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Recycling and remanufacturing of 3D printed continuous carbon fiber reinforced PLA composites

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ABSTRACT

A cleaner production pattern for high-performance continuous carbon fiber reinforced thermoplastic composites (CFRTPCs) has been proposed on the base of recycling and remanufacturing of 3D printed continuous carbon fiber reinforced (CFR) PLA composites. Continuous carbon fiber and PLA matrix was recycled in the form of PLA impregnated carbon fiber filament from 3D printed composite components and reused as the raw material for further 3D printing process. The original printing trajectory is reversely applied, allowing for a 100% recycling of the continuous fiber without any effect on the mechanical properties. Tensile performance of recycled carbon fiber filaments was evaluated, which was higher than that of originally printed composites. Remanufactured CFRTPCs specimens also exhibited a 25% higher bending strength than that of original ones, which experimentally demonstrated the first non-downgrade recycling process for CFRTPCs. A material recovery rate of 100% for continuous carbon fiber and 73% for PLA matrix were achieved for a better environmental impact. Energy consumption of 67.7 and 66 MJ/kg respectively for recycling and remanufacturing processes was detected and compared with conventional methods. The proposed cleaner production pattern offered a potential strategy for the low-cost industrial application of fully recyclable composites.

1. Introduction

Carbon fiber reinforced polymer composites provide design engineers with superior quality and long life span. Higher strength, lower weight and less maintenance have led to many engineering applications, which are increasingly used to replace metals in numbers of industrial, sporting and transport applications (Stewart, 2011; Yang et al., 2012). However composite materials, as a special category of engineering materials have not yet been properly recycled. Down cycling, such as energy or fuel recovery with little materials recovery such as reinforcement fiber was normally used in the laboratory and industrial reality. This is mainly due to their inherent heterogeneous nature of the matrix and the reinforcement, leading to poor materials recyclability, in particular the thermoset based composites (Yang et al., 2012). So, the use of thermoplastics as a matrix material in fiber reinforced composites has been growing steadily, especially in automotive and aerospace applications, largely due to the materials' recyclability and ability to be processed rapidly (Stewart, 2011). Recently, there are quite a few researches to investigate the fabrication process and performance of fiber reinforced thermoplastic composites, which are mainly utilizing the conventional fabrication processes, including thermoplastic prepreg tape placement (Kim et al., 2014; Qureshi et al., 2014), injection molding (Luo et al., 2014), and others (Leal et al., 2016; Schneider et al., 2015; Sorrentino et al., 2014). Meanwhile, some interdisciplinary researches have also been conducted to fabricate composite components by using additive manufacturing technology, also called 3D printing (Wohlers, 2015), by which the components are fabricated by joining materials from 3D model data, usually layer upon layer as opposed to subtractive manufacturing methods. 3D printing process integrates the materials preparation process and forming process together, which provide a wide design flexibility and a reduced product development cycle. Short fiber reinforced thermoplastic composites have been prepared by fused deposition modeling (Ning et al., 2015; Tekinalp et al., 2014) and selective laser sintering processes

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(Goodridge et al., 2011; Yan et al., 2011). However, how to efficiently recycle the fabricated thermoplastic composites without downcycling was still rarely considered.

Actually, very seldom researches have been conducted on the recycling and remanufacturing of fiber reinforced thermoplastic composites. A closed loop material recycling for fiber reinforced thermoplastic composites was proposed and verified experimentally, in which a degradation recycling pattern was utilized for carbon fiber and matrix, from continuous FRTPs, long FRTPs, short FRTPs, finally to powder reinforced plastics (Colucci et al., 2015; Kemmochi et al., 1995). A concept of direct structural recycling of thermoplastic composites was also put forward, by which that large composite products can be cut into small-size structural pieces that can be directly used to produce smaller composite products (Asmatulu et al., 2014; Schinner et al., 1996). Nevertheless, fully recovering continuous fiber and matrix is still a challenge for the development and application of fiber reinforced thermoplastic composites (Oliveux et al., 2015). Development of new and better recyclable composite materials as well as fabrication process is needed for the further development in order to meet simultaneously the end-use properties and recyclability.

Recently, continuous carbon fiber reinforced polylactide (PLA) thermoplastic composites were successfully fabricated by an innovative 3D printing process in the authors' research group (Tian et al., 2016), which shows a promising prospect for the low-cost fabrication of composite component. PLA, a biodegradable polyester produced from renewable resources (Castro-Aguirre et al., 2016), has a key-position in the market of biopolymers for various applications such as biomedical, packaging, textile fibers and technical items, which is one of the most promising candidates for further developments of composites due to its inherent properties (Murariu and Dubois, 2016). 3D printing of continuous carbon fiber reinforced thermoplastic composites (CFRTPCs) provided both excellent mechanical performance and possibility for fully recycling even remanufacturing due to the orderly distribution of continuous carbon fiber tows.

In the present research, a fully recyclable production pattern for CFRTPCs was proposed and investigated on the base of 3D printing of CFRTPCs, which took overall considerations on the fabrication, recycling, and remanufacturing of 3D printed PLA CFRTPCs. A recycling and remanufacturing process based on 3D printing process was firstly established for CFRTPCs. Then, the mechanical performance of recycled carbon filament and remanufactured CFRTPCs were systematically studied by analyzing the microstructures and interfacial properties of the printed composites. Aging process of the PLA matrix and its influence on the performance of the composites were also investigated by comparing the changes in the molecular weight of PLA matrix. Economical and environmental issues have been taken into considerations by analyzing the material recovery rate and energy consumption during the recycling process. Based upon these results, a new concept for cleaner production pattern of composites was conceived and discussed for the future development and application of high performance composites. Finally, technical perspectives of the proposed process were also summarized in order to transfer this innovative concept to a real industrial application.

2. Material and methods

2.1. Experimental platform

As shown in Fig. 1a, the FDM-based 3D printing method for CFRTPCs was utilized, which consists of extrusion head, control system, building platform, X-Y motion mechanism etc. Detailed investigation on the process parameters has been conducted in a previously published article (Tian et al., 2016). In the 3D printing process of CFRTPCs, thermoplastic filaments were fed into and melt in the printer head, forming a melting pool, into which the continuous carbon fiber was drawn and impregnated with melt matrix. Extrusion happened when the printing head moved according to the geometrical information of the layer. Thus, the CFRTPCs components were fabricated by solidification and bonding of the matrix including the continuous fiber. The distribution of carbon fiber in the printed components is schematically shown in Fig. 1b, in which continuous fiber are regularly arranged and multiple interfaces are formed among fiber, matrix, lines, and layers. Orderly distribution of continuous fiber made the recycling process feasible.

According to the structural characters shown in Fig. 1b, a recycling and remanufacturing strategy was put forward in the present paper. As shown in Fig. 2a, basically it is a reverse process to the 3D printing of CFRTPCs. A hot air gun was employed to locally remelt matrix material on the 3D printed CFRTPCs according the reverse path of the printing process, as shown in Fig. 2b. Then, the carbon fiber was pulled out gently and continuously with the movement of the hot air gun. Resolidified thermoplastic material adhered to the fiber and formed an impregnated carbon fiber filament with a relatively rough surface. To smooth the filament surface, a remolding nozzle with a diameter of 0.8 mm was used to melt the thermoplastic matrix, as shown in Fig. 2c. There was no obvious damage observed on the recycled carbon fiber filament due to the protection layer of thermoplastics. The obtained thermoplastic impregnated carbon fiber filament could be rolled up or directly fed back into the 3D printing process for the remanufacturing process, as show in Fig. 2d and e. Standard samples and components were remanufactured and studied by using this recycling and remanufacturing strategy in the present research.

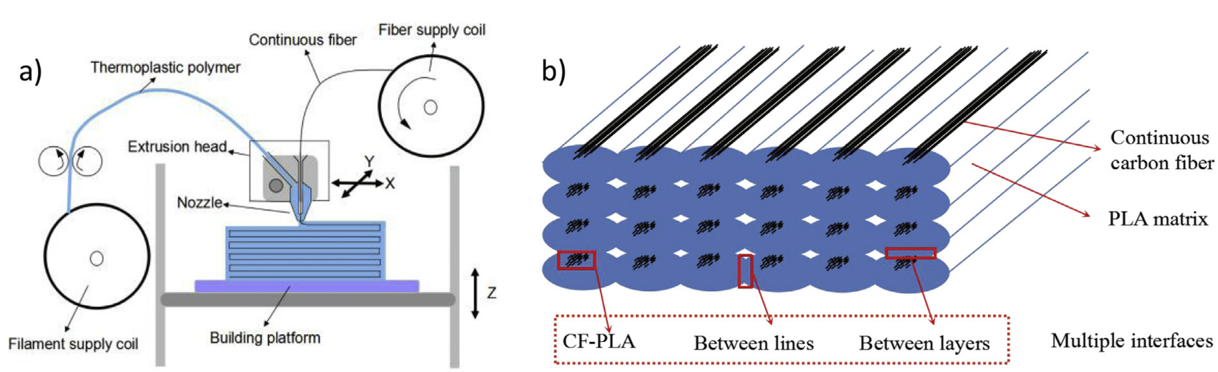

Fig. 1. Scheme of 3D printing for CFR PLA composites a), and fiber distributions in the printed composites b) (Tian et al., 2016).

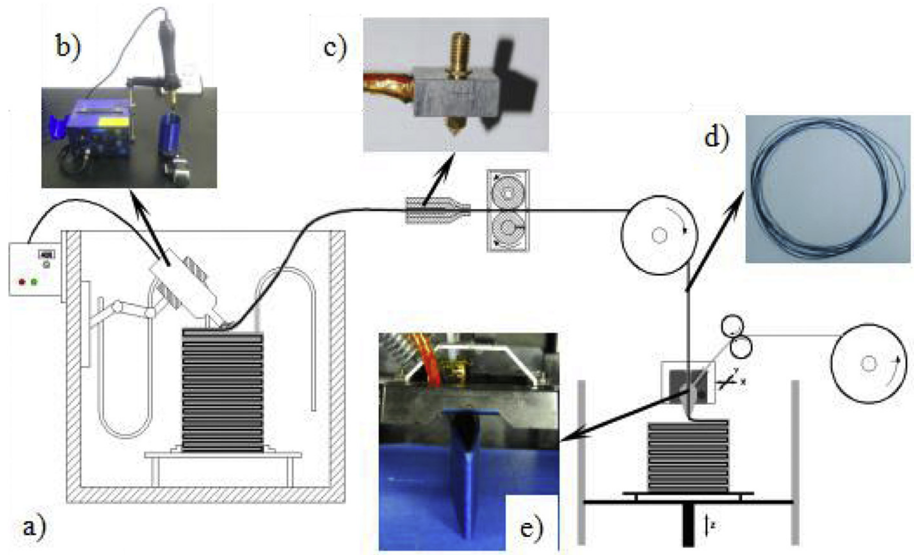

Fig. 2. Scheme of recycling and remanufacturing of 3D printed CFRTPCs a), and key elements for each step: b) hot air gun system, c) remolding nozzle, d) recycled impregnated filament, e) remanufacturing process.

2.2. Raw materials and experimental procedure

In the present research, polylactide (PLA/1.75 mm) from FLASHFORGE Corp in China has been used as the thermoplastic material, and 1K carbon fiber tows from TENAX-J Corp in Japan has been used as the reinforcement. No further surface sizing was conducted in the present research. All the samples were prepared on the aforementioned experimental equipment.

All the parameters for the 3D printing process have been already investigated. In order to well understand the process parameters, the scheme for printing head is reused in the present research, as shown in Fig. 3. According to the previous research, process parameters for the 3D printing were chosen as shown in Table 1. In the remanufacturing stage, same parameters except the feeding rate of the filament were used as the original printing process in order to compare the properties of remanufactured specimen with the original ones. Considering the recycled carbon fiber filaments have already contained few thermoplastics, the feed rate of filament was reduced slightly from 100 mm/min to 80 mm/min to keep a similar fiber content with the originally printed samples.

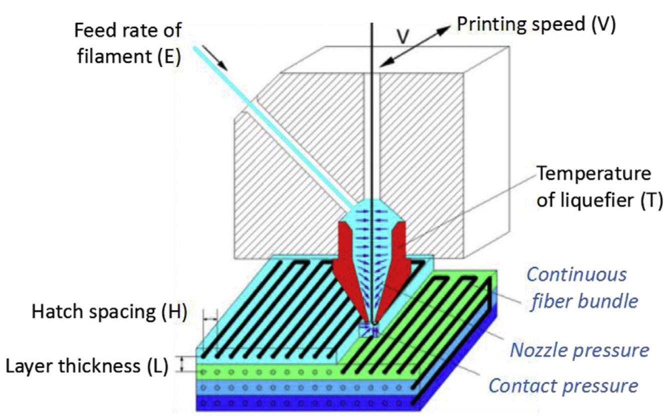

Fig. 3. Process parameters for the 3D printing process of CFRTPCs (Tian et al., 2016).

In the recycling process, temperature in the remelting area was observed by using a thermal image camera when the hot air gun was running. Remelting temperature was set from 240 to 300 °C, which was a little bit higher than that of printing head. Temperature lower than 240 °C would cause difficulties in stripping the fiber, and even break the carbon fiber. A remolding nozzle with a diameter of 0.8 mm was chosen to smooth the surface of the filament. When the nozzle diameter was larger than 0.8 mm, no remolding effect took place. On the contrary, small diameter would produce too much drag force and break the continuous carbon fiber due to the shear force. The temperature of remolding nozzle was set as 240 °C when the drawing out speed was 200 mm/min. A portion of thermoplastic materials was removed when the carbon fiber went through the remolding nozzle. Thus, during the remanufacturing process, pure PLA filament was fed into the printing head to compensate the loss of matrix, also renew the recycled matrix with thermoplastics without thermal degradation.

Standard specimens for characterization have been prepared in

Table 1
Process parameters for three different process stages.

Parameters	Process stages		
	Original printing	Recycling	Remanufacturing
Hatch spacing (H, mm)	1	/	1
Layer thickness (L, mm)	0.5	/	0.5
Printing or pulling speed (V, mm/min)	100	200	100
Temperature of liquefier (T, °C)	210	240	210
Feed rate of filament (E, mm/min)	100	/	80
Diameter of nozzle (mm)	2	0.8	2
Remelting temperature (T, °C)	/	240~300	/

different process stages by using pure PLA, pure PLA and virginal carbon fiber (original printing), pure PLA and recycled carbon fiber impregnated filament (remanufacturing), respectively. Mechanical properties and microstructures of the composites, aging character of matrix, energy consumption and material recovery rate of the process were carefully studied and compared. Finally, a recycling and remanufacturing process for a 3D printed CFRTPCs component was conducted to demonstrate a cleaner production pattern for high performance composites.

2.3. Characterization of material properties

To evaluate the performance of 3D printed CFR PLA composites, several measurements were conducted. Flexural strength and interlaminar shear strength were measured using universal testing machine (PLD-5kN, LETRY Corp., China) according to the standard of GB/T 1449:2005 and JC/T773-2010 (ISO14130:1997) on 3D printed composite specimens with a size of 100 × 15 × 2 mm, and 20 × 10 × 2 mm, respectively. Tensile strength was measured using universal testing machine (PLD-5kN, LETRY Corp., China) according to the standard of GB/T 1447:2005 on 3D printed composite specimens. Impact strength was measured using charpy impact machine (XJJ-50,HUIPU Corp.,China) according to the standard of GB/T 1043:1993 on 3D printed composite unnotched specimens with a size of 80 × 10 × 4 mm. Molecular weight was measured by using GPC (Gel Permeation Chromatography Waters 2695, Waters Corp.,US) to obtain the distribution of matrix molecular weight. Thermal imaging camera (SC7300M, FLIR Systems AB Corp., Sweden) was used to observe the temperature distribution of remelting area in the recycling process. Energy consumption was measured by using energy meter (DDS2015, ELECALL Corp., China) during the forming and recycling process. Fracture surfaces of tested specimens were observed with a Hitachi S-3000N SEM to evaluate the interfaces between deposited lines as well as fibers in matrix. For each experimental group, five specimens were prepared to obtain an average value of the targeted properties. For all the specimens, mechanical properties testing has been conducted along the orientation of carbon fiber.

3. Results

3.1. Mechanical properties of recycled and re-manufactured composites

Using traditional chemical, thermal, and mechanical recycling processes, composites can only be recycled to a lower material level, and so could be mostly reused in less critical applications. Material states and mechanical properties of the recycled and reused composites are always the most important consideration when evaluating a recycling process for composites. In this section, basic mechanical properties of 3D printed composite specimens, impregnated carbon fiber filament, and recycled and remanufactured CFRTPCs were investigated and compared.

3.1.1. Tensile strength

When recycling continuous fiber reinforced composites with traditional ways, only short fiber normally can be obtained due to the cutting and grinding process before chemical or thermal recycling. Degradation of fiber properties is inevitable when recycling continuous fiber into short fiber. However, in the present research, an impregnated carbon fiber filament was obtained after recycling 3D printed CFRTPCs without sacrificing the fiber properties. Tensile properties of the originally printed carbon fiber reinforced filaments and recycled ones were measured to verify the changes in the fiber filament properties. As shown in Fig. 4, misalignment of carbon fibers in a tow happened and caused the nonsynchronous breakage, which lowered the tensile properties of virgin carbon fiber tow. The originally printed CF/PLA filament had a higher fracture force (about 118N) than that of virgin fiber tow (about 80N). However, fiber pull-out was still observed as shown by the middle picture in Fig. 4 due to the poor impregnation of matrix into the carbon fiber tow. After recycling, PLA matrix was fully impregnated into the carbon fiber tows, which achieved a better reinforcement effect. Synchronous breakage of carbon fiber without any pull-out promoted the mechanical performance of carbon fiber filament to a higher level (about 142N) as shown by the right picture in Fig. 4, thus a non-downgrade recycling process for carbon fiber reinforced composites was obtained instead of down cycling.

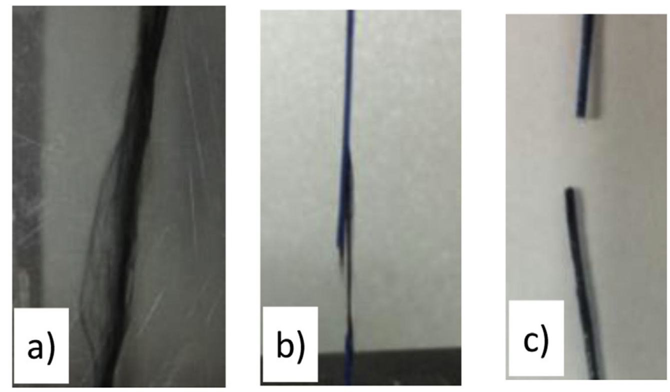

Fig. 4. Fracture patterns for a) virgin carbon fiber tows, b) originally printed, and c) recycled carbon fiber filament, with linear densities of 0.067 g/m, 0.98 g/m, 0.64 g/m respectively.

To further validate the feasibility of the remanufacturing process, specimens were prepared by using the recycled carbon fiber impregnated filament. Two control groups of specimens, pure PLA and virginal carbon fiber reinforced PLA, were also prepared and measured. Results of tensile strength are shown in Fig. 5. Pure PLA samples showed a very low tensile strength of 62 MPa, tensile modulus of 4.2 GPa. When using continuous fiber reinforcement, the samples exhibited a dramatic increase in tensile strength and modulus to 256 MPa and 20.6 GPa, respectively. The tensile

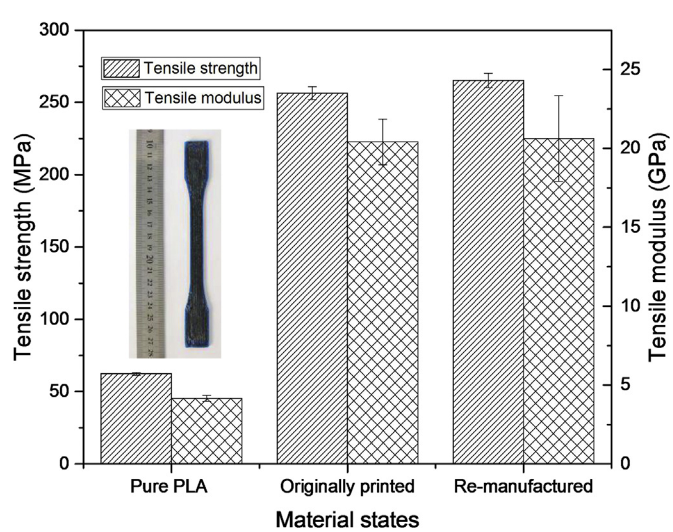

Fig. 5. Tensile strength and modulus of pure PLA, originally printed and re-manufactured composites specimens.

strength was increased almost four times than that of pure PLA. This demonstrated an excellent reinforcement of continuous fiber to the PLA matrix. Moreover, after the carbon fiber was recycled into an impregnated filament and reused in the remanufacturing process, there was no obvious improvement for tensile strength and modulus probably due to unidirectional character of produced composites, by which the tensile force was sustained mostly by the carbon fiber instead of interfaces.

3.1.2. Flexural strength

Flexural strength was further measured to investigate the influence of recycling and remanufacturing process on the mechanical properties of composites. The results are shown in Fig. 6. An average flexural strength of 263 MPa was obtained for the remanufactured composite specimens. In comparison with tensile strength shown in Fig. 5, remanufacturing process led to a relatively larger (about 25%) improvement on the flexural strength over the originally printed composites specimens. During tensile measurement, the force was mainly undertaken by the carbon fibers considering the consistent orientation. However, in the bending measurement, the loading path of the force was more complicated due to the multiple interfaces among fiber, matrix, lines and layers, as shown in Fig. 1. Thus, the flexural strength was mainly determined by both the carbon fiber and the interfaces. Large improvement in flexural strength must be the evidence for the improvement of interfaces, especially between the fiber tow and matrix. Recycling and remanufacturing processes provided extra melting impregnation functions for a better interface, also for an obvious improvement of flexural strength. However, the modulus of remanufactured composite specimens was slightly decreased from 14.5 GPa of originally printed composites specimens to 13.3 GPa, as shown in Fig. 6. It was probably due to the degradation of thermoplastic PLA matrix during the recycling and remanufacturing processes. The mechanical properties of unidirectional CF/PLA composites prepared by using different processes were compared, as shown in Table 2. Flexural strength and modulus of 3D printed composites were higher than that of solution pre-impregnated and hot pressed specimens with similar carbon fiber content of 25 vol%. Recycled and remanufactured CF/PLA specimens with carbon fiber content of 8.9 vol% had a flexural strength of 263 MPa, which was higher than that of hot pressed samples (220 MPa) with carbon fiber content of 20 vol%. However, the flexural modulus was still lower than that of high carbon fiber content (see Table 2).

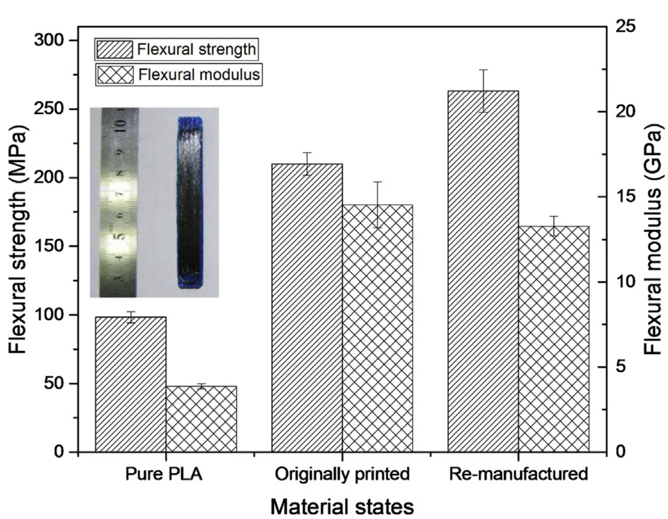

Fig. 6. Flexural strength and modulus of pure PLA, originally printed and remanufactured composites specimens.

3.1.3. Charpy-impact strength

Composite impact strength is a very important character to the comprehensive performance, which is related with stiffness and strength of fabricated composite components. Three mechanism of energy absorption and dissipating during impact for fiber reinforced composites are fiber and matrix debonding (fiber pull-out), delamination, and fiber breakage. Fiber content and interfacial properties are critical to the impact strength. In the present research, the carbon fiber content for all the printed specimens were controlled to be around 10 wt% or 8.9 vol%. Thus, the difference in the impact strength was mainly determined by the interfacial properties, including fiber with matrix, deposited lines and layers. Results are shown in Fig. 7. Unlike tensile strength shown in Fig. 5, the impact strength of the originally printed CF/PLA (34.5 kJ/m^2) didn't exhibit a multifold improvement over pure PLA (20.0 kJ/m^2). The low failure strain of carbon fiber may cause the limited improvement in impact strength. Carbon fiber pull-out and breakage were observed on the fractured surface of composites specimen, as shown in Fig. 7b. Carbon fiber without full impregnation with matrix was obviously the reason for the carbon fiber pull-out. However, when the carbon fiber was recycled and transformed into impregnated carbon fiber filament, the remanufactured composite specimen showed a completely different break mechanism. No fiber pull-out and only fiber breakage happened on the sample after impact testing, as shown in Fig. 7c. Impact strength was slightly improved to 38.7 kJ/m^2 from 34.5 kJ/m^2 of the originally printed specimens.

Similar results were obtained for the interlaminar shear strength, which was 5.69 $\pm$ 0.32 MPa, 20.25 $\pm$ 0.61 MPa, and 22.67 $\pm$ 0.82 MPa, respectively for pure PLA, originally printed and re-manufactured composite specimens. No obvious improvement was obtained after recycling and remanufacturing. Moreover, if compared with tensile and flexural strength, interlaminar shear strength was quit low due to the character of layer-wised fabrication for 3D printing.

According to the comparison of originally printed and remanufactured CF/PLA specimens, flexural strength were obviously

Table 2
Comparison of the mechanical strength for 3D printed and conventionally fabricated CF/PLA composites.

Unidirectional composites	Processes	Carbon fiber content (vol %)	Flexural strength (MPa)	Flexural modulus (GPa)	Source
CF/PLA	3D printing	25	335	30	(Tian et al., 2016)
CF/PLA	Recycling, and then remanufacturing by 3D printing	8.9	263	13.3	Present work
CF/PLA	Solvent casting plus compression molding technique	25	280	30	(Wan et al., 2001)
CF/HA (2.5wt%)+PLA	Solution pre-impregnating and hot pressing	20	220	20	(Shen et al., 2009)

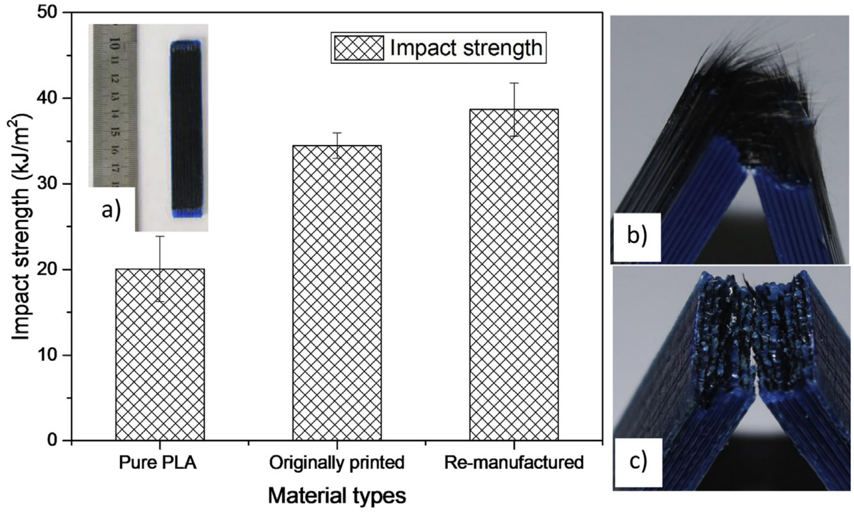

Fig. 7. Impact strength of pure PLA, originally printed and re-manufactured composites specimens, inserted pictures are standard specimen a), broken specimen from original printing b), and remanufacturing c), respectively.

improved to certain extent after the recycling and remanufacturing process. Tensile strength, impact strength, as well as interlaminar shear strength were improved but not so significantly. No carbon fiber was damaged during this recycling process. Meanwhile, thermal treatment in the recycling process may play a vital role to improve the bonding and impregnation between fiber and matrix, and create a superior interfacial properties.

3.2. Microstructures of recycled and remanufactured composites

Macroscopic mechanical properties are always determined by microstructure, especially interfaces for fiber reinforced composites. When virgin carbon fiber was fed into the printing nozzle, the pure PLA was melt and formed a melt pool in the temperature of 210 °C as shown in Fig. 3. In-situ impregnation took place between carbon fiber tow and melt PLA in this melting pool. However, impregnation period was extremely short depending on the printing speed and may be not efficient for the melt thermoplastic matrix to fully penetrate into the carbon fiber tow. Besides the period, temperature and pressure in the impregnation process were also important, which have been proved in the previous research (Tian et al., 2016). However, recycling may promote the impregnation and make a high level recycled material. Microstructure of originally printed and recycled single carbon fiber reinforced filaments were observed, as shown in Fig. 8. Originally printed carbon fiber filament were only surrounded by the thermoplastic matrix, and no obvious penetration was observed in the Fig. 8a. Only the fibers outside the tow was impregnated and inside fibers were loosely packaged, which was consistent to the fracture pattern show in Figs. 4 and 7b. The reinforcement effect was of course limited. However, after debonding at 240–300 °C and remolding at 240 °C as shown in Fig. 2, recycled carbon fiber filament showed a different interface, as shown in Fig. 8b. Fully penetration of thermoplastic matrix into the fiber tow were achieved. Even though there were still micro pores around the interface (Fig. 8b), the following remanufacturing process would enrich the interfaces, which were verified by the microstructure of remanufactured composite specimens as shown in Fig. 9.

Fractured surface of originally printed and remanufactured composite specimens were investigated, as shown in Fig. 9. There was a fiber layer formed in the originally printed composite specimen, but no obvious penetration of matrix into the carbon fiber tow. It was similar with the microstructure of originally printed single carbon fiber filament, as shown in Fig. 8a. In the remanufacturing process, recycled single impregnated carbon fiber filament was reused to replace the virgin carbon fiber together with pure PLA, as shown in Fig. 2. A remelting and re-impregnating process happened, which further enhanced the interfaces and improved the mechanical properties. Almost fully impregnation were obtained after the remanufacturing process as shown in

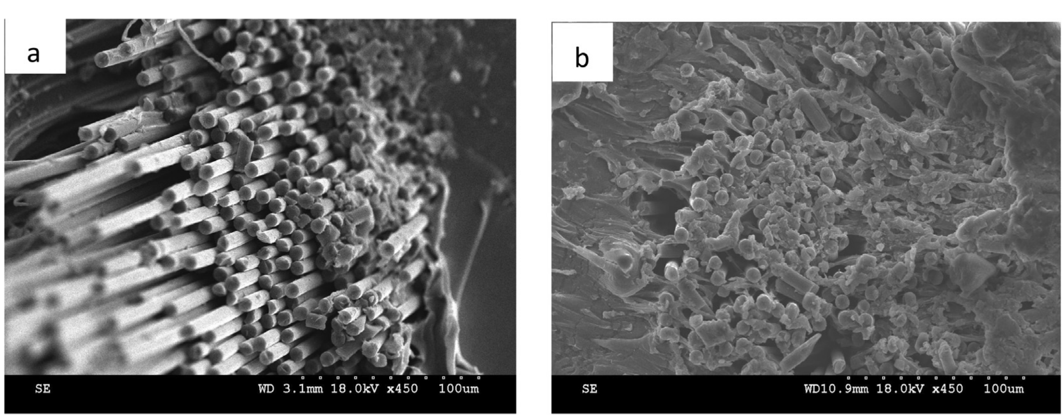

Fig. 8. Microstructure of single tow carbon fiber reinforced filament, originally printed a), and recycled single impregnated filament b).

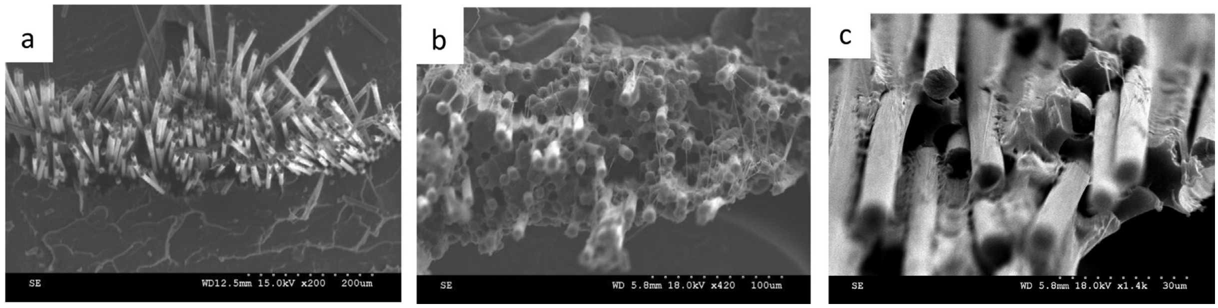

Fig. 9. Microstructures of carbon fiber reinforced composite specimen, originally printed a) and remanufactured b)and c).

Fig. 9b and c, and a higher mechanical properties was certainly achieved. However, the macroscopic mechanical properties have not been promoted dramatically yet, for instance, max 25% percentage increasement for the flexural strength. Carbon fiber sizing compatibility and multiple interfaces between lines and layers may also determine the final properties to some extent respectively, which was still unclear and need further investigation.

3.3. Aging of thermoplastic PLA matrix

As mentioned in the previous section, temperature was the key factor influencing the performance of the 3D printed and remanufactured CFRTPCs. Heating happened at several different stages in whole process shown in Fig. 2. Increasing temperature always produced a larger melt flow rate (MFR) or better flowability, shorter molecular chain and lower melt viscosity. It was positive to promote the impregnation of thermoplastic into carbon fiber tow (Tian et al., 2016). However, thermal cycles would also cause decomposition of thermoplastics, which was an aging process and would reduce the mechanical performance of the thermoplastic matrix. In order to understand the influence of multiple heating cycles on the performance of PLA matrix, molecular distributions of PLA matrix in each process stage were measured and compared, as shown in Fig. 10.

Recycling process started from debonding of carbon fiber in the already fabricated sample at the temperature of 240–300 °C, and then debonded filament went through the remolding nozzle with a temperature of 240 °C. These two thermal cycles obviously reduced

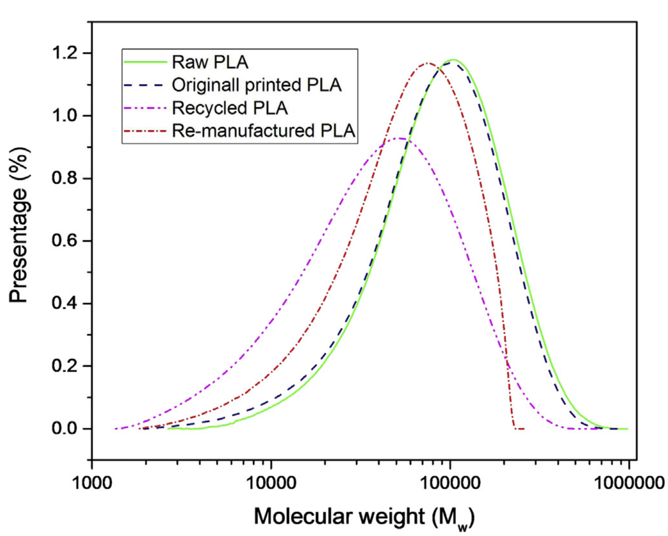

Fig. 10. Molecular weight distribution of PLA in different material states.

the molecular weight of the PLA matrix and made the widest molecular weight distribution, as shown in Fig. 10. Meanwhile, lower molecular weight decreased melt viscosity of PLA and promoted the impregnation of carbon fiber filament, which was consistent with the microstructure shown in Fig. 8. The following remanufacturing process was a 3D printing process using pure PLA filament and recycled carbon fiber filament instead of virgin carbon fiber. It has been proved by the molecular weight distribution in Fig. 10 that 3D printing of PLA at a temperature of 210 °C had very slight influence on the PLA molecular weight. Using pure PLA filament in the remanufacturing process would compensate the loss of molecular weight and minimize its negative influence on the performance of remanufactured composite components. Finally, the molecular weight of remanufactured PLA matrix was improved to some extent by mixing recycled PLA with originally printed one, as shown in Fig. 10. Actually, after thermal cycles in recycling and remanufacturing process, not only the impregnation was improved by decreasing the melt viscosity, but PLA matrix performance was also ensured by compensating the molecular weight loss with new PLA filament. Eventually, 3D printed CF/PLA was fully recycled and remanufactured with higher mechanical properties.

4. Discussion

4.1. Economical and environmental considerations

In the existing recycling processes of composites, such as mechanical, thermal, and chemical recycling, seldom materials can be retrieved at the similar level of performance. Down cycling always happens by recovering little raw materials like polymer monomer from matrix, and shortened reinforcement fiber. Quality of recycled materials are not comparable to the virgin materials, and also difficult to be handled in the reuse process. It is often impossible to be used in a similar application. Also, the price of recycled material is even higher than the virgin ones. These are all the challenges for recycling composites. In the present research, a recycling and remanufacturing process for 3D printed CFRTPCs has been put forward, which provided a fully recyclable composite materials with mechanical properties even higher than the original ones. This provides a possibility to realize a "green" composite for the future based on 3D printing without considering the usage of carbon fibers. Besides the mechanical performance, considerations must be taken on the economical and environmental issues. Wastes or materials recovery rate, and energy consumption for the recycling process should be discussed.

4.1.1. Materials recovery rate

Reinforcement fiber and PLA matrix were not separately recycled in the present method. An impregnated carbon fiber filament was obtained after recycling process. The materials recovery rate can be easily calculated by the weight ratio of recycled filament to the original composite component. An overall material recovery rate of 75% has been achieved, in which continuous carbon fiber is 100% recovered and transformed into an impregnated filament without any damage on the properties of carbon fiber. 25% weight loss in the recycling process was mainly caused by the remolding process when the debonded filament went through the remolding nozzle with a diameter of 0.8 mm, in which redundant PLA was blocked by the remolding nozzle. With the 3D printing process parameters shown in Table 1, fiber content of the fabricated composite specimens was about 10 wt% or 8.9 vol%. Thus, the recovered PLA in the impregnated filament was about 73 wt%. Actually, the blocked PLA material could be collected and used again even though the molecular chain was shortened during the recycling process as shown in Fig. 10. In summary, continuous carbon fiber can be fully recycled to impregnated filaments with an improved interfacial and mechanical performance. Almost all the PLA matrix can be recycled and reused, 73 wt% of which was recovered in the impregnated filament together with the continuous carbon fiber, and the rest can be collected for further usage even with slight degradation in molecular weight. The excellent material recovery efficiency would make fully recyclable “green” composites possible.

4.1.2. Energy consumption

In comparison with energy consumption of movement mechanisms, energy was mainly consumed in multiple heating processes. Thermal energy was utilized in both recycling and remanufacturing processes. In the recycling process, hot wind gun was used to locally heat the composite components, leading to debonding. Remolding nozzle was heated to melt the PLA adhering to the carbon fiber. A power meter has been used to detect the energy consumption. An overall energy consumption of 67.7 MJ/kg has been detected in the recycling process, which was much higher than the conventional mechanical, thermal, and chemical recycling processes, as shown in Table 3. In the present setup for recycling, a hot wind gun of 250w was utilized to locally heat the composite component in an open environment. Pulling speed used was relatively low, only 200 mm/min. Thus, most energy was dissipated in the environment instead of absorbed by the composites. A closed chamber for recycling could be better, but putting the whole composites into a higher temperature environment would exacerbate the aging process of the matrix. Proper recycling strategy is still under investigation. Anyway, even using the current setup, the energy used for recycling is still much lower than the fabrication of virgin carbon fiber. Energy saving will be more significant when the recycling strategy is optimized.

Remanufacturing is a 3D printing process of CFRTPCs using recycled carbon fiber filament, in which energy are mainly consumed by heating and moving the printing head. A energy consumption of 66 MJ/kg has been monitored by a power meter, which was much larger than the average energy consumption for the conventional manufacturing process, as shown in Table 3. The power required by the 3D printer was about 95 W, which was slightly affected by the velocity of mechanism motions. In the present 3D printing process, the working platform was also in an open air, from which thermal energy can dissipate into the environment. With a relatively low printing speed of 100 mm/min, a composite component was printed in a longer period. A high energy consumption was certainly caused by the low fabrication efficiency. Energy consumption in the remanufacturing process would be reduced by either enclosing the working platform in an insulated chamber or increasing the fabrication efficiency. The former measure may bring thermal effects on the mechanical components and cause instability of long-term printing process, which is still under testing. Another measure is to accelerate the printing process. The influence of printing speed or fabrication efficiency on the average energy consumption for a standard specimen is shown in Fig. 11. Energy consumption has been dramatically reduced with the increasing printing speed. With a printing speed of 300 mm/min, energy consumption is about 20 MJ/kg, which is comparable to the autoclave molding or injection molding. However, when the printing speed is higher, the impregnation period of fiber and melt PLA matrix in the printing nozzle is reduced in an equal proportion. Interface, mechanical properties and surface quality of the fabricated composites may also be negatively affected even through part weight doesn't change so much (Fig. 11). A

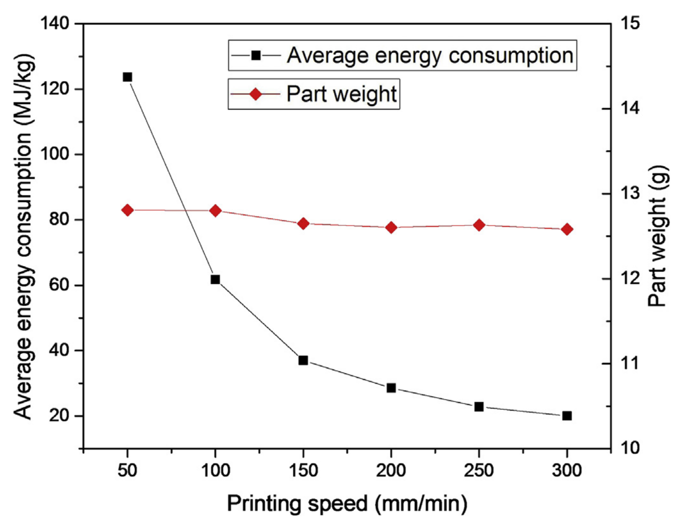

Fig. 11. Average energy consumption changes with the printing speed-the fabrication efficiency.

Table 3
Comparison of energy consumption in fabrication and recycling composites (Castro-Aguirre et al., 2016; Oliveux et al., 2015; Song et al., 2009).

Processes		Energy intensity (MJ/kg)
Raw material	Carbon fiber	183-286
	PLA	41.739
Forming processes	Autoclave molding	21.9
	Rein transfer molding (RTM)	12.8
	Filament winding	2.7
	Pultrusion	3.1
	Injection molding	19
	3D printing of CFRTPCs[a]	**66**
Recycling processes for carbon fiber	Ground CFRC	0.27
	Thermo -chemical recycling	10.3-35.7
	Recycling of 3D printed CFRTPCs[a]	**67.7**

[a] Results from the present research.

balance must be found between the fabrication efficiency and performance to reduce the energy consumption as larger as possible.

4.2. A cleaner production pattern of composites for future

Currently, carbon fiber reinforced composites have not yet been properly recycled probably due to their inherent heterogeneous nature of matrix and the reinforcement, leading to poor materials recyclability, in particular the thermoset composites. Design and manufacturing processes are usually conducted only for a light weight and higher mechanical performance, without any consideration of end of life (EOL) treatment. For the future composites design and manufacturing, the use of thermoplastics might be much more preferable than non-remeltable thermoset matrix. And more easily recyclable composites are strongly needed. Thus, innovative concept is required for future development in order to meet simultaneously the end-use properties and the recyclability, which are normally in contradictory with each other (Yang et al., 2012).

Recycling strategy is always linked with the material types and manufacturing process. Based on the recycling and remanufacturing process of 3D printed CFRTPCs, a cleaner production pattern of composites for the future can be conceived as shown in Fig. 12. A biodegradable thermoplastics PLA is used for the matrix of composites, which can be made from renewable materials like corn by photosynthesis functions. 3D printing process is utilized to produce a CFR PLA composites. 3D printing process itself is a clean manufacturing method without any waste of raw material and harmful emission. The performance of 3D printed composite components is considerable according to the achieved experimental results. Moreover, the printing trajectory could be reversely used for the recycling process which is a big advantage compared to other processes. After usage of printed composite components, a recycling process can be employed to transfer EOL composites to intermediate products, the impregnated carbon fiber filament, which can be directly used for the following remanufacturing process. As exhibited in the present paper, a better interface and mechanical performance has been obtained due to the recycling process. For the first time, this results show a non-downgrade recycling process for the composite. The more interesting point is that the remanufactured composite components may experience more recycling and remanufacturing cycles. The times of these cycles could be determined by the aging of PLA matrix, which still can be optimized or compensated by refilling new PLA materials into the remanufacturing process. In this overall process, continuous carbon fiber is fully recycled and reused without any damage and degradation due to the protection of PLA matrix. The requirement for the virgin carbon fiber would be significantly reduced. Further more, real green composites will be produced in the future when high performance natural fibers like flax are used by 3D printing process. This innovative concept includes all the aspects of how to avoid environmental impact of composites, reducing the expensive raw material-carbon fiber, using renewable materials, fully recycling of composites to an up level, and remanufacturing with a higher performance. This four "Re"s production pattern for CFRTPCs is a so prefect concept for future composites that efforts must be made to realize the real industrial application.

4.3. Technical perspectives

Any innovative concept is always accompanied by technical limitations to be solved. For recycling and remanufacturing of 3D printed CFRTPCs, only process principle is demonstrated in the

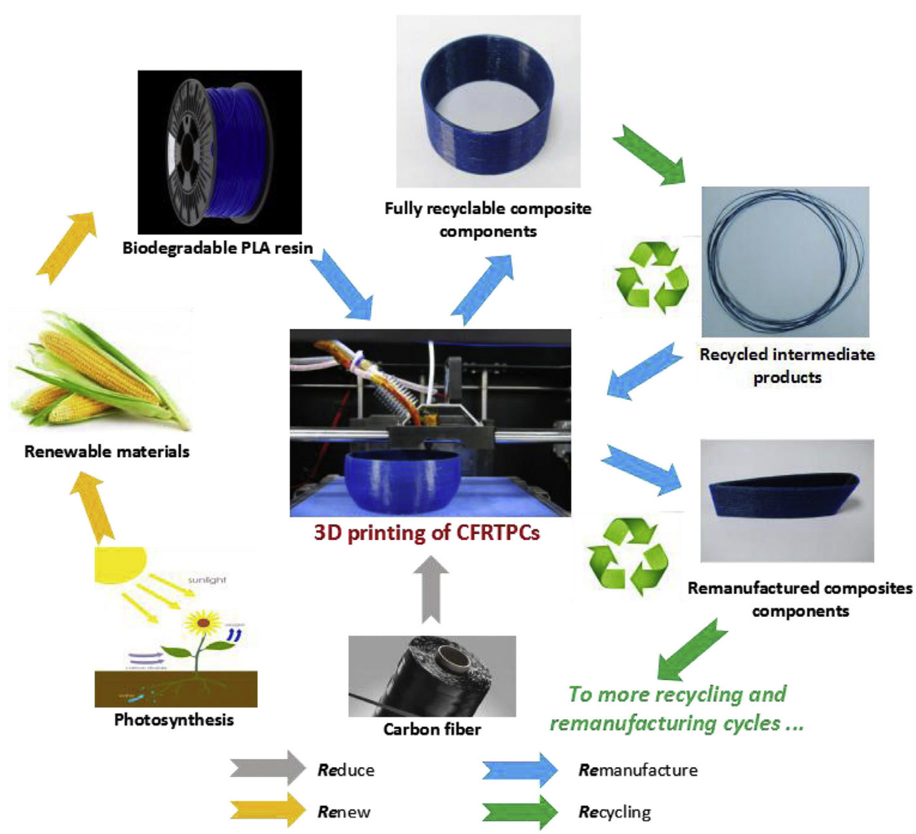

Fig. 12. A four-"**Re**"s cleaner production pattern for CFRTPCs.

laboratory environment. Further technology improvements are urgently required at least in the following research topics.

a) Performance of 3D printed CFRTPCs are still not satisfactory considering the advanced application field. Materials for matrix should be extended to a wider spectrum for better properties, such as heat resistance, chemical stability, and toughness. Meanwhile, the interfaces between fiber and matrix, deposited lines and layers should also be improved, which is vital to the comprehensive properties.
b) Production efficiency should be scaled up to certain extent in order to meet the requirement of industrial production. 3D printing is fundamentally a time-consuming process, in particular for 1K carbon fiber reinforced composites. Higher K (i.e. 10k, 50k) tow might be further utilized to achieve a higher fabrication efficiency without sacrificing the end-use properties. Significant modifications of the current 3D printing process, for example, controllable pressure in the printing head, would be required to obtain a fully impregnation for the high carbon fiber tows.
c) Innovations on 3D printing of CFRTPCs are still required to overcome the inherent shortcomings, like poor inter-lamination bonding. Reinforcement in the “Z” direction between layers is necessary to be integrated into the composite components without sacrificing the recyclability. 3D printing on curved surface by using a multiple degree of freedom is surely quite interesting and attractive to deposit the carbon fiber along to the load path of the composite structure.
d) Adoption of 3D printing process and fabricated components in industrial application is the driving force for the ongoing development. Design strategy of composite structures considering recycling and remanufacturing of 3D printed CFRTPCs will be the ultimate pushing force for the technological development.

5. Conclusions

An innovative recycling and remanufacturing process based on 3D printing of CFRTPCs was proposed and systematically investigated in the present research. Continuous carbon fiber was recycled from 3D printed CFRTPCs to impregnated carbon fiber filament, which possesses a higher tensile force (142N) than the originally printed filament (118N) due to the improved interfacial properties. Remanufacturing has been demonstrated by 3D printing process utilizing recycled carbon fiber impregnated filament and pure PLA as raw materials. Remanufactured composite specimens achieved a comparable and even higher mechanical properties, such as 25% improvement of flexural strength in comparison with the originally 3D printed composites. Even though aging of thermoplastic PLA matrix was observed, the performance of remanufactured composites still maintained a high quality due to the compensation of pure PLA in the remanufacturing process. For the first time, a non-downgrade recycling of high performance composites was experimentally demonstrated. Moreover, high material recovery rates for both carbon fiber (100%) and PLA matrix (73%) were directly achieved due to the unique character of 3D printed CFRTPCs. An overall energy consumption for recycling process and remanufacturing was about 67.7 MJ/kg and 66 MJ/kg, respectively, which was higher than the conventional recycling and manufacturing process and could be further improved by increasing the production efficiency. Based on the experimental results, a four ”Re”s cleaner production pattern for future composites was conceived and further technical perspectives were deduced in order to overcome the current technical limitation.

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