Macromolecular Symposia
www.ms-journal.de

Production of PLA-Milled Carbon Fibers (MCF) filled filaments for Fused Filament Fabrication (FFF) printing

Claudio Tosto,* Eugenio Pergolizzi, Libera Vitiello, Giovanni Filippone, and Gianluca Cicala

Polylactide (PLA) filaments for fused filament fabrication (FFF) printing with high content of milled carbon fibers (MCF, average length of 1000 nm) are produced. The selected MCF are obtained from commercial sources that derives them from pyrolysis of carbon fibers composites. Twin-screw extruder equipped with volumetric and side feeders are used to melt mix different content of MCF (i.e., from 10 to 30 wt%) prior to filament extrusion. The produced reinforced filaments are used for 3D printing specimens that are characterized in terms of their thermomechanical properties. Higher mechanical properties compared to commercial reinforced filaments are obtained with the filament modified with 30 wt% of MCF.

1. Introduction

Although fused filament fabrication (FFF) printing is simple to use, it is well recognized that the components it produces have inferior properties than identical parts produced by traditional processes such as injection molding, due to voids and weak interlaminar bonding.[1] Incorporating reinforcing fillers, such as fibers or nanoparticles, into the filament's polymer matrix is one option to address this issue. As outlined in recent papers [2–6] the current state of the art for reinforced filament is limited to systems with low fiber content (i.e., ≤20 wt). The aim of this work was to overcome the currently used contents of fiber reaching up to 30 wt% of milled carbon fibers (MCF, average length 1000 nm). The obtained filaments were tested on a commercial FFF printer, and the printed parts thoroughly characterized.

2. Experimental Section

The manufacturing of filaments containing up to 30 wt% CFs was done using a thermoplastic matrix of polylactide acid resin (PLA) (**Table 1**).

PLA, grade 4032D from Natureworks LCC (Nebraska, USA) was selected as it is a routinely polymer used for FFF filament. Milled carbon fibers obtained from pyrolysis was purchased from Easycomposites (England, UK). The filaments were manufactured using a Brabender GmbH & Co. Compounding KETSE 20/40 twin-screw extruder. To avoid the creation of air bubbles in the filament and clogging of the nozzle during extrusion, the PLA pellets were first dried in a special oven at a temperature of 50–60°C. The final diameter of the filament was equal to 2.85 ± 0.2 mm. The printed samples for mechanical testing (ASTM D638) were obtained using the Ultimaker S5 printer (**Figure 1**) with optimized printing parameters (**Table 2**). For printing pure PLA and PLA+CFs nozzles with a diameter of 0.4 and 0.6 mm, respectively were used.

Rheological tests were performed on the pellets obtained by cutting the extruded filament by using a stress-controlled rotational rheometer (mod. AR-G2 by TA Instruments) in parallel plate geometry (plate diameter 25 mm). Sequences of oscillatory shear experiments were performed to obtain the complex viscosity (η^*) in the linear viscoelastic regime, whose limits were assessed through preliminary strain amplitude shear tests. The frequency scans were carried out at 210°C from frequency $\omega = 600$ rad s^{-1} down to $\omega = 0.06$ rad s^{-1} in air atmosphere. The samples were previously dried at 85°C overnight under vacuum.

All the samples were tensile tested in accordance with ASTM D638, on an Instron 5985 universal testing machine (Instron, Milan, Italy) equipped with a 10 kN load cell, in strain control mode at a speed of 2 mm min^{-1}.

3. Results and Discussion

3.1. Rheological Characterization

The rheological behavior of the pure and loaded filaments was investigated by performing consecutive frequency scans on the same sample. The typical result of this analysis is reported in **Figure 2** for pure PLA and PLA+CF30. The magnitude of the complex viscosity progressively decreases while testing due to degradation.

C. Tosto, E. Pergolizzi, G. Cicala
Department of Civil Engineering and Architecture
University of Catania
V.le Andrea Doria 6, Catania 95125, Italy
E-mail: gianluca.cicala@unict.it

L. Vitiello, G. Filippone
Department of Chemical
Materials and Production Engineering
University of Naples Federico II
Piazzale Tecchio 80, Napoli 80125, Italy

DOI: 10.1002/masy.202100417

Table 1. ID of studied formulations.

ID	PLA content [wt%]	CFs content [wt%]
PLA	100	0
PLA+CF10	90	10
PLA+CF20	80	20
PLA+CF30	70	30

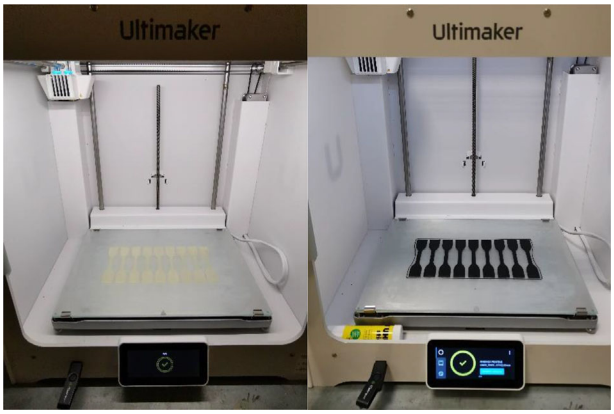

Figure 1. 3D printed samples by PLA (left) and PLA CF-reinforced (right) extruded filaments.

Table 2. Printing parameters on Ultimaker S5.

Printing parameter	Unit	Value
Nozzle diameter	mm	0.4–0.6
Wall thickness	mm	1
Wall line count	-	3
Layer thickness	mm	0.2
Infill	%	100
Raster angles	deg	[0]
Printing temperature	°C	200–210
Plate temperature	°C	60
Print speed	mm s^{-1}	70
Fan speed	%	100
Retraction distance	mm	6.5
Retraction speed	mm s^{-1}	25

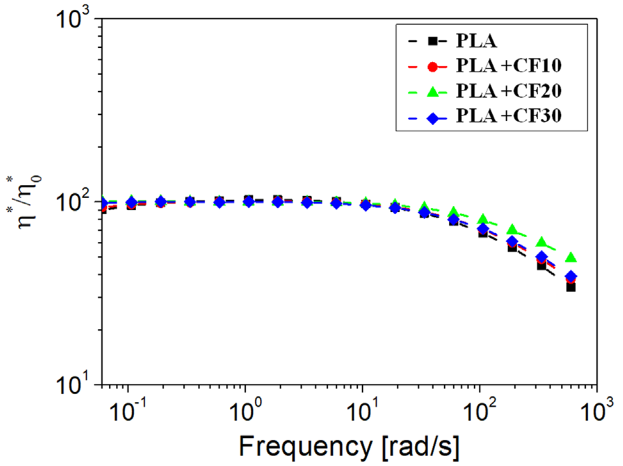

Figure 3. First frequency scan of the normalized zero-frequency complex viscosity for all the samples analyzed.

Figure 3 compares the complex viscosities of samples at different filler content as collected during the first frequency scan. Data were normalized by dividing them by the low-frequency plateau of the complex viscosity (η_0^*). None of the samples exhibits shear thinning behavior in the studied frequency range. This absence of any increase of the complex viscosity curves at low frequency suggests that the percolation is not achieved for the considered fiber contents.[7]

The time evolution of η_0^* can be taken as a reference for monitoring the advancement of degradation for samples at different fiber content.[7] To facilitate the comparison, the parameters time (t) and η_0^* are normalized with respect to their initial value (t_0 and $\eta_0^{\prime *}$) (**Figure 4**). The initial slope of the curves provides a measure of the rate of the degradation phenomenon. Considering that the degradation rates are comparable, and taking into account that no clear trends can be recognized, it can be concluded that the effect of fibers on matrix degradation, if any, is negligible. The decrease of the viscosity over time can be ascribed to the inherent thermal degradation of the PLA matrix.

3.2. Mechanical Characterization

After generating the experimental plan, the following response observations were collected: Young's modulus (E), ultimate

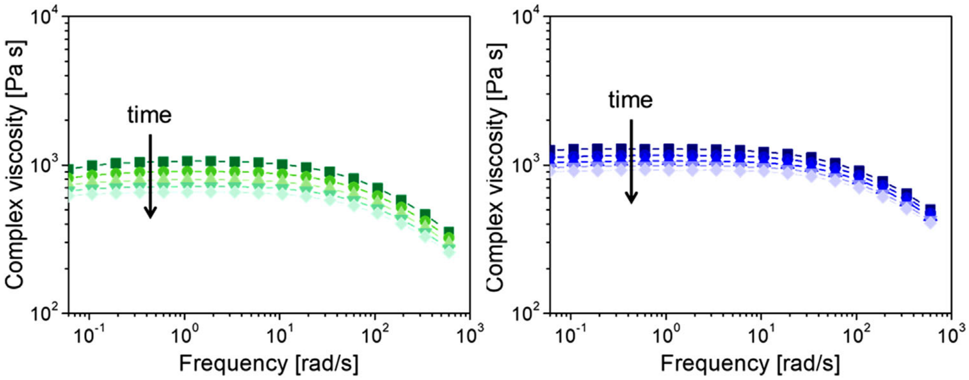

Figure 2. The complex viscosity as collected through consecutive frequency scans over ≈1 h for A) pure PLA and B) PLA+CF30 composites.

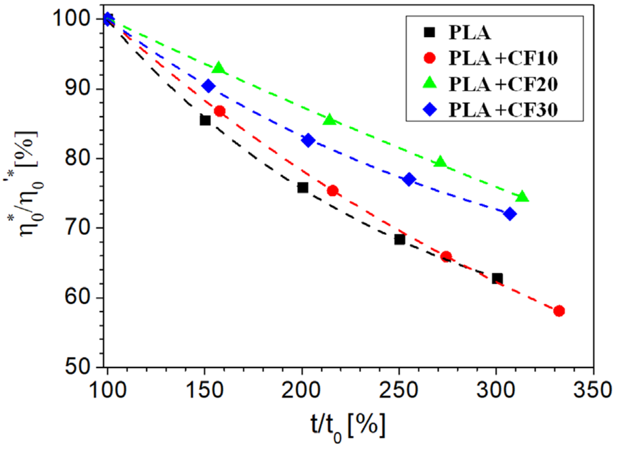

Figure 4. Time evolution of the normalized zero-frequency complex viscosity for all the samples analyzed.

Figure 5. 3D printing components by PLA+CF30.

Table 3. Comparison of PLA filaments.

Filaments	E [GPa]	UTS [MPa]	ϵ [%]	Manufacturer
PLA	5.22	89.67	2.19	This study
PLA	-	63.00	4.00	Verbatim
PLA	2.35	45.60	5.20	Ultimaker
PLA	2.19	25.40	2.49	FiberForce
PLA+CF10	5.39	57.10	1.64	This study
PLA+CF15	6.56	96.00	-	Proto-Pasta
PLA+CF15	4.23	51.00	2.08	3DXTECH
PLA+CF20	7.05	51.46	1.07	This study
PLA+CF20	4.95	48.00	2.00	3DXTECH
PLA+CF20	4.80	47.90	2.00	SD3D
PLA+CF30	8.56	62.68	1.00	This study

tensile strength (UTS), and elongation at break (ϵ). An ANOVA study was performed using the Minitab software (Pennsylvania, USA). The responses E, UTS, ϵ varied in the range between 5.19 and 8.63 GPa, 51.45 and 92.09 MPa, 0.84% and 2.39%, respectively. The models appear to have a good robustness to define the observed responses with high R-squared values of 99.81%, 99.09%, and 96.89%, respectively for E, UTS, and ϵ.

A comparison of the mechanical properties measured for the filaments developed in this study with those available commercially can be found in **Table 3**. The comparison clearly shows that the manufactured filaments outperform the commercial filaments available commercially due to the higher content of reinforcing fibers used. **Figure 5** depicts some components showing the excellent printability and the good surface quality for the filaments developed.

4. Conclusions

PLA filaments filled with milled carbon fibers ranging from 10 up to 30 wt% were manufactured and tested on a commercial FFF printer. The filaments showed consistent quality allowing to print good specimens and part with complex shape. The extruded filaments were thoroughly characterized by mean of rheology showing that no significant degradation occurred upon fiber addition. The thermal degradation measured by rheology was like what is normally reported with pure PLA. This is a positive result with highly filled filaments as it proofs that the filled filament can be used continuously as for the pure PLA filament. The latter results were confirmed by printing trials as showed in the paper. The filaments were also tested by printing samples for mechanical testing. The tensile properties measured showed that the high content of reinforcements used greatly improved the mechanical properties overcoming, as expected, the commercial filaments that have lower fiber's content. Further improvements can be achieved if higher fiber content or longer fibers can be used. This poses some technological issues that needs to be addressed to improve further the use of FFF for functional parts and for the use of degradable systems.[8]

Acknowledgements

Claudio Tosto acknowledges the MIUR funding of his PhD within the PON Ricerca e Innovazione 2014–2020 Asse I "Investimenti in Capitale Umano" -Azione I.1 "Dottorati Innovativi Con Caratterizzazione Industriale" Project Title "Advanced Materials for Additive manufacturing" (AMA) (CUP E67I18001120006). Gianluca Cicala acknowledges MIUR funding through the grant MAMMA under the PRIN scheme (CUP E64I17000260001).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

additive manufacturing, fused filament fabrication (FFF), mechanical properties, PLA, recycled carbon fibers

Received: October 12, 2021
Revised: October 26, 2021

- [1] C. Tosto, L. Saitta, E. Pergolizzi, I. Blanco, G. Celano, G. Cicala, *Appl. Sci.* **2020**, *10*, 3195.
- [2] B. Brenken, E. Barocio, A. Favaloro, V. Kunc, R. Byron, *Addit. Manuf.* **2018**, *21*, 1.
- [3] S. M. F. Kabir, K. Mathur1, A. F. M. Seyam, *Compos. Struct.* **2020**, *232*, 111476.
- [4] N. Werken, H. Tekinalp, P. Khanbolouki, S. Ozcan, A. Williams, M. Tehrani, *Addit. Manuf.* **2020**, *31*, 100962.
- [5] V. Mazzanti, L. Malagutti, F. Mollica, *Polymers* **2019**, *11*, 1094.
- [6] L. G. Blok, M. L. Longana, H. Yu, B. K. S. Woods, *Addit. Manuf.* **2018**, *22*, 176.
- [7] G. Filippone, S. C. Carroccio, G. Curcuruto, E. Passaglia, C. Gambarotti, N. T. Dintcheva, *Polymer* **2015**, *73*, 102.
- [8] V. Mazzanti, M. S. de Luna, R. Pariante, F. Mollica, G. Filippone, *Composites, Part A* **2020**, *137*, 105990.