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Thesis:	Title: Novel composite manufacturing techniques toward high performance and sustainable materials.	
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Start of the work:	
Intermediate presentation (Zwischenpräsentation):	
Final presentation (Endepräsentation):	
Deadline delivery final report:	

Introduction

The market for glass fibre (GF) reinforced polymer composites has been growing rapidly, mainly due to their attractive performance to price ratio[1]. The newer class of thermoplastic (TP) polymers, offers a simple and more sustainable processing route than thermosets since only temperature and/or pressure are required to manufacture such composite[2].
Nonetheless, there are still two main drawbacks that are limiting the wider application of this type of material, namely weak fibre-matrix interface and recyclability. The first one, arises from sub-optimal sizing development and lack of research in the field, yielding decreased mechanical properties of the resulting composite[3]. The latter, is still not fully proven due to the heterogeneity and lower MW of the recycled polymer which results in lower final mechanical properties[4].
Solid-state polymerisation appears to be a promising approach to overcome the current limitations in terms of the sustainability and performance of thermoplastic composites.
As the name suggests, this reaction is carried out in the solid-state, at temperatures between the glass transition and the melting ones. This condition promotes mobility of the reactive

[1] Thomason, J.L., 2019. Glass fibre sizing: A review. *Composites Part A: Applied Science and Manufacturing*, *127*, p.105619.
[2] Karger-Kocsis, J., Mahmood, H. and Pegoretti, A., 2015. Recent advances in fiber/matrix interphase engineering for polymer composites. *Progress in Materials Science*, *73*, pp.1-43.
[3] J L Thomason and LJ Adzima. Sizing up the interphase: an insider's guide to the science of sizing. Composites Part A: Applied Science and Manufacturing, 32(3-4):313–321, 2001
[4] Singh, A.K., Bedi, R. and Kaith, B.S., 2021. Composite materials based on recycled polyethylene terephthalate and their properties–A comprehensive review. *Composites Part B: Engineering*, p.108928.

functional groups in the amorphous region, increasing the probability of chemical interaction. Furthermore, by keeping the temperature below the melting one, the ordered crystalline fraction is not altered during the process, thus preventing degradation and depolymerisation**Error! Bookmark not defined.**.

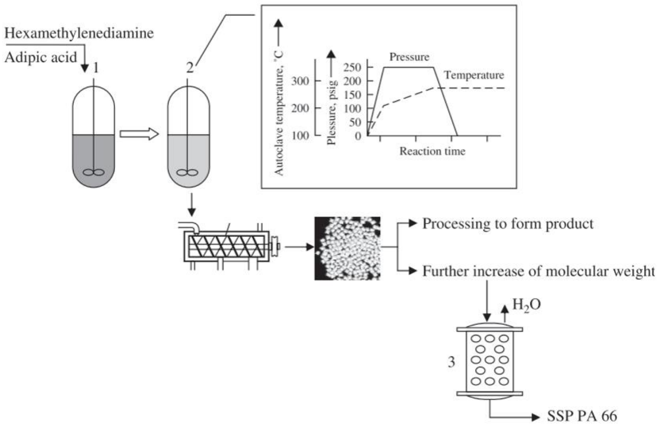

Figure 1: Industrial production of PA66 with SSP finishing step.

In terms of performance improvements, SSP can be advantageous in many ways. First, as the reaction proceeds, the molecular weight increase improves the mechanical performance of the polymer and, consequently, of the entire composite[5].
Then, SSP has the potential to improve the interface properties from a chemical point of view. The amorphous fraction that contains the reactive chain ends can chemically link to the glass, yielding covalent bonds between the components. Lastly, interfacial properties can be further boosted in terms of physical interaction[6].

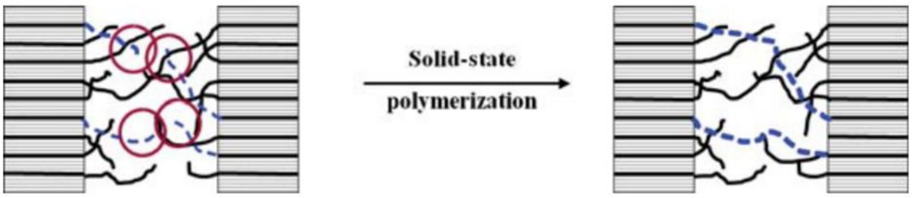

Figure 2: Industrial production of PA66 with SSP finishing step.

In terms of sustainability, a well-known problem of recycled polymer is the lower mechanical performance, which does not allow the direct re-use of such materials. This is due to a lower MW, arising from depolymerisation during the recycling process; and a wide distribution of MW, arising from a wide range of recycled material grades/quality[7]. These issues can be solved via SSP, as it has been shown that this reaction can homogenise and increase the MW of the recycled polymer back to virgin matrix values.

[5] Achilias, D.S., Gerakis, K., Giliopoulos, D.J., Triantafyllidis, K.S. and Bikiaris, D.N., 2016. Effect of high surface area mesoporous silica fillers (MCF and SBA-15) on solid state polymerization of PET. *European Polymer Journal*, *81*, pp.347-364.
[6] Duh, B., 2001. Reaction kinetics for solid-state polymerization of poly (ethylene terephthalate). *Journal of applied polymer science*, *81*(7), pp.1748-1761.
[7] Singh, A.K., Bedi, R. and Kaith, B.S., 2021. Composite materials based on recycled polyethylene terephthalate and their properties–A comprehensive review. *Composites Part B: Engineering*, p.108928.

Objectives

The present thesis proposal aims to investigate novel composite manufacturing routes to overcome the current limitations. The main scope is to investigate the potential of solid-state polymerization reaction toward the manufacturing of composite materials with superior mechanical properties and improved environmental compliance. The long term vision is to enable the production of composite by using plastic wastes so to move toward a circular economy approach.

In terms of composites, there is not much research available, even though the potential to improve processing, sustainability and performance are present. Therefore, the main objective of this thesis is to showcase the potential of SSP for the manufacturing of high performance & sustainable composite. More specifically, this will be done via lab based SSP reaction optimisation for BCF.

To easily process the material, initial viscosity plays an important role. Due to the high processing speed, viscosities larger than 1 Pa*s results in fibre breakage. Commercial grades PET have a melt viscosity of at least 350 Pa*s. To overcome this limitation, a reactive extrusion will be carried out, where a commercial grade PET will be reacted with different amount of co-monomer (ethelyene glycol). Then, this material will be solid state polymerised. Therefore, the first task of this thesis is to characterise the reactive extrusion process. This will identify the influence of initial viscosity on solid state polymerisation, and therefore the condition with the largest ΔMW can be selected.

The second, and main task, is to characterise the core reaction of the process; composite solid state polymerisaiton. This will involve quantifying the influence of catylst and processing aids (like silica nanoparticle) on reaction time, final MW and fiber-matrix interaction. This will be done directly on produced BCF, via different thermal, rheological and chemical analysis techniques like, but not limited to, DSC, TGA, complex rheometry, IR and SEM imaging.
A good starting point for this optimisation is the publication from Duh[8], Karayannidis et al[9] and Achilias[10] in terms of processing aids, Vouyiouka et al[11] and Duh[12] in terms of temperature and time influence.
Moreover, in order to produce the needed material, a minimal process optimisation will have to be carried out, to reliably produce BCF. Parameters like fiber withdrawing speed and initial polymer viscosity are thought to have the largest influence on the process. Yan *et al.* publications are a good starting point for the processing and manufacturing set-up[13,14].

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[8] Ben Duh. Effects of crystallinity on solid-state polymerization of poly(ethyleneterephthalate). Journal of applied polymer science, 102(1):623–632, 2006.

[9] George P Karayannidis, Demetris E Kokkalas, and Demetris N Bikiaris. Solid-statepolycondensation of poly (ethylene terephthalate) recycled from postconsumer soft-drink bottles. i.Journal of applied polymer science, 50(12):2135–2142, 1993.

[10] Achilias, D.S., Gerakis, K., Giliopoulos, D.J., Triantafyllidis, K.S. and Bikiaris, D.N., 2016. Effect of high surface area mesoporous silica fillers (MCF and SBA-15) on solid state polymerization of PET. *European Polymer Journal*, *81*, pp.347-364.

[11] SN Vouyiouka, EK Karakatsani, and CD Papaspyrides. Solid state polymerization.Progress in polymer science, 30(1):10–37, 2005

[12] Ben Duh. Reaction kinetics for solid-state polymerization of poly (ethylene tereph-thalate).Journal of applied polymer science, 81(7):1748–1761, 2001

[13] Yan, W., Han, K., Qin, L. and Yu, M., 2004. Study on long fiber–reinforced thermoplastic composites prepared by in situ solid-state polycondensation. *Journal of applied polymer science*, *91*(6), pp.3959-3965.

[14] Yan, W., Han, K., Zhou, H. and Yu, M., 2006. Study on the grafting of PET onto the glass fiber surface during in situ solid-state polycondensation. *Journal of applied polymer science*, *99*(3), pp.775-781.

The third and conclusive task of this thesis, will be to produce and characterise a recycled PET-GF composite. The knowledge previously gathered about reactive extrusion, SSP and BCF processing will allow a faster implementation and more efficient production of the new composite. Then, with the previously used characterisation techniques, the material will be compared to virgin PET-GF composites.

Work breakdown

The work will be mainly subdivided into the following tasks:

1. Literature review of conventional SSP, composite recycling and SSP for composites
2. Reactive extrusion, process characterisation (effect of EG concentration on the viscosity)
3. Reactive extrusion, process influence on SSP (effect of initial viscosity on final MW)
4. Reproducible production of PET-GF BCF specimens
5. Parametric study of SSP reaction (T,t) influence on MW
6. Parametric study of processing aids (catalyst, SiNP) influence on the MW and reaction time
7. Sample characterisation via thermal analysis, rheology, chemical composition and imaging
8. If time allows, recycled PET-GF BCF production, optimisation and characterisation
9. Report write up

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4. Singh, A.K., Bedi, R. and Kaith, B.S., 2021. Composite materials based on recycled polyethylene terephthalate and their properties–A comprehensive review. *Composites Part B: Engineering*, p.108928.
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Please consider

- ❖ Directives and useful information about Student Projects at the Laboratory of Composite Materials and Adaptive Structures are available online at:

Zurich, 09/12/2021

Supervisor:	Advisor:	Student:
Prof. P. Ermanni	Oliver Vetterli,	

http://www.structures.ethz.ch/content/dam/ethz/special-interest/mavt/design-materials-fabrication/composite-materials-dam/Education/Informationen/CMAS_Richtlinien_Studienarbeiten_EN.pdf

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