Novel Processing Route for PET-GF Composite Manufacturing Via SSP

Other Conference Item

Author(s):
Vetterli, Oliver; Pappas, Georgios A.; Ermanni, Paolo

Publication date:
2023

Permanent link:
https://doi.org/https://doi.org/10.3929/ethz-b-000651131

NOVEL PROCESSING ROUTE FOR PET-GF COMPOSITE MANUFACTURING VIA SSP

O. Vetterli, G. A. Pappas, P. Ermanni
Laboratory of Composite Materials and Adaptive Structures,
ETH Zürich, 8092 Zürich, Switzerland.

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.
3. N. Aegerter, A. Luijten, D. Massella, P. Ermanni, Production of highly concentrated commodity thermoplastic np suspensions with 3d printed confined impinging jet mixers and efficient downstream operations, Powder Technology 410 (2022) 117835

Introduction – TP Composites & challenges

- **Why Thermoplastic?**

Price to performance ratio

Increased fracture toughness

Sustainability potential

- **Processing challenges:**

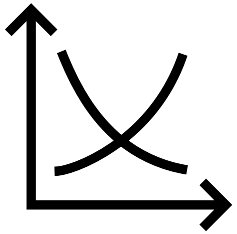
Dissolution in solvents:
- Expensive
- Compatibility
- Sustainability

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

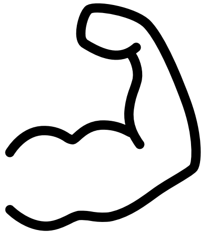
1. J. L. Thomason, Glass fibre sizing: A review, Composites Part A: Applied Science and Manufacturing 127 (2019) 105619.
2. C. Schneeberger, J. C. Wong, P. Ermanni, Hybrid bicomponent fibres for thermoplastic composite preforms, Composites Part A: Applied Science and Manufacturing 103 (2017) 69–73.
3. N. Aegerter, A. Luijten, D. Massella, P. Ermanni, Production of highly concentrated commodity thermoplastic np suspensions with 3d printed confined impinging jet mixers and efficient downstream operations, Powder Technology 410 (2022) 117835

Introduction – TP Composites & challenges

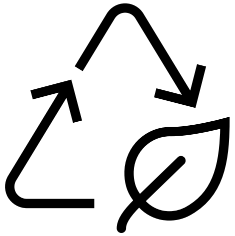
- **Why Thermoplastic?**



Price to performance ratio

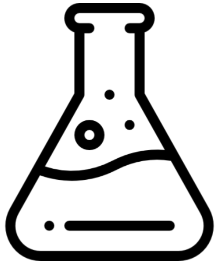


Increased fracture toughness

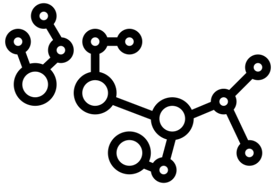


Sustainability potential

- **Processing challenges:**

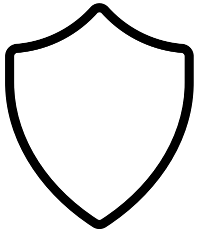


Dissolution in solvents:
- Expensive
- Compatibility
- Sustainability



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

- **Matrix Fibre interaction:**

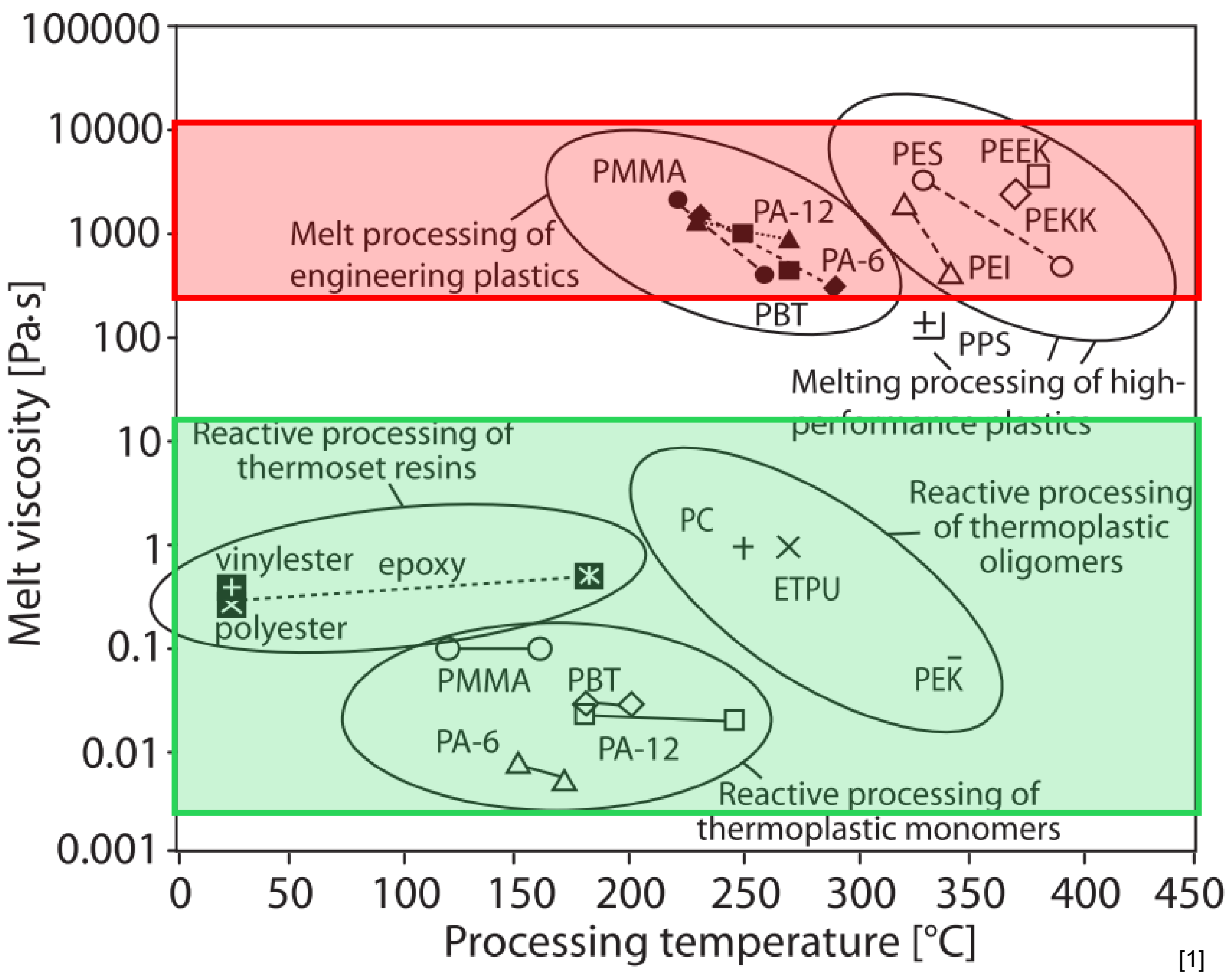


Weak link:
- $\sigma_{interface}$ < Yield
- Sizing not optimized for TP
- No covalent bond – VdW

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.
3. N. Aegerter, A. Luijten, D. Massella, P. Ermanni, Production of highly concentrated commodity thermoplastic np suspensions with 3d printed confined impinging jet mixers and efficient downstream operations, Powder Technology 410 (2022) 117835

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**

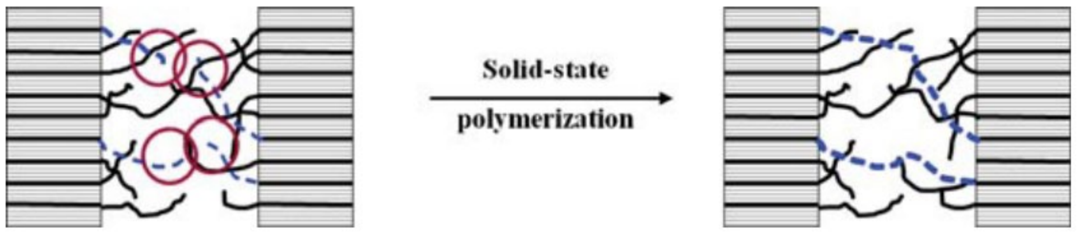


[1]

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.

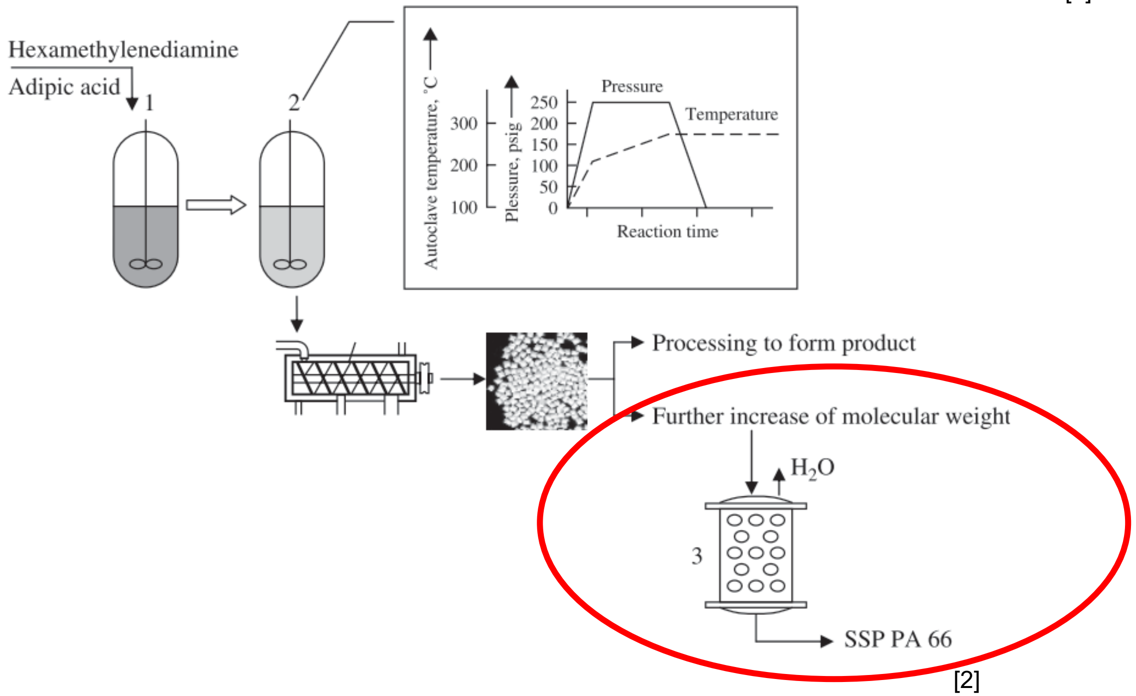
What is SSP?

- 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



[1]

- Potential advantages for composites?
  - **Processability & Sustainability**
  - **Interface improvement**

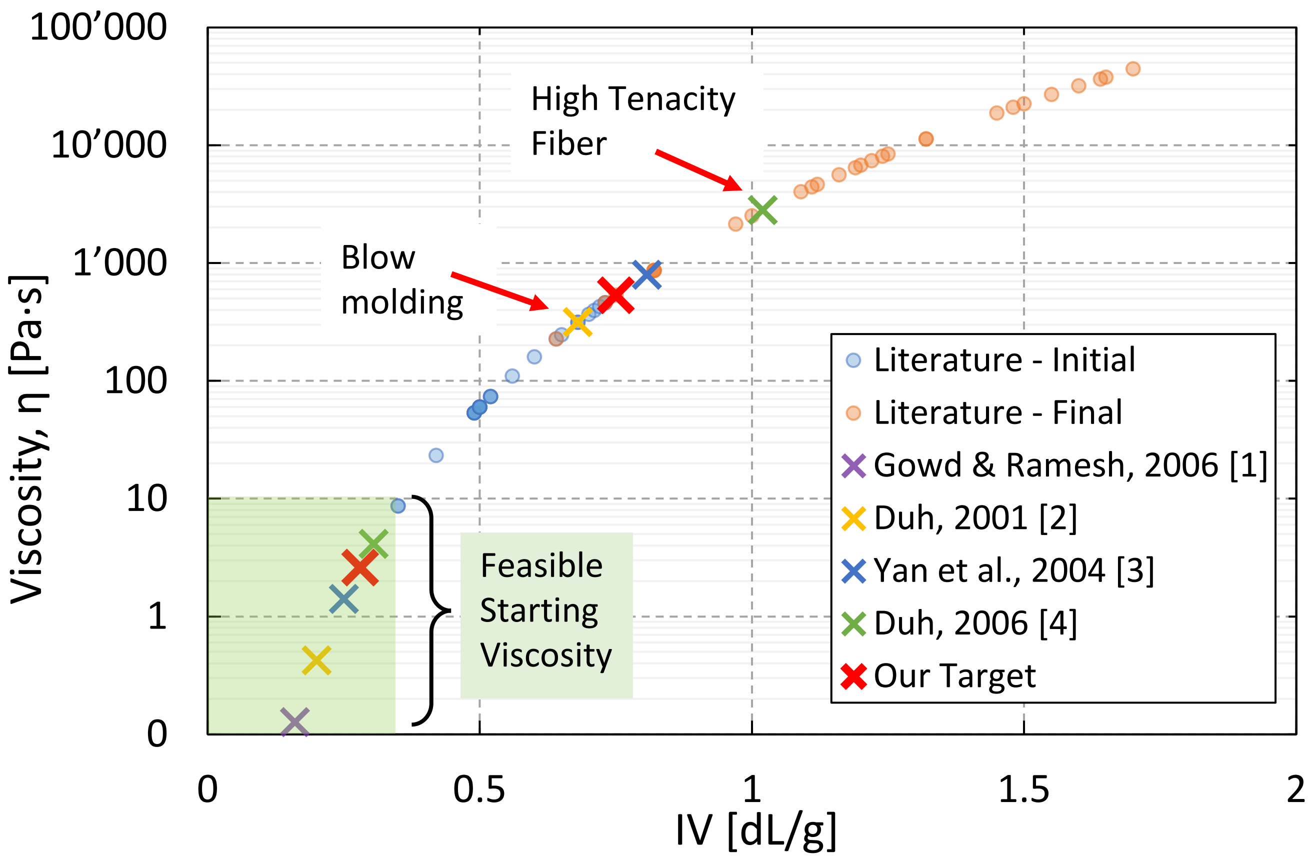


[2]

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



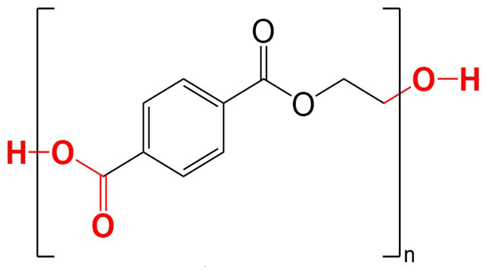
Impregnate TP like TS → Efficient & high-quality

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

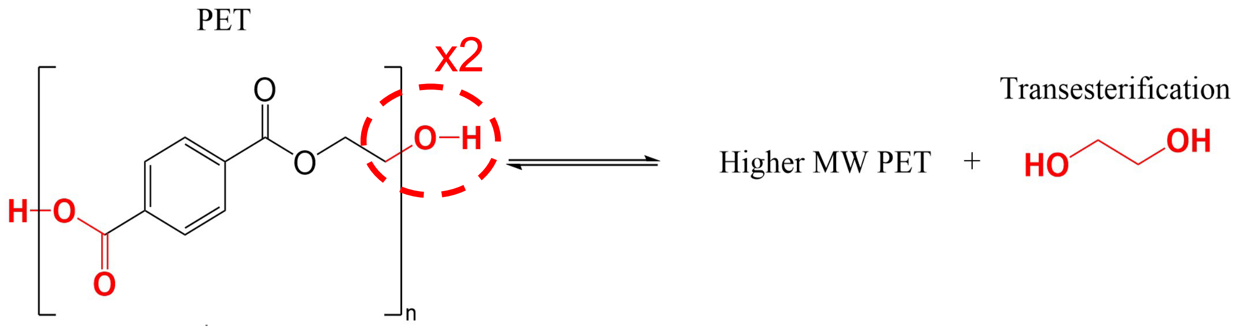
PET



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.

SSP for composite application – interface advantages

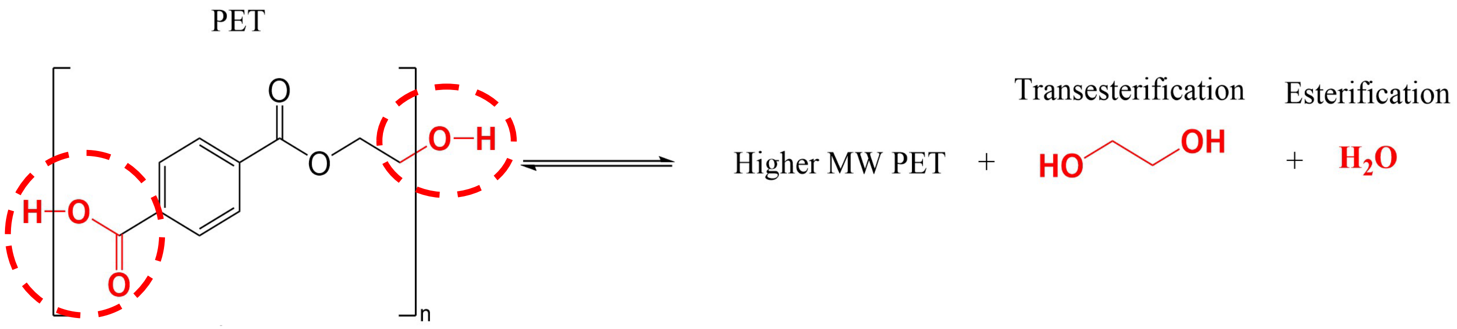
- Chemical groups involved in **SSP can react with GF surface**
  - Covalent bond between GF-PET
  - Stronger interface



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.

SSP for composite application – interface advantages

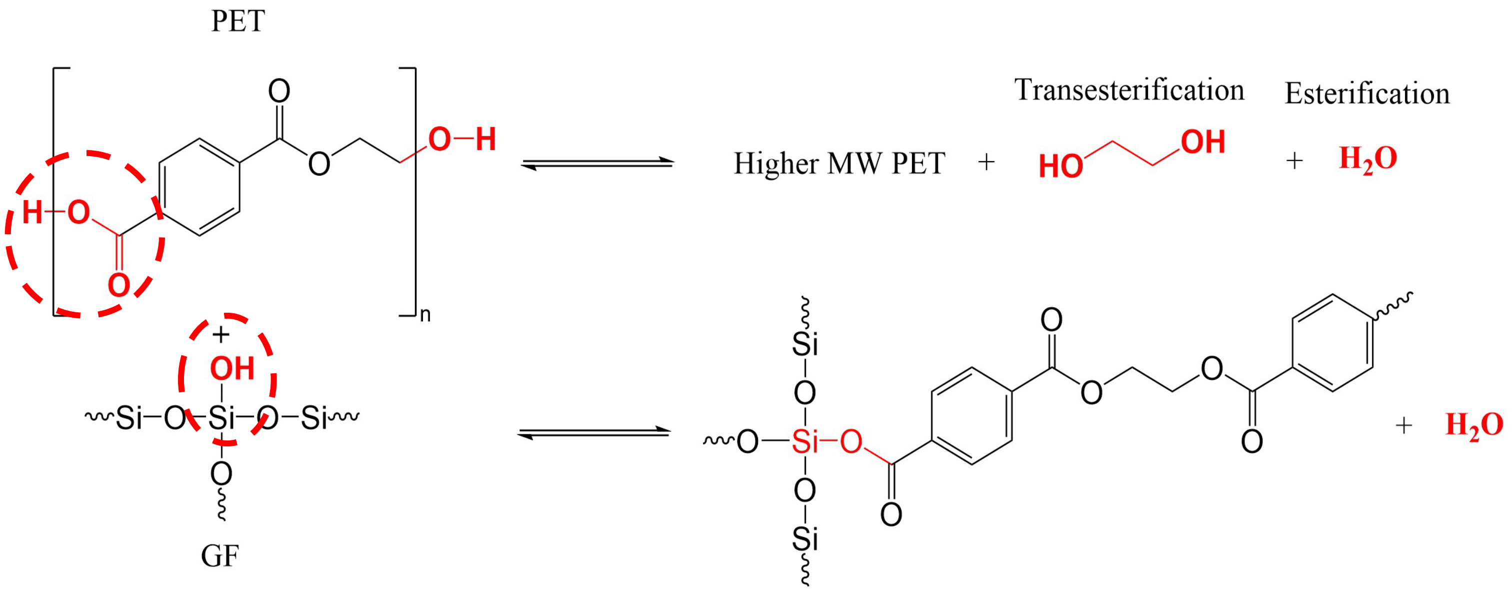
- Chemical groups involved in **SSP can react with GF surface**
  - Covalent bond between GF-PET
  - Stronger interface



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.

SSP for composite application – interface advantages

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



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)
  - Measured in [Pa*s]
  - **Only on pure polymer**

Polymer Characterization methods

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

- Polymer Industry → Intrinsic viscosity (IV)
  - Via capillary viscometer, Cannon-Feske
  - Measure flowing time of dilute solution
  - Measured in [dL/g]

$$[\eta] = K * \overline{M_w^{\alpha}}$$

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

Polymer Characterization methods

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

- Polymer Industry → Intrinsic viscosity (IV)
  - Via capillary viscometer, Cannon-Feske
  - Measure flowing time of dilute solution
  - Measured in [dL/g]

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

$$[\eta] = K * \overline{M_w^{\alpha}}$$

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

Polymer Characterization methods

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

- Polymer Industry → Intrinsic viscosity (IV)
  - Via capillary viscometer, Cannon-Feske
  - Measure flowing time of dilute solution
  - Measured in [dL/g]

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

	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

Low MW pre-polymer → Impregnation → **PET-GF Low *η* Composite** → Post processing via in-situ SSP

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

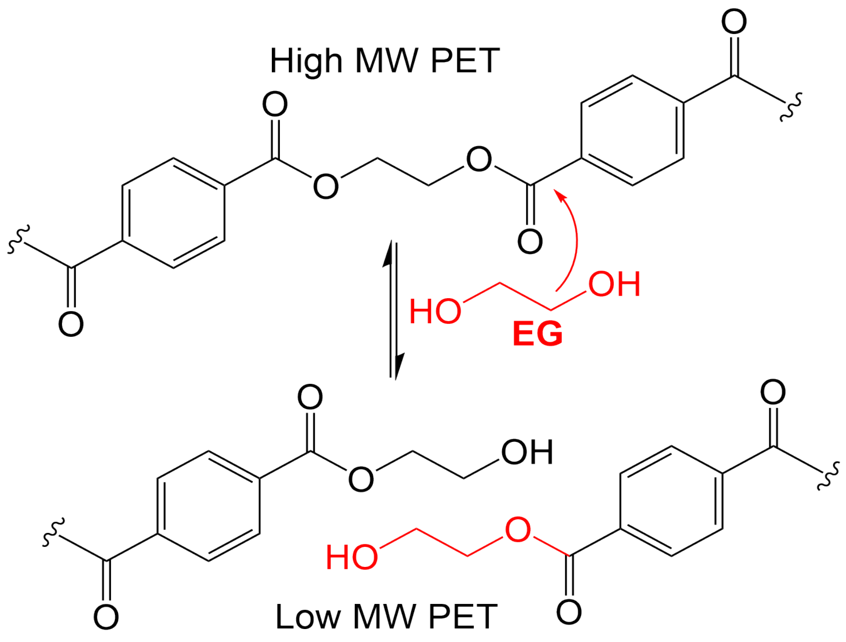
Impregnation
- With low η oligomer
- Fast
- Low P required

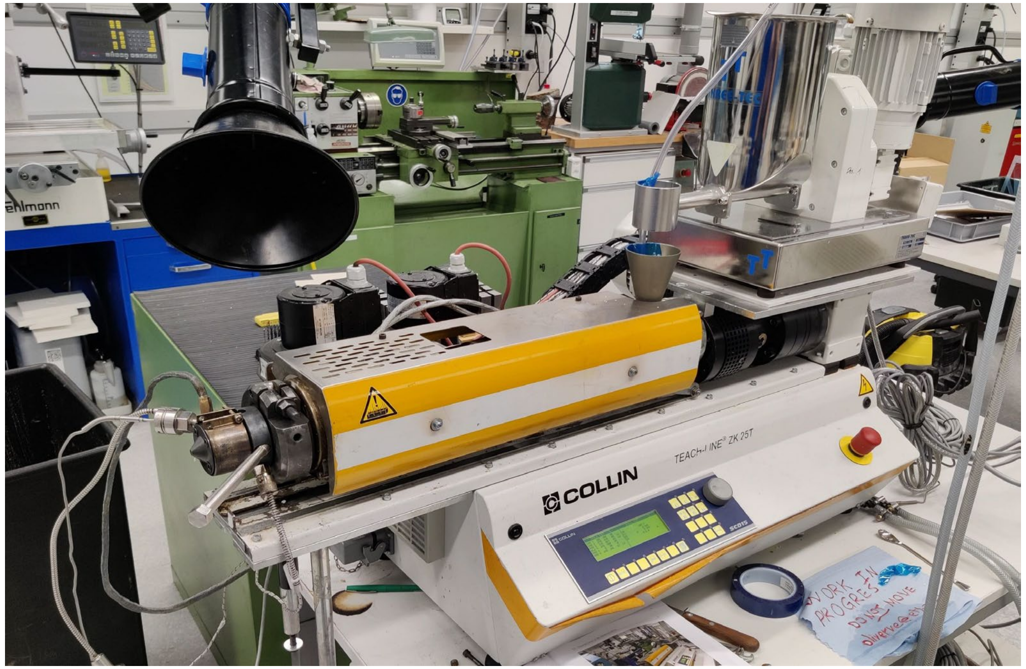
Post processing via in-situ SSP
- **Improve polymer properties**
- **Improve interface properties**

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



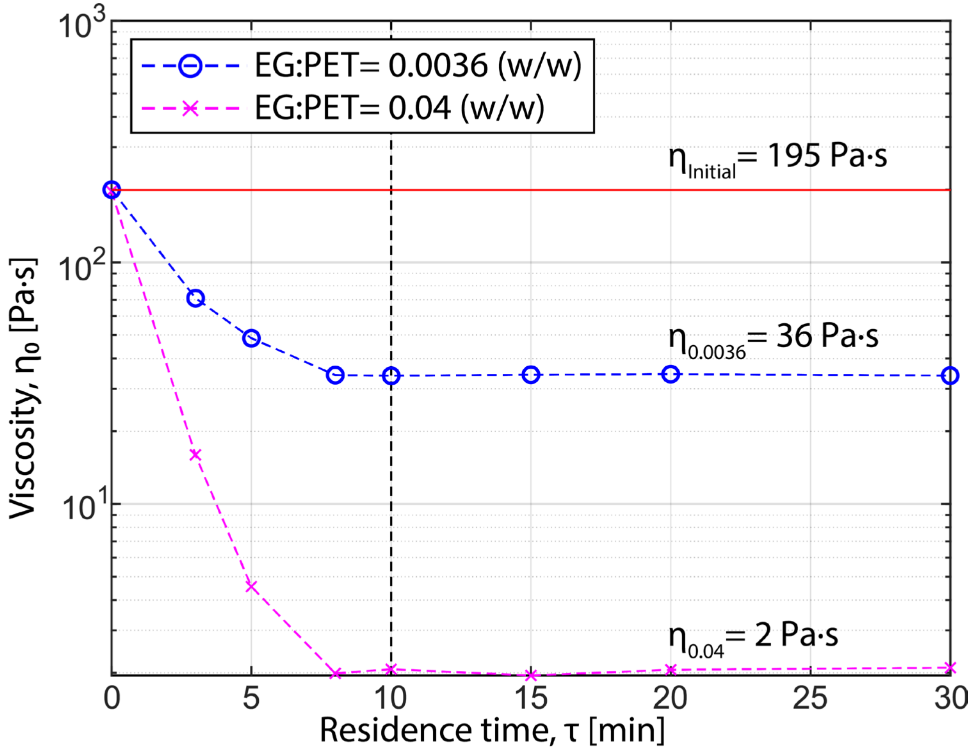


[1]

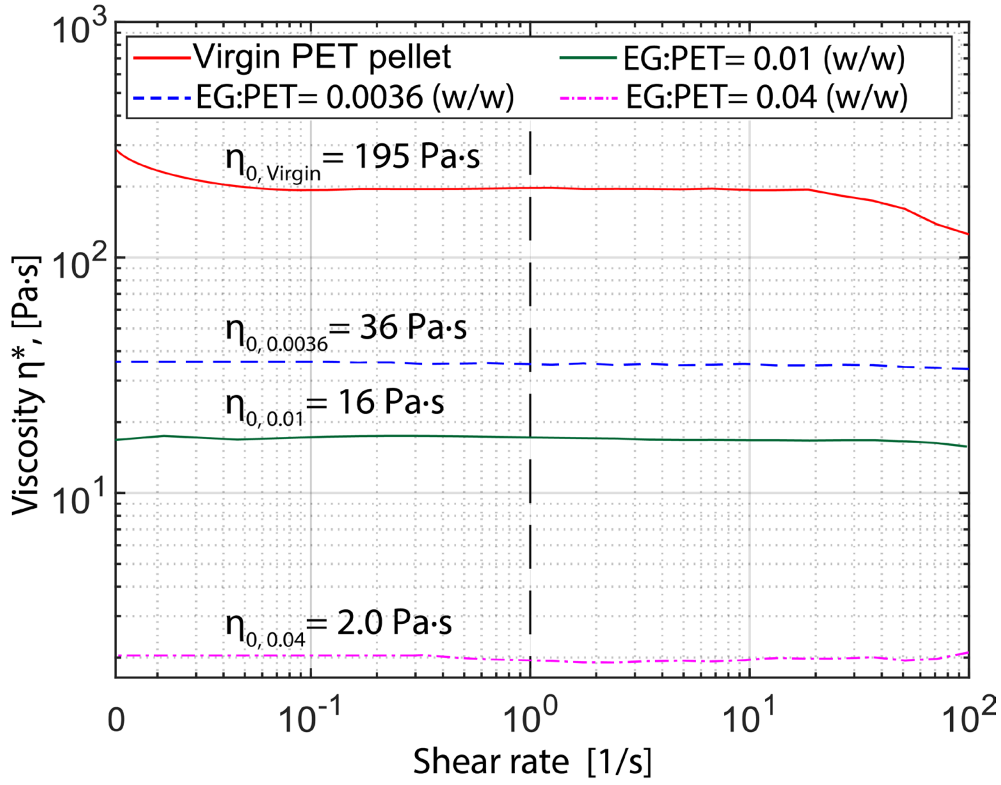
1. SoftMAT Lab, ETH Zürich

Reactive extrusion - Results

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

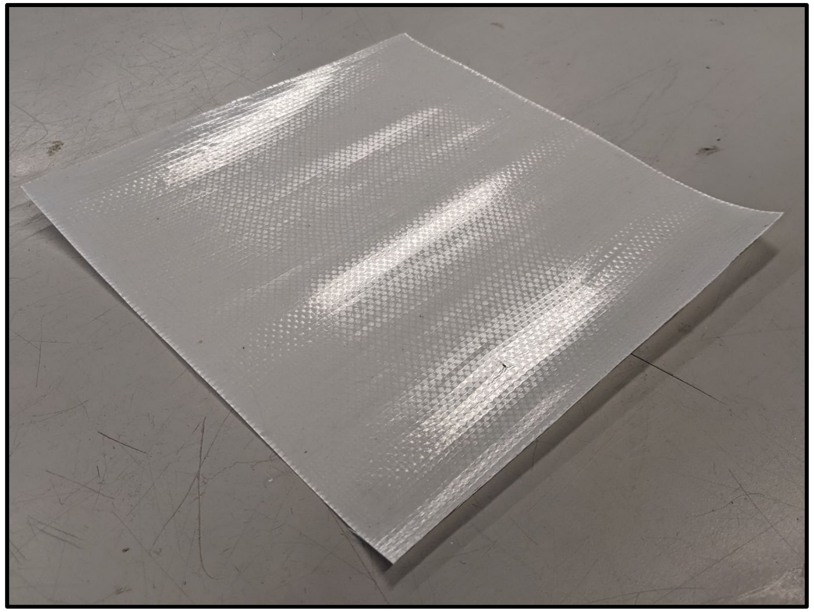


- Easy to produce a wide range of viscosities
- Low *η* → Newtonian fluid behavior
- Homogeneous reaction → no high MW chains



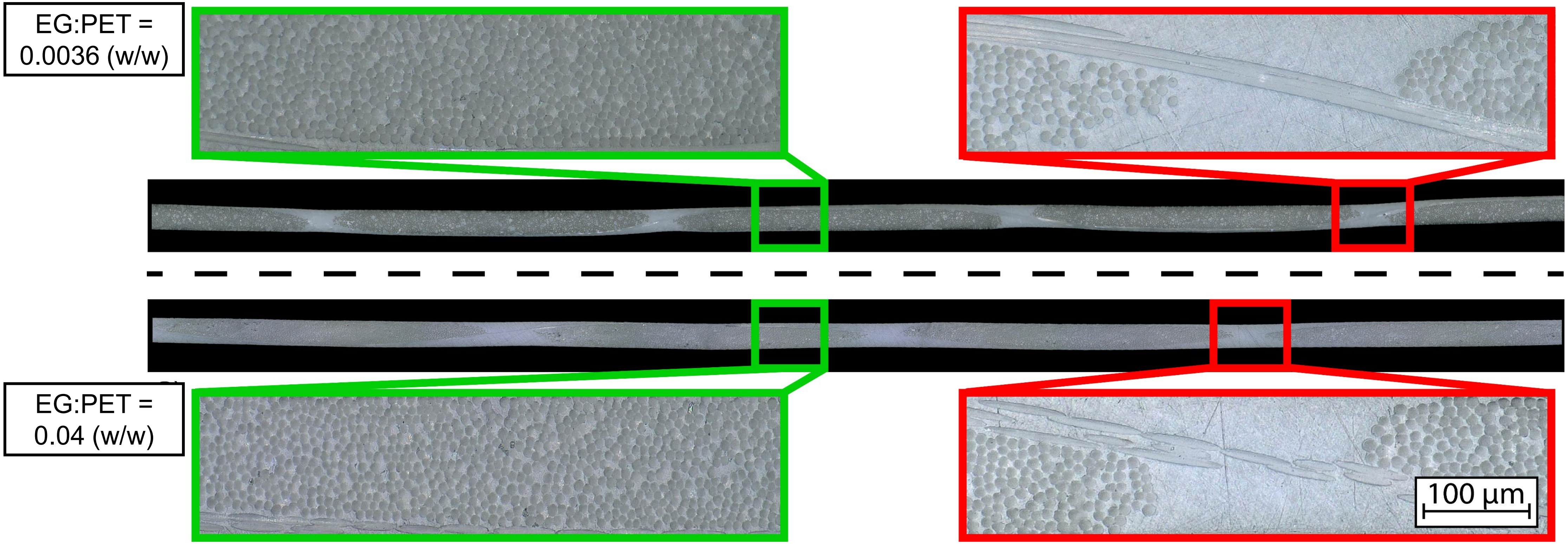
Impregnation – Process

- 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



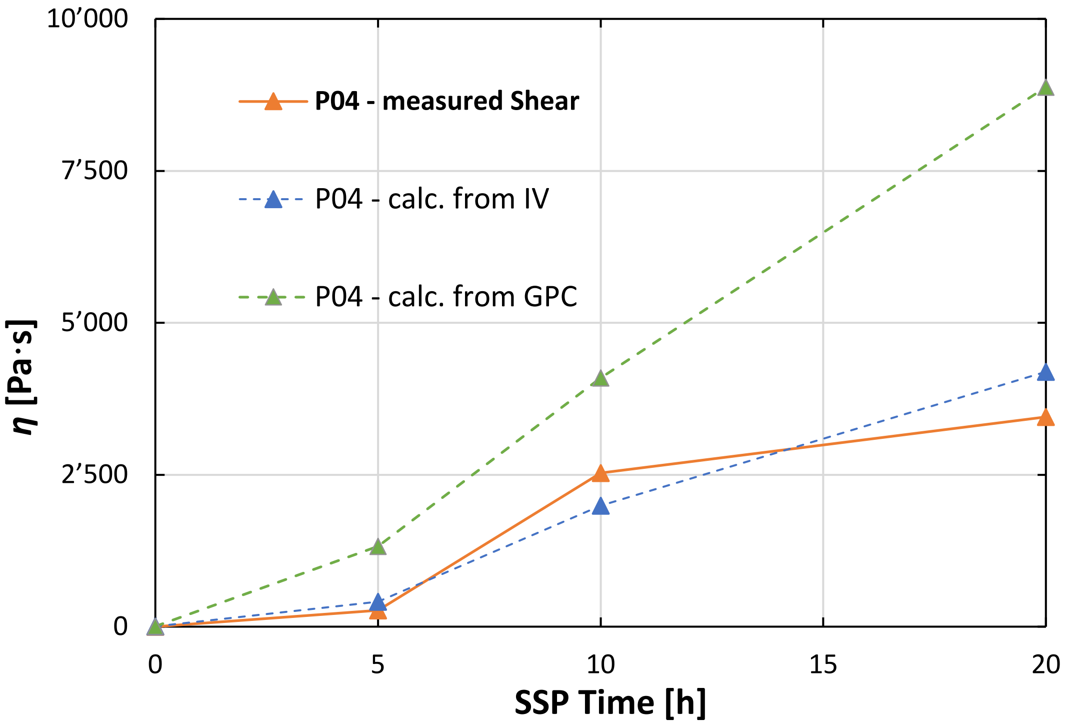
Solid State Polymerisation - Process

- 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

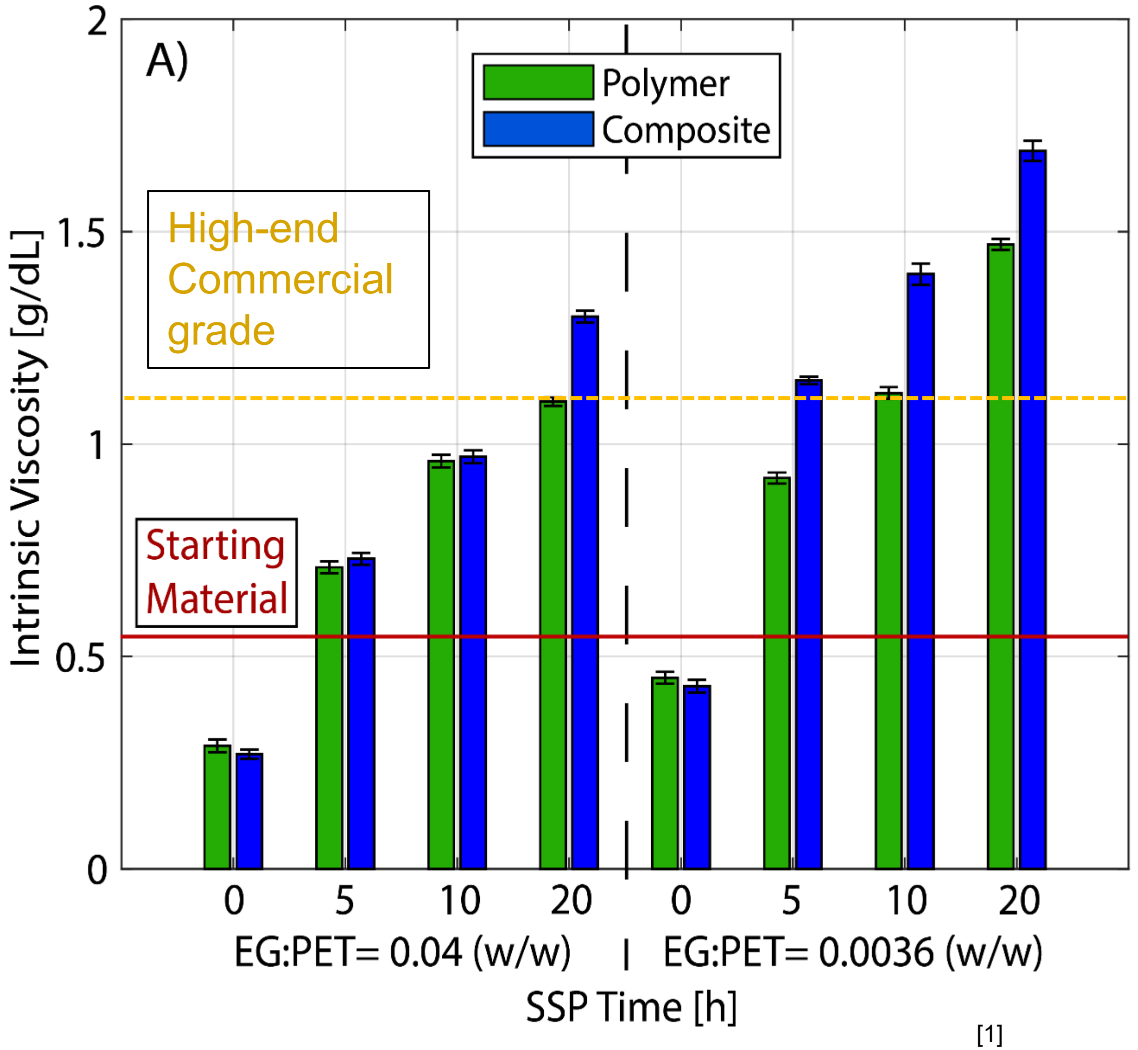
Single GF ply

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



Solid State Polymerisation - Results

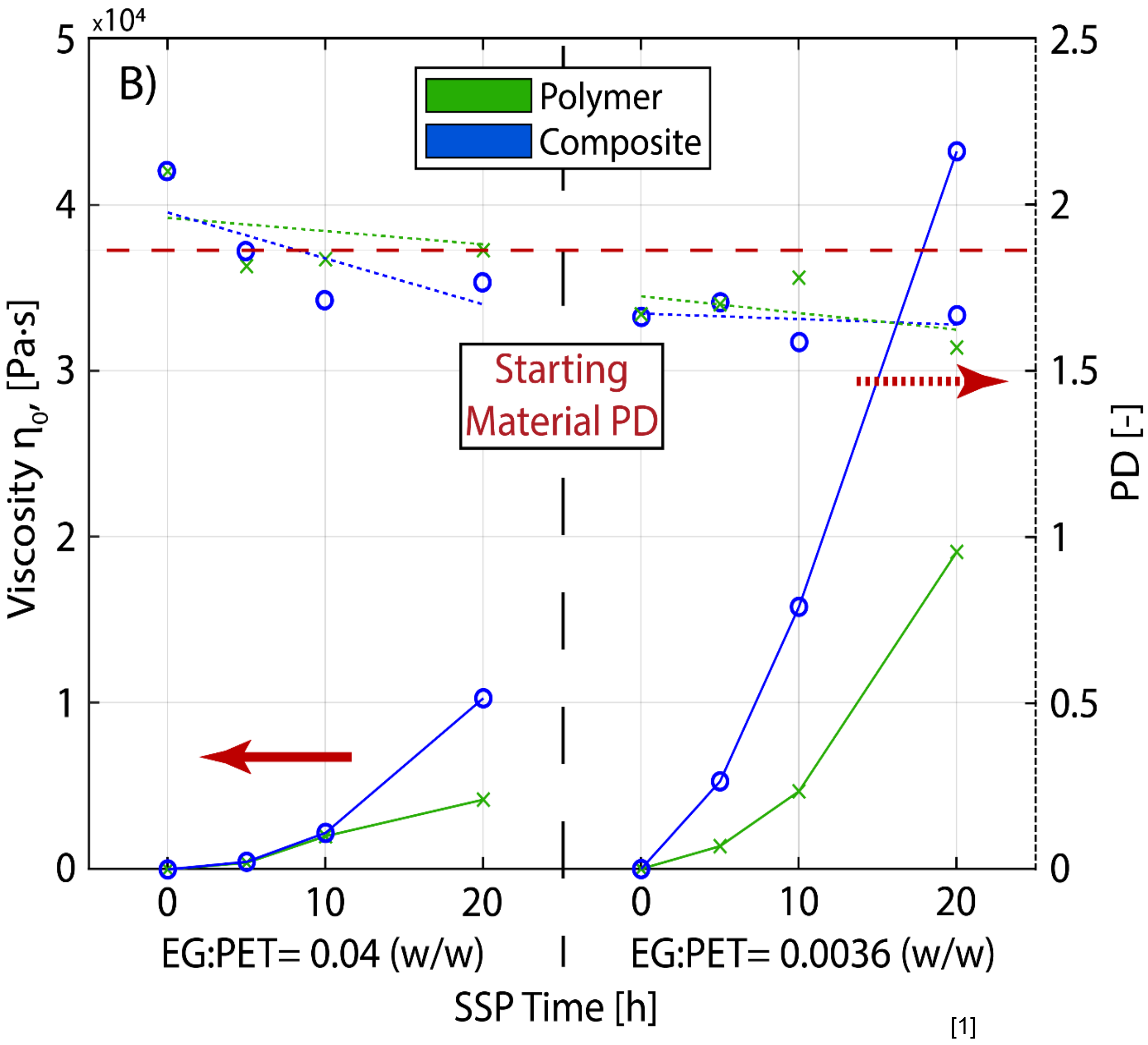
- < 5h starting material IV reached & exceeded
- < 20h IV of highest commercial grade exceeded
- Presence of fibre does not inhibit the reaction
- Due to the favorable geometry thin ply even faster



[1]

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

oliverve@ethz.ch

Acknowledgments:

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