ETH zürich

CMASLab

NOVEL PROCESSING ROUTE FOR PET-GF COMPOSITE MANUFACTURING VIA SSP

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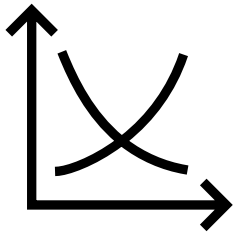
Agenda

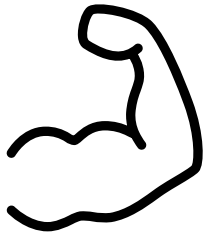
- Introduction
  - Thermoplastics Composites & challenges
  - Technology screen
  - Background on SSP
  - SSP Processing & Interface advantages for composites manufacturing
- Characterization methods
- Workflow – Overview
- Results
- Conclusion & Outlook

Introduction – TP Composites & challenges

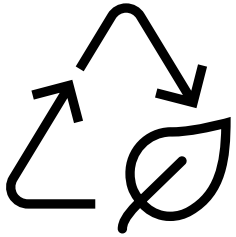
- **Why Thermoplastic?**



Price to performance ratio



Increased fracture toughness



Sustainability potential

1. J. L. Thomason, Glass fibre sizing: A review, Composites Part A: Applied Science and Manufacturing 127 (2019) 105619.
2. C. Schneeberger, J. C. Wong, P. Ermanni, Hybrid bicomponent fibres for thermoplastic composite preforms, Composites Part A: Applied Science and Manufacturing 103 (2017) 69–73.
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Introduction – TP Composites & challenges

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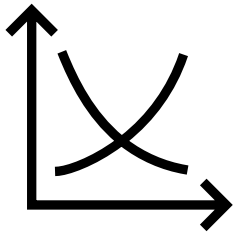

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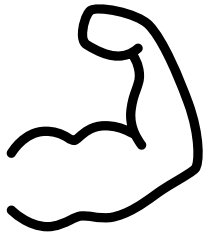

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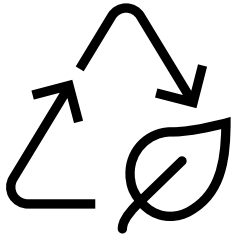

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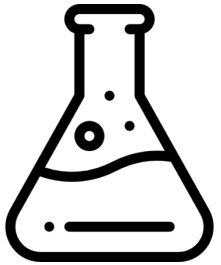
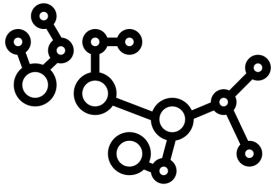
- **Processing challenges:**



Dissolution in solvents:
- Expensive
- Compatibility
- Sustainability



In-situ reaction:
- Time consuming
- By-products
- Demanding conditions

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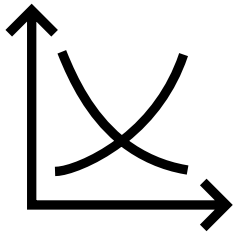

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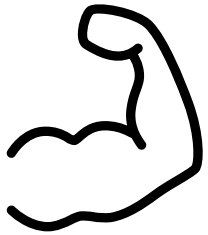

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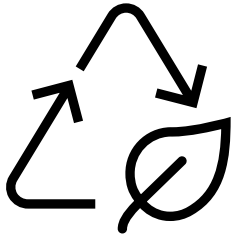

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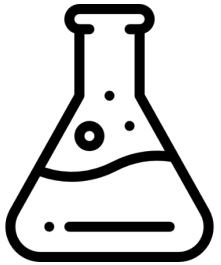

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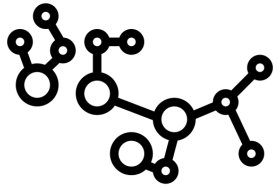
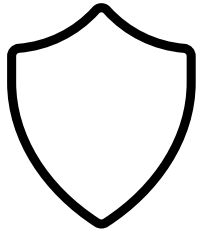


In-situ reaction:
- Time consuming
- By-products
- Demanding conditions

- **Matrix Fibre interaction:**



Weak link:
- $\sigma_{interface}$ < Yield
- Sizing not optimized for TP
- No covalent bond – VdW

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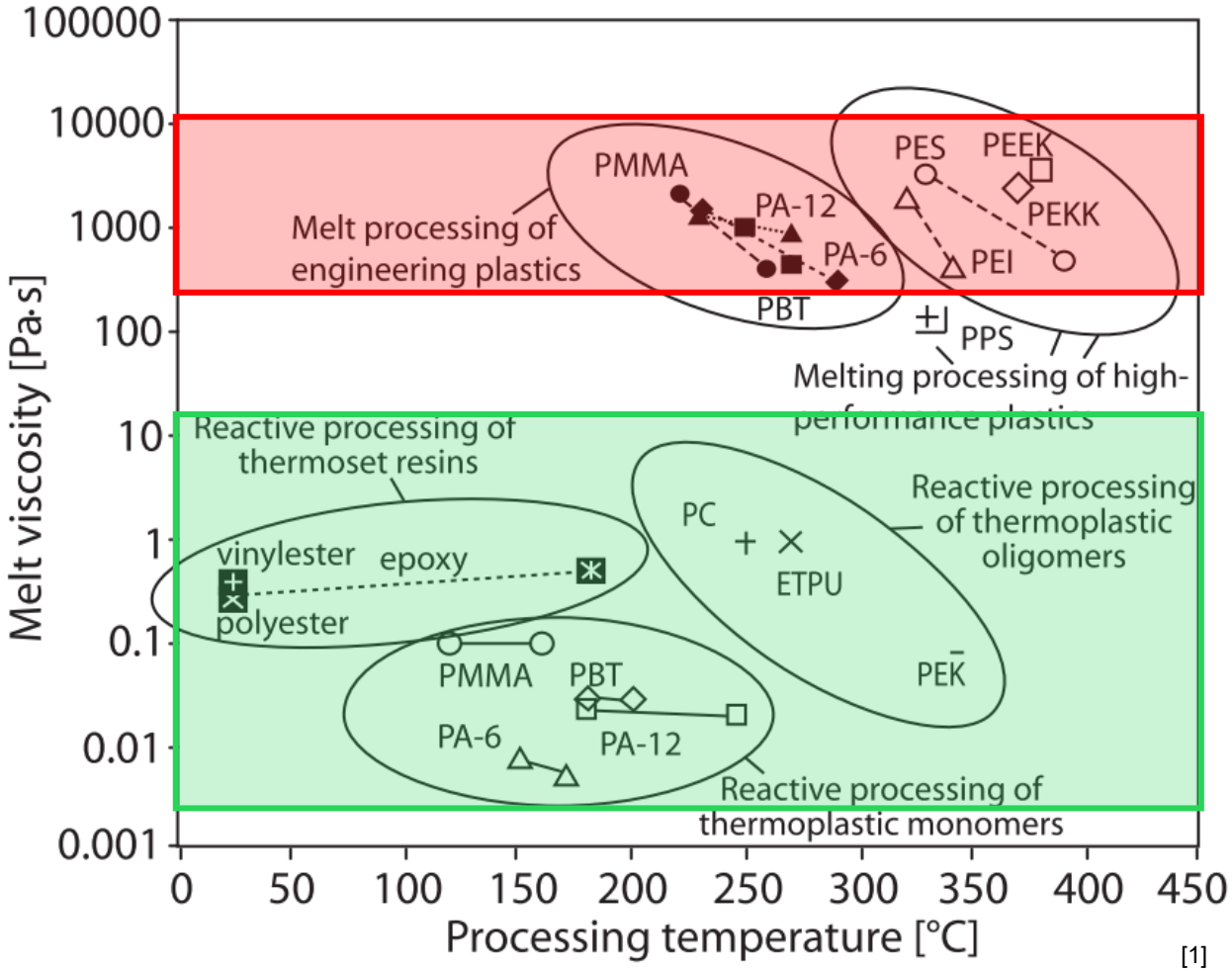
Introduction - Technology screen

- What is needed?
  - Ease of processing → **Low MW** (low η)
  - High performance → **High MW** (high η)
- How do we get that?
  - Reactive Processing of Monomers
    → Too slow & demanding conditions
  - Particle suspension
    → Complex set up & solvents
  - Liquid crystal polymer (LCP)
    → Still to viscous &/or need solvents
  - **Solid State Polymerisation**

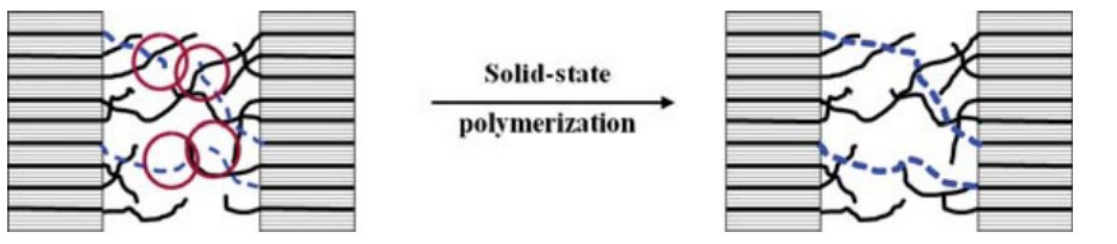


[1]

1. Van Rijswijk, K., and H. E. N. Bersee. "Reactive processing of textile fiber-reinforced thermoplastic composites–An overview." *Composites Part A: Applied Science and Manufacturing* 38.3 (2007): 666-681.

What is SSP?

- Polycondensation polymers → PAs, Polyesters (PET)
- MW increase in the Solid State
  - Mild conditions $T_g < T < T_m$
  - Between amorphous regions
  - By-products: H_2O and EG
- Potential advantages for composites?
  - **Processability & Sustainability**
  - **Interface improvement**



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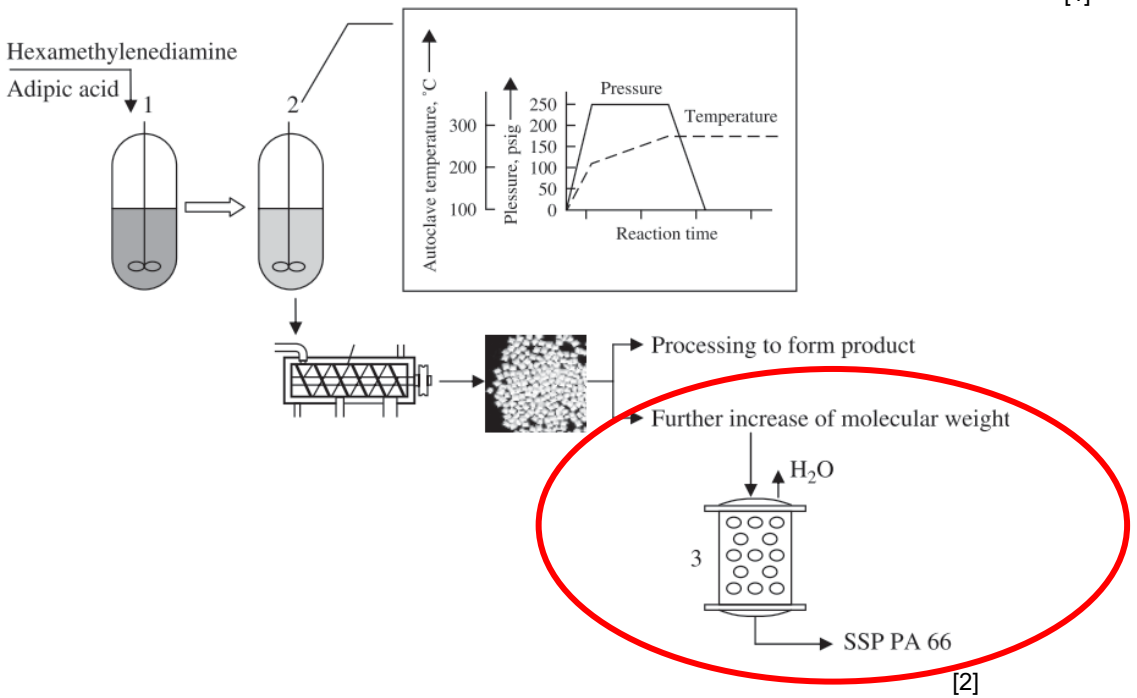
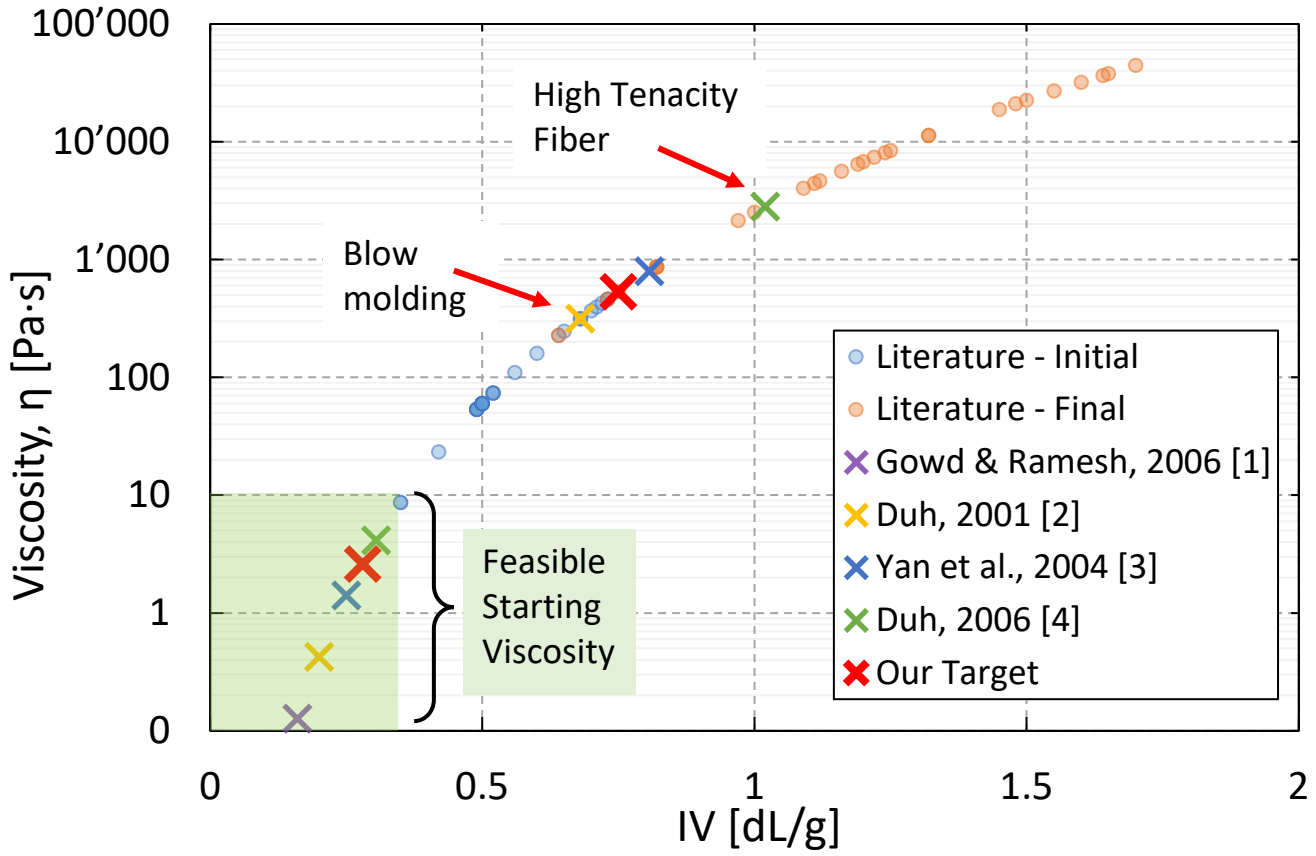


[2]

1. Solid State Polymerisation, by C.D. Papaspyrides & S. N. Vouyiouka, Book
2. Handbook of Thermoplastics by Olagoke Olabisi, Kalopo Adewle, Book

SSP for composite application – processing advantages

- Impregnation speed
  - Commercial product η: 400 -3'000 Pa·s
  - Our aim 1-10 Pa·s
  - **Substantial time saved**
- Composite quality → **practically void-free**
- No solvent, nor other chemicals
- Reaction in the solid state
  - Recover & improve mechanical properties
  - **Off-line & bulk** → "drying stage"
- Literature:
  - Feasibility on pure polymer proved
  - All reached commercial grade quality



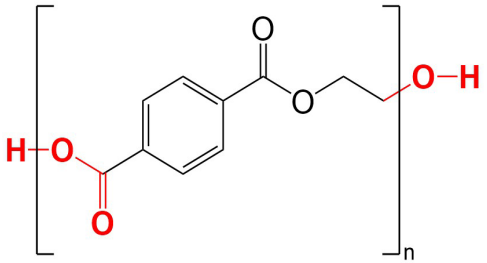
Impregnate TP like TS → Efficient & high-quality

1. Gowd, E. Bhoje, and C. Ramesh. "Effect of poly (ethylene glycol) on the solid-state polymerization of poly (ethylene terephthalate)." *Polymer international* 55.3 (2006): 340-345.
2. Duh, Ben. "Reaction kinetics for solid-state polymerization of poly (ethylene terephthalate)." *Journal of applied polymer science* 81.7 (2001): 1748-1761.
3. Yan, Weixia, et al. "Study on long fiber–reinforced thermoplastic composites prepared by in situ solid-state polycondensation." *Journal of applied polymer science* 91.6 (2004): 3959-3965.
4. Duh, Ben. "Effects of crystallinity on solid-state polymerization of poly (ethylene terephthalate)." *Journal of applied polymer science* 102.1 (2006): 623-632.

SSP for composite application – interface advantages

- Chemical groups involved in **SSP can react with GF surface**
  - Covalent bond between GF-PET
  - Stronger interface

PET



1. Achilias, D.S., Bikiaris, D.N., Karavelidis, V. and Karayannidis, G.P., 2008. Effect of silica nanoparticles on solid state polymerization of poly (ethylene terephthalate). *European polymer journal*, *44*(10), pp.3096-3107.

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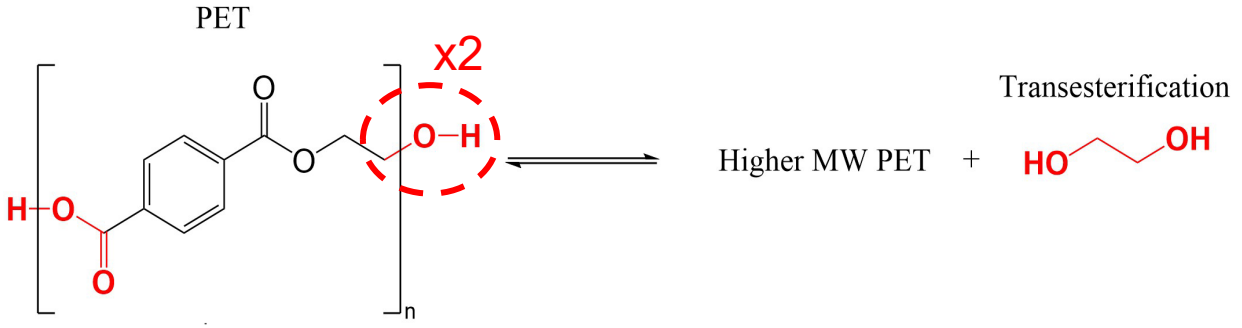

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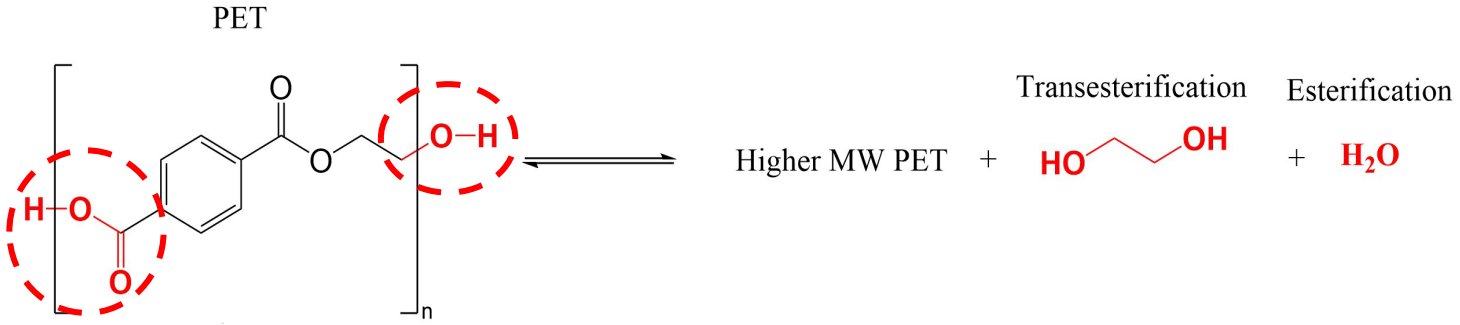

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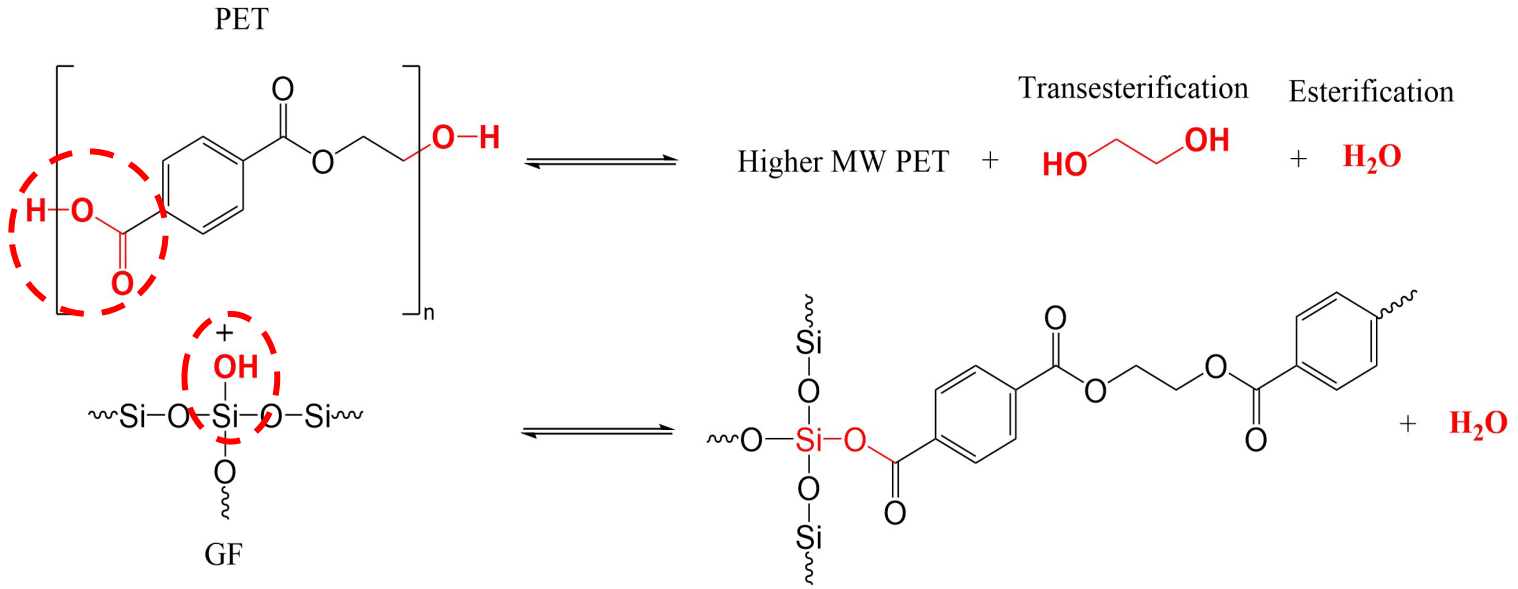

Matrix-fiber form a covalent link → Stronger bonds than with sizing solution

1. Achilias, D.S., Bikiaris, D.N., Karavelidis, V. and Karayannidis, G.P., 2008. Effect of silica nanoparticles on solid state polymerization of poly (ethylene terephthalate). *European polymer journal*, *44*(10), pp.3096-3107.

Polymer Characterization methods

- Processing → Melt viscosity (η)
  - Rheology, measure complex shear → get η_0
  - At processing Temperature (> T_M)
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  - **Only on pure polymer**

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- Polymer Industry → Intrinsic viscosity (IV)
  - Via capillary viscometer, Cannon-Feske
  - Measure flowing time of dilute solution
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$$[\eta] = K * \overline{M_w^{\alpha}}$$

- Shear viscosity: $K = 3.2 * 10^{-14}, \alpha = 3.5$
- Intrinsic viscosity :$K = 7.4 * 10^{-4}, \alpha = 0.648$

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- Polymer science → MW distribution
  - Via Gel Permeation Column (GPC)
  - Actual measurement of MW, not correlation
  - Measure distribution polymer → quality

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	IV [dL/g]	Melt η [Pa*s]	MW_w [kg/mol]
High-end Commercial grade	1.1 – 1.2	3'500 – 6'000	78 – 90
Average Commercial grade	0.7 – 0.73	350 – 450	39 – 41
Our initial grade aim	0.25 – 0.35	1 – 10	8 – 13,5

TP-GF Composite Manufacturing via SSP- Workflow

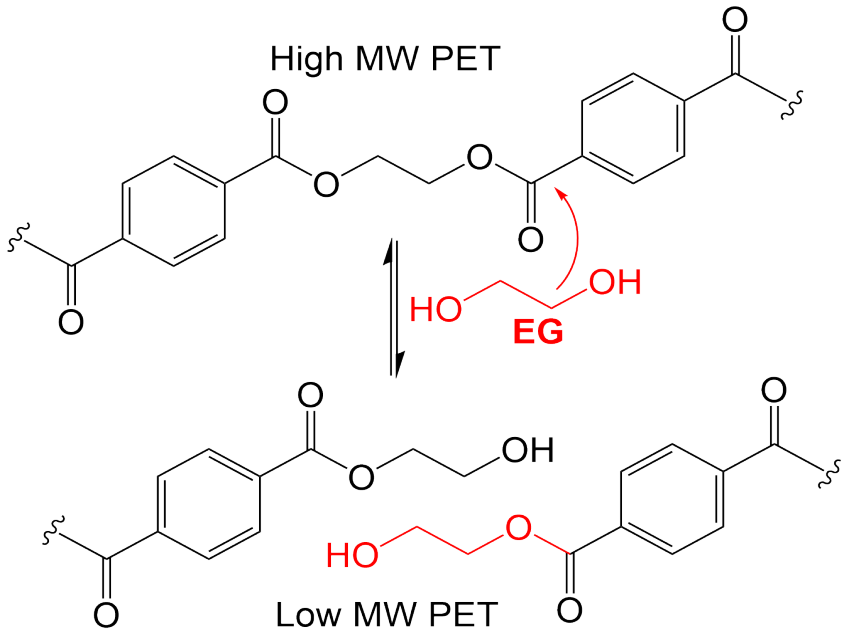
- Oligomer
- Low η < 10 Pa·s
- No solvent
- Obtained via Reactive extrusion

- With low η oligomer
- Fast
- Low P required

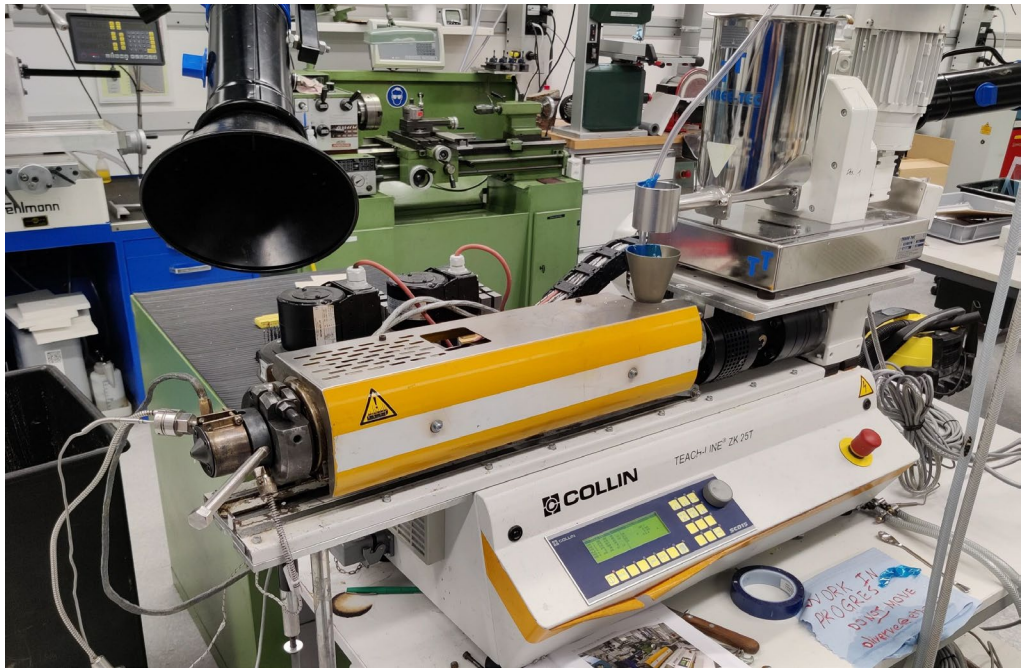
- **Improve polymer properties**
- **Improve interface properties**

Reactive extrusion - Process

- Need lower η than commercially available
- Many depolymerization options → Glycolysis
- PET + EG (co-monomer) → Oligomer
- Tune ratio EG/PET to achieve different η
- Heat & Mixing → Twin screw extruder



Condition	VPET	HIGH η	MEDIUM η	LOW η
EG:PET ratio	0	0.0036	0.01	0.04
η [Pa*s]	195	36	16	2



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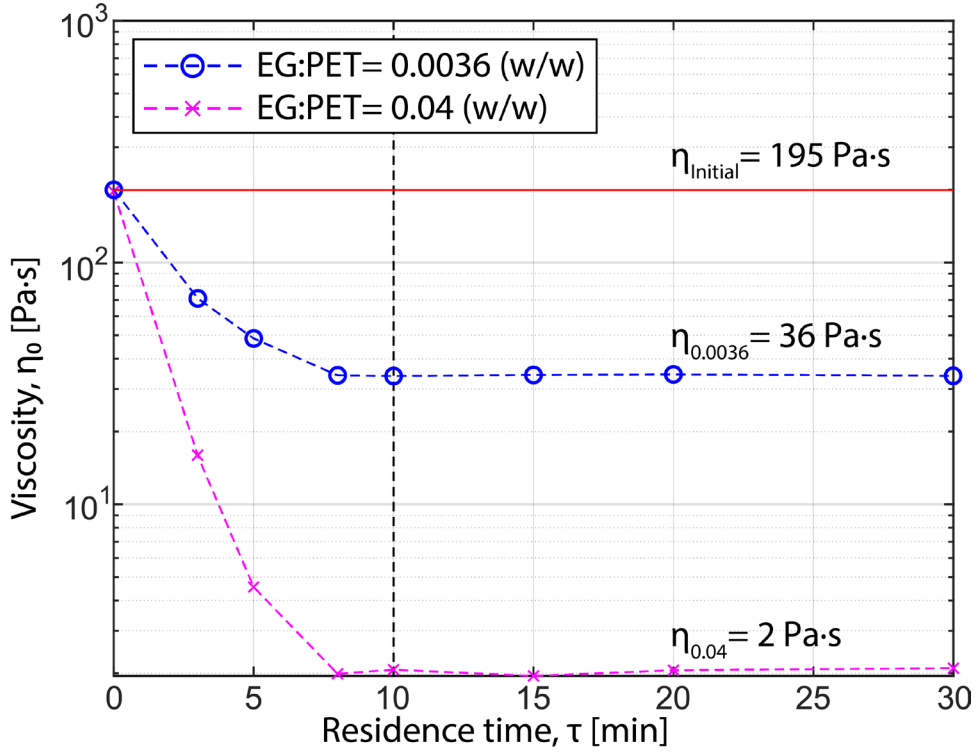
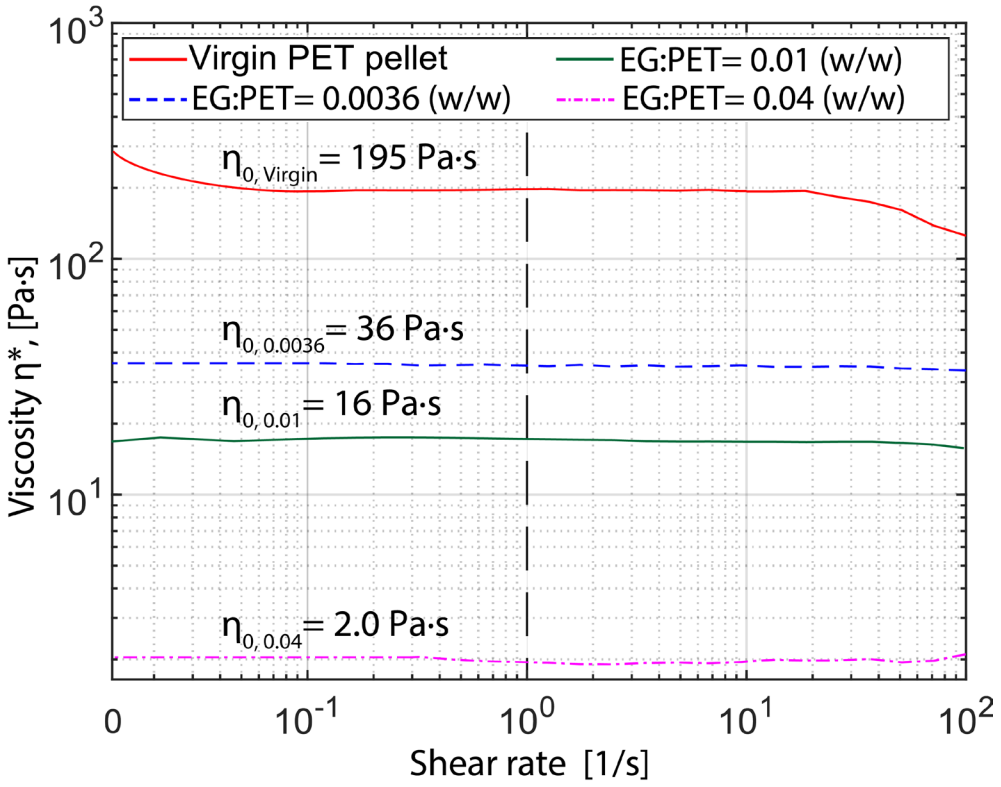
1. SoftMAT Lab, ETH Zürich

Reactive extrusion - Results

- <10 min of reaction time for all the grades
- No further degradation within 30 min

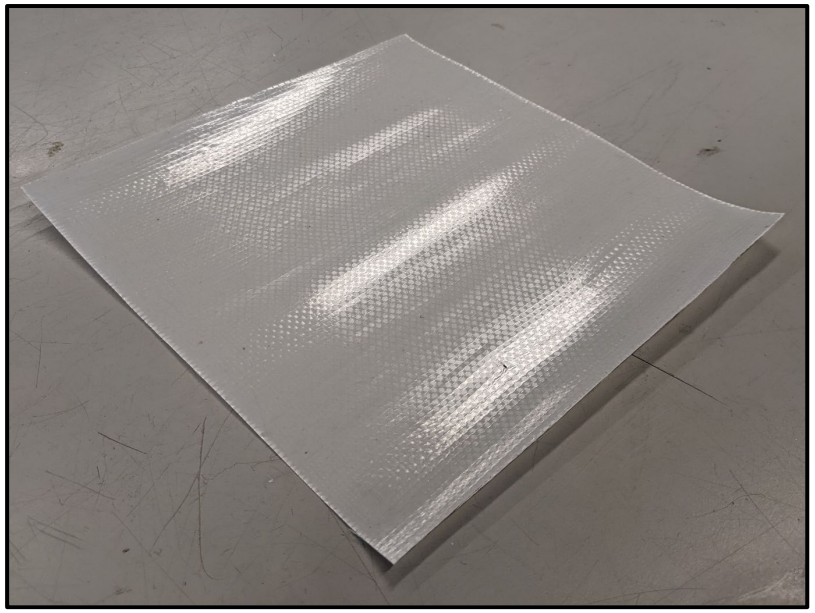


- Easy to produce a wide range of viscosities
- Low η → Newtonian fluid behavior
- Homogeneous reaction → no high MW chains



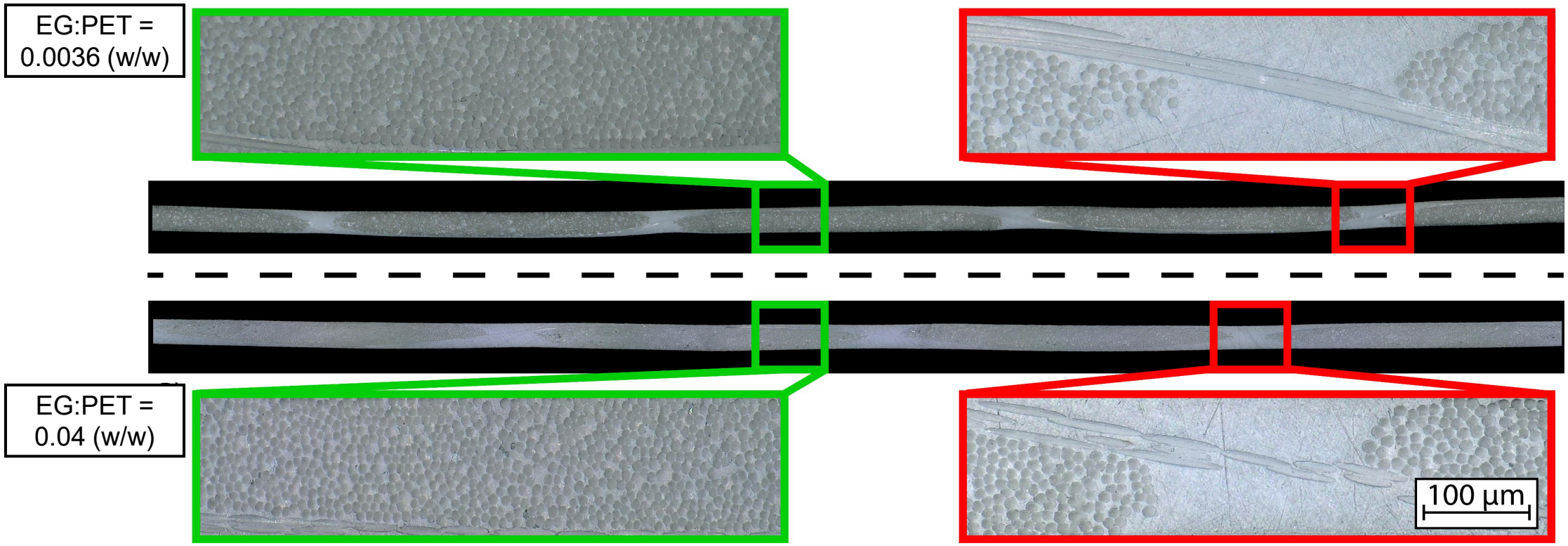
Impregnation – Process

- High temp. compression molding under vacuum
  - Process temperature: 270°C
  - Process pressure: 2 – 4 Bar
- On single ply → not diffusion limited
- GF textile: UD 200 gsm
- Composite with ~ 50% FVF



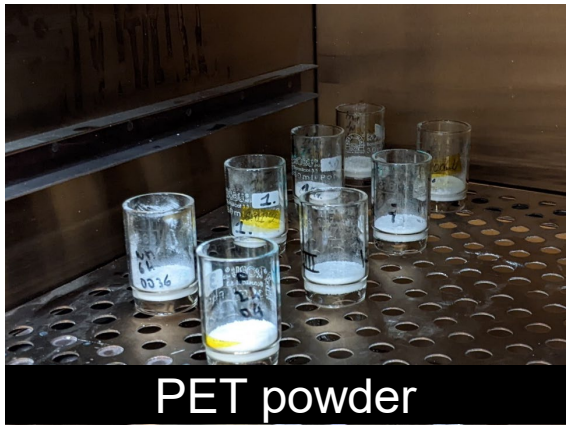
Impregnation – Results

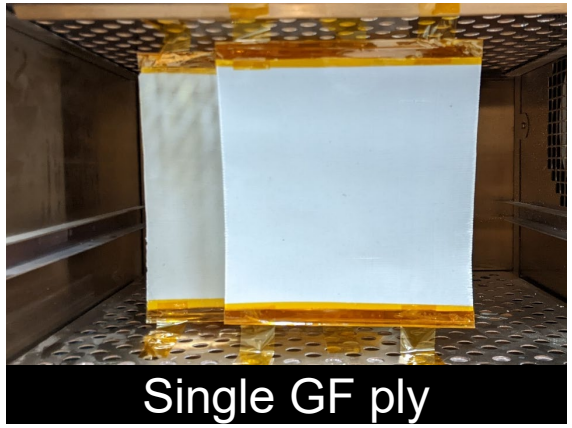
- Very low pressure required
- Low viscosity → opposite problem of TP
- Practically voidless
- Textile structure maintained



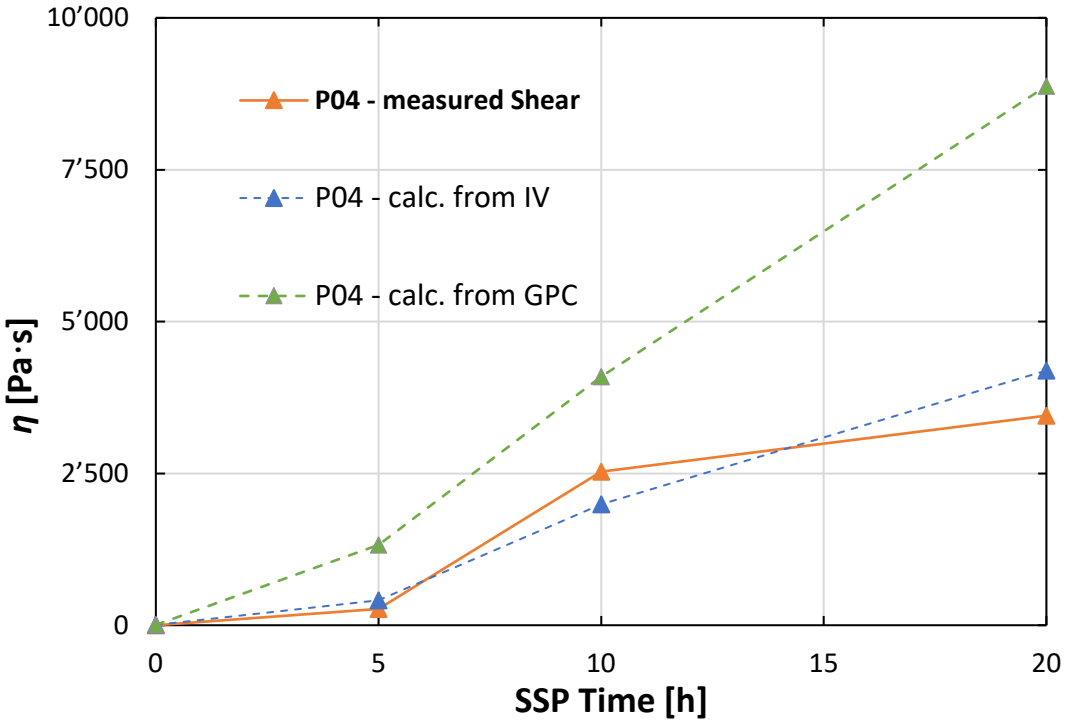
Solid State Polymerisation - Process

- Flushing N_2 oven → to remove by-products
- Up to 20h of reaction → to monitor η vs t
- Single ply & powder → shortest path for diffusion
- Powder → correlation η & IV & GPC


PET powder

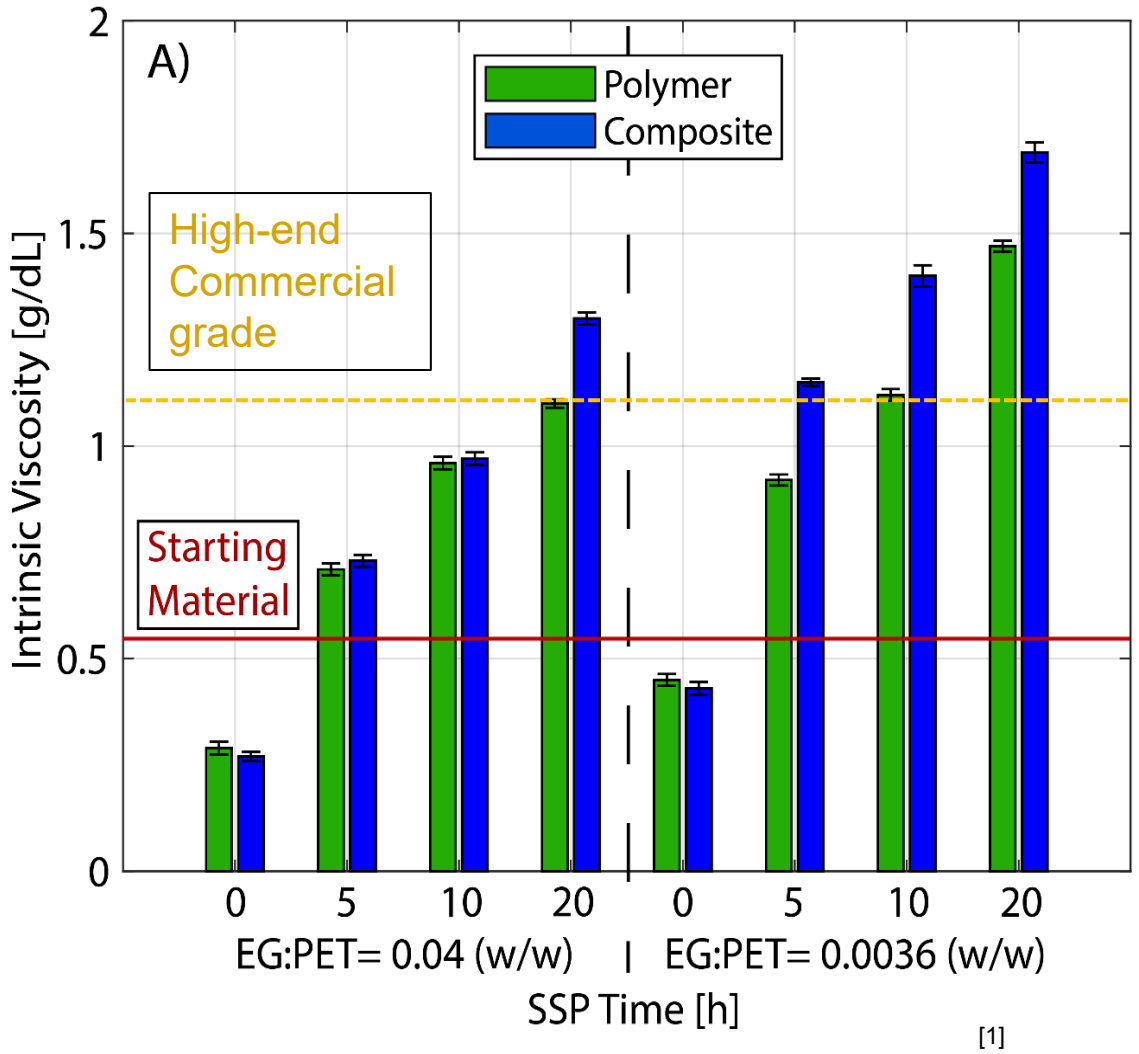

Single GF ply

- Correlation:
  - Process variable → η
  - All correlated via MW
  - IV ↔ η most precise & easy to measure



Solid State Polymerisation - Results

- < 5h starting material IV reached & exceeded
- < 20h IV of highest commercial grade exceeded
- Presence of fibre does not inhibit the reaction
- Due to the favorable geometry thin ply even faster



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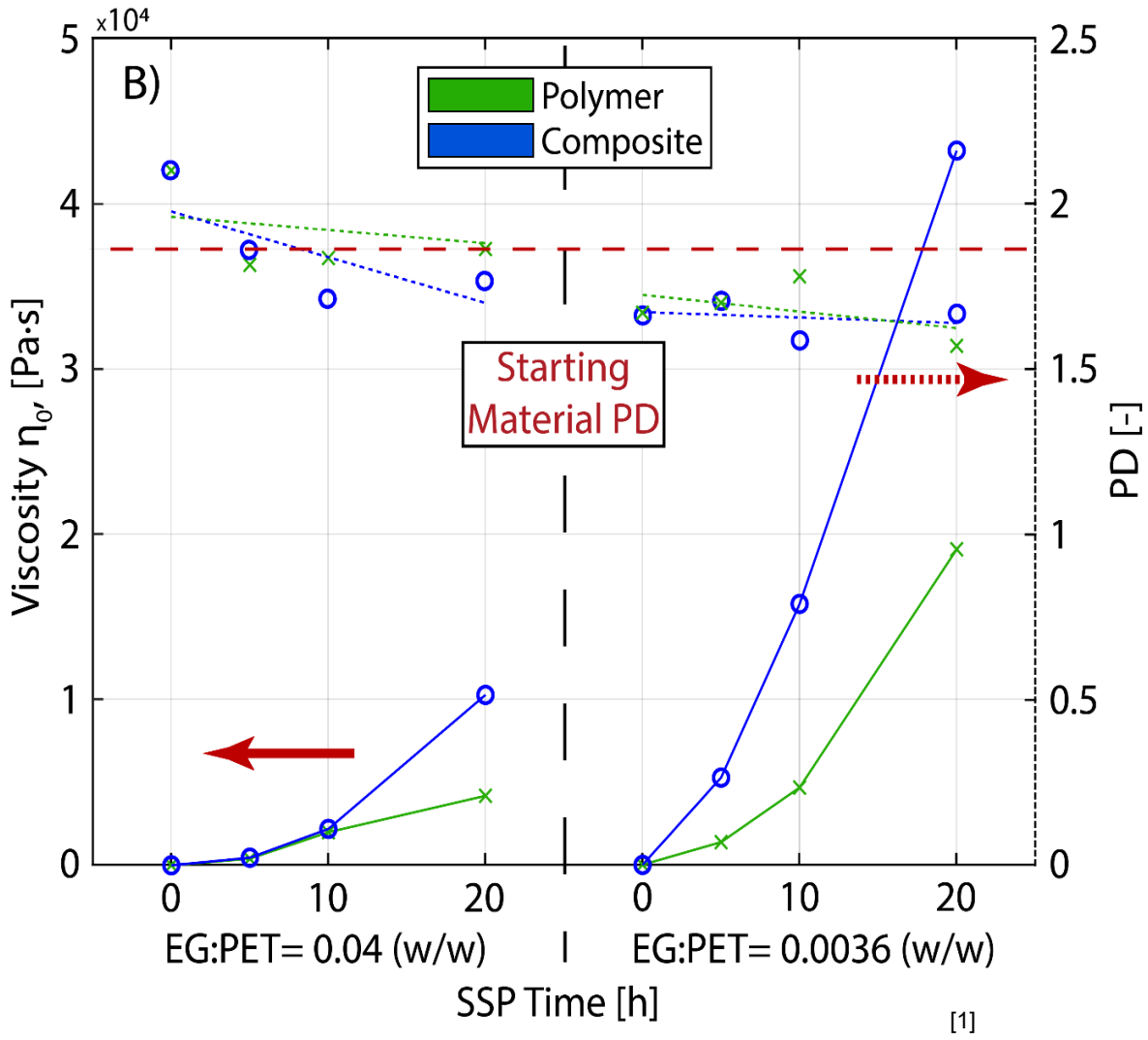
Solid State Polymerisation - Results

- η has a stronger dependency to MW (3.5 vs 0.65)
- The reaction may further advance post 20h
- Virtually un-processable >40’000 Pa·s
- Polymer quality increase with time (PD decrease)



1. In collaboration with Dr. Daniel Lester, Haddleton Group, Warwick University

Conclusions

- Step 1) Reactive extrusion
  - ✓ Fast and effective – in 10 minutes the reaction is over
  - ✓ Can easily modify polymer viscosity w/o degradation – from 2 to 40 Pa*s
- Step 2) Impregnation
  - ✓ Can impregnate GF with minimal pressure maintaining textile shape and no voids
- Step 3) Composite level SSP
  - ✓ The presence of fibre does not inhibit or slow down the reaction
  - ✓ Quickly reach initial polymer quality and with longer time exceed highest commercial grades
  - ✓ Produce an improved quality polymer

Work in progress & Outlook

- Mechanical testing to identify
  - Influence of the process on the polymer
  - Influence of the process on the interface

- Even if the reaction is proceeding, is the interface improving too? I.e. when do we saturate the interface bonds?

- How much thicker can we manufacture plies via SSP while maintaining constant MW?

- What happens if GF is substituted with CF?

Thanks for your attention.

Vetterli Oliver

Doctoral Candidate by CMAS Lab

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Acknowledgments:

- Dr. Lester Daniel, Haddleton Group, Warwick University
- Dr. Feldman Kirill, SoftMAT Lab, ETH Zürich

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