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Investigation on the recycling potential of additively manufactured carbon fiber reinforced PA 6.6

C. Lohr [a,*], A. Trauth [b], J. Schukraft [b], S. Leher [b], K.A. Weidenmann [b]

[a] Technische Hochschule Ingolstadt, Ingolstadt, Germany
[b] University of Augsburg, Institute for Materials Resource Management, Augsburg, Germany

ABSTRACT

Carbon fiber reinforced polymers (CFRP) are already used in a wide range of applications such as automotive, aerospace and renewable energy industries and demand on this material class is increasing steadily. As demand increases, the amount of CFRP waste, either from production or at the end of life of components, increases simultaneously and sustainable solutions such as disposal, reuse or recycling of fiber reinforced materials getting more and more important.

In this paper one possibility for recycling short carbon fiber reinforced polyamide 6.6 (CF/PA 6.6) is presented. The recycling process includes shredding of the material, drying and filament extrusion to enable a reuse of the material with an additive manufacturing process. The focus of this investigation is on the mechanical properties of the recycled filaments itself as well as on the 3D printed specimen considered recycled filaments. The properties at different stages of the short carbon fiber reinforced polyamide 6.6 recycling process were investigated, including the juvenile CF/PA 6.6 as well as specimens made from one- or two-times recycled material. Mechanical performance was evaluated by tensile, bending and impact testing. Experimental results pointed out that no significant difference in performance of juvenile and recycled materials was observed for tensile and flexural loads. The impact strength of the recycled specimen decreased to a small extent.

1. Introduction

Global climate change, reduction of greenhouse gases, substitution of fossil energies by renewable energies, energy efficiency and sustainability are major challenges for policy and the industrialized nations in current days. One crucial task is to reduce greenhouse gases, above all carbon dioxide (CO_2). [1].

In addition to the use of renewable energy sources, lightweight construction represents a key technology for reducing carbon dioxide, especially in the transportation sector [2,3]. In the search for lightweight materials, carbon fiber reinforced plastics (CFRP) are in high demand, since CFRPs are characterized by their excellent specific material properties and a wide range of possible applications [4,5].

Carbon fiber reinforced composites can be manufactured by a wide range of different process techniques. Within this study components made from additive manufacturing (3D printing) are considered. The technical performance of 3D printing is particularly convincing due to tool-free shaping and the possibility to print any geometry, even with cavities or overhangs. [6] Another advantage results from the reduction of production waste due to the high material utilization rate [7]. In 2010 the global demand for CFRP was 51,000 tons. This figure more than doubled by 2018. The forecasted demand for 2026 is 157,500 tons. [8] As demand increases, so does the amount of CFRP waste. CFRP production waste is estimated to be 20,000 to 30,000 tons by 2025 especially due to aerospace, automotive and wind energy industries. The end-of-life cycle of CFRP components ranges between 10 to 30 years, depending on the application. Due to the cost- and energy-intensive manufacturing process of carbon fibers [9], resource-conservation and recycling are advancing. [10].

Not only components at their end of life, but also waste made from CFRP are important to consider developing novel recycling strategies. Basically, CFRP waste can be divided into three types: (1) dry fibers from e.g. production residues or offcuts, (2) pre-impregnated fibers from production residues or offcuts from prepreg materials, as well as (3) defective or “end-of-life” CFRP components with hardened matrix. [10].

In general, two recycling methods can be differentiated.

First, recycling is possible by separating the fiber and the matrix to reuse the reinforcing fibers of a composite (reclamation of the fibers) with a novel matrix material to form new parts by fused deposition molding for example [11–14]. This separation can be achieved by thermal or chemical methods. Thermal separation, e.g., pyrolysis, takes place in an inert atmosphere in a temperature range of 400 °C to 700 °C, usually after mechanical comminution of the CFRP components. Due to the exclusion of oxidizing agents (e.g., oxygen), the matrix does not burn, but is broken down into short-chain molecules and then coked. The quality of the recovered carbon fibers depends on the selected

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* Corresponding author.
E-mail address: christoph.lohr@thi.de (C. Lohr).

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pyrolysis process parameters, as well as the proportion and composition of the polymer matrix. [15–17] The high tendency of the carbon fibers to oxidize from a temperature of 600 °C is problematic, as it has a considerable effect on the mechanical properties. In addition, pyrolysis dissolves the sizing on the fiber surface and, depending on the matrix material, a small percentage of residual coke remains on the fiber surface. This negatively affects the subsequent further processing and the renewed adhesion between the recycled fibers and the new matrix. A chemical separation process to separate fiber and matrix is the solvolysis process, that is based on depolymerizing of the matrix with a solvent to short-chain fragments, most of which are present in the liquid phase. Compared to pyrolysis, the energy level of solvolysis is lower. A distinction can be made between HTP solvolysis (high temperatures and pressures; above 200 °C) and LTP solvolysis (low temperatures and pressures; 80 °C to 200 °C). [18–20] Several studies report on the mechanical properties of chemical or thermal recycled carbon fibers [17,20].

Second, mechanical approaches are feasible to recycle components made from CFRP at the end of their usage. Mechanical recycling is based on shredding of the composite to obtain fragments featuring a size of 50 mm to 100 mm. Further mechanical comminution is possible with the help of hammer mills or high-speed milling machines to achieve fragments ranging from 50 μm to 10 mm. The shredded material can then be used as reinforcement or filler in a new CFRP component. [21–24] For thermoplastic matrices, it is possible to reuse the material after a mechanical recycling process in form of pellets for a subsequent extrusion or injection molding processes [25,26], as well as in additive manufacturing [27]. A disadvantage of this recycling method is the shortening of the fibers and the associated reduction in the mechanical properties. Hence with mechanically recycled material only short fiber reinforcement is feasible. [27].

3D printing is a promising approach to reuse polymers and to reduce the environmental impact of these materials since printable filaments can be made from a variety of thermoplastic materials, including those from recycling [28,29]. A comparison of mechanical performance of specimens printed from virgin polylactic acid with specimens made from PLA obtained by grounding up some of the printed parts (one-time and twice) to extrude a recycled filament showed that short beam strength was comparable to specimens made from virgin material. However, a third recycling cycle led to a decrease in short beam strength and a higher variability of the results [30]. The same approach (virgin and recycled PLA specimens made from 3D printed parts) highlighted that with the recycled filament, tensile strength and hardness slightly decreased (by 10.9 % and 2.4 %, respectively), shear strength increased (6.8 %) and tensile modulus of elasticity was statistically unchanged. It held generally true, that results of the recycled filament showed more variability [31].

By considering post-consumer products, e.g. used plastic bags [32] or from food packages and car dashboards [33], the grinded polymeric material can be reinforced by fibrous materials to form reinforced filaments for the manufacturing of 3D printed novel components. A similar approach considers recycled polymeric materials to which continuous fibers can be added in a 3D printing process to manufacture parts with improved mechanical performance. Whereas tensile properties were slightly lower for the recycled matrix material, flexural properties were nearly the same for the recycled and virgin matrix material. [34].

Furthermore, the reuse of grinded and extruded waste of fiber reinforced composite, for example preliminary used for wind turbines, could successfully be integrated in a polymeric filament to be reused with 3D printing [13,35,36]. A similar approach, based on regranulation followed by the remelting and injection molding has successfully been proven to lead recycled parts showing no significant degradation of mechanical, thermal and morphological properties [25]. For fused filament fabrication (FFF), the literature reports the recyclability of printed parts, filaments and the production of novel materials containing virgin and recycled materials in blends utilizing an extrusion device. Typical polymers for FFF 3D printing like Low-density Polyethylene (LDPE), High-density Polyethylene (HDPE), Polyethylene (PE), Polypropylene (PP) [29,37–40] and Nylon [41,42] are used in several studies. The research group around Vidakis et al. [43–48] intensively studied the recyclability of different unreinforced polymers for the 3D printing (fused filament fabrication) using filament extrusion. Therefore, the mechanical and thermal properties were investigated utilizing tensile, flexural, impact, and microhardness tests along with DSC, TGA, Raman spectroscopy, and SEM analyses. Using up to six recycling cycles and associated additive manufacturing of specimen the different studies showed the influence and mechanical response of the polymers over multiple recycling processes. They found, that for Polyamide 12 [44], Polyethylene Terephthalate Glycol [45], Polypropylene [46], Acrylonitrile-Butadiene-Styrene [47] and High-Density Polyethylene [48] the mechanical properties improved in general between the 3rd and 5th recycling process in a range of 10 % to 30 % depending on polymer and property. [43–48].

Literature review clearly showed that different techniques to use recycled materials for 3D printing have already been investigated and their potential to reduce the amount of polymeric waste has successfully been demonstrated. However, there is little knowledge so far that focuses on the properties of recycled 3D printed carbon fiber reinforced materials, such as misprints, support structures, and purge lines to be used in additive manufacturing again, although industry always considers such approaches. Hence, the aim of the study at hand aims to generate knowledge to understand recycling potential of fiber reinforced waste resulting from 3D printing. For this approach 3D printed parts made from fiber reinforced polymers were shredded to granulate and extruded to a recycled fiber reinforced filament. Mechanical performance of the virgin and recycled parts is compared to understand material degradation resulting from recycling. To further address the effect of repeated recycling processes on the mechanic response of the PA6.6 reinforced with carbon fibers via extrusion, a variety of mechanical tests were conducted on 3D-printed specimens including flexion and Charpy impact tests per recycle repetition. Tensile testing was done on the filament (virgin, recycled and of the different recycling sources). The findings prove that the mechanical response of the recycled PA6.6/CF polymer is generally improved over the recycling repetitions and differ from the source material (misprints, support structures, purge lines).

2. Materials and manufacturing

2.1. Investigated material

To investigate the recycling potential of carbon fiber reinforced PA 6.6 filament, type Onyx [49], from Markforged (Waltham, MA, USA) was considered. The PA6.6 CF composite was chosen in this study because it is a high-quality material with very high mechanical properties – therefore it is expected that minor degradation leads to reusable material with still high mechanical properties. It is also a rather expensive material (~250€/1000 cm^3) for 3D printing which could be commercially interesting in future large scale recycling processes. The manufacturer describes Onyx as a carbon fiber reinforced nylon and states a tensile modulus of 2,4 GPa, tensile strength of 37 MPa and impact strength of 330 J/m [49]. Furthermore, residues printed with Onyx material from a precedent additive manufacturing process, e.g., support structures, purge lines and misprints, were provided by Vocus3D (Augsburg, Germany). Polyamide 6.6 is characterized by the excellent strength, toughness, stiffness and dimensional stability under heat [50,51]. Due to its structural composition, PA 6.6 tends to hygroscopic properties, i.e., high moisture absorption. In addition to an increase in volume, this leads to a change in density and the mechanical properties are affected [51,52]. Hence, if processed via additive manufacturing, it is important to ensure low humidity in the environment. Too high humidity has a negative influence on the print quality [51] and the used filament in this study was dried to the manufacturers recommendation.

2.2. Additive manufacturing of the specimens

The specimens for the experimental investigation were manufactured with a Markforgeds Mark Two 3D printer. According to DIN EN ISO 178 and DIN EN ISO 179 specimens featured dimensions of 80 × 10 × 4 mm^3 (c.f. Fig. 1).

Before the specimens were printed, a CAD model of the specimens was created with Solid Edge 2020, which was imported as STL-file (Standard Tessellation Language) into the Markforged slicer software Eiger (Eiger Markforged, Somerville, MA, USA). After the printing job has been transmitted to the printer via the software Eiger, the printing bed is covered with thin layer of glue (type: ELMERS Washable School Glue Stick) to prevent the printed object from detaching from the print bed during printing, since the printing bed of the Mark Two printer is not heated. Without adhesive, the material would contract due to the crystallization that occurs as a result of cooling [37]. Then appropriate printing parameters have been defined starting with given process parameters by the printer's manufacturer for virgin PA6.6/CF and refined with a pre-trial test run for the chosen material (c.f. Table 1). The printing temperature is set to 275 °C. During printing, the bed is moved upwards along the z-axis to the printing head, that is movable in x- and y- direction. Printing always starts with a purge line at the edge of the print bed, which ensures that there is enough filament in the print head for the following print. In addition, the purge line can be used to identify, for example, excessively wet filament or under-extrusion. [53].

Figs. 2 and 3 show the first and second layer of a specimen. The solid fill pattern and the fill density of 100 % are clearly recognizable. The lines of layers one and two are oriented at a 90° angle to each other and are constantly alternating up to the last layer.

2.3. Recycling process

2.3.1. Shredding

After the initial mechanical characterization considering bending and charpy impact tests, the specimens were shredded with a shredder from 3devo (Shred IT) to gain granules in two comminution steps (c.f. Fig. 4).

To investigate the recyclability of carbon fiber-reinforced PA 6.6, specimens manufactured from a juvenile filament (c.f. Fig. 5 (a)) as well as support structures (c.f. Fig. 5 (b)) and purge lines (c.f. Fig. 5 (c)) from the company Focus 3D were shredded. Depending on the initial form of the material, granules or flakes were obtained (c.f. Fig. 5).

2.3.2. Drying

As a result of the hygroscopic property of PA 6.6.-based CFRP [54], the shredding of the material is followed by a drying process of at least four hours in a polymer dryer (AIRID, 3devo) regarding the manufacturer recommendation [55], since humidity can have a negative effect on subsequent filament extrusion and a high moisture content can cause, for example, voids in the inside of the filament or lead to a rough filament surface [50]. During the drying process, the granulate is continuously stirred in a container at 80 °C with a kind of dough hook. This process ensures a uniform reduction of the moisture. Essential parameters for drying are temperature, duration, rotation speed, size of the material (e.g., flakes, granules, powder) and the filling quantity. Starting with given process parameters by the extruder's manufacturer for PA6.6/CF material the final processing parameters were refined with a pre-trial test run. The exact values considered for drying within this study are summarized in Table 2.

Fig. 1. Specimen manufactured by Markforgeds Mark Two 3D printer.

Table 1
Printing parameters to manufacture the specimens.

General:	
Material	Onyx
Printer Type	Markforged 3D Mark Two
Settings:	
Layer Height (mm)	0.100
Infill:	
Fill Pattern	Solid Fill
Fill Density	100 %
Wall Layers (0.80 mm)	2
Total Number of Layers	40

2.4. Filament extrusion

In view of the increase in surface area due to the granulate production, the tendency of the carbon fiber-reinforced polyamide to hygroscopy. Due to this, filament extrusion was immediately linked to the drying process. The extruder used (Composer 450, 3devo) is shown in Fig. 6.

Before extrusion begins, an empty filament spool is attached to the designated holder on the side of the extruder. The dimensions of the spool are noted in the extruder software, which is essential for the automated winding of the filament.

Inside the extruder is the rotatable extruder screw. It is surrounded by four heating zones where the temperatures can be adjusted independently of each other. The pellets fall through a hopper down to the extruder screw and are transported forward by the rotation. As a result of the friction created and the high temperatures of the heating zones, the granulate melts into a homogeneous mass. The mass is pressed out of a 2 mm nozzle and cooled directly by two fans located to the left and right of the nozzle. The still warm filament is fed to two drive rollers underneath and a sensor. The sensor ensures a constant measurement of the diameter. Until the extruder has settled down to the intended diameter, there is a loss of material and thus a smaller number of samples can be produced in the subsequent print. Once the desired size has been reached, the filament is cut off and the spooling process can be started. The steps of the spooling process just listed must be carried out quickly to keep the filament under tension and thus achieve a flawless result. While the spool rotates clockwise, the position holder moves from left to right at a low speed, laying the filament side by side. The extrusion parameter data differs depending on the polymer used. Table 3 lists the specially defined values for filament production from carbon fiber reinforced PA 6.6. In addition to purge lines and support structures, specimens printed with the virgin Onyx filament from Markforged were recycled to simulate the recycling of misprints. The parameters have been found by a pre-trial based on processing data to virgin PA6.6/CF from the machine manufacturer. The described procedure ensures a versatile test of the recyclability of carbon fiber reinforced PA 6.6.

In total, five groups of specimens were obtained:

1) Specimens made from **virgin Onyx filament**
2) Specimens made from mechanically loaded specimens of group 1, that were shredded and extruded to **one-time recycled filament** to emulate misprints of virgin Onyx material
3) Specimens made from mechanically loaded specimens of group 2, that were shredded and extruded to **two-times recycled filament** to emulate misprints of one-time recycled filament
4) Specimens made from filament obtained by shredding and extruding of **purge lines**

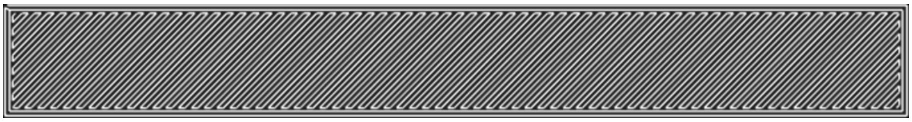

Fig. 2. First layer of a specimen (2D).

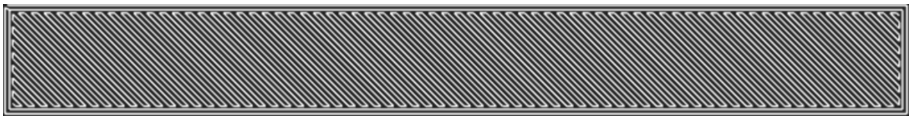

Fig. 3. Second layer of a specimen (2D).

Fig. 4. Components of the shredder from 3devo.

5) Specimens made from filament obtained by shredding and extruding of **support structures**

After recycling the filament from the different sources (purge line, misprints, support structure) at different recycle runs (as shown above), the recycled 3D printing filament is fed into the Markforgeds Mark Two 3D printer. Similar to virgin PA6.6/CF the recycled material is processed and printed with the same parameters (see chapter 2.2) to avoid a different thermal influence on the polymer structure.

3. Methods

Mechanical characterization, explained in the following, aimed to answer the following research questions.

- To what extent do the different recycling cycles influence the mechanical properties of the material? (Investigation based on bending and charpy impact testing)
- Do the various filaments show different mechanical behavior before printing the specimens? (Investigation based on tensile testing)

All specimens were stored for at least 24 h in a standard climate (23 °C and 50 % humidity) before mechanical characterization. Dimensions of the specimens were determined using a vernier caliper before loading. In the following the different testing procedures are described in detail.

3.1. Tensile testing of the filaments

To assess whether the printing process has an impact on the material properties, the filaments were subjected to a mechanical test directly after the recycling process without any further processing. This allows to observe of the influence of recycling of the material. The tensile properties of the different filaments were determined according to the guidelines of DIN EN ISO 527–1 and DIN EN ISO 572–4. Five types of filaments were considered:

1) Virgin Onyx filament
2) Onyx filament recycled one time
3) Onyx filament recycled two times
4) Shredded and extruded support structures
5) Shredded and extruded purge lines

The filaments were cut to 8 cm long parts and tested in two test series. Half of the cut filaments were dried for 72 h at 60 °C in a vacuum oven. To counteract the predetermined curvature of the filaments, the specimens were individually stored in specially made plastic tubes with a length of about 9 cm long and a diameter of 6–7 mm. The second half of the cut filaments was first stored in the tubes for at least 24 h in a standard climate (23 °C and 50 % humidity) before placing them in the vacuum oven at 60 °C (according to DIN EN ISO 291).

Each specimen was clamped into a universal testing machine (type: Z010, ZwickRoell) pre-loaded with a force of about 10 N to minimize the influence of the still slightly present curvature and to position two measuring marks correctly in a distance of 5 cm in the middle of the preloaded filaments. Elongation was measured with an extensometer (videoXtens by ZwickRoell) on the measuring marks. Tensile tests were carried out a test speed of 5 mm/min, after the pre-load was increased to 15 N. The tensile modulus and tensile strength of the filaments were determined using linear regression.

3.2. Bending testing of printed specimens

Mechanical characterization regarding the bending properties of the material was carried out according to the specifications of DIN EN ISO 178. A Zwick universal testing machine (type Z010, ZwickRoell) was used for the 3-point bending test. A radius of 3 mm was selected for the supports. The upper fin had a radius of 5 mm and the support distance was 64 mm. Preload was set to 0.1 N and applied with a speed of 5 mm/min. Applied load and deflection, hence movement of the crosshead, were measured continuously. To determine the bending modulus, in the linear-elastic region load was applied with a speed of 2 mm/min. Then, the testing speed was increased to 10 mm/min. Loading was stopped as soon as the specimen failed or a maximum displacement of 20 mm of the upper loading nose was reached. The stress–strain

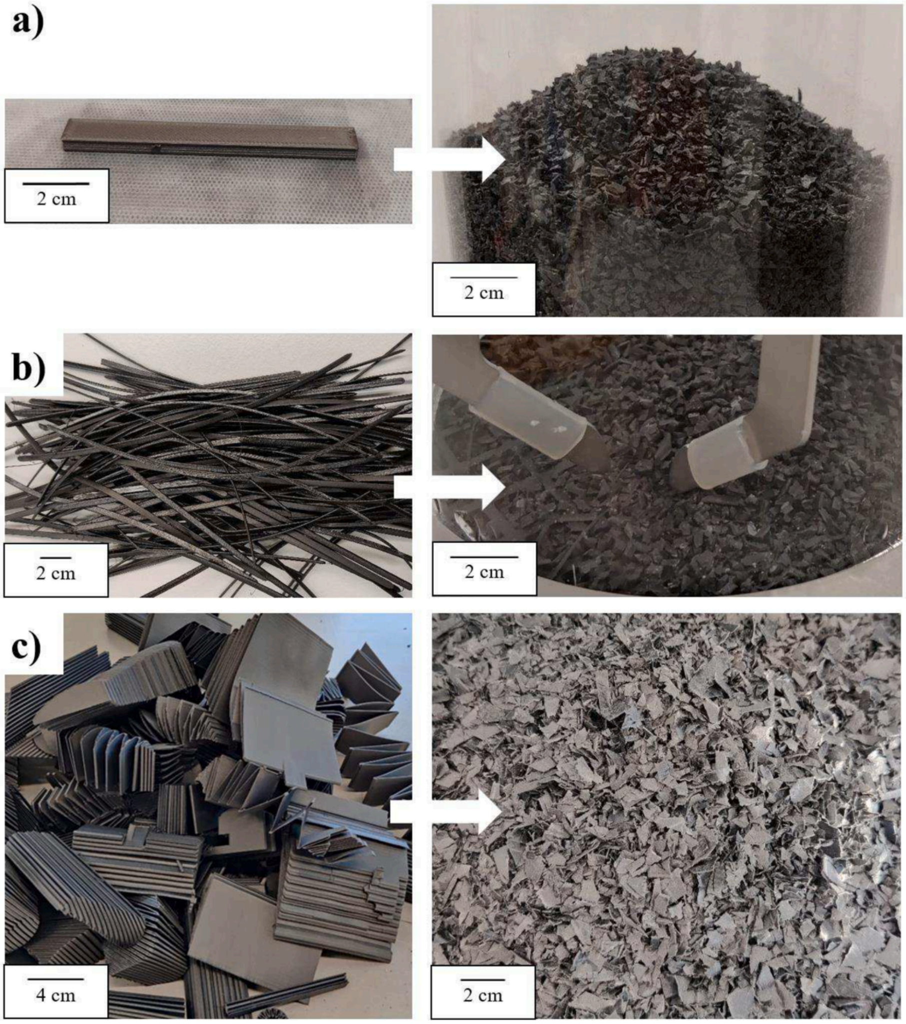

Fig. 5. Sources of recycling material from the initial material. a) 3D-printed specimen, b) purge lines, and c) support structure.

Table 2
Parameters and setting for drying the granules.

Drying temperature	80 °C
Automatic blower speed	on
Mixer speed	8 rpm
Drying duration	at least 4 h, cf. [42]

diagram was used to determine the characteristic values required for mechanical characterization. Accordingly, the bending modulus and the bending strength were determined.

3.3. *Charpy impact testing of printed specimens*

A Charpy impact test aims to measure energy absorption introduced into a specimen by a swinging pendulum. Energy absorption is a decisive indicator for the toughness of the tested material [56]. Impact testing was carried out according to DIN EN ISO 179–1 and Charpy impact strength refers to the impact energy absorbed during fracture in relation to the initial cross-sectional area of the specimen. It is given in the unit kJ/m^2. For testing, specimens were placed in the center of the holder provided by means of a positioner. The pendulum was then deflected at a 150° angle and fixed in place. After the impact pendulum was released, the pendulum struck the unnotched specimen on the narrow side. The machine records the maximum angle of the pendulum that is reached after impact on the specimen. In this way, the impact energy absorbed can be determined. The results of the Charpy impact test are described in detail in chapter 4.3.

4. Results and Discussion

Processing the PA6.6/CF material on the described lab scaled machines showed no serious issues about processibility. Comparing the recycled 3D printing filament to virgin PA6.6/CF some minor feeding issues with the recycled flakes into the extruder and some (rare) feeding issues in the 3d printer due to thickness variations of the filament occurred.

4.1. *Tensile testing of the filament*

The tensile was one possibility to test the mechanical properties of the different filaments prior to the printing process. The tensile strength and the tensile modulus were determined in each case. Furthermore, the filaments were tested in a standard climate condition and a dried condition. Due to the hygroscopy of polyamide 6.6, the mechanical properties are affected. The tensile modulus is reduced by the moisture absorption in the standard climate and lower values are reached than for the dried condition. 3.64 GPa were reached for the filament recycled once in standard climate in comparison to 4.22 GPa for the same filament in the dried condition. The highest tensile modulus reached for the juvenile filament at standard climate conditions was 4.05 GPa in. The lowest value was measured for the filament made from purge lines

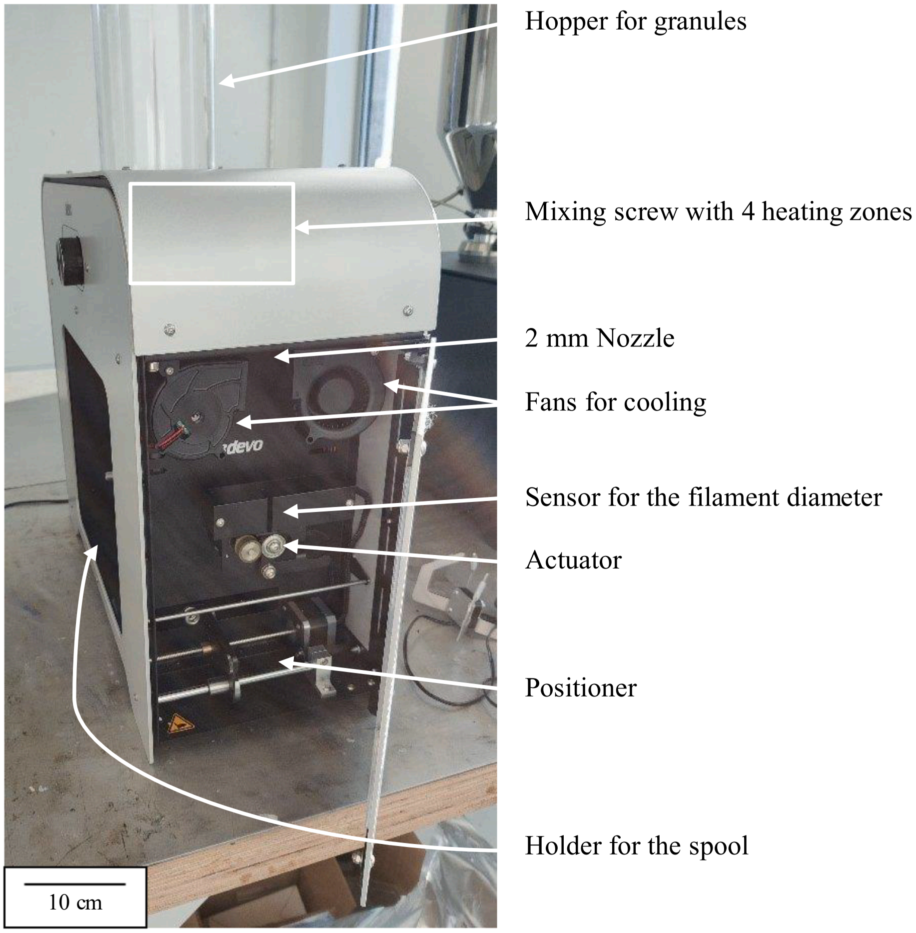

Fig. 6. Filament extruder with all essential components.

Table 3
Setting for the filament extrusion.

Fan Speed	90 %
Screw Speed	6.8 RPM
Heater 1	238 °C
Heater 2	260 °C
Heater 3	260 °C
Heater 4	250 °C
Filament Diameter	1.75 mm

(2.52 GPa). The filament recycled twice, and the purge line filament were about 1.5 GPa below the tensile modulus of the juvenile filament. Compared to the first recycling, there was a drop in tensile modulus after the second recycling by 28.9 % (cf. table 4). The tensile modulus of the support structures in the dried condition was 4.8 GPa and about 15 to 20 % higher than the other four filaments. Only three specimens could be included to evaluate the tensile modulus of the support structures, which makes it difficult to make a definite statement about potential causes for the higher value. Possibly, the filament from support structures has a deviating fiber orientation due to the different initial shape (flakes) or higher crystallinity lead to the increase of mechanical properties. For PA12 [44], which was recycled and manufactured in a similar process for 3D printing with the number of recycling cycles the crystallinity of the material decreases.

Fig. 7 shows a bar chart with the tensile moduli of all filaments in dried and standard condition. The individual bars represent the mean values of each filament with the appropriate standard deviation.

The tensile strength of the juvenile filament was 71.23 MPa in standard climate condition. The one-time recycled filament as well as the purge line filament and the support structure filament exhibited tensile strengths of about 70 MPa in the standard climate. On average the four recycled filaments were 6.6 % lower than the juvenile filament. The filament recycled once was 5.2 % below the tensile strength of the juvenile filament and the filament recycled twice was 19.5 % below. A tensile strength of 57.33 MPa was determined for the two times recycled filament. Thus, the tensile strength decreased from the first to the second recycling by 15.1 %. This decrease could be caused by damaged fibers due to the repeated comminution and re-extrusion.

All filaments tested in dried conditions showed higher tensile strength than the filaments tested in standard climate with a lower standard deviation. The juvenile filament was at 84.22 MPa in the dried condition. No significant differences in tensile strength were observed for the juvenile filament, the purge line filament and the support structure filament. All three filaments had a tensile strength of about 85 MPa. The once and twice recycled filaments were about 12 % lower at 74.05 MPa and 75.82 MPa. The once recycled filament and the filaments made from purge lines and support structures each went through the recycling cycle once. The reason for the different tensile strengths of the three filaments could be due to the different granule shapes and thus to different fiber orientations. All values for the filaments tested in standard and dried condition can be taken from table 5.

Fig. 8 shows a bar chart with the tensile strength of all filaments in dried and standard condition. The individual bars represent the mean values of each filament with the appropriate standard deviation. The lower standard deviation for the samples in dried condition can be explained by the better performance of the matrix material in the absence of moisture. The melting and solidification of the polyamide during filament extrusion could have an influence on the chemical

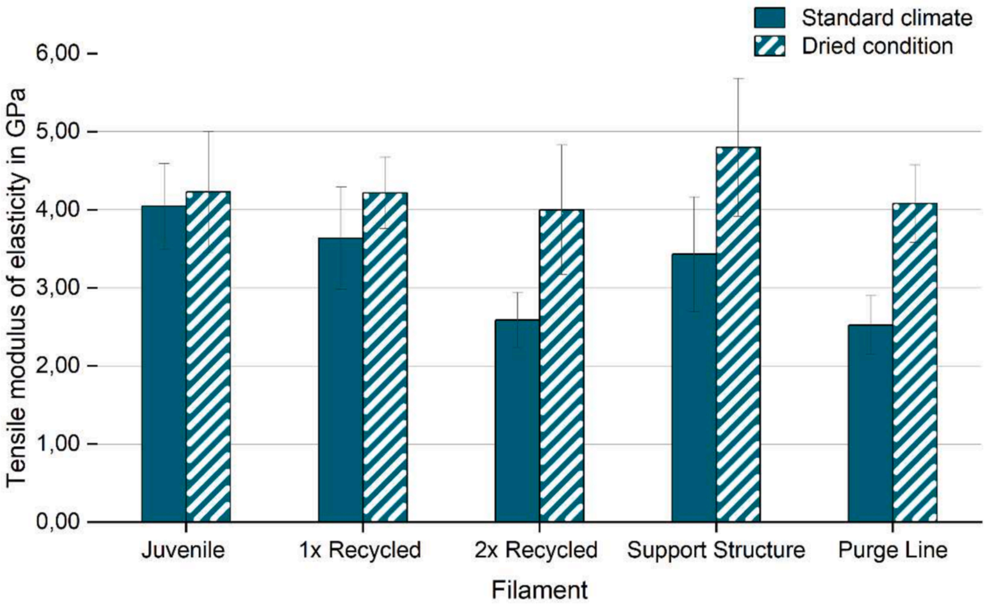

Fig. 7. Tensile modulus of elasticity of the filaments in standard climate and dried condition.

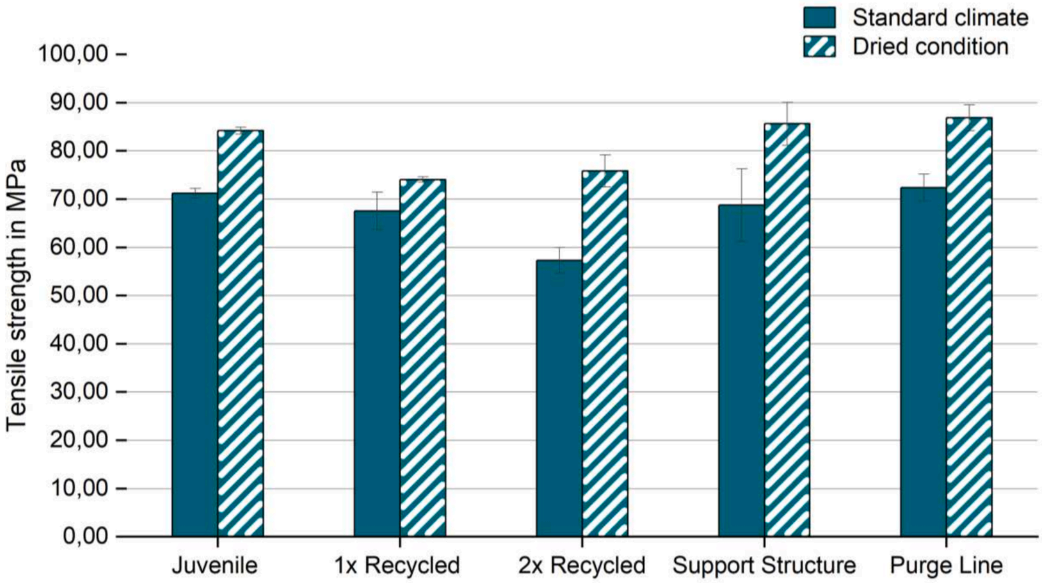

Fig. 8. Tensile stress over tensile strain of specific filament specimen in standard climate (top) and dried condition (bottom).

structure. Due to the changed structure, increased water absorption would be a conceivable reason for the reduced tensile modulus of the recycled filaments. A decrease in tensile modulus due to recycling was also observed by Colucci et al. [25]. They recycled artificially aged carbon short fiber reinforced PA 6.6 by injection molding and observed a decrease in tensile modulus by 12.7 % compared to untreated samples. In addition, the complex viscosity decreased from 4263.1 Pa-s (untreated) to 3757.4 Pa-s (aged, recycled) [25]. For tensile strength investigation, Colucci et al. observed a 20.4 % reduction in the recycled carbon short fiber reinforced PA 6.6 compared to the untreated specimens [25]. Evens et al. [26] investigated the tensile strength for injection molding recycled carbon fiber reinforced PP and observed a decrease of 6.5 % in tensile strength after the first recycling cycle. After the second cycle a reduction of 13 % and after ten cycles, a reduction of 25 % in tensile strength was measured [26]. This is comparable with the extrusion process, used in this study, where the tensile strength decreased in average for all four different recycling processes after the first cycle about 6.6 %. In the second cycle a decrease of about 15 % is measured and proofs a comparable destructive load in the injection molding and extrusion process for short fibers (cf. Vaxman et al. [44]). In the dried condition, the higher performance of the matrix dominates the failure mechanism and the influence of the fibers become a minor effect, which is not visible in the tensile strength (cf. Fig. 8).

Fig. 9 shows the Tensile stress over tensile strain of specific filament specimen in standard climate (left) and dried condition (right). The source of material and conditioning have a significant influence on the mechanical properties of the filament. Comparing the graphs for juvenile, 1x recycled and 2x recycled it is evident, that – for standard climate – the maximum stress decreases with the elongation at break increases with the number of recycling times.

When dried, the 2x recycled filament has higher tensile strength with lower elongation at break (cf. 11 bottom; cf. Fig. 10). Literature [42,44]

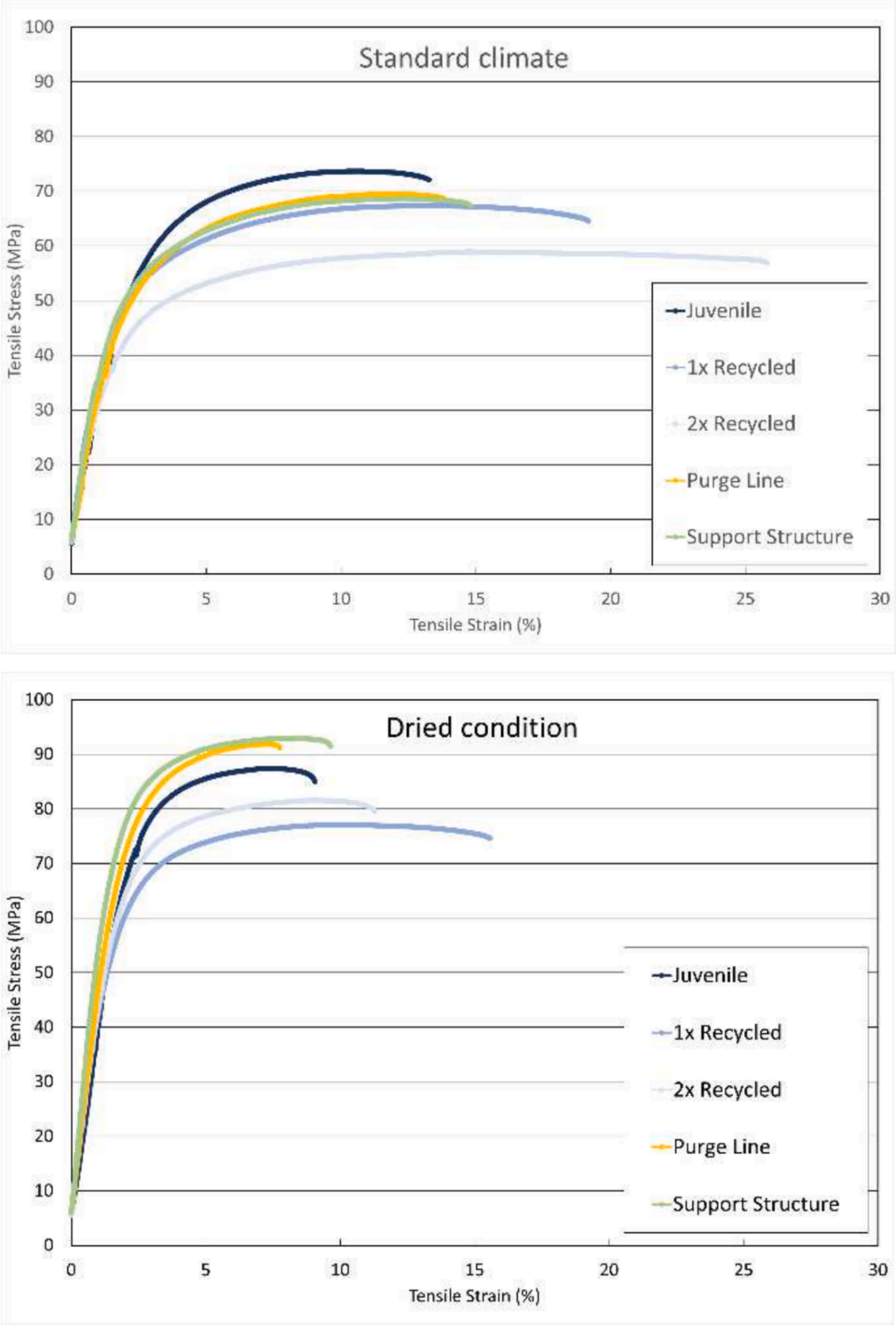

Fig. 9. Tensile strength of the filaments in standard climate and dried condition.

indicates that for polyamide a reduction in crystallinity typically diminishes the ability of material molecules to organize and form crystalline regions. In the context of polymer recycling, this decrease in crystallinity suggests that chain branching or cross-linking may occur alongside chain scission during extrusion-based recycling. Such changes in crystallinity can affect the material's mechanical properties, like the modulus. Notably, the variation in polymer chain lengths due to repeated recycling impacts crystallite quality and degree of crystallinity, cross-linking likely contributes to reduced mechanical performance. It is also seen in literature, that after several recycling cycles (e.g. six times for PA 12 studied in [44]) an inability to further process the material on an extruder or 3D printer occurs. In this study the filament was recycled a maximum of two times and no such processing problems have occurred.

4.2. *Bending test of the specimens*

Due to the material properties and the selected test parameters, none of the specimens broke during the bending test. In every case, the specified failure criterion of a maximum deformation of 20 mm has been considered. For the specimens made of the original onyx, a flexural modulus of 1.67 GPa and a standard deviation of 0.04 GPa could be determined (cf. Fig. 11). The flexural strength showed a value of 57.58 MPa and a standard deviation of 0.84 MPa (cf. Fig. 12). The flexural modulus of the once-recycled specimens could be determined to have a mean value of 2.02 GPa. The standard deviation was 0.16 GPa (cf. Fig. 11). The flexural strength was found to be 68.94 MPa with a standard deviation of 5.08 MPa (cf. Fig. 12). The sample group of twice-recycled filament had an average flexural modulus of 1.68 GPa and a

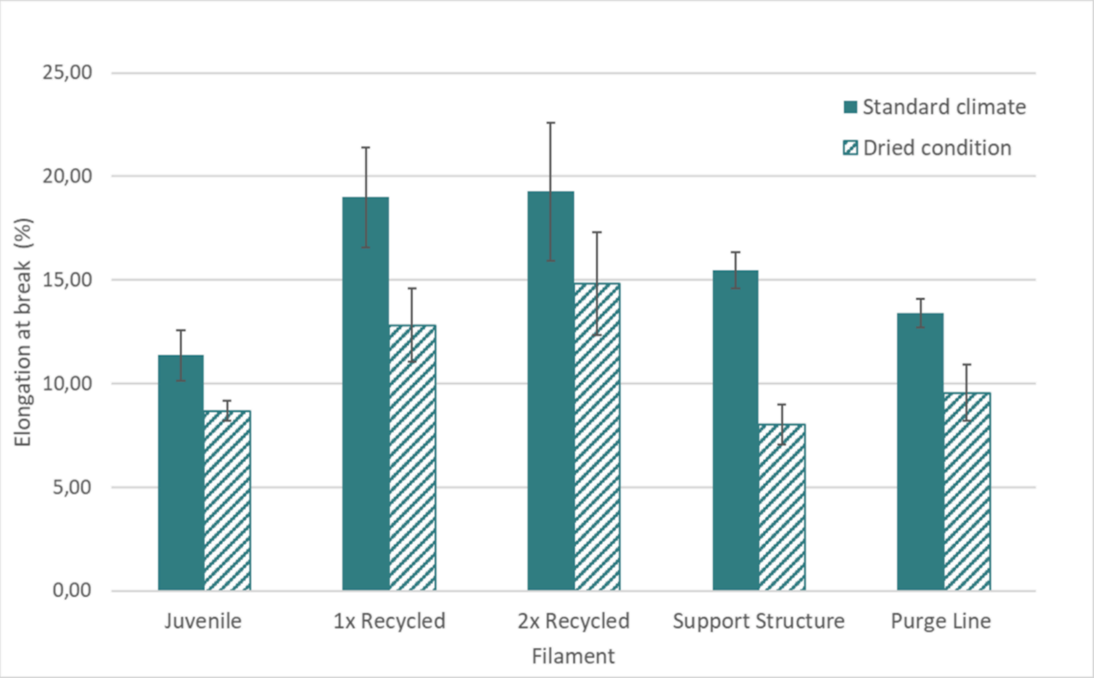

Fig. 10. Elongation at break (in %) of the filaments in standard climate and dried condition.

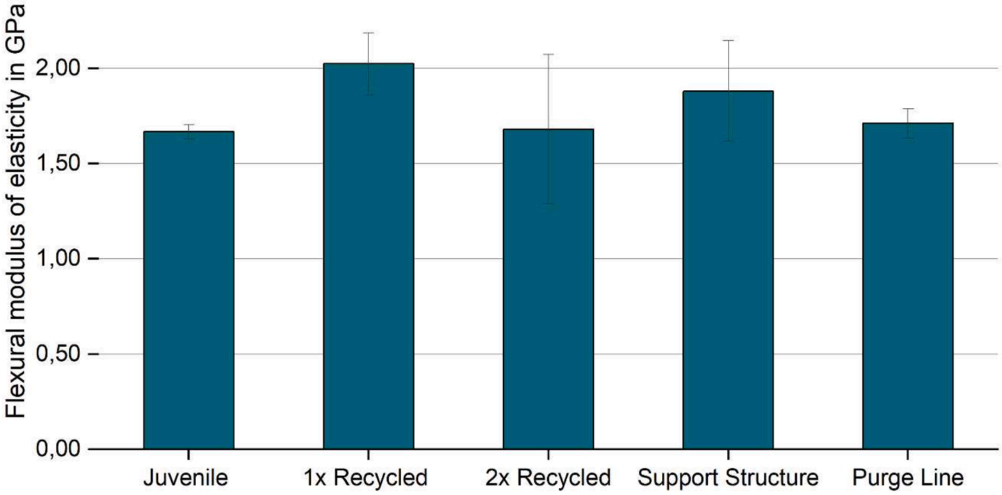

Fig. 11. Flexural modulus of elasticity of the different investigated material conditions.

standard deviation of 0.39 GPa (cf. Fig. 11). Flexural strength had an average value of 55.35 MPa with a standard deviation of 11.82 MPa (cf. Fig. 12). For the specimens from the support structure filament, a flexural modulus of 1.88 GPa was determined. The standard deviation was 0.26 GPa (cf. Fig. 11). A value of 62.45 MPa was calculated for the average flexural strength of this series of specimens. The value of the standard deviation was 7.86 MPa (cf. Fig. 12). The average flexural modulus of the purge line filament sample series had a value of 1.71 GPa with a standard deviation of 0.08 GPa (cf. Fig. 11). The mean value of the flexural strength was 57.25 MPa and there was a standard deviation of 1.86 MPa (cf. Fig. 12).

Fig. 13 shows the flexural stress over flexural strain of specific specimen. Flexural properties follow a different trend than the tensile properties of the filament. Both flexural strength and modulus of elasticity peaking in the 1x recycling cycle. In the 2x recycled cycle, both properties begin to decrease.

The “stiffness” of the material at bending remains in a narrow area of properties, as the elongation at maximum stress is at ~ 6,9 % for all material sources and recycling cycles (cf. Fig. 14).

The once-recycled specimens, as well as the specimens from support structures, showed an increased flexural modulus of elasticity of 12 % and 20 %, respectively, compared to the original onyx specimens (1.67 GPa). This is in good agreement with the results of Vidakis et al for unreinforced polymer such as PA 12 [44], ABS [47] and HDPE [43].

The specimens from purge lines were minimally higher than the flexural modulus of elasticity of the untreated Onyx at 1.71 GPa. Due to filament extrusion, orientation of the short carbon fibers could conceivably be the reason for the improved flexural modulus of elasticity. Furthermore, a change in the chemical structure of the polyamide due to the repeated melting and solidification is conceivable – as mentioned in [44] on the study on mechanical properties over recycling time on PA 12.

The flexural modulus of elasticity decreased in the following order from the once-recycled specimens to the support structure specimens,

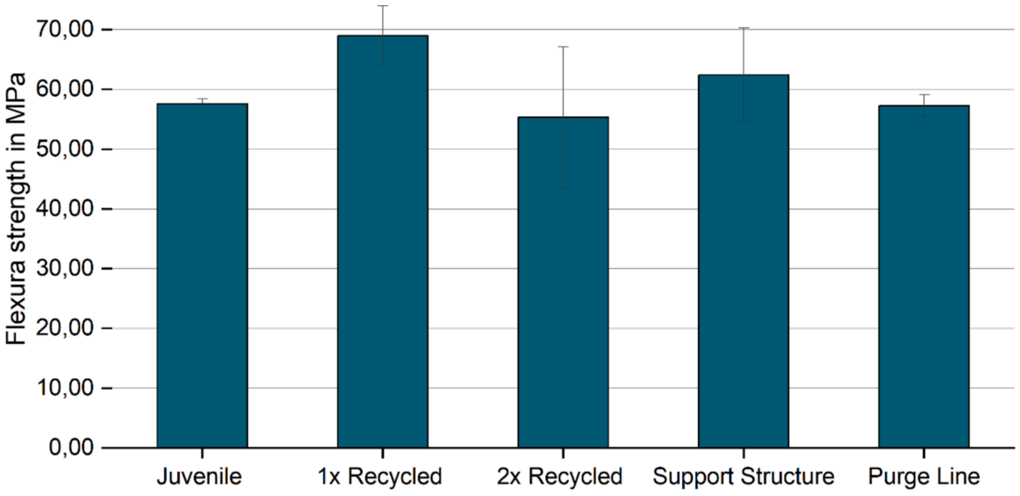

Fig. 12. Flexural strength of the different investigated material conditions.

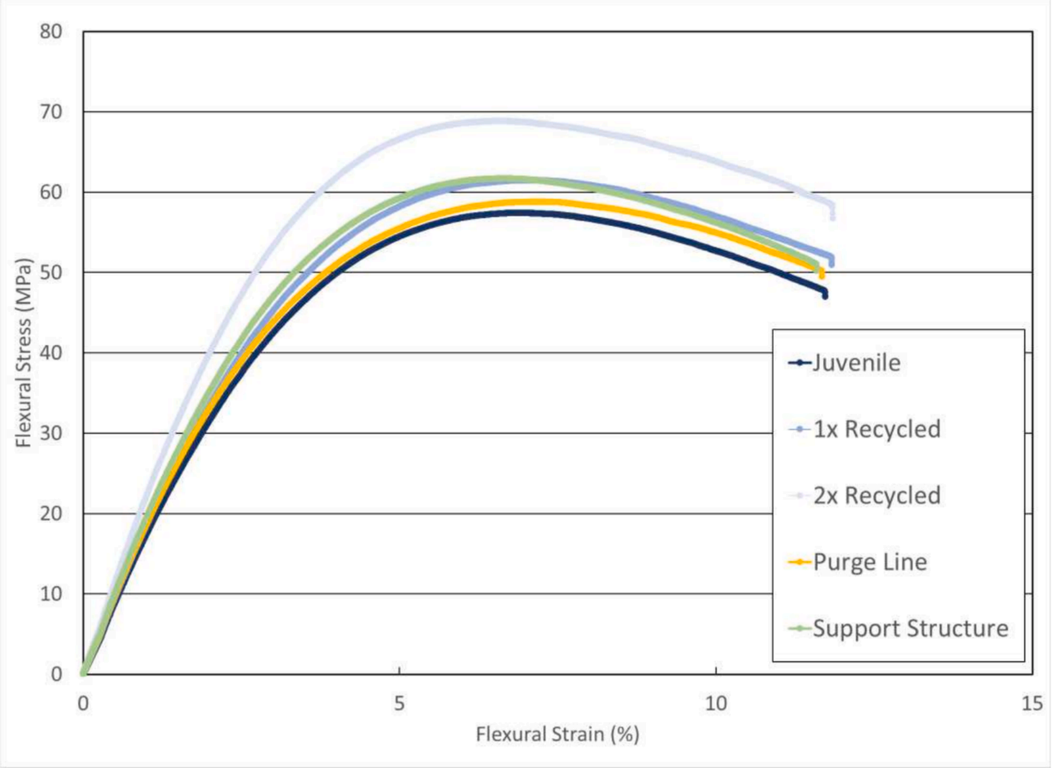

Fig. 13. Flexural stress over Flexural strain of specific specimen.

and finally the purge line specimens. The difference between these values can be explained by the three different initial shapes before recycling. The samples, support structures and purge lines are manufactured in different ways in the 3D printer. The purge line is extruded in one layer as an approx. 5 mm wide line, while the sample and the support structures are specific to the printed part as they are printed over several layers and differ in terms of shape, size, filling pattern. These differences are still present in the granules or flakes. With a different fiber orientation this could also be the reason for the deviating characteristic values. In contrast to Evens et al. [26], a comparable flexural modulus to the original samples could be determined in this work after the second recycling cycle (1.67 GPa and 1.68 GPa). The decrease in the value from the first to the second cycle is caused by fiber breakage occurring during the processing by the shear forces acting on the shredder and extruder. Such a behavior was shown for short fiber reinforced thermoplastics by Vaxman et al. [57].

Furthermore, thermal degradation (as shown in [44] for PA 12) of the polymer could also lead to a decrease in the flexural modulus after the second cycle. The incorporated short CF fibers could also lead to a higher temperature while processing due to the high shear rate inside the material further degrading the polymer material.

4.3. *Charpy impact testing of the specimens*

For the specimens from the juvenile filament, an average value of 43.70 kJ/m^2 was determined. The average values of the other specimens were 62.48 kJ/m^2 (recycled 1x), 43.37 kJ/m^2 (recycled 2x), 51.57 kJ/m^2 (support structure) and 88.26 kJ/m^2 (purge line). The

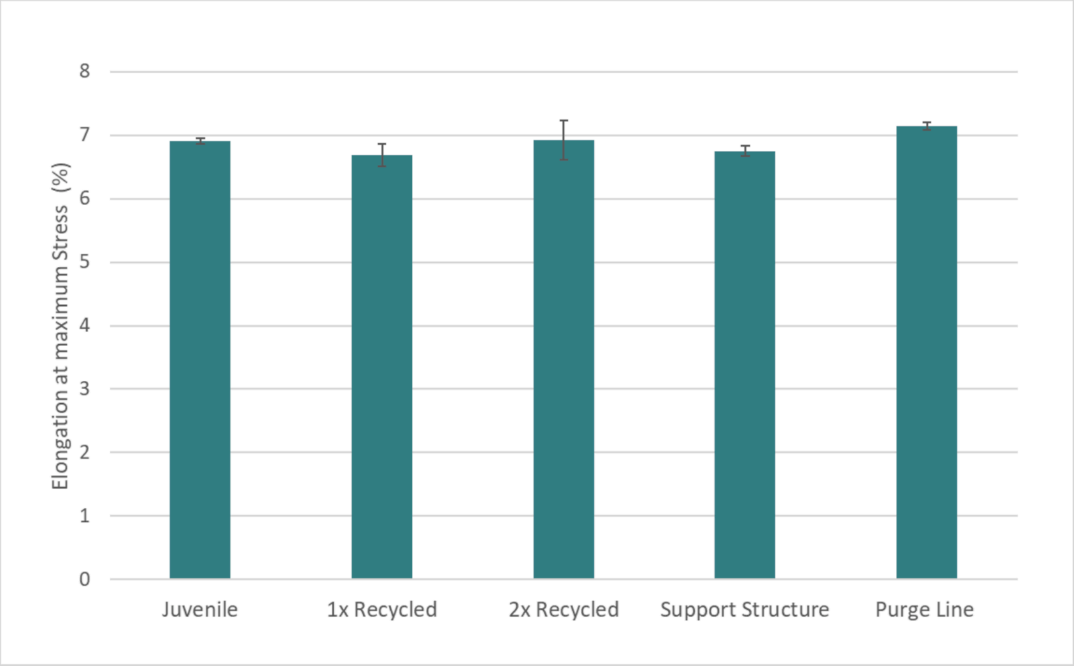

Fig. 14. Elongation (in %) at maximum flexural stress.

purge line specimens exhibited twice the average impact strength of the juvenile specimens. The specimens from once-recycled Onyx were 62.48 kJ/m^2, which is about 40 % higher than the juvenile Onyx and about 30 % lower than the purge line specimens. The specimens from support structures were about 18 % lower than the one-time recycled specimens. All materials that went through the recycling once (recycled once, purge line, support structure), an improved impact strength of 54.3 % was achieved compared to the juvenile specimens.

Fiber orientation initiated by filament extrusion was already mentioned for flexural modulus of elasticity and flexural strength and is a confirming the explanation for the improved impact strength after the first recycling. The improved impact strength could be also explained due to a change in structure of the matrix material because of the multiple heat exposure.

A comparative graph of the Charpy impact strength can be found in Fig. 15. The individual bars represent the mean values of each tested material with the appropriate standard deviation. The improvement after first recycling is dominant for the impact strength of the material system. The filament, once recycled, has a 40 % higher impact strength then the juvenile filament. In average for all once recycled filaments (including the purge line and the support structure), an increase in 54.3 % was reached. The via injection molding recycled fiber reinforced filament by Evens et al. [26], reached an increase of 50 % in impact strength only after ten recycling cycles. After the first cycle, the value increased by only 2 % and after the second cycle by 5 % [26]. Differences between the once recycled purge lines, support structures and juvenile filament can be explained, analogous to the flexural strength, by the processing of the recycling and the orientation during 3D printing.

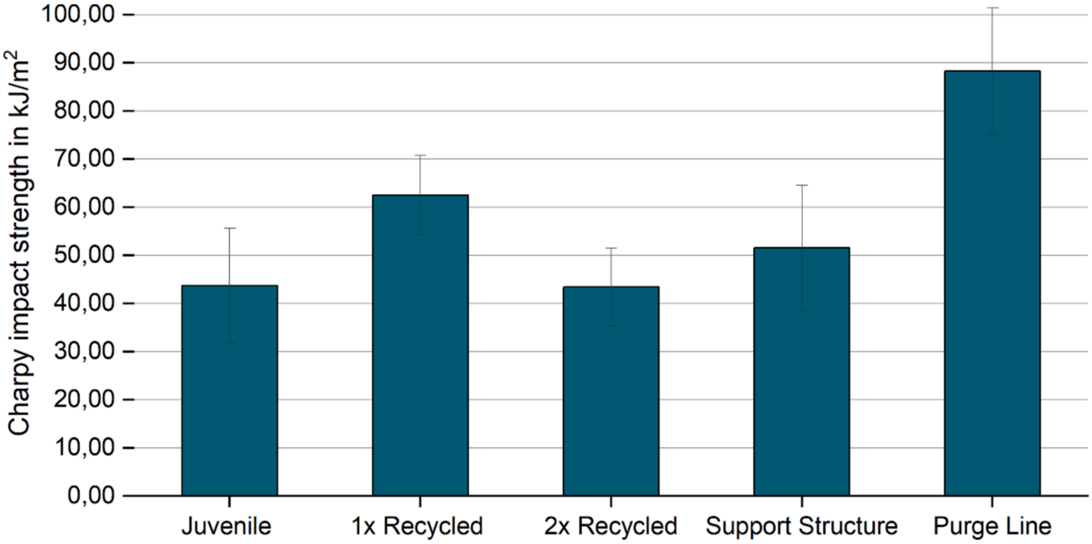

Fig. 15. Charpy impact strength of the five different specimens.

5. Summary and conclusion

A PA 6.6 filament type Onyx by Markforged was tested in the juvenile state, once and twice recycled, as well as the shredded and extruded purge lines and support structures. Besides filament testing, mechanical tests were carried out on 3D printed parts via bending and sharpy impact testing. The filament has shown the potential of recyclability and allow one time recycling without a decrease but even an increase of mechanical properties. Therefore, it is a promising approach to reuse the purge lines and support structures of 3D printing processes and to increase the material yield during processing. For the second recycling cycle, a decrease in the mechanical properties has been recognized, a spread in deviation and partly decrease in average properties in comparison with the juvenile, like the flexural strength. This shows the need of considering the application and the required component quality, before a – multiple times – recycled material can be used for 3D printing processes. Applications of the recycling process of the shown PA6.6/CF material could be in larger on demand 3D printing companies where the waste material (support structure, purge line e.g.) could be rebuilt to filament and reused for new parts – provided the mechanical properties are acceptable for future use. For this application cost efficiency in recycling is an interesting topic and key for industrializing these methods. In future studies the findings of this study on the mechanical properties over cycle times lay the foundation for a cost-benefit analysis of the recycling stream based on the available material quantities and sources.

CRediT authorship contribution statement

C. Lohr: Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation, Conceptualization. **A. Trauth:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **J. Schukraft:** Writing – original draft, Visualization, Methodology, Formal analysis. **S. Leher:** Writing – original draft, Visualization, Methodology, Investigation, Data curation, Conceptualization. **K.A. Weidenmann:** Writing – review & editing, Supervision, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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