RECYCLING OF LONG CARBON FIBERS, PART II: DEVELOPMENT OF A BINDER TAPE MANUFACTURING PROCESS FOR PROCESSING IN AUTOMATED TAPE LAYING

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Abstract

Current approaches for FRPC recycling usually not exploit the potential of endless fibers due to shortening and improper alignment during recycling processes. Hence, the presented work aimed at the development of a recycling process for long recycled carbon fibers (LrCF), where fiber length is preserved and load-related fiber orientation is possible.
The starting point for the presented work were so-called slivers, which are long bundles of fibers resulting from a carding process that has been applied to fiber scrap resulting from pyrolysis. The main focus of this work was on the development of a binder mesh application rig that processes the sliver to a binder tape, processable in an automated tape laying process. The binder tape preform manufactured this way two alternative routes for composite manufacturing were tested. First the amount of binder was set so high, that direct thermoplastic pressing of the preforms was possible. Second, the amount of binder was minimized and the preforms were infiltrated with a thermoset resin system via resin transfer molding. While the thermoplastic route showed very deficient fiber-matrix-adhesion, with the thermoset route ≈ 68% of stiffness and ≈ 31% of strength of virgin fiber-based composites could be achieved in fiber direction in an unidirectional lay-up.

1. Introduction

1.1. Motivation

Since 2010 the global demand of carbon fibers (CF) has more than doubled, resulting in a forecasted demand of 77,000 tons in 2018 [1]. But not all CF end in final parts. Already along the multiple steps in the production chain of carbon fiber reinforced plastic composites (CFRPC), 30% to 40% of the input material is lost as production waste [2]. This leads to an increase in production waste which is directly correlated to CF demand, and represents the first of two significant CF waste streams. The second, in the near future at least as important as the first waste stream, will be end-of-life (EoL) parts. Despite this fact, recycling of the expensive carbon fibers is still not industrially established, since there is no closed material cycle as it is the case in the metal or plastic industry.

1.2. State of the art: recycling of carbon fibers

When regarding mechanical properties, it is favorable to use rCF with the highest residual length possible with load-related orientation within the recycled part. In [3] the influence of fiber lengths and alignment on mechanical properties was investigated. Although the authors did not use rCF, but virgin fibers with sizing, a clear influence of both – the fiber length and the alignment – on mechanical properties could be observed. Unidirectional (UD) tapes made of CF (type Toray T300) and fiber volume content (FVC) of 40% had been tested. The tensile strength decreased by 8% for realigned fibers of 100 mm length and by 28% for realigned fibers of 50 mm length, compared to continuous, but realigned fiber. The tensile modulus was not significantly affected, although for 50 mm CF the values showed a higher scatter. Regarding the alignment, shorter fiber lengths combined with an off-axis angle of 15% severed the decrease in strength. In general, an off-axis angle of 15% led to a maximum decrease in tensile strength of 15% (50 mm CF length) [3]. In the latter case, a decrease of 15% was rather a positive result compared to [4]. In this calculated case for glass fiber (GF) composite with epoxy as matrix, a 15% off-axis angle leads to a decrease in strength of about 50%. Carding processes are suitable to align up to 90% of rCF, although it leads to a broad fiber length distribution from under 1 mm up to the original input length. Usually this fiber distribution is corresponding to a Gaussian curve. The average fiber length is depending on process management and topic of current research [5–7]. The carding process needs to be adopted for the treatment of carbon fibers, but it shows a high potential for aligned rCF SFPs in sufficient output rates while preserving the fiber length the best possible.

When using rCF material the most challenging points are to prevent the following:

- Misalignment of fibers: As mentioned above, already a small amount of misalignment of the fibers away from the ideal 0°-direction leads to a significant decrease of strength and stiffness.
- Lack of fiber sizing: The fiber sizing is operating as a coupling agent for fiber-matrix adhesion and is therefore crucial to load transmission in composites.
- Damage of fibers: Any damage of fibers occurring at any point of the recycling process, for example due to local notches or kinks is a possible source for crack initiation.
- Fiber length: Composites reinforced with short rCF are considered to be a down-cycling of the material.

2. Objective

The presented work aimed at the development of a recycling process for long recycled carbon fibers (LrCF), where fiber length is preserved and load-related fiber orientation is possible.
Following the presented state of the art, an expedient approach for best use of the properties of recycled carbon fibers is processing via automated tape laying (ATL) as costly textile processing can be avoided and fibers can be place related to loads applied on the part.
The starting point for the presented work were so-called slivers, which are long bundles of fibers resulting from a carding & drawing process that has been applied to fiber scrap (see Figure 1). The main focus of this work was on the development of a binder mesh application rig, which processes the sliver to a binder tape, processable in an ATL process, and a subsequent composite manufacturing process.

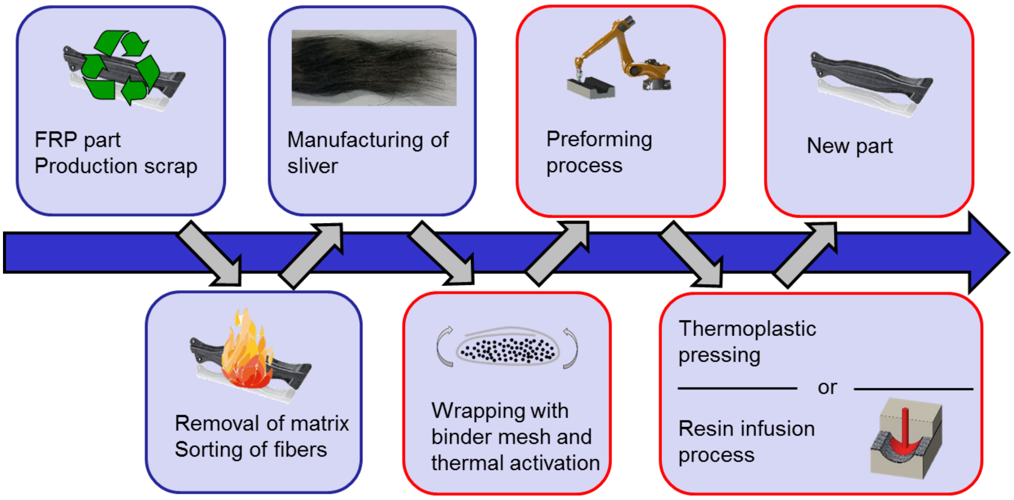

Figure 1: Depiction of conducted process chain

This paper presents the developments on the binder mesh process including a validation consisting of laminate manufacturing via hot pressing and Resin Transfer Molding respectively.

3. Materials and methods

In the following, input materials as well as used machinery and processes for laminate manufacturing are described.

3.1. Sliver material

The basis for the considered process is a sliver material, which is a strand of limited length fibers mostly aligned in length direction of the product as can be seen in Figure 2.

Figure 2: Sliver material, bending due to gravity shows low bending stiffness

The sliver is the result of a carding process performed by ELG Carbon Fibre Ltd. with subsequent drawing process by Deutsche Institute für Textil+Faserforschung Denkendorf. The input material for the carding process was carbon fiber material which was regained from pyrolyzed virgin carbon fibers with a length of 150 mm. During the carding process the fiber balls resulting from Pyrolysis are untangled and the sliver is pre-formed. The drawing process is required for optimization of fiber alignment and material homogeneity. During these processes, auxiliary thermoplastic fibers like PA6 can be added for better processing with less fiber shortening. These can also be used as matrix material as will be shown below. The sliver material used in this work had a length weight of ≈ 4 g/m. Due to the lack of stabilizing structure or auxiliary material, the sliver shows only little cohesion that is achieved by friction between single fibers. For this reason, the application of a binder material is necessary to ensure sufficient cohesion for automated processing of the material. One severe drawback of recycled material is the possible variation in weight per length and the resulting inhomogeneities during processing. Besides possible rupture of the material due to local weaknesses, also jamming of the machines due to local accumulations can occur. Furthermore, variations of length weight impose problems during later steps as the produced preforms suffer from variations of local thickness. For the material processes in this work, local variations in weight per length of 50% have been observed.

3.2. Part manufacturing for validation tests

To validate the developed binder manufacturing process two possible process routes for manufacturing of a finished laminate were considered: a thermoplastic and a thermoset route. Both draw back on preforms manufactured out of the novel binder mesh tapes via a Dry Fiber Placement process (Figure 3). Subsequently, the two alternative routes were followed as detailed in the following.

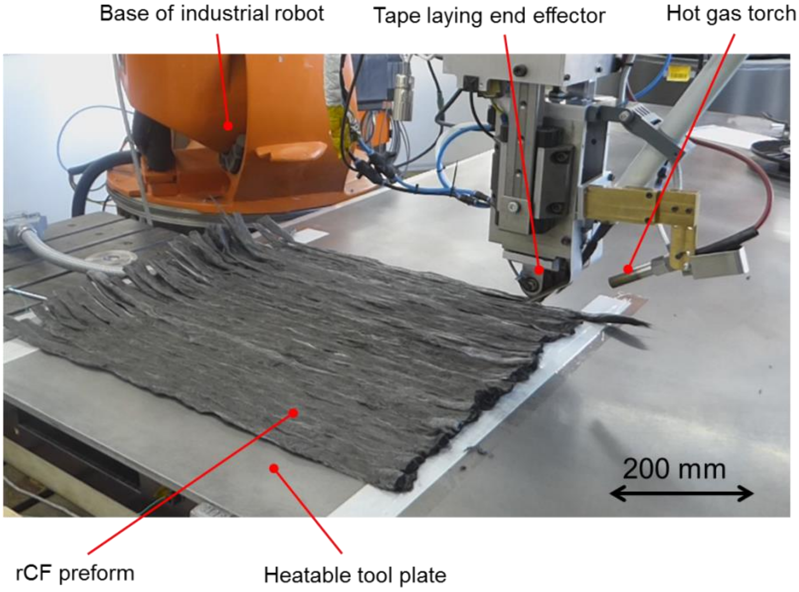

Figure 3: Dry fiber lay-up process with industrial robot

3.2.1. Thermoplastic route

As already mentioned, auxiliary fibers like PA6 might be added during sliver manufacturing. Depending on the amount, it can be expedient to follow a thermoplastic process route. This means that the amount of auxiliary fibers added is sufficient to achieve complete impregnation of the finished part at 50% fiber volume content. Due to not perfectly aligned fibers, higher intended fiber volume contents could possibly lead to local voids due to shortage of matrix. After manufacturing the preform, it can subsequently be consolidated to the finished laminate using a pressing process that can either produce a flat plate or form the preform into net shape. For the validation tests, preforms with pure unidirectional lay-up were manufactured by ATL. To reach a FVC of 50% at the thickness of 2 mm during pressing, a total sliver mass of 2943 g/m² was used. The preforms were then pressed with 20 bar at 250°C for 30 min and following cooled down again.

3.2.2. Thermoset route

The preform resulting from the Dry Fiber Placement is porous and can also be processed in a Resin Transfer Molding (RTM) process. During RTM the porous preform is impregnated with a thermoset resin system in a closed tool. For this process chain the amount of auxiliary thermoplastic fibers added during sliver manufacturing is critical as adhesion between the thermoplastic fibers and the surrounding thermoset matrix might be deficient and the presence of thermoplastic fibers reduces the available space within the composite for impregnation of carbon fibers. For these reasons, in the thermoset route, no thermoplastic fibers were used. Still, binder material was added as will be discussed later. For the validation tests, preforms with pure unidirectional lay-up were manufactured by ATL. To reach a FVC of 50% at the thickness of 2 mm during pressing, a fiber mass of this preform (not containing auxiliary PA6 fibers) of 1615 g/m² was used. As mentioned in section 3.1, variations in the sliver’s length weight also result in variations of preform thickness. Due to this reason, the reachable FVC is limited for preforms with larger thickness variations as local agglomerations lead to blockage of tool closing. In the experiments conducted for this work, FVC was limited to 34% due to this effect for the thermoset plate. For input materials with more homogeneous weight per length, 50% FVC can easily be achieved.

For the injections a Resin Transfer Molding process was used, in which the preform was placed in a closed metal tool and vacuum was applied. The system RIMR 935 / RIMH 936 by Huntsman was injected at an overpressure of 4 bar with curing of 3 hours a 100 °C.

3.3. Mechanical testing and plate characterization

The properties of the plates after thermoplastic pressing or RTM respectively, have been tested using tensile testing (DIN EN ISO 527-5), 3-point bending tests (DIN EN ISO 178) and scanning electron microscopy.

4. Development of binder application process

As already discussed, the sliver resulting from the carding and drawing process does not possess a sufficient cohesion for further processing in ATL. For this reason, a suitable semi-finished product has to be manufactured. This SFP has to possess sufficient tensile stability and inherent cohesion as well as cohesion between single strands after lay-up. To meet these requirements different alternatives were evaluated. One common technique used in ATL processes for binder application is the use of powdery binder. However, powder binder needs a large amount of binder material to provide a sufficient cohesion of the SFP. The second alternative, which was implemented in the end, was to envelop the sliver with a thermoplastic binder mesh material, which can subsequently be molten and pressed on the sliver to attach it. This patented procedure has been adapted to a lab scale binder application machine that is presented here [8]. An overview of the machine can be seen in Figure 4.

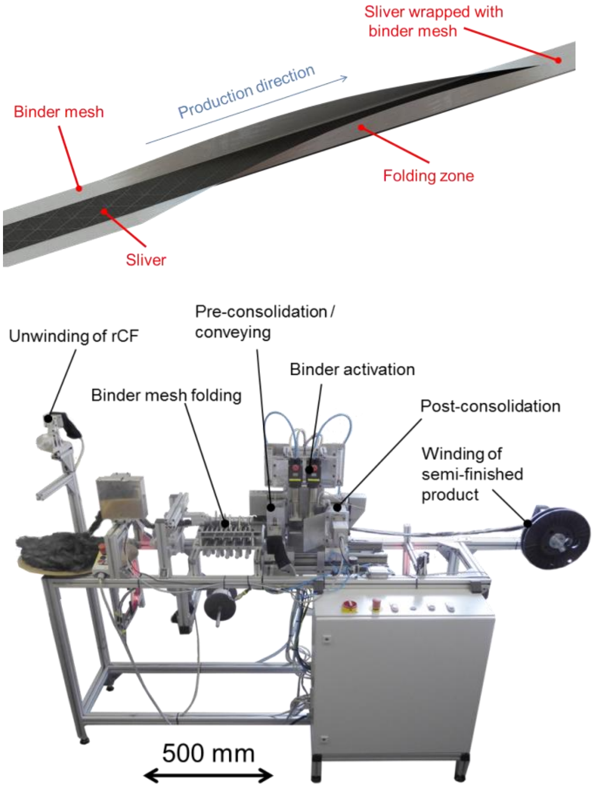

Figure 4: Principle of binder mesh folding (top) and overview of binder tape manufacturing machine (bottom)

The manufacturing of the semi-finished product, the binder tape, from the sliver, several process steps have to be conducted subsequently. In a first step, the delivered sliver material has to be conveyed. If the material is already on a spool, it has to be unwound. For controlled unwinding speed, certain material sag is allowed and measured using light barriers. The unwinding speed is then adjusted for constant material sag. The binder mesh material is continuously supplied from below and the two material streams are then merged. In a folding unit, rod shapers, adjustable in both position and angle, fold the binder mesh around the sliver. Due to the adjustability, a large variety of input materials with various length weights (sliver) and areal weights (mesh) can be processed. When the sliver is completely surrounded by the mesh material, the compound is pre-compacted by a propelled pair of rolls with adjustable pressure. In a heating unit, two hot air fans with adjustable temperature and air diffusors heat-up the compound in order to allow a slight melting of the binder material. In a subsequent consolidation step, the binder tape is fixed and cooled by another propelled pair of rolls with adjustable pressure. For enhancement of fiber orientation, a speed difference between the pre-consolidation and final consolidation can be set. The stretched state of the fibers under tension can be frozen with the binder mesh. After a second roll pair for consolidation for cooling and compaction, the material can be wound up on a spool for transport to the subsequent automated lay-up step. In conclusion, a very flexible process and machinery for binder mesh application has been developed. Length weights from 3 g/m up to 20 g/m can be processed at speed up to 20 m/min. A future scale-up to faster process speeds and higher length weights seems expedient and feasible.

5. Mechanical Testing

5.1. Tensile testing process direction (0°)

In the results of 0° tensile tests (Figure 5), it can be seen that tensile strength is reduced to less than 25% for the thermoplastic plate compared to a plate manufactured by Dry Fiber Placement with virgin fibers. For the plates with recycled fibers, it was observed by visual inspection that a large amount of fibers is pulled-out of the matrix on the fracture surface. The fibers seem dry and do not show any residuals of the PA6 matrix. This could be one possible reason for this significant reduction of strength compared to a new fiber, as it indicates a very deficient fiber/matrix-adhesion. When regarding modulus, the reduction is about 50%. As discussed above, the modulus is mainly influenced by fiber orientation, whereby the lack of sizing has a minor influence on measured modulus. Furthermore, deficient fiber orientation has a larger influence on measured modulus.

For the thermoset plate, only a fiber volume of 34% was reached as discussed above. For comparison reasons, the values were recalculated to 50% for the 0° tensile test for comparison. Better fiber alignment has been reached at the binder application compared to for the thermoplastic plate, possibly due to the different fiber sliding behavior without auxiliary thermoplastic fibers. This can especially be seen in the achieved modulus. Strength is higher than for the thermoplastic plate as well, this behavior can be explained by better fiber-matrix cohesion observed in visual inspection and SEM (scanning electron microscopy) due to the better bonding behavior of epoxy matrix compared to PA6. Compared to commercially available rCF mat material, strength and modulus are significantly higher. It can thus be stated that the efforts aligning the fibers in load direction pay-off by achieving better properties compared to random fiber alignment.

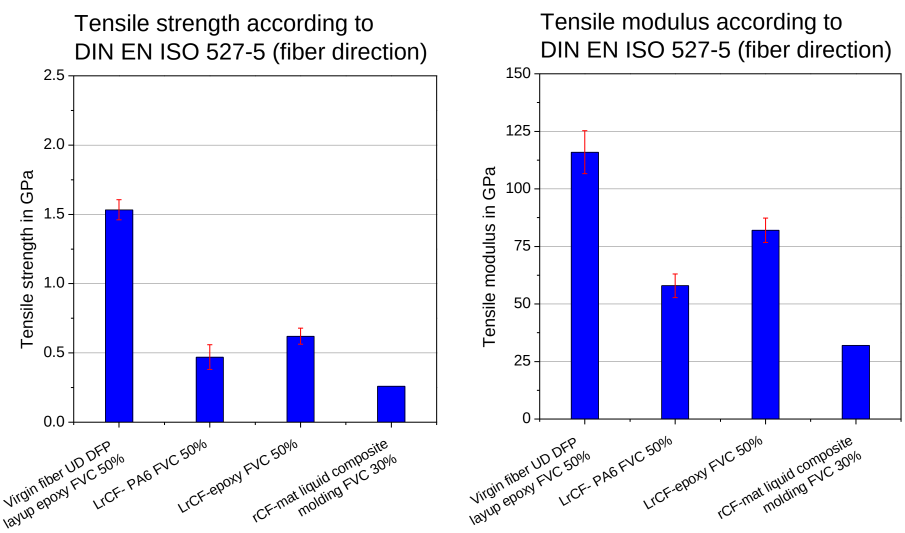

Figure 5: Results of tensile testing in fiber direction and comparison with virgin fiber (DFP preforming, 50 % FVC, epoxy matrix) and commercially available rCF-mat [9].

5.2. Tensile testing transverse to processing direction (90°)

To determine the properties transverse to process direction, tensile tests have been conducted (Figure 6). The results show a stiffness and strength of about 15% compared to the respective values for 0° direction and thus a high anisotropy of ≈ 1:7. The high anisotropy indicates a high degree of fiber orientation. Compared to a random fiber mat material (virgin fibers), the values are significantly lower in this direction as the random fiber mat material is transversely isotropic. Compared to the unreinforced EP resin, strength is similar while a significant reinforcement can be observed in modulus. This is due to a certain amount of fibers not oriented in 90° direction.

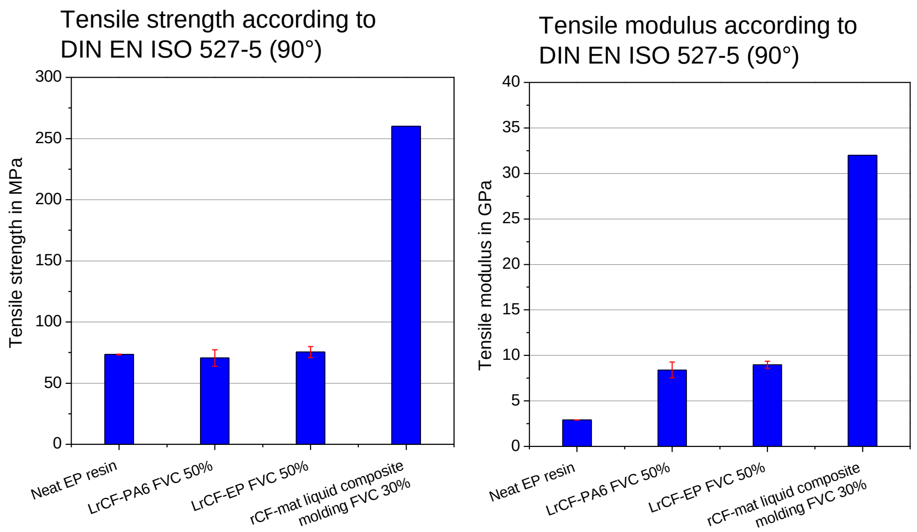

Figure 6: Results of mechanical testing transverse to fiber direction (90°) and comparison commercially available rCF-mat [9]

5.3. 3-point bending tests

To determine the bending properties of the material, bending tests have been conducted. For the bending properties, the values of the LrCF-thermoset have not been scaled to 50% FVC mathematically as this is only reasonable for 0° tensile tests. Still, comparable properties to those of the thermoplastic at 50% have been achieved. Once again, possible reasons are better fiber alignment for the stiffness and in case of strength the better bonding between fibers and matrix. As a reference, the values of a similar sliver material used by STFI [10] have been added which is manufactured by impregnation with an EP-resin as well.

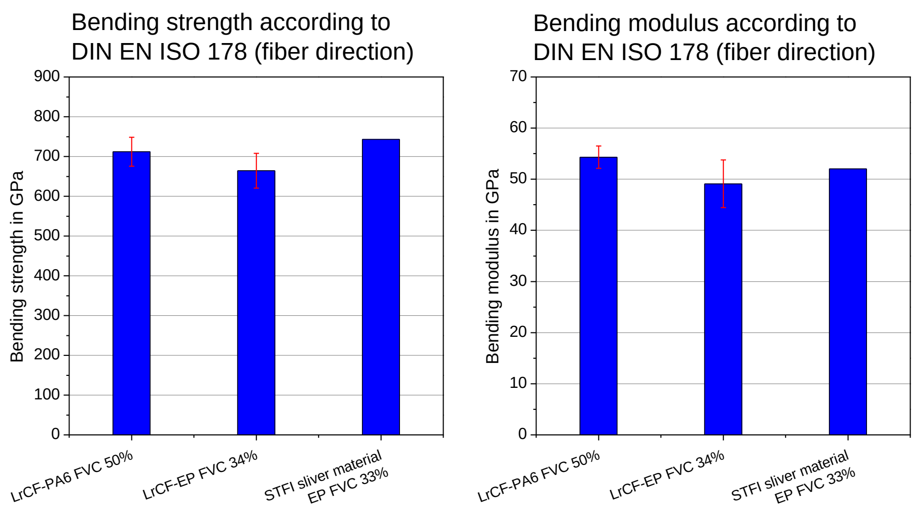

Figure 7: Results of bending test and comparison with STFI sliver material [10]

6. Summary

In the present work, a process chain for the manufacturing of new parts made of long recycled carbon fibers (LrCF) has been suggested. One of the core elements of this process chain is a machine producing LrCF binder tapes out of sliver input material using wrapping with a binder mesh material which has been developed and validated within this study. These binder tapes can be further processed in an automated tape laying process because of the good cohesion and the contained binder material. During the binder application, further stretching of the sliver and freezing this state using binder material has been implemented. The process chain has validated by manufacturing thermoplastic and thermoset plates for material characterization via thermoforming and Resin Transfer Molding, respectively. The mechanical characterization revealed that compared to random virgin fiber mat material, fiber properties can be used more effectively by using anisotropy effects. Still, compared to virgin fibers, there is a considerable decrease of properties. Possible reasons are less-than-ideal fiber alignment and deficient fiber-matrix cohesion. The issue of fiber-matrix adhesion has especially been shown for a thermoplastic FRPC.

All in all, the shown process chain bears a large potential for recycling of carbon fibers by using more of their potential than common recycling techniques. In future work, fiber alignment has to be further improved as well as homogeneity of sliver input material. Adding a sizing or using dry scrap with sizing on fibers for better fiber-matrix adhesion should be considered in future steps as well. The experiments have been conducted on lab-scale. For further use, adaption of the machinery for industrial-scale application is advisable.

Acknowledgement

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