RESEARCH ARTICLE

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Production of Thermoplastic Composite Filaments for Additive Manufacturing using Recycled Carbon Fibers

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The present work reports the use of recycled carbon fibers (rCF), obtained from pyro-gasification treatment of carbon fibers reinforced polymers (CFRP), to produce a thermoplastic composite filament for additive manufacturing, in particular fused deposition modeling (FDM) process. Polylactic acid (PLA), a thermoplastic biobased and biodegradable polymer, is used as matrix for the composite filament, as it is the most common plastic used in FDM due to its good mechanical properties, stiffness, and strength. Upon production process optimization, filaments with rCF loadings of 5 and 10% wt are produced and analyzed. A particular attention is devoted to the evaluation of the production process on the carbon fibers (CFs) length and the study of the thermal and mechanical properties of the obtained composite materials.

1. Introduction

In the latest years, carbon fibers (CFs), due to their lightweight and excellent mechanical properties, are used to produce high performance materials applied in an increasing number of fields, such as automotive, aerospace and defense, wind turbines, sport, and leisure. Over 97% of CFs are used as reinforcement in composite materials (CFRPs) whose applications have just recently had a boost reaching a market size of 197,000 tons in 2023.[1]

Although the production of CFRP has been optimized to fulfill the increasing demand, there is still the issue of the end-of-life product of CFRPs and waste scraps deriving from production processes. Different technological approaches have been recently put forward for CFRPs recycling. [2] Among them, the pyro-gasification treatment is a promising process to obtain clean recycled carbon fibers from CFRP waste and end-of-life products.[3] It is worth noting that CFs are a raw material with high added value and a very energy intense production process (183-286 MJ kg^{-1}), thus their recovery and re-use will be very interesting from the economic and environmental point of view.[4] This thermal process consists of a first step under an oxygen deprived atmosphere (pyrolysis), which leads to a solid residue composed of mainly unmodified carbon fibers covered in a carbonaceous layer (char), which can be removed through a further oxidative treatment (gasification) leading to fibers with properties not far from virgin ones.[5]

The recycled CFs (rCFs) were thus added to polylactic acid (PLA), a thermoplastic aliphatic polyester widely used for 3D printing PLA, [6] which is biobased and biodegradable; despite its considerable cost, it represents one of the most common materials used in Fused Deposition Modeling (FDM), thanks to its good mechanical properties and processability.[7] A number of different approaches can be used to modify PLA, but CFs seem to lead to good results without significant weight increase.[8,9]

In the present work, PLA was mixed with different amount of rCFs (5 and 10% wt, **Table 1**) with the aim to obtain a filament suitable for 3D printing technology. The production process of the filaments was optimized in each step by checking the final properties of the composite material, mostly examining their thermal properties and the average CFs length. It is worth to underline that the PLA polar structure should be able to positively interact with the oxygen-rich surface of rCFs, thus promoting adhesion without the requirement of an additional sizing process.[10] Furthermore, CFs reinforced PLA filaments are already available on the market, and the possibility to re-use CFs recovered by scraps or end-of-life products, will reduce considerably their cost. This latter point is even more significant when considering that CFs have to be strongly downsized for applications such as FDM, and this is a further boost for using rCFs, which do require downsizing for their application.

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Table 1. Produced filament and compositions.

Material	Matrix	Reinforcement	Reinforcement Content [% wt_{tot}]
PLA	PLA	—	—
PLA/rCF5	PLA	rCF	5
PLA/rCF10	PLA	rCF	10

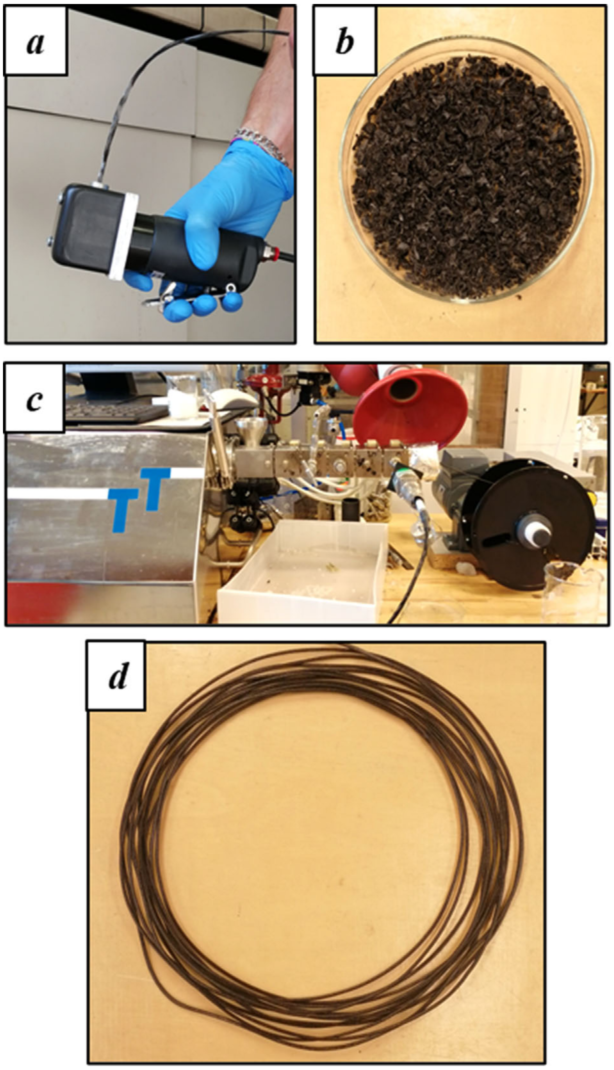

Figure 1. **a)** Working compress air chopper gun; **b)** compound material after grinding; **c)** extrusion of composite filament; and **(d)** CFs reinforced PLA filament.

2. Results and Discussion

Recycled carbon fibers were obtained by pyro-gasification of production scraps and cutouts, as previously reported, [4] and consist of bundle of fibers of different lengths (from 5 to 40 cm). So, they were downsized to 7 mm using a compress-air chopper gun (**Figure 1**a).

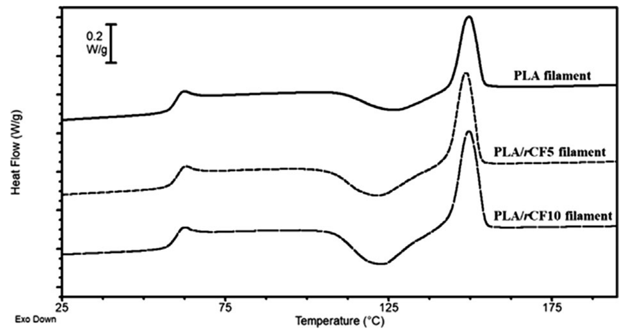

Figure 2. Second heating scan of DSC analysis of CF reinforced filaments and reference filament (neat PLA).

With the aim to avoid PLA degradation with a consequent drastic drop of its mechanical properties due to the presence of moisture, all the chopped fibers and PLA were kept in a vacuum oven at 100°C for 5 h before use.

Dried raw materials were then compounded in a double-screw mixer (PLASTI-CORDER, BrabenderTM, Germany). This step was optimized by varying the processing parameters, such as temperature of the three heating zones, screw speed and processing time, with the aim of avoiding the degradation of the matrix and to provide an optimal CFs dispersion. First, plain PLA was put in the double-screw mixer at 170°C and kept for 2 min to ensure the total melting of the polymer. Then, CFs were added to the molten PLA (at 170°C and 75 rpm screw speed) and the compound was mixed for 5 min obtaining a bulk blended material. Then, the compounded material was ground (Figure 1b) using an electric grinder and extruded (Figure 1c) on a ZE 12 (L/D = 25) co-rotating twin-screw extruder (ThreeTecTM, Switzerland) thus producing the 3D printing filament (Figure 1d). The extrusion step was optimized by varying several parameters (screw speed, five heating zones temperature, post-extrusion traction). In particular, neat PLA (used as reference) was extruded with a temperature profile 155°C/160°C/165°C/160°C/155°C and a screws speed equal to 100 rpm. The extrusion of the reinforced materials was carried out with temperatures slightly higher than for neat PLA (160°C/165°C/170°C/165°C/160°C) in order to reduce the viscosity of melt PLA and ensure an optimal CFs dispersion.

Thermal properties of composite filaments were determined by differential scanning calorimetry (DSC Q2000, TA Instruments, USA) and compared with neat PLA filament (**Figure 2**).

Figure 2 shows the DSC thermograms of neat PLA, PLA/rCF5, and PLA/rCF10 obtained at a heating rate of 10°C min^{-1}: all the samples display a second order transition at around 60°C, which can be ascribed to the glass transition temperature (T_g) of the PLA matrix. Furthermore, all the thermograms show an endothermic transition at around 150°C (melting temperature of PLA) and an exothermic one at lower temperature. Such a behavior is typical of PLA, which is a semi-crystalline polymer characterized by a slow crystallization that leads to the so-called "cold crystallization."[7] As shown in Figure 2, the "cold crystallization" peak is more intense and set to lower temperature for reinforced PLA (both PLA/rCF5 and PLA/rCF10) than neat PLA. Such a behavior seems to suggest that CFs act as a nucleating agent, thus promoting the crystallization of PLA: this aspect might lead to an improvement of the mechanical properties of the material.

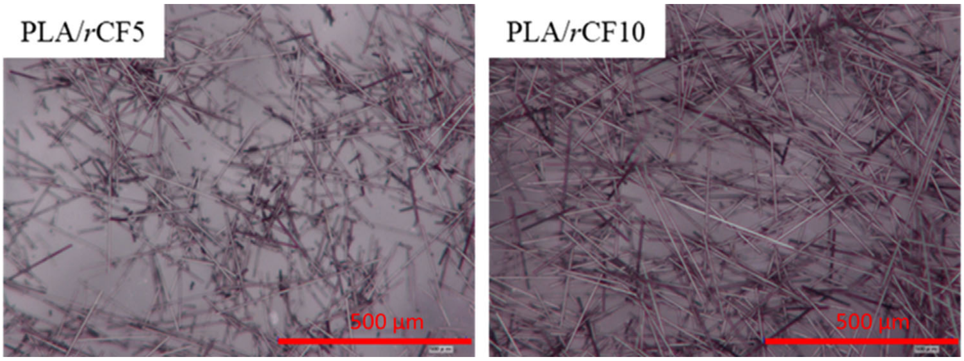

Figure 3. Optical microscope images of CFs reinforced PLA samples. Reference scale bar corresponds to 500 µm.

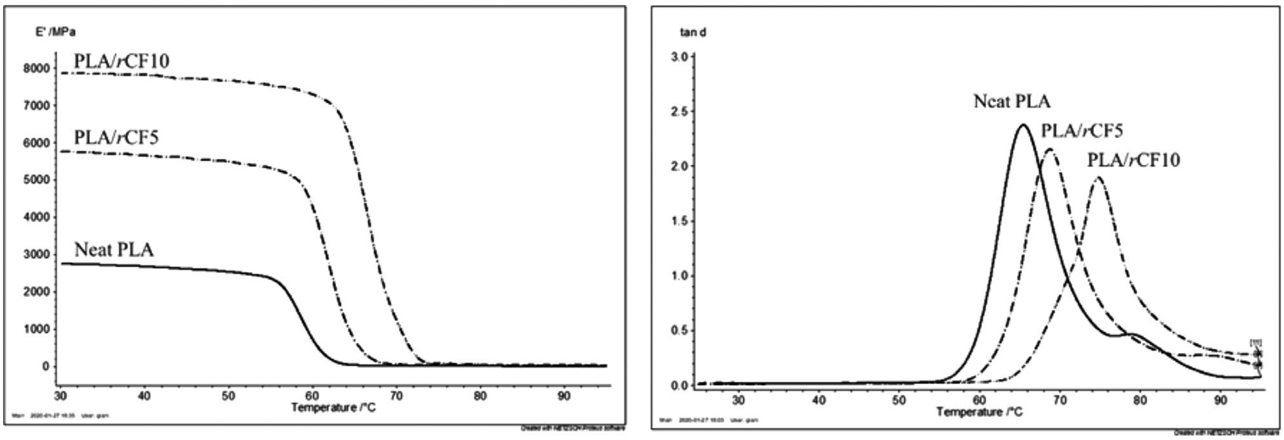

Figure 4. DMA analysis of neat PLA, PLA/rCF5 and PLA/rCF10: (left) Storage modulus (E') versus T. (right) tanδ versus T.

The composite filaments were analyzed by thermogravimetric analysis (TGA) with three replicas in order to evaluate the real CF content. The analysis led to non-reproducible results, probably because of reduced amount of sample used (in the order of few mg), thus suggesting a certain extent of inhomogeneity in the fiber content along the filament. The CFs content determination was then carried out by pyro-gasification of 1 g of sample in a muffle oven. In particular, each sample was heated in inert atmosphere (N_2) up to 500°C with a ramp of 10°C min^{-1}, and then oxidized in air at 500°C to remove the char created in the first step accordingly to a previously reported method.[4] The obtained results show that the filaments CFs content is very close to the expected one, i.e., 5% wt. and 10% wt, respectively, supporting the hypothesis of homogeneous CF distribution along the filament. The residues of CFs obtained from the matrix degradation test were also investigated by optical microscopy, with HX 7700 Hirox 3D Multifocal Microscope, to evaluate the effect of the whole production process on the CF length. The latter is an important parameter for the printability of the filament, since a too large size of the reinforcement additive leads to printing troubles, such as nozzle clogging. So, CFs must be shorter than the nozzle diameter that typically is 0.4 mm. As shown in **Figure 3**, all the samples contain fibers in the range 150–250 µm.

Mechanical properties of filaments were studied by dynamic mechanical analysis (DMA), using a DMA Artemis 242E (Netzsch, Germany). The analysis was carried out heating the specimen from 25°C to 100°C, at a heating rate of 3°C min^{-1}; samples were measured in tensile mode, applying a maximum force of 8.0 N and 40 µm deformation of the filament (**Figure 4**).

As a guideline, five samples for each formulation were analyzed. DMA spectra, reported in Figure 4, show that higher mechanical performances were obtained for composite filaments with respect to plain PLA: the storage modulus (Figure 4 on the left) increases from 2500 to about 5500 MPa for 5% wt reinforced filaments and over 7500 MPa for 10% wt rCFs contain ones. Furthermore, the glass transition temperature (T_g), calculated both as the onset temperature of E' first loss and tanδ peak, increases as a function of the rCFs content.

3. Conclusion

The present work demonstrates that recycled carbon fibers might represent a viable alternative to pristine carbon fibers for modification and reinforcement of PLA intended for 3D printing. Upon optimization of the whole CF addition process, a significant increment of thermal (T_g) and mechanical (E') properties were obtained, using pyrogassified CF recovered from CFRP end-of-life components. This observation might pave the way to a further massive application of such recycled fibers, in filed where downsizing is a requirement.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

additive manufacturing, composite materials, poly(lactic) acid, recycled carbon fibers

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