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Thermal and mechanical properties of Fdmed biocomposites in polylactic acid and food flour waste

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Abstract. In the last few years, fused deposition modelling (FDM) has been explored as an innovative technology for processing thermoplastic green composite materials. However, not all FDM filaments are ecologically beneficial due to their release of toxic compounds during printing. Moreover, they have a dangerous environmental impact, as they are obtained from petroleum. The researches on biofilament manufacturing for FDM are of great interest, thus attracting a lot of attention. The low cost of such filaments could help minimize the use of petroleum-based plastics. In this frame, this work deals with a 3d printer PLA filament neat and additive by food flour waste percentage was created. The innovative filament was analyzed by calorimetric and thermogravimetric analysis, and its printability was evaluated by manufacturing specimens of suitable dimensions for flexural tests. The mechanical tests were carried out to assess the use of the innovative 3d printed biocomposite in place of traditional plastics in packaging or to make films for food use.

Introduction

Plastics derived from natural sources have attracted extraordinary attention as they do not contribute to the depletion of fossil resources, ensuring reduced carbon dioxide production during synthesis and transformation. Therefore, they generate a lower environmental impact than petroleum-derived ones. As a result, PLA is one of the most widely used bioplastics. Still, its intrinsic characteristics, such as fragility, often limit its use in particularly demanding applications unless strategies such as mixing with other polymers or including suitable additives are used. With these approaches, new environmentally sustainable materials are obtained, with better performance and which guarantee the reduction of environmental contamination associated with plastic [1-5].

The most common manufacturing technologies for thermoplastic-based green composites are extrusion, compression moulding and injection moulding [6]. Nevertheless, fused deposition modelling (FDM) has been explored as an innovative technology for processing thermoplastic green composite materials [7-11]. The many advantages of FDM, the reduction of production time and costs, and the possibility to create highly elaborated geometries are the most interesting aspects that make this manufacturing technique promising for making green composite components [12]. FDM has gained interest in several fields, such as aerospace, automotive, research, medical architecture, food, and design [13-15]. It is an additive manufacturing method which applies different thermoplastics materials for composites and biocomposites [16]. A thermoplastic filament is heated and crushed out on the printing plate by a nozzle. The product is created by depositing material layer by layer that solidifies after fusing to produce the components [17,18].

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The market demand for 3D printing filament is estimated to reach high gain values by 2027 at an annual growth rate of about 20%. Plastic filaments have recently led the printing press industry due to the high demand for filaments [19]. However, not all FDM filaments are ecologically beneficial due to their release of toxic compounds during printing. In addition, they have a dangerous impact on the environment, as they are obtained from petroleum [20].

The growing use of industrial and domestic FDM 3D printing further increases plastic waste. Such technology could gradually displace and replace some cheap and non-biodegradable plastic waste in ambient conditions posing a threat to the environment. To address the above-described problems, the researches on biofilament manufacturing for FDM are of great interest thus attracting a lot of attention. The low cost of such filaments could help minimize the use of petroleum-based plastics. Although many works have been done on biomaterials, most concern biomedical applications [21-23].

In this frame, combining biodegradable polymers with agricultural waste, marine waste, or industrial residues from wood processing has gained particular interest in producing composite materials with high mechanical performance [1-5]. Often these fibres come from processing waste typical of the areas of research sites, such as flour deriving from hazelnut processing waste [24] or bamboo [25].

This work created a 3d printer PLA filament neat and additived by food flour waste percentage. The innovative filament was analyzed by calorimetric and thermogravimetric analysis, and its printability was evaluated by manufacturing specimens of suitable dimensions for flexural tests. The mechanical tests were carried out to assess the use of the innovative 3d printed biocomposite in place of traditional plastics in packaging for food use.

Materials

Investigated systems were based on a commercial polylactic acid (PLA) supplied by Biowares.r.l. with the trade name Luminy LX175 (density: 1.24 g/cm3, MFI@210°C/2.16 Kg: 6g/10 min, Tg: 60°C) and food flour waste (FW) supplied by a local pasta factory.

From PLA pellets (100% wt.), cleaned and filled filament (FW) was produced using a 3Devo Composer 450 Filament Maker (Utrecht, The Netherlands) with a single screw extruder equipped with four heating zones, reaching a maximum T=450°C.

For the extrusion of the PLA_FW, the four heat zones reached a temperature between 70° and 190°, in about twenty-five minutes, with a first increasing sequence to favor the melting of the granules of raw material inserted into the feed hopper (Fig. 1), and then decreasing to favor the extraction of the extruded filament. Once the temperature T=190°C was reached, the extruded filament was wound onto a reel via the rotating shaft of the extruder itself. At the exit, the filament is further cooled by two fans, as the extruder expels it through a nozzle at a temperature of about 170°, corresponding to the last heat zone. The diameter of the extruded filament has been controlled by a sensor which guarantees maximum uniformity of the diameter. Finally, neat and filled PLA filaments with a 1.75 ± 0.2 mm diameter were produced.

Fig. 1. Granules of raw material neat and infilled by flour waste.

3D Printer Setup

The samples were manufactured using the Sharebot 42 3D printer, which uses FDM (Fused Deposition Modeling) as an additive manufacturing technique. The 3D printer is 450x420x470 mm in size and has a printing volume of 250x220x220 mm, while the Z resolution is 50 microns. CAD 3D of the samples were modelled with Solidworks software. Then, they were imported into the Simplify3D software. The heated printing bed, the printing bed autocalibration system, the easy detach system and the filament sensor are integrated into the 3D printer. 100% infill density, a line infill pattern and a -45°/+45° raster orientation were adopted. Layers height was fixed equal to 0.2 mm. Plate temperature equal to 90°C, a deposition speed equal to 70 mm/s and an extruder temperature equal to 215°C were selected for all samples.

Thermal Analysis

Extruded compounds were thermally analyzed using a TA Instruments DSC Q2000 differential scanning calorimeter (New Castle, DE, USA) by applying a typical three-stage procedure involving a first heating step from 30°C to 220°C, a cooling step from 220°C to 30°C and further heating from 30°C to 220°C. All the steps were carried out on 8-10 mg of material at a rate of 10°C/min. Processing of collected thermograms allowed the evaluation of some typical parameters, such as the temperature and the enthalpy of the main transitions evaluated as the peak temperature and the area underlying the respective calorimetric signal.

Thermogravimetric analyses were carried out by a Perkin Elmer Pyris Diamond analyzer (TGA) model. At this purpose, materials were heated starting from a temperature of 25℃ up to a temperature of 800℃ in a flow of nitrogen at a heating rate of 10℃/min.

All the investigated materials were compared with neat PLA processed under the same conditions.

Mechanical Tests

Bending measurements determined the mechanical performances of the explored materials. Specifically, bending tests were conducted on 12.7x3.2x4 mm3 specimens, according to ASTM D790 standard [23] using a Galdabini QUASAR 50 materials testing machine with a test speed equal to 3mm/min.

For each sample, five specimens were tested to verify the reproducibility of the data.

Results and Discussion

Calorimetric results.

Table 1 summarises the results obtained from the calorimetric analysis of the materials under study. The glass transition temperature (T_g) and the melting temperature (T_m) values, characteristic of the hosting matrix, are not substantially affected by waste flours. On the contrary, the inclusion of this filler significantly increases the melting and cold crystallization enthalpy values (H_m and H_{cc}, respectively), slightly anticipating the cold crystallization temperature (T_{cc}). In other words, it is evident that the filler alters the crystalline structure of the host matrix and probably favours its crystallization.

Table 1. DSC results.

Material	T_g[°C]	T_{cc}[°C]	ΔH_{cc}[J/g]	T_m [°C]	ΔH_m[J/g]
PLA	59.2	124.2	8.9	150.3	14.9
PLA+1%FW	59.6	116	13.9	149.9	21.9
PLA+3%FW	58.9	117.7	15.9	149.5	21.5
PLA+5%FW	59.4	118.4	13.9	149.6	19.6

TGA results.

The results obtained on all examined samples are collected in Table 2 regarding key parameters. In addition, the temperatures corresponding to a weight loss equal to 1% and 5% ($T_{1\%}$ and $T_{5\%}$, respectively), the temperature at which the massive degradation of the material (T_d) occurs and the residual mass percentage remaining at the end of the applied thermal scan are reported.

The inclusion of waste flours causes a progressive reduction in the material's thermal stability. However, this effect, usually catalyzed in the presence of organic fillers, appears to be not marked up to a composition of 3% by weight.

In the presence of 5 wt% of FW, on the other hand, perhaps also due to the higher moisture content brought internally to the composite by the organic filler included, the first parameter $T_{1\%}$ is strongly anticipated.

Concerning the amount of the residue, this parameter, resulting to be not zero even for the reference matrix, increases with the filler content, assuming values not easily comparable with the nominal content of waste flours included.

Table 2. TGA results.

Material	$T_{1\%}$ [°C]	$T_{5\%}$ [°C]	T_d[°C]	Residue [%]
ExtrudedPLA	290	307	351	0.5
PLA+1%FW	262	285	320	1.1
PLA+3%FW	261	292	324	1.8
PLA+5%FW	160	286	322	3.1

Mechanical results.

Flexural tests results have been reported in Fig. 2 and Table 3 where the flexural strength, $σ_f$, and the correspondent maximum deflection, d_{max}, are reported for each material tested.

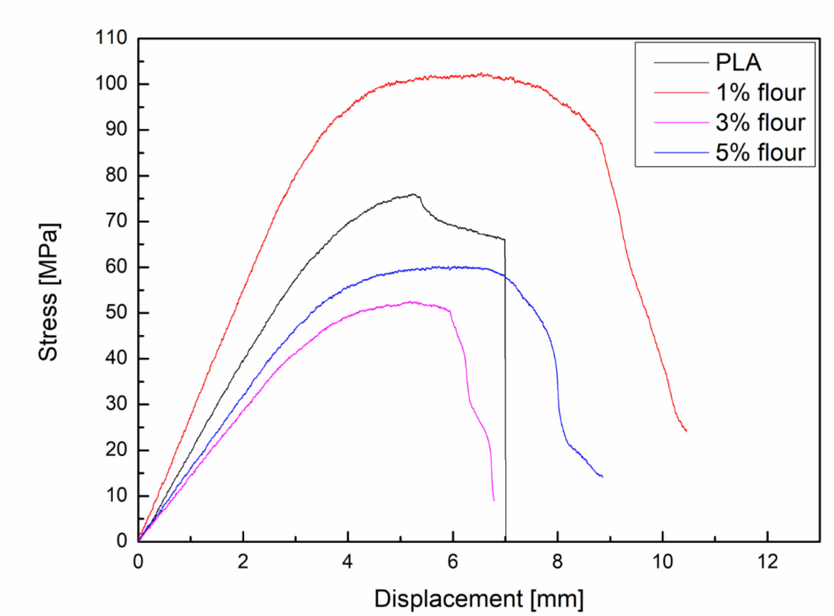

Fig. 2. Stress displacement curves for all materials tested.

As visible in Fig. 2, the printed samples with a percentage of flour waste of 1%wt show a maximum load higher respect to neat PLA, also offering the ability to hold the load over a longer displacement range. On the other hand, increasing the FW content determines increasing material embrittlement, as confirmed by the visual inspections of the bent specimens (see Fig. 3). Clearly, samples of extruded PLA or containing 1% wt of FW show a crack at the load's application point, while ones filled with 3% and 5% by weight of FW yield at the load application point undergo a brittle break.

Table 3. Flexural tests results.

Material	σ_f [MPa]	d_{max} [mm]
ExtrudedPLA	75.91± 2.5	5.20± 0.2
PLA+1%FW	100.21± 3.0	6.66± 0.5
PLA+3%FW	50.99± 2.6	5.30± 0.3
PLA+5%FW	58.61± 3.2	6.00± 0.6

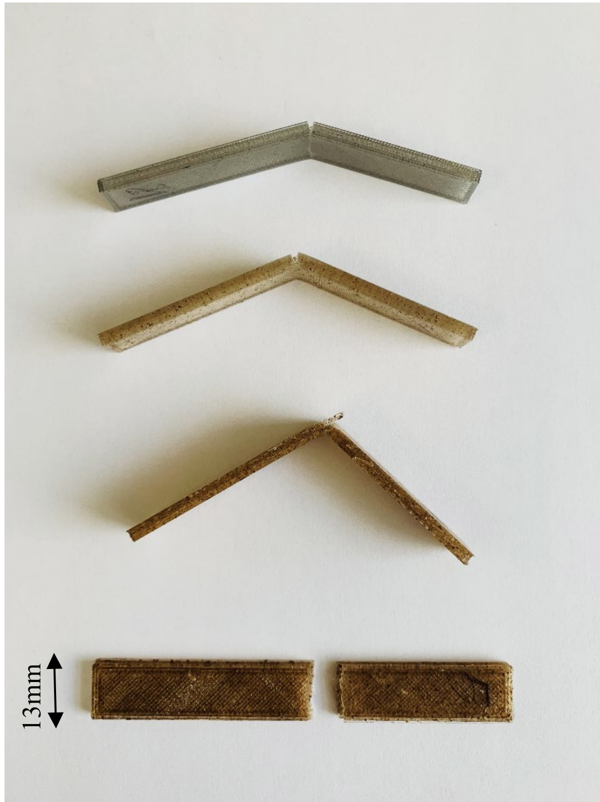

Fig. 3. Bending specimens after test.

These considerations are further highlighted by bending features values at break obtained for all the materials studied on at least 5 specimens tested for each sample (see Table 3).

Summary

The work's aim is to propose innovative biodegradable filament made of PLA and different flour waste percentages to explore the potential of 3d printed composites for sustainable industrial applications. The attention was focused on food flour waste in huge quantities on the national territory, especially in Southern Italy, where there is a large consumption of products such as pasta and bread.

The filament produced appears constant in diameter, equal to 1.75mm. Thermal and mechanical analysis of samples based on poly (lactic) acid-containing food flour waste have indicated an improvement in the mechanical parameters in bending behaviour compared to those characteristics of the polymeric reference matrix only for FW=1%. Also, material toughness decreases with the flour waste content over FW=1%. This behaviour is typical for micro composites, including filler having a poor chemical affinity with the surrounding matrix. It is supported by the morphological observations performed on fractured cryogenic sections of the samples.

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