FILAMENTS FOR ADDITIVE MANUFACTURING REINFORCED WITH CARBON FIBERS FROM WASTE STREAM

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Abstract
The work presents one of the preliminary efforts to process high performance PPS based filaments with CF reinforcements coming from discarded production waste stream. The processing and performance of the filaments are discussed along with a preliminary LCA to have an idea on the potential environmental impacts of theses new rCF based filaments.

1. Introduction

Thermoplastics can be used efficiently in products as customized material systems. Their use as a bespoke/customizable material system means that a particular matrix system can be functionalized to tailor certain properties – strength, stiffness, etc. This is often achieved by the introduction of reinforcements such as continuous fiber tows. Such semi-finished products are mainly used in advanced manufacturing processes with high performance requirements (aviation, automotive, etc) and market potential. The market volume for continuous fiber-reinforced materials for additive manufacturing was estimated at USD 127 million in 2019 and is expected to grow at a CAGR of 21.5% to USD 733 million by 2028 [1]. However, to the best of our knowledge, when it comes to carbon fiber based reinforcement, most of it is comprised of virgin material. With the push towards a more sustainable composite industry and the eventual enforcement of EU's ecodesign requirements, it may soon be stipulated to have a minimum rate of recycled materials in such products. This will undoubtedly increase the demand for recycled materials based semi-finished products in the near future.

With the continued commitment towards excellence and innovation in the field of composites, the Institute of Lightweight Systems (SY) of the German Aerospace Center (DLR) has embarked on the path towards developing filaments via extrusion for additive manufacturing using carbon fibers from waste stream (production and/or recycled) as the main reinforcements. To help adapt existing infrastructure, demonstrate its processing and to give a new service life, this current work demonstrates filaments reinforced with carbon fiber tows entirely from production rejects. The filaments are processed using DLR's state-of-art ENDLOS Effekt co-extrusion [2,3] line with high performance thermoplastic matrix (Polyphenylene sulfide, PPS). Herein, the process parameters' influence on the properties (polymer crystallinity, strength, etc) is presented, which will be complemented by microstructural characterization of the filament to investigate the void contents. Additionally, in DLR's continued effort towards sustainability, an initial preliminary cradle-to-gate Life Cycle Assessment (LCA) of the production process is presented to establish the potential environmental impacts of the filament processing. The LCA is based on measurements of relevant gate-to-gate Life Cycle Inventory (LCI) data including the main process steps, for instance materials flows and the electricity consumption of heating elements, extruder and Sonotrode. The assessment is considering data gaps and necessary steps for a potential industrialization of the whole process.

2. Results and Discussion

2.1 Filament processing and void analysis

Filaments were processed in DLR's ENDLOS Effekt fibre impregnation line *(Fig. 1)* with PPS as the main polymer reinforced with 'fuzzy' carbon fibers. Tows containing damanged carbon fibers after production are rejected as waste – destined to be otherwise disposed, and are termed as 'fuzzy' lot. It is such fibers *(referred to as recycled or rCF from here on)* that has been used to process these novel filaments to provide a new life to these discarded waste. DLR implemented a unique co-extrusion line to impregnate and manufacture endless fibre-reinforced filaments for 3D printing with high-performance thermoplastic polymers and 12K fiber rovings. It consists of a dedicated co-extrusion tool followed by 1-2 ultrasound impregnation cells *(Sonotrode, Fig. 1)*. Followed by a downstream of the impregnation unit, a multinozzle concept with hydraulic decoupling is used to shape and consolidate the filament. Additionally, a heating concept is implemented to modify crystallinity of the solidifying filament.

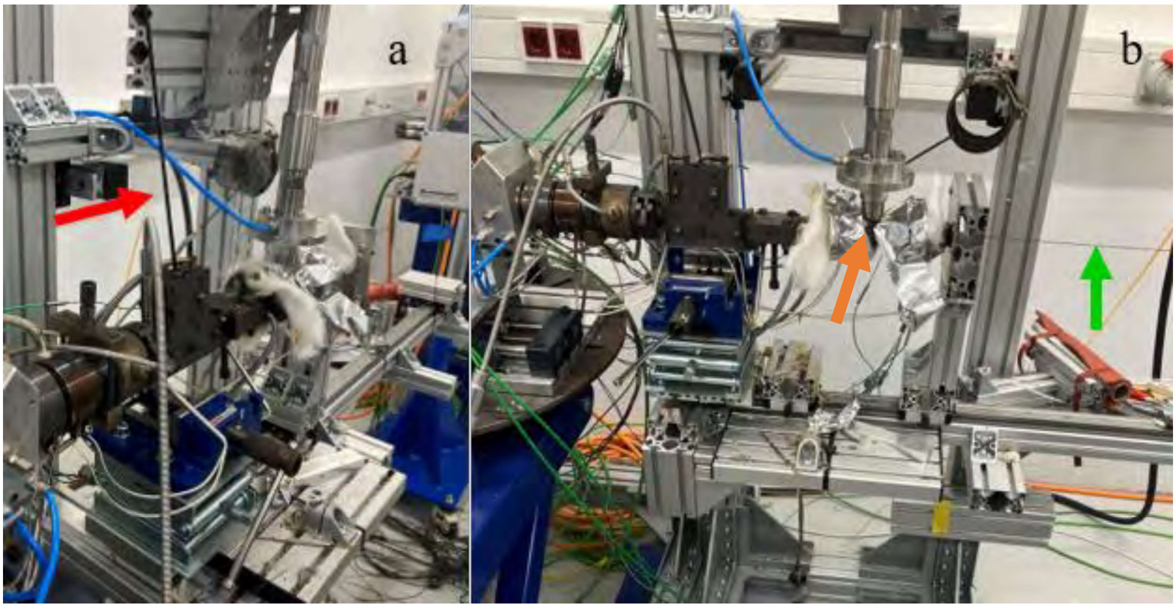

Figure 1: Shows the ENDLOS Effekt line with the fiber insertion point (red arrow) and finished filament (green arrow). The Sonotrode is marked with a orange arrow.

The Sonotrode has been successfully tested *(representative in Fig. 2)* to reduce entanglement of the polymerchains, reducing the wall friction and the viscosity to maintain processability in a longer tool and improve fluidity in combination with a change in the melt flow field. Further information about the effect can be found in Ref [4].

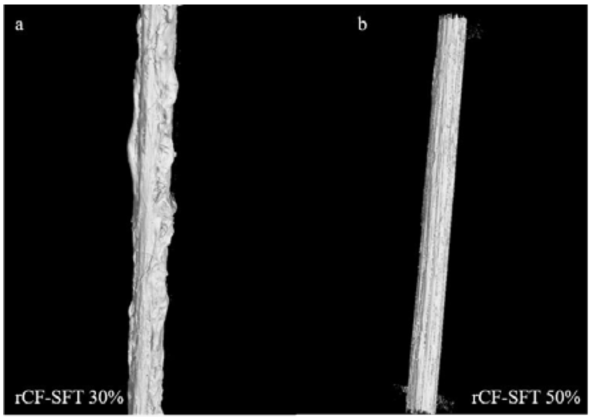

Figure 2: Effect of the Ultrasound energy imparted by the sonotrode on the polymer wetting as seen via micro-CT *(FIBRE, Bremen)*. At 30% sound intensity (a) a significant roughness of the polymer is visible which seemed to be smoothed out at 50% sound intensity (b). This indicates at better fiber wetting which is expected to influence and the pore formation within the filaments

Generally, voids appear in different scales. A common approach to classify void is to use the size and location of the voids. Medhikani et al. [5] uses macro, meso and micro-voids for the same. Macro-voids are denoted as a dry area in the composite but more relevant for the investigated applications of rovings in a filament are the meso- and micro-voids as elucidated next.

Micro-Voids appear in areas of small channels between single fibers. They appear mostly in areas of comparatively higher fiber volume content. Whereas, meso-voids appear in larger channels in areas of lower fiber content. The conducted void analysis uses automated image processing *(with a python script)* to detect the voids which appear as black in optical micrographs *(imaged with Keyence VHX-7100 in coxial mode)*.

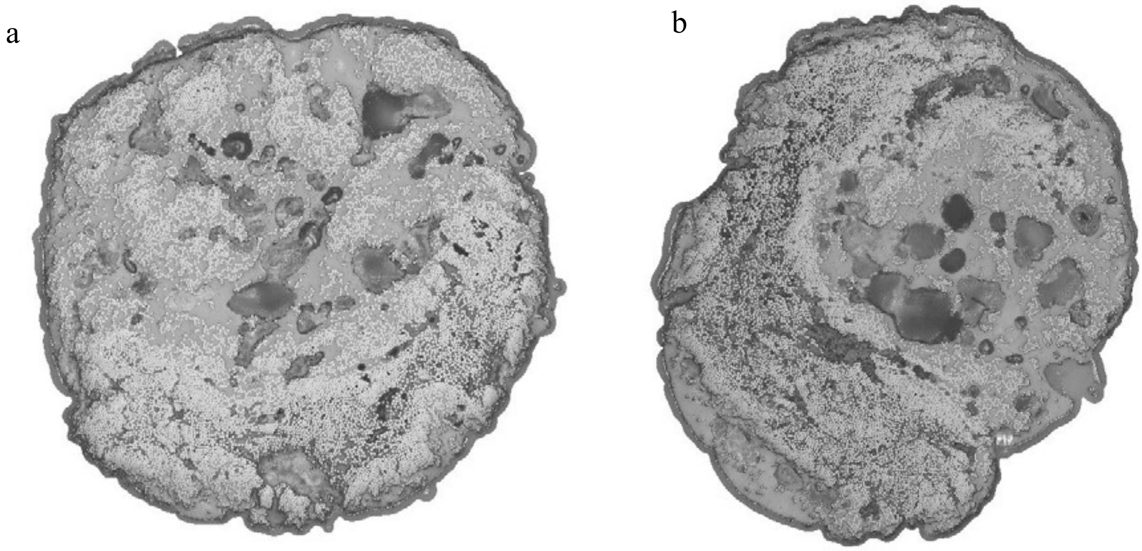

Figure. 3. Cross sectional micrographs of filaments processed with a) 30% ultrasound and b) 50% ultrasound amplitudes. For analysis details please refer to the poster ID: I9SKB.

Fig. 3 shows a cross section optical micrograph of the filament manufactured using rCF-rovings and PPS *(as shown Fig. 1 & 2)* with an ultrasound amplitude of 30% and 50%. The analysis reveals an overall void content of 11% *(average of the sample lot is 12% for 30% US-amplitude and 22% for 50% US-amplitude, for details please refer to Table 1)* using identical manufacturing parameters as filaments with virgin CF reinforcements. Additional darker areas in the crosssectional image indicate voids are underneath the top surface. Further analysis indicate a uniform distribution of the voids along the fiber length and hence, a crosssectional image can be used to indicate the volumetric void content.

From these micrographs *(Fig. 3)*, it can be seen that the fibers are not evenly distributed that can result in different channel sizes leading to varying local permeabilities that can cause the evolution of voids. The used rCF contain a sizing to keep them in shape for ease of entry into the tool during the manufacturing process. Thermal measurements *(DSC)* and previous in-house analysis have indicated an increased void content when using sized fibers. Filaments using 50% *(~15µm)* ultrasound amplitude are seen to increase the void content, which is currently being investigated if its a consequence of manufacturing parameters. Optimitzation trials are currently being conducted for a better understanding of this hypothesized infiltration behavior.

2.2 Crytallinity via Dynamic Scanning Calorimetry (DSC)

A crystallinity comparison between the commercial and the rCF based filaments were carried out from the melting enthalpy data from the heat flow curve of the 2nd heating run of the Dynamic Scanning Calometry *(DSC2 STAR System, Mettler Toledo, run: 25°C-350°C @ 10°C/min under N_2)*. Since it is not common to use production rejects as reinforcements and it has already been widely reported crystallinity of the polymer is generally influenced via various factors [6, 7, 8]. Given the unknown about how these fibers influence the polymer, a comparison was made to get an impression if the fibers have any impact on the inherent properties of the PPS.

This is another step towards benchmarking the filaments as well as given the additional pointer that ultrasound energy imparted by the sonotrode at varying amplitudes was also used to aid in fiber wetting. Overall anylsis shows *(Fig. 4)* an improvement in crystallinity when rCF is used as reinforcements in comparison to virgin tows with 50% ultrasound for processing. This is even so when the ultrasound is reduced to 30% intensity *(Table 1)*, which indicates at possible improved bulk properties which is currently being investigated in-house. The glass transition temperature *(T_g, °C)* remains fairly unchanged indicating minimal thermal impact.

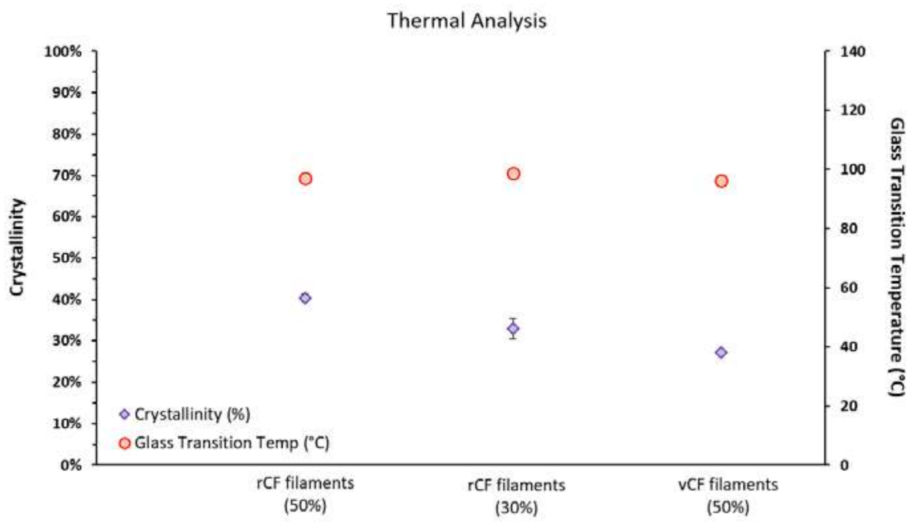

Figure. 4. Comaprative DSC analysis of the filaments show the variation in PPS crystallinity *(%)* and glass transition temperature *(T_g, °C)*.

2.3 Tension Performance

Since our goal is to use these filaments in advanced manufacturing processes, the load bearing capability of the filaments were assessed under tension in a Zwick Roell Z005 universal testing machine with a 5kN load cell at a test speed of 2mm/min under 23°C and 50% relative humidity. Filaments processed with virgin and rCF tows processed with 50% ultrasound intensity was tested for comparative purposes and presented in Figure 5. As can be seen, the tension performance in both aspect appear to be comparable with minimal deviation between the 2 carbon fiber sources at same ultrasound energy is indicative of an encouraging prospect.

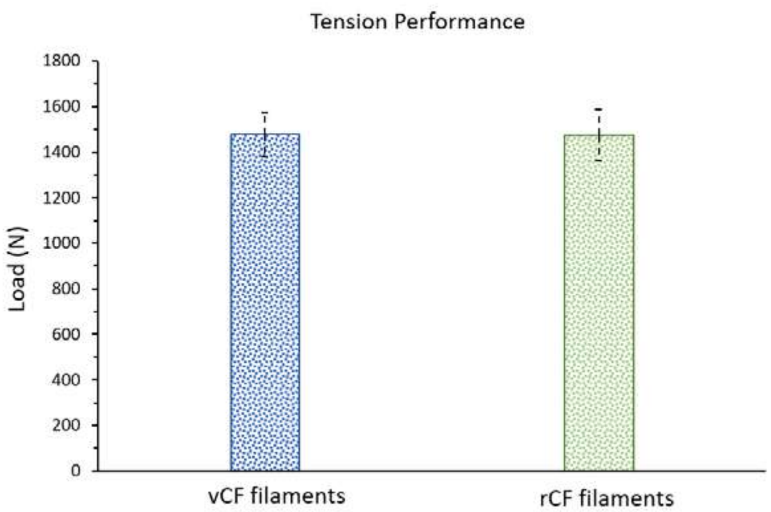

Figure 5. Tension performance comparision between PPS filament processed with virgin and recycled CF rovings with 50% ultrasound energy.

Tests are planned for filaments processed with 30% ultrasound energy to investigate if the ultrasound itself has any impact on the structural performance of these fiaments.

Table 1: Summary of the analysis details

Sample	Fiber type	Void Content		Crystallinity		Tg	Tension performance (N)	
		Avg (%)	*SD (%)*	*Avg.*	*SD*	*(°C)*	*Avg.*	*SD*
rCF-PPS filament_50%	Fuzzy production reject	22.0	2.5	40.4%	0.9%	97.1	1476	± 111
rCF-PPS filament_30%	Fuzzy production reject	13.5	2.2	32.9%	2.5%	98.6	--	--
vCF-PPS filament_50%	Virgin	14.3	1.5	27.2%	0.1%	96.4	1477	± 96

2.4 Life Cycle Assessment (LCA)

With the concept of sustainability gaining an increasingly important role in today's world, the UN adopted 17 Sustainable Development Goals (SDGs) in 2015 as agreed by the heads of state and government of the member states [9]. The SDGs are based on the three pillars of sustainability: social, economic and ecologic. With this in mind, to assess the ecological perspective, a Life Cycle Assessment (LCA) according to EN ISO 14040/44 [10, 11] is used to assess the potential environmental impacts of these new rCF reinforced filament presented in this work including the production of materials in a preliminary cradle-to-gate approach. Figure 6 shows a SWOT-Analysis which gives a peek in the window for the rationale to assess the sustainability of the process using LCA as a tool. This new rCF applicability lowers the dependency on virgin material. An additional opportunity is that the assessment of the environmental impacts lead to the possibility to optimize the technology if necessary with a feedback of the hot spots.

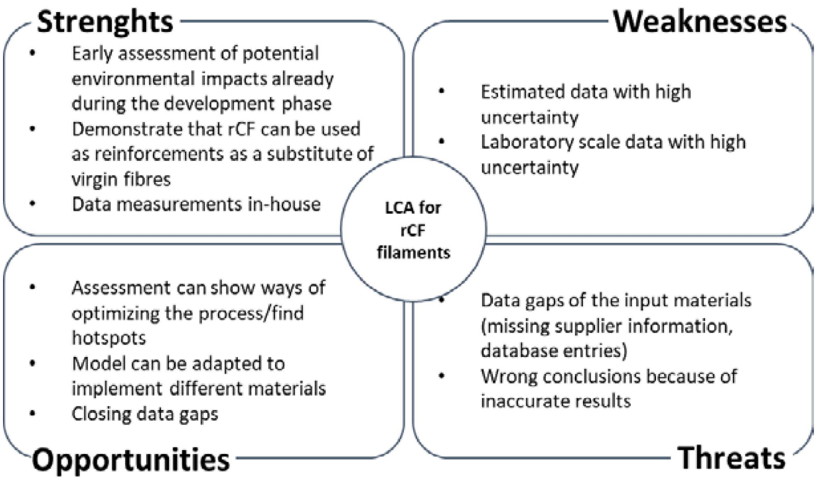

Figure 6. SWOT-Analysis of doing LCA for the rCF filaments

The process flow is shown in Figure 7 and shows the system boundaries of this new filament production including the production steps with their in- and outputs. Data will be collected for all shown process steps within the foreground system. Since it is an in-house process all relevant data will be measured and/or estimated. Details of electricity consumption is measured as well as the mass flows of materials including losses/waste to have a through understanding. The preliminary modeling of this new filament production contributes to closing the data gaps which LCA professionals are faced with and will also give feedback to the process developers for potential improvements from environmental point of view. In further measurements, the reproducibility of the technology will be verifierd, the collection of measurement data which is relevant for LCA will be expanded and described in an upcoming publication planned for later in the year.

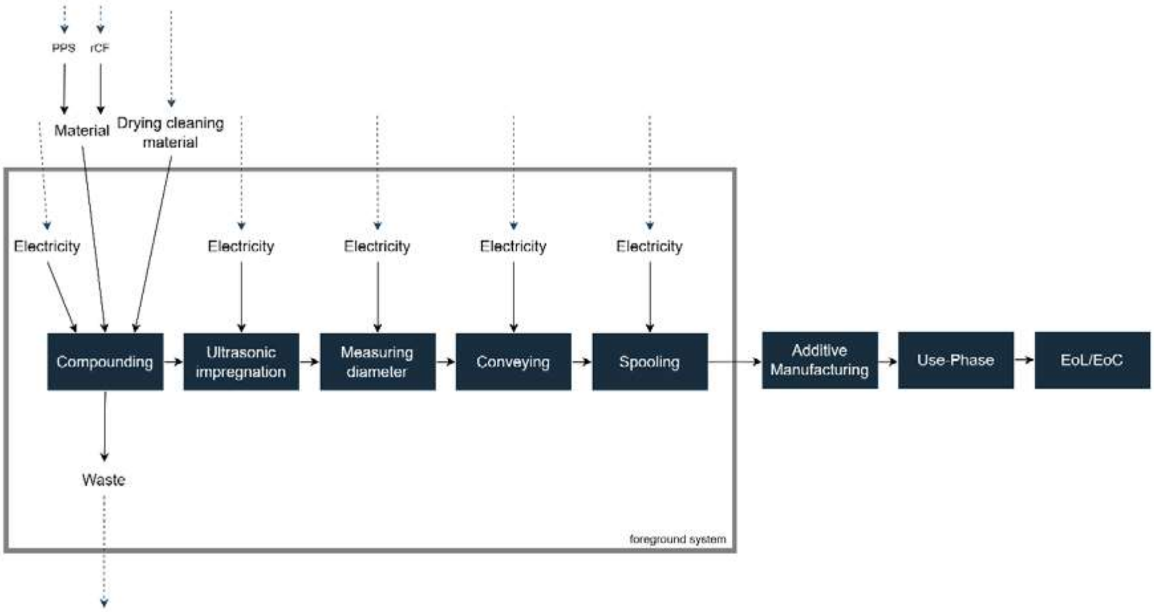

Figure 7. Process model with the main production steps of the rCF filament production as the foreground system and the following life cycle phases

3. Conclusion

This work presents the initial trails carried out by the DLR team to develop a filament intended for high-preformance usage reinforced entirely with rCF. A preliminary assessment of its microstructural and polymer characteristics along with the first assessment of its bulk performance shows that although some variation in void content is obersvered with differing ultrasound intensity, the structural performance remains fairly comparable. Futher investigations on the bulk performance is being carried out in-house to better understand the evolution of the voids and the impact (or not) it has on the bulk properties. It has been shown that the application of the LCA has a meaningful use and with further trials the model will be expanded.

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