Synthesis and process engineering of glycerol based polyesters as toughness enhancers for commercial bioplastics

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Presentation outline

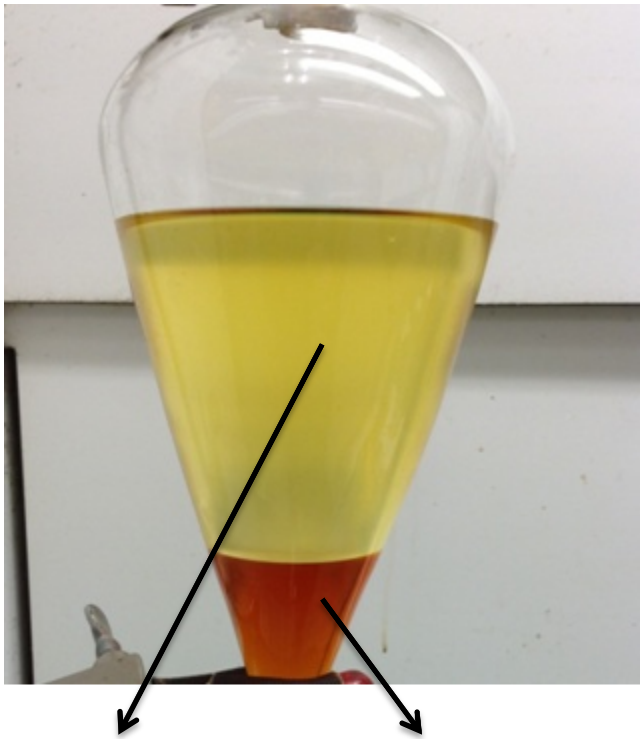
Introduction

1. Glycerol from biorefineries → 2. Glycerol for synthesis of materials

Results and discussion

3. Examples of application of glycerol based materials → 4. Summary and discussion

Glycerol facts and statistics

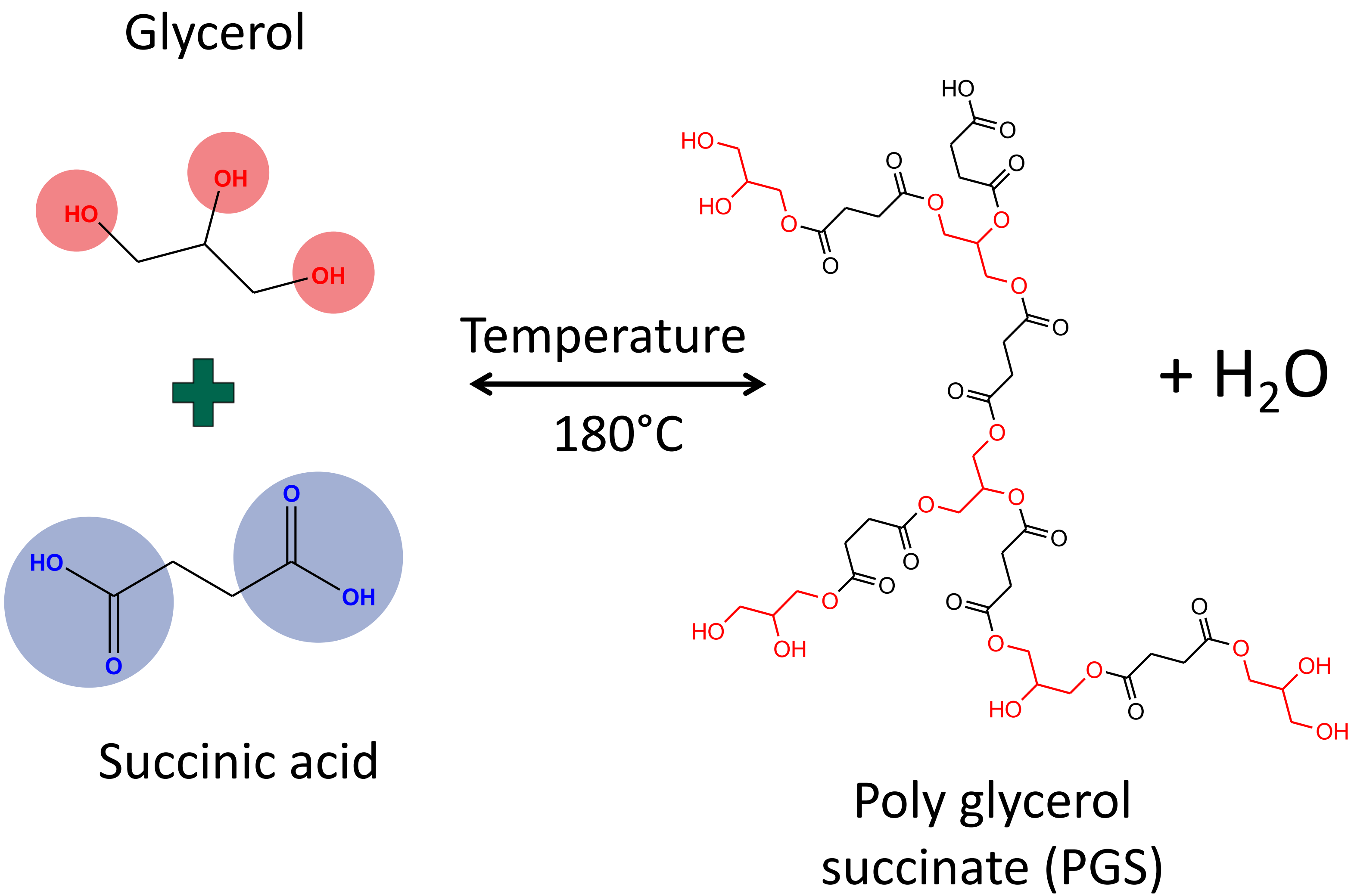


Glycerol numbers

- **Worlwide production > 1.1 billion lbs/year[1]**
- **Estimated production by 2020 = 5.8 billion lbs/year [2]**
- **Projected market by 2018 = $2.1 billion [3]**

1. Top value added chemicals from biomass, U.S. Department of Energy, 2004
2. M. Ayoub, A.Z. Abdullah. Renew. And Sustain. Energy Reviews, 2012, 16, 2671-2686
3. http://www.biofuels-news.com/industry_news.php?item_id=7794, from 20 May 2014

Glycerol polycondensation



Valerio, O., Horvath, T., Pond, C., Misra, M., & Mohanty, A.K. *Industrial Crops and Products* 78 (2015): 141-147.

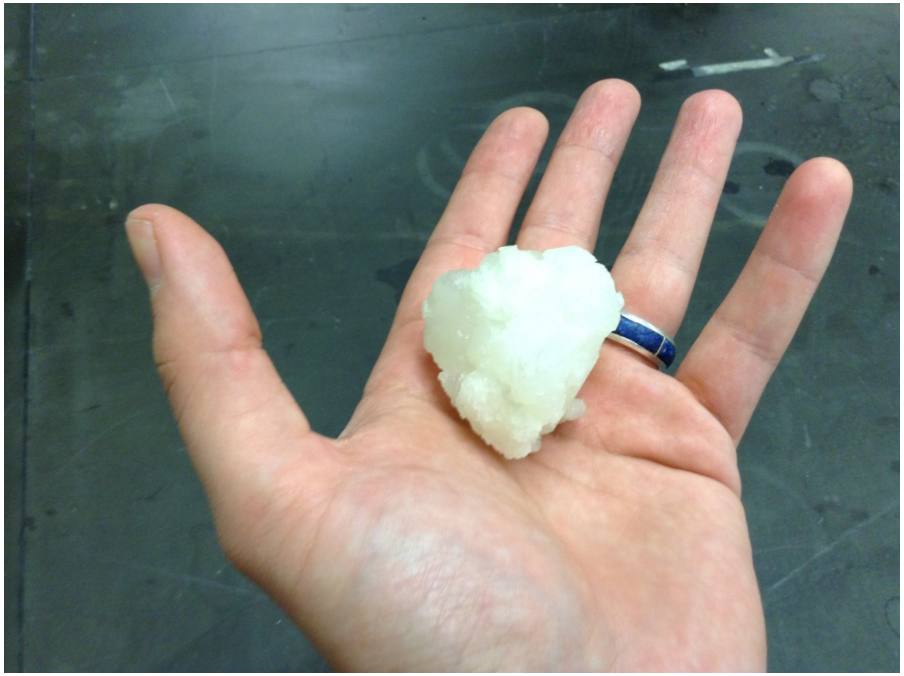
Glycerol polycondensation

- **Advantages**
  - One pot procedure
  - Usage of biobased monomers
  - Can be synthesized in bulk (with no solvent addition)
  - No toxic monomers or co products formed

- **Challenges**
  - Gelation control (crosslinks at high conversion)
  - Homogeneous synthesis of gel products
  - Difficult to purify
  - Low molecular weight

PGS products

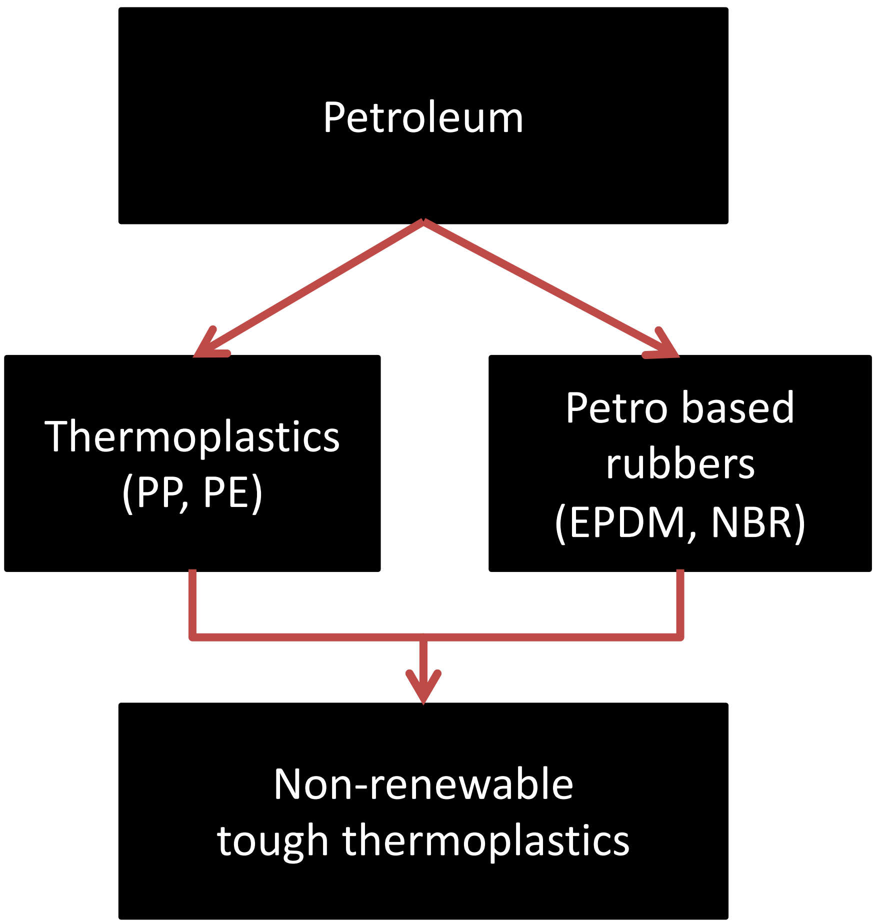
Liquid poly glycerol succinate
(stopped before gel onset)



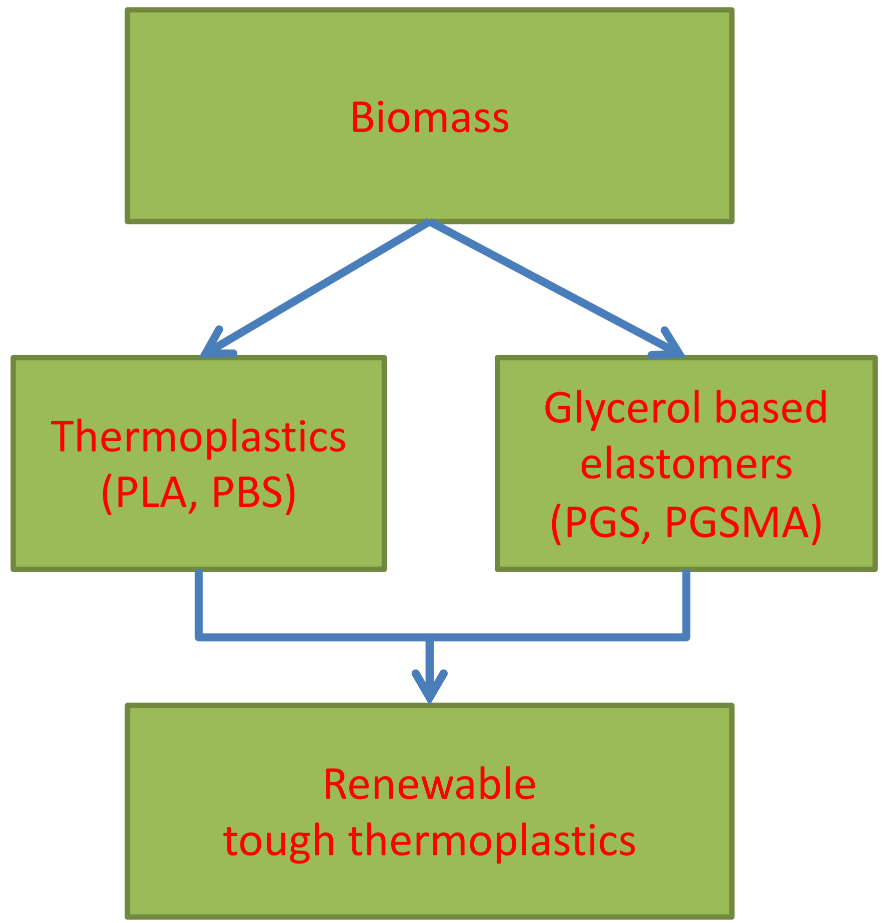
Elastomer poly glycerol succinate
(stopped after gel onset)

Toughening of bioplastics with PGS

Conventional oil refinery



Biorefinery

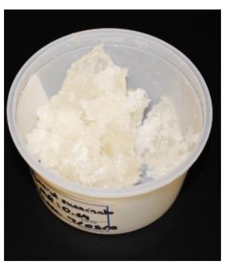


PGS blending with bioplastics: Example 1

Glycerol polyester (PGS) blending with Poly butylene succinate (PBS)

Poly (butylene succinate) (PBS)

+



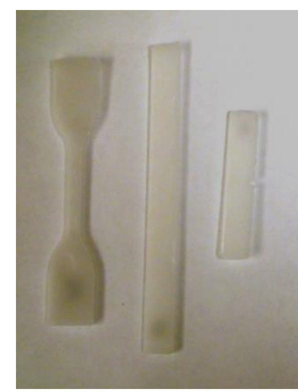
Gel Poly glycerol succinate (PGS)

Twin screw extruder

Tprocess = 150°C
2 min mixing, 100 rpm
Tmold = 30°C

Injection molding

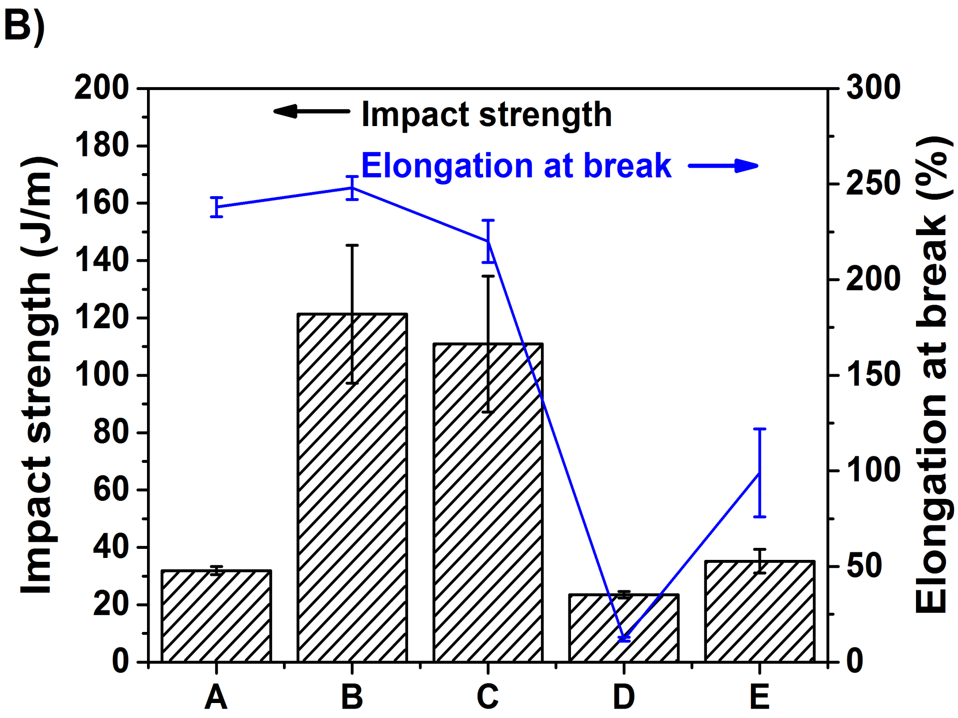
Samples for mechanical testing



Valerio, O., Misra, M. & Mohanty, A.K. J Polym Environ (2017). doi:10.1007/s10924-017-1015-4

PGS blending with bioplastics: Example 1

- PBS impact resistance increased 250% with 30wt% addition of gel PGS
- Tensile strength reduction of 35%
- Pure glycerol based PGS yields higher impact to PBS



A: Pure PBS
B, C: 70/30 PBS/PGS (PGS from pure and technical glycerol)
D, E: 70/30 PBS/PGS (PGS from crude glycerol)

Valerio, O., Misra, M. & Mohanty, A.K. J Polym Environ (2017). doi:10.1007/s10924-017-1015-4

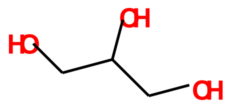
PGS blending with bioplastics: Example 2

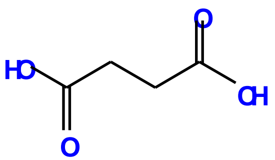
Glycerol polyester (PGS) **reactive** blending with Poly lactic acid (PLA)

Step 1: Synthesis of PGS containing unsaturation points by using maleic anhydride as comonomer

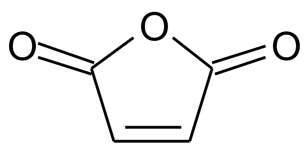
Poly glycerol succinate co maleate (PGSMA)

Glycerol



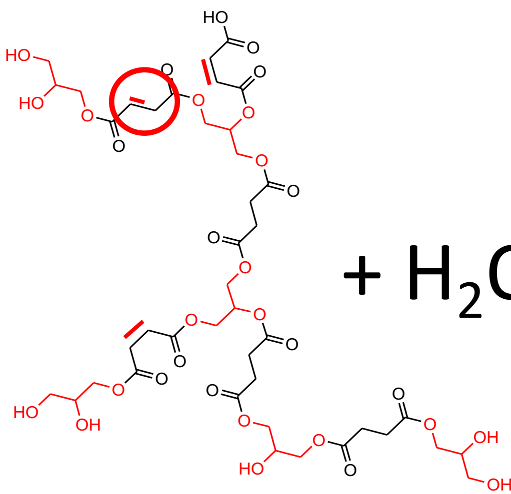


Succinic acid



Maleic anhydride

Temperature



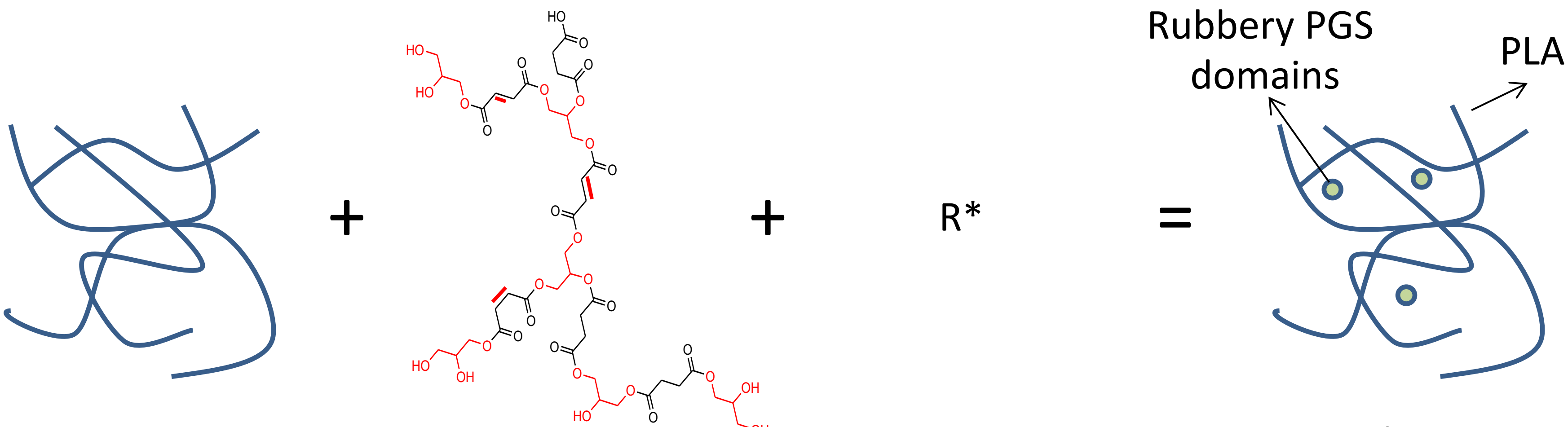
+ H_2O

Valerio, O., Pin, J.M., Misra, M., & Mohanty, A.K. *ACS Omega* 1, no. 6 (2016): 1284-1295.

PGS blending with bioplastics: Example 2

Glycerol polyester (PGS) **reactive** blending with Poly lactic acid (PLA)

Step 2: Reactive blending of PGS and PLA in presence of a free radical initiator induces PGS crosslinking *in situ*



PLA chains | PGSMA oligomers | Radical initiator | PLA/PGSMA system

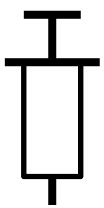
Valerio, O., Pin, J.M., Misra, M., & Mohanty, A.K. *ACS Omega* 1, no. 6 (2016): 1284-1295.

PGS blending with bioplastics: Example 2

Glycerol polyester (PGS) blending with Poly lactic acid (PLA)

Poly lactic acid (PLA)

+



Liquid Poly glycerol succinate (PGS)

+

Radical initiator (L) (Luperox)

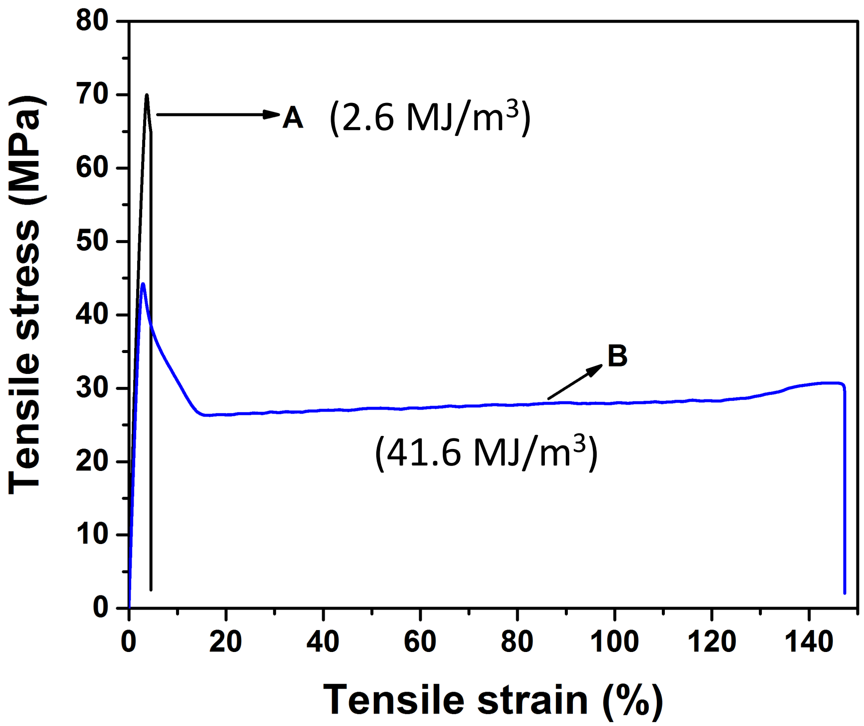
Reactive extrusion
Twin screw extruder

Tprocess = 180°C
2 min mixing, 100 rpm
Tmold = 30°C

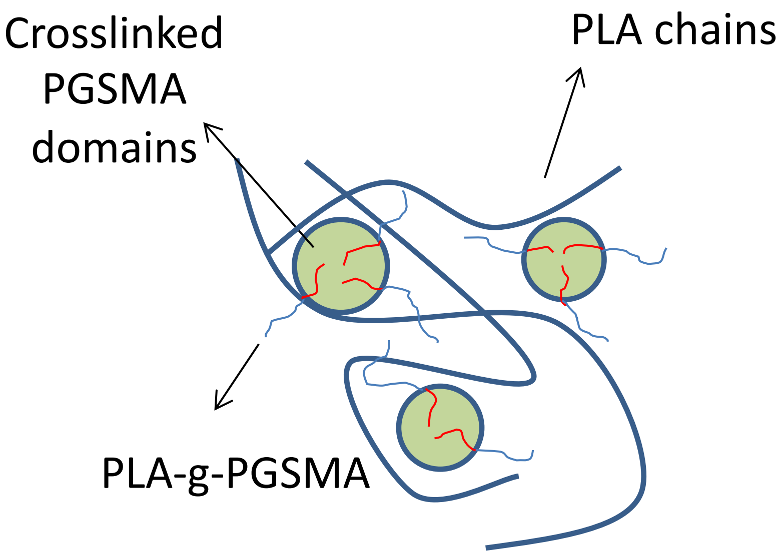
Injection molding

Samples for mechanical testing

PGS blending with bioplastics: Example 2



A: neat PLA 3251D Ingeo + Luperox (L)
B: 80/20 PLA/PGS + L



Addition of 20 wt% of PGS to PLA on reactive extrusion mode increased elongation at break in 140%

Valerio, O., Pin, J.M., Misra, M., & Mohanty, A.K. *ACS Omega* 1, no. 6 (2016): 1284-1295.

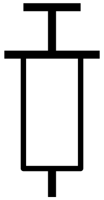
Can we create a biobased thermoplastic blend using PGS with similar mechanical properties to polypropylene?

PGS blending with bioplastics

PGSMA blending with Poly lactic acid (PLA) and Poly butylene succinate (PBS)

PLA and PBS pellets

+



Liquid Poly glycerol succinate (PGS)

+

Radical initiator (L) (Luperox)

Reactive extrusion
Twin screw extruder

Tprocess = 180°C
2 min mixing, 100 rpm
Tmold = 30°C

Injection molding

Samples for mechanical testing

Target mechanical properties

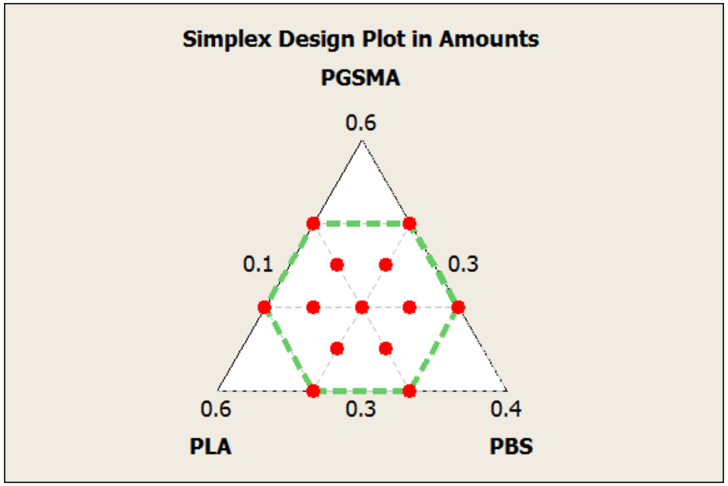
Table 1: Examples of commercial polypropylene properties

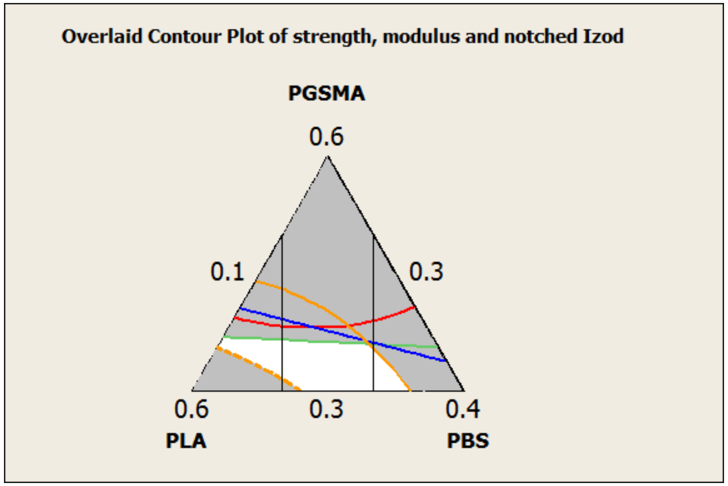
Polypropylene	Tensile stress at yield (MPa)	Tensile modulus (GPa)	Notched Izod impact (J/m)	ref
LB Adstif EA5075	30	1600	50	1
LB Pro-fax 7523	27	1150	100	2
PP 2135N	23	1100	186	3
SABIC 49MK45	29	1400	65	4

- Tensile stress at yield: 25 - 40 MPa
- Tensile modulus: 1 – 2 GPa
- Notched Izod impact (23°C): 50 – 200 J/m

1. https://www.lyondellbasell.com/en/polymers/p/Adstif-EA5075/9f1f3cc4-b0ef-4379-a9e9-2b781d7b45ad
2. https://www.lyondellbasell.com/en/polymers/p/Pro-fax-7523/dad5e94a-e1e1-4696-b572-f3253ebfdf18
3. http://www.pinnaclepolymers.com/datasds.php
4. https://www.sabic.com/en/products/polymers/polypropylene-pp/sabic-pp

Design of experiments and optimization





- Mixture design of experiments allowed screening for optimal combination of PGSMA, PLA and PBS
- A feasibility region was found, where mechanical properties are in the range of target properties:
- Tensile stress at yield: 25 - 40 MPa
- Tensile modulus: 1 – 2 GPa
- Notched Izod impact : 50 – 200 J/m

Valerio, O., Misra, M., & Mohanty, A.K. *Polymer testing* 65, (2018): 420-428.

Thermoplastic blend of PGSMA

Table 2: Comparison of PGSMA blends and polypropylene

Material	Tensile stress at yield (MPa)	Tensile modulus (GPa)	Notched Izod impact (J/m)	ref
LB Adstif EA5075	30	1.600	50	1
LB Pro-fax 7523	27	1.150	100	2
PP 2135N	23	1.100	186	3
SABIC 49MK45	29	1.400	65	4
35/40/25 PGSMA/PLA/PBS	33.8	1.470	159	

- An example of PGSMA/PLA/PBS blend is displaying similar mechanical performance to PP
- Properties can be adjusted by changing the formulation

1. https://www.lyondellbasell.com/en/polymers/p/Adstif-EA5075/9f1f3cc4-b0ef-4379-a9e9-2b781d7b45ad
2. https://www.lyondellbasell.com/en/polymers/p/Pro-fax-7523/dad5e94a-e1e1-4696-b572-f3253ebfdf18
3. http://www.pinnaclepolymers.com/datasds.php
4. https://www.sabic.com/en/products/polymers/polypropylene-pp/sabic-pp

Summary

- PGS can be synthesized in short and simple procedures using biobased monomers
- PGS gel has shown capability of improving impact resistance for poly(butylene succinate)
- PGSMA can be used for increasing elongation at break of PLA in reactive extrusion mode
- PGSMA was successfully used in ternary blends with PLA and PBS for creating a material with similar mechanical properties to petro-based polypropylene
- Overall PGS is a promising bioplastic for the modification of commercial thermoplastics mechanical behavior by melt blending

Acknowledgements

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Questions?

Thank you!