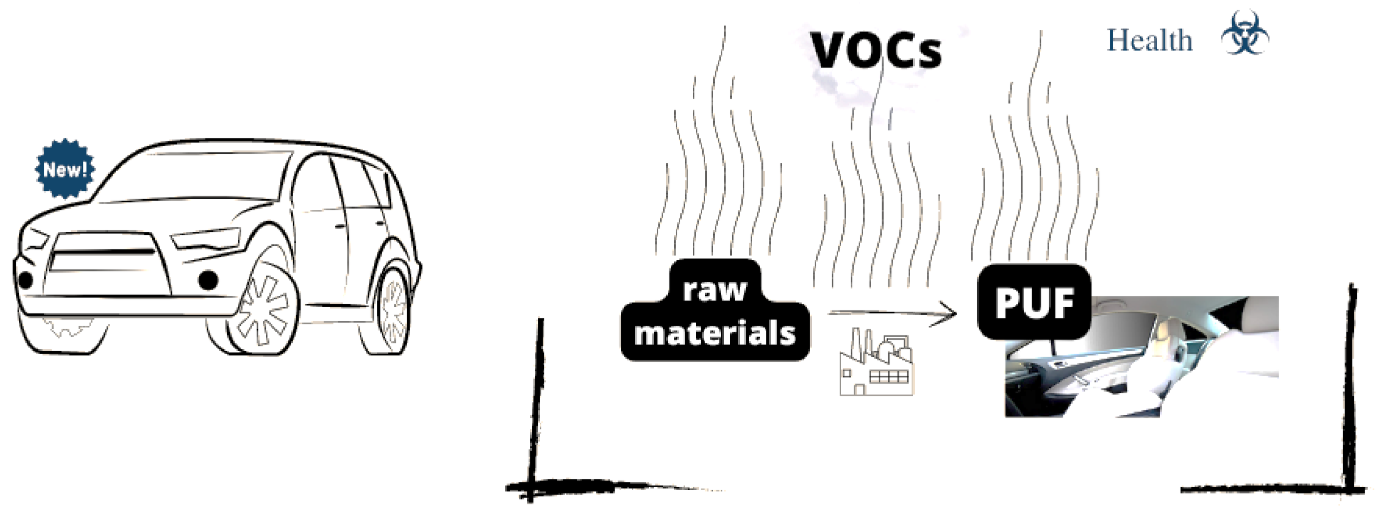
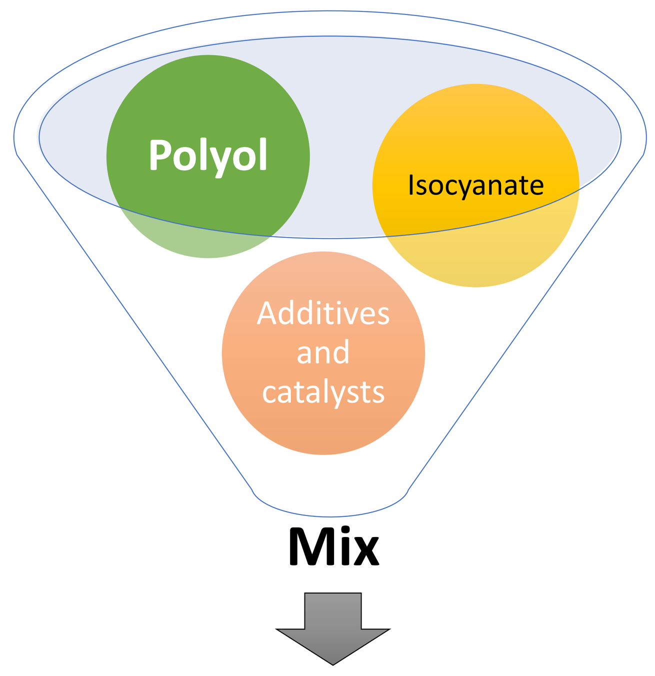
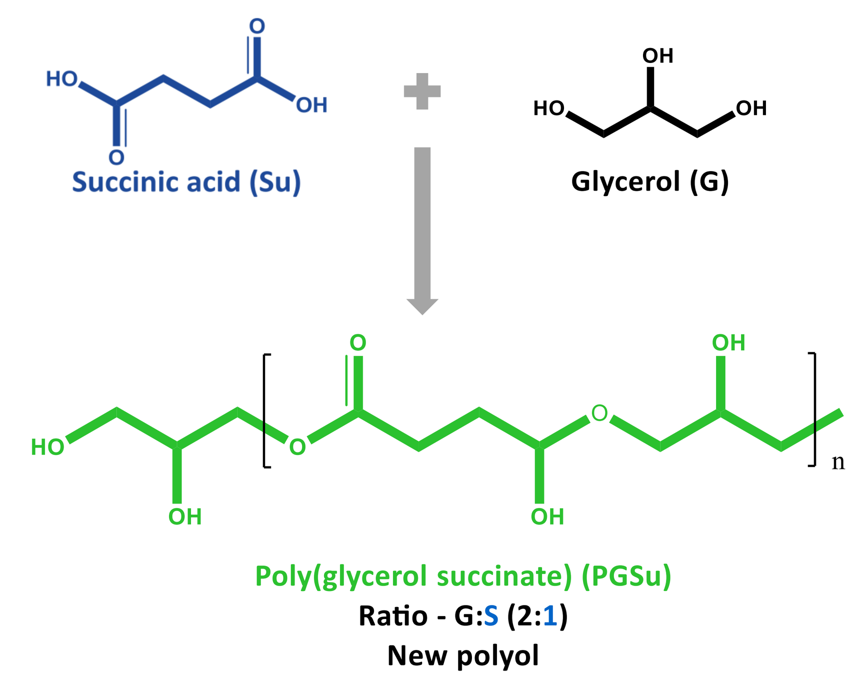
INTRODUCTION

Polyurethane foams (PUF) are commonly manufactured using **polyols, isocyanates, and additives**. Although widely used in the automotive and construction sectors, these foams release **volatile organic compounds (VOCs)** during production and use, posing **health risks** to its users.[1]

Problem







Standard foam
Lab scale

Potential solution
Polyol PGSu as a potential substitute for commercial polyols

The **GreenAuto project** seeks to modernize the automotive sector by advancing towards more **sustainable, safer, and healthier vehicles**. Inspired by the principles of **green chemistry**, we explored the **synthesis of polyols** from **bio-based monomers**. This approach is intended to avoid **VOCs** from petrochemical refineries.

METHODOLOGIES AND RESULTS

Polyol PGSu (2:1) synthesis

PARR reactor with thermal jacket produced by us

Polycondensation synthesis example:

Reactants	*Conditions*
Glycerol → 100g	150ºC
Succinic acid → 54.3g	Nitrogen flow
No catalyst	150 RPM
	7 hours

Polyol PGSu (2:1) properties
Acid value: 38.7 mg KOH/g
Viscosity: 7600 mPa.s
Hydroxyl number: 780 mg KOH/g
Functionality: between 3 – 8
Colour: yellowish clear

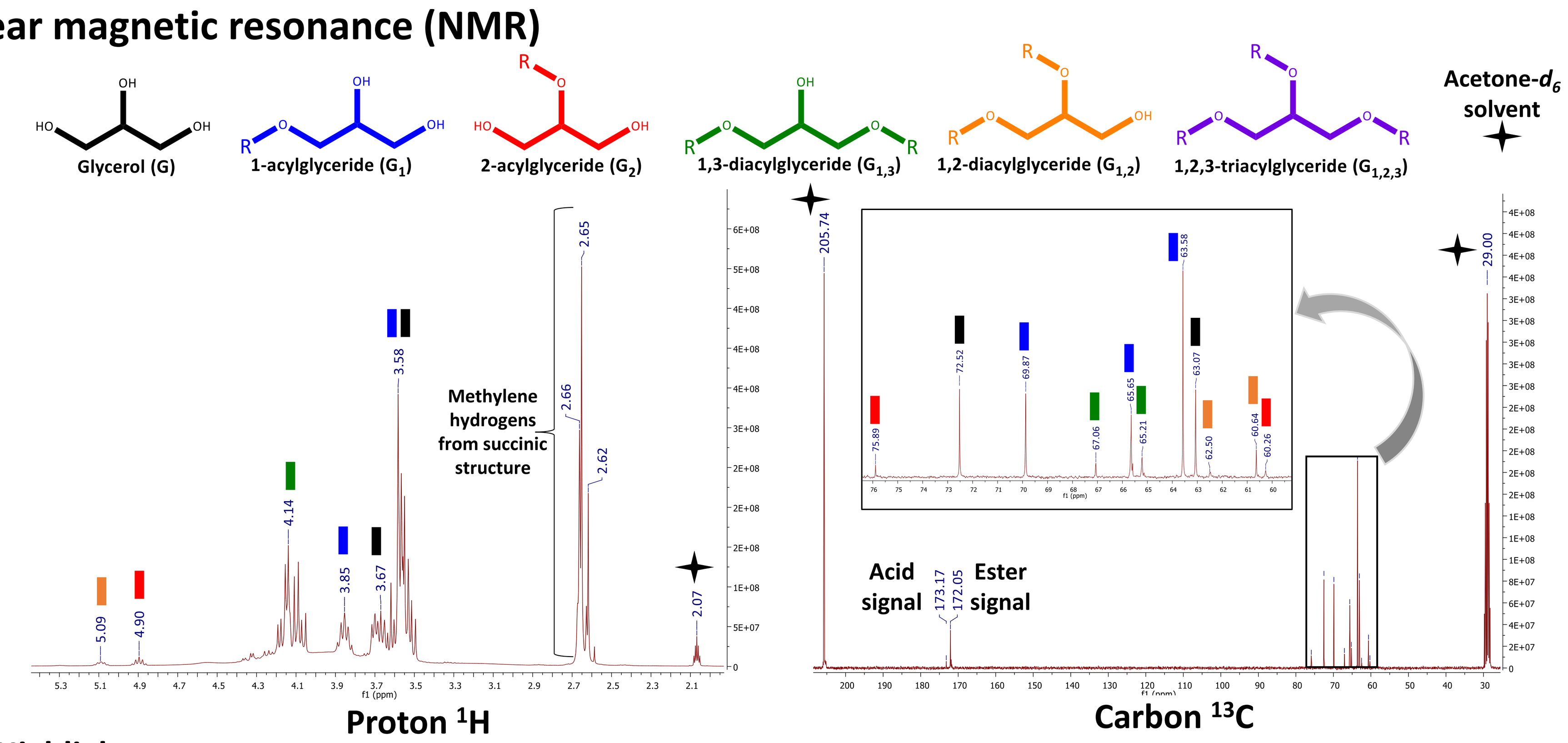
Standard foam production

Foam production example:

Reactants
Polyol Repsol R-2510 → 18g (or partial substitution with PGSu)
Isocyanate MDI → 19.5g
Catalyst DMCHA → 0.16g
Blowing agent (water) → 0.35g
Surfactant → 0.36g

Conditions
Room temperature and paper cup as recipient.
1º mix 1000 RPM for 20 seconds (Polyols, Catalyst, Water and Surfactant)
2º mix 1000 RPM for 60 seconds (after addition of Isocyanate MDI)
Final: Waiting for the foam growing

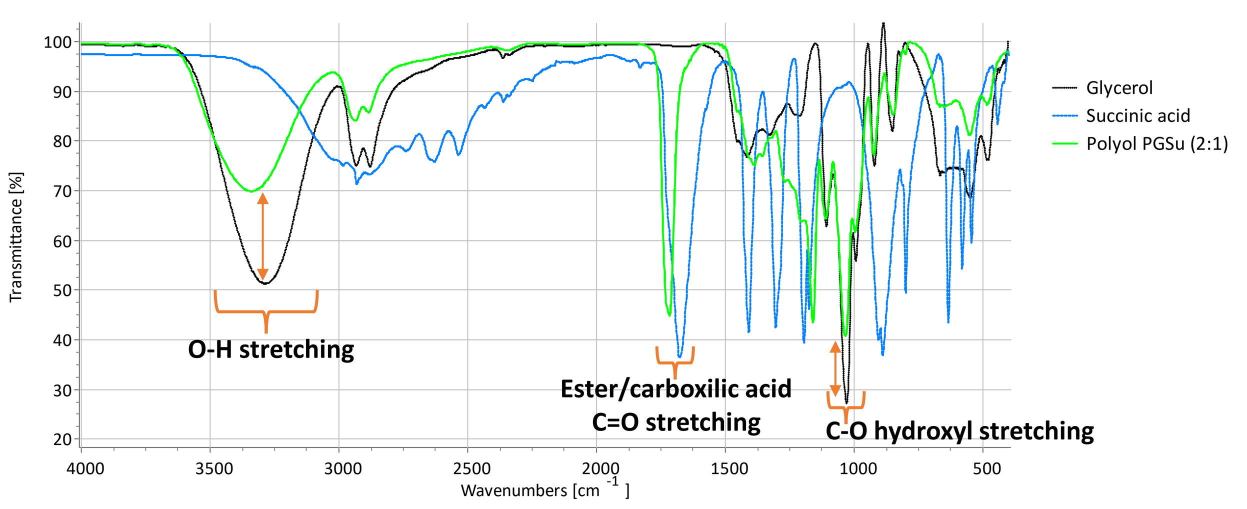
Nuclear magnetic resonance (NMR)



NMR Highlights

- **Branched structure signals (1,2,3 - triacylglyceride) were not found.**
- Primary hydroxyl groups were the most reactive with **strong 1-acylglyceride** and **1,3-acylglyceride** signals.
- Secondary hydroxyl groups also reacted, primarily as **end points of the structure (2-acylglyceride), and 1,2-acylglyceride was also detected.**
- The **signal** from the **acid groups is weak**. The **ester bonds** signal is **nine times more intense**. This agrees with the acid value (38.7 mg KOH/g) obtained.
- All these **NMR** results **support** the **FTIR and ESI-MS analyses.**

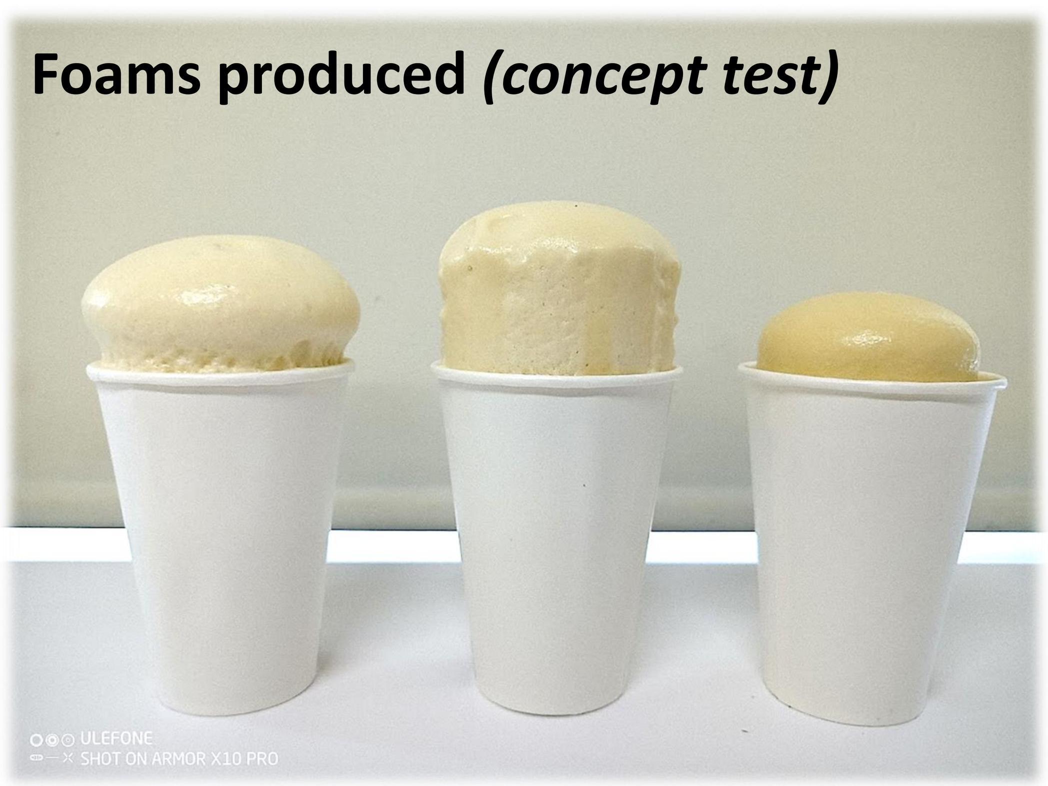
Fourier-transform infrared spectroscopy (FTIR)



FTIR Highlights

- **Hydroxyl groups of glycerol were consumed to produced polyol PGSu** (decrease bands intensity 3500 – 3000 cm^{-1} and 1034 cm^{-1}).
- **Acid groups of succinic acid were consumed to produce ester bonds** (shift from acid C=O 1675 cm^{-1} to ester C=O 1722 cm^{-1})

Foams produced *(concept test)*



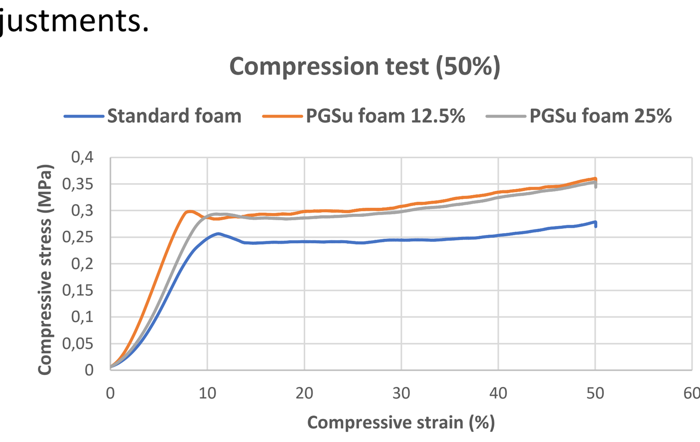
Standard foam	PGSu foam 12.5%	PGSu foam 25%
Polyol Repsol R-2510	Polyol Repsol R-2510	Polyol Repsol R-2510
100%	**87.5%**	**75%**
Polyol PGSu	Polyol PGSu	Polyol PGSu
0%	**12.5%**	**25%**

Foam Produce Highlights

Polyol PGSu was used **as replacement of** commercial polyol (Repsol R-2510): **12.5%** and **25% (wt/wt)**

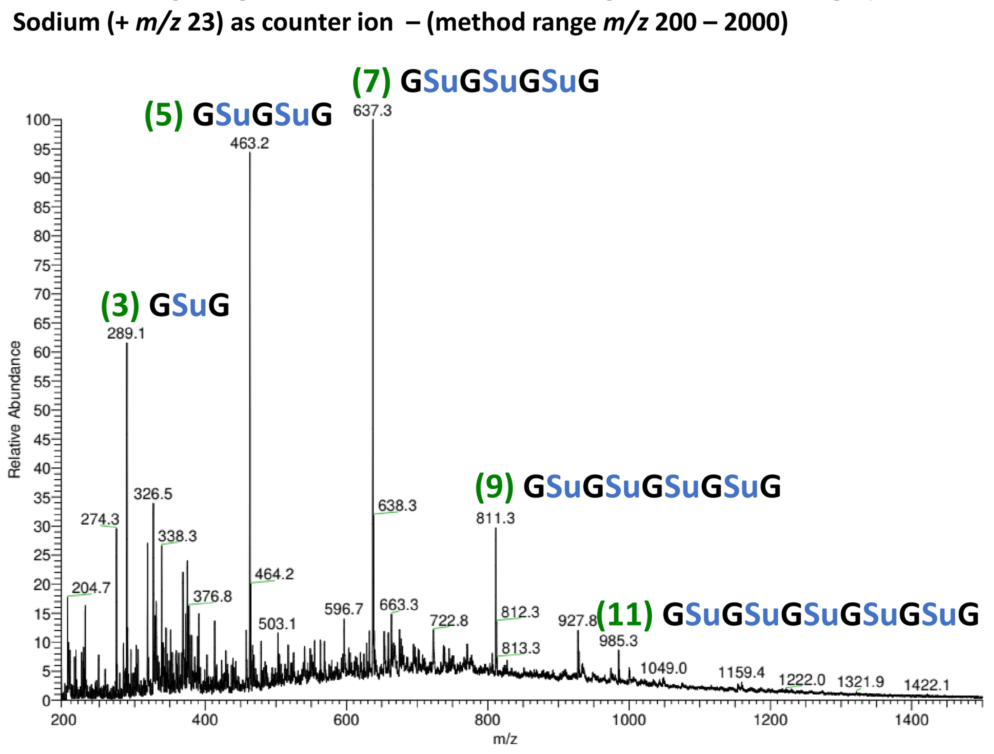
A **12.5% substitution** did **not affect significantly the expansion volume**, but it was noticed that the final **expansion is maintained** with the **memory of the cup shape**. There is no mushrooming effect, as was the case with the standard formulation.

A **25% substitution reduced the expansion volume**, indicating that this formulation cannot tolerate such a high polyol substitution, without any extra adjustments.



Electrospray ionization mass spectrometry (ESI-MS)

Sodium (+ m/z 23) as counter ion – (method range m/z 200 – 2000)



ESI-MS Highlights

- **Five principal oligomers identified**

Relative abundance Trimer 63	**(3) GSuG** Mw: 266 g/mol
Relative abundance Pentamer 94	**(5) GSuGSuG** Mw: 440 g/mol
Relative abundance Heptamer 100	**(7) GSuGSuGSuG** Mw: 614 g/mol
Relative abundance Enneamer 30	**(9) GSuGSuGSuGSuG** Mw: 788 g/mol
Relative abundance Hendecamer 8	**(11) GSuGSuGSuGSuGSuG** Mw: 962 g/mol

- The five identified masses can be justified by **linear oligomer structures that have glycerol as terminal unit.**
- The **polyol PGSu** is composed essentially of **oligomers** with **less than 650 g/mol**.

CONCLUSIONS

Polyol PGSu is composed of **linear polymeric structures** with varying **functionality (3-8),** and a molecular mass **lower than 1000g/mol.**

The use of PGSu polyol as a direct replacement for **commercial polyol up to 12.5%** appears to **have potential for success**, without the need for extra formulation adjustments.

The **exploratory concept** presented here was performed based on a single polyurethane foam formulation. However, It seams that the **polyol PGSu has the potential** to be used, **at least, as** an **oligomeric chain extender** in the production of polyurethane foams.

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