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New filaments with natural fillers for FDM 3D printing and their applications in biomedical field

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Abstract

Current Fused Deposition Modelling (FDM) techniques have promoted the extension of 3D printing technologies to new applications ranging from the biomedical, aerospace, and submarine fields, to some specific applications in manufacturing and civil fields. The expansion of the fields of application, generally, entails considering peculiar characteristics, such as complex geometries or requirements as low density. Furthermore, the breathability, the pleasantness to the touch, aesthetic appearance and a strong visual identity, that can be achieved by means of 3D printing, are especially requested for some applications such as biomedical. For the improvement of the manufacturing of these parts, the design of a dedicated filament is a relevant issue to be taken into account. polylactic acid (PLA) and organic by-products from agricultural waste. The study includes a preliminary illustration of the main properties of these materials and a biomedical application of such bio-plastic compounds through experimental testing in order to assess the suitability to FDM printing. In particular, the performance in terms of lightweight, strength and roughness have been evaluated. The interesting final properties make these materials suitable for biomedical applications as it is shown in this study for the neck collar prototype reported. In addition, such innovative bio-composite materials allow reducing the cost of environmental impact as well as the production management costs.

Keywords: Organic bio-composite filament; Bio-plastic compounds; Additive Manufacturing capability; Roughness; Mechanical properties; Biomedical applications

1. Introduction

Chemurgy, a branch of industry and applied chemistry which studies the integration of agricultural and natural biomasses, has emerged since 1930s with the aim to give an input to the secondary industry for the production of fuels, chemical compounds and materials [1].

As such, this "industrial symbiosis" model allows integrating peculiar features of certain biologic materials in order to eliminate the use of traditional petrochemical modifying agents, by realizing plastic materials with improved ecological properties. The adherence to some of the principles set out in the 'European strategy for plastic in the circular economy' further confirms the environmental benefit of this production paradigm [2,3]. Biomass fillers not only allow to completely substitute the toxic and polluting additives, but they are also able to improve material performance. In fact, biomasses are added in much higher percentages, ranging from 15% to 60%, with respect to chemical additives, so leading to significant savings of the plastic material. In this way, two points are achieved simultaneously: *i)* reduction of dangerous substances in materials and *ii)* raw materials

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replacement with wastes from production cycles (meeting waste framework directive [4] 'reuse before recycling' indications).

Concerning the first point, the environmental impact of plastics, at various levels is well recognized [5]. One of the worst effects is produced by the so-called microplastics, that is, plastic particles ranging between 5 and 330 µm. Noteworthy, these latter can reach any terrestrial environment due to their size. Recent studies have further demonstrated that they can travel hundreds of kilometers, carried by the wind, clouds and rain [6]. Nevertheless, microplastics can strike living organisms so that a human could assume up to 5 grams (the equivalent of a credit card) per week in the worst perspective, (UN News, 2017). Moreover, most of the impact caused by microplastics directly depends on the additives contained within them. Indeed, the additive agents release their toxicity to the environment where microplastics deposit and accumulate. In other words, the small plastic particles act as a simple vector [7,8]. The so-called secondary microplastics differ from the primary ones in which they are not directly produced in that size: it is the case of plastic particles used in cosmetic products or those making up fibers for clothes they separate from plastic objects due to mechanical, thermal or chemical deterioration.

Since the additives - core problem is their intrinsic toxicity, the new paradigm exposed could be an excellent perspective using completely non-toxic and biodegradable materials. The paradigm of circular economy is generally applicable to manufactured parts including multi material components [9] and parts obtained by means of Additive Manufacturing (AM) [10], which can be implemented with different manufacturing processes [11].

Herein, two novel organic bio-composite filaments, so-called HEMP and WEED, made of polylactic acid (PLA) filled with organic by-products [12] are illustrated together with an example of application to the biomedical field by using Additive Manufacturing. Such novel "environmental-friendly" plastics are totally biodegradable and biocompatible, making them appropriate for the manufacture of products in food, cosmetics, pharmaceutical and biomedical fields.

Furthermore, these bio-plastic compounds have different physical, mechanical, and visual features which depend on different agricultural supply chains (by-products) employed.

Concerning the biomedical field, these materials are particularly recommended for the realization of objects, such as orthoses. In fact, AM owns a great versatility in design and efficiency if an appropriate design framework is provided [13]. For instance, devices like orthoses require a patient-specific approach where the customization undoubtedly gives an added value: often, the preoperative planning is finalized to the realization of 3D printed models [14], patient specific instruments [15], customized orthopaedic devices [16], customized dental implant systems [17]. It is noteworthy that in all these applications AM also makes possible the production of one single customized item at reasonable prices. Moreover, AM enables the production of complex geometries almost impossible to be manufactured such as scaffolds for tissue engineering, which nowadays sparks a highlight interest, [18,19].

The reduced environmental impact, the recyclability, the optimized disposal and, especially, the limited management and production costs, are relevant characteristics that convey numerous advantages over its competitors.

More striking, compared to traditional thermoplastic materials, our compounds also reach an improvement of their performance in terms of mechanical properties and weight reduction, as outlined in the present paper. Besides, since European standards requires 20% biobased [4], the secondary sectors related to thermoplastic industries, can exploit efficaciously these new inputs from agricultural wastes.

2. Bio-plastic compounds fabrication

Fundamentally, our novel bio-plastic materials here described are composite materials, constituted by two or more different phases with a distinct interface: *i)* the matrix or continuous phase and *ii)* the filler/reinforcement phase, surrounded by matrix material [20, 21].

The final composite material shows improved mechanical/physical characteristics than pristine components despite of the individual phases preserving their own features [22]. Nevertheless, composite materials exhibit remarkable anisotropy, that is, their properties change considerably when observed in different directions [22]. Commonly, in artificial usage, the continuous phase is based on synthetic thermosetting or thermoplastic polymers, depending on the type of technological applications, whereas inorganic fibers or particulates (e.g. glass, carbon, etc.) can be employed as the filler phase for ensuring strength and stiffness to the resultant composite material [22].

Compared to synthetic and artificial composite compounds, our materials are completely natural-based: a matrix made of Polylactic Acid (PLA), a 100% bio-based plastics (purchased from Ingeo Biopolymer 3D450 by NatureWorks), and a reinforcement that consists of different particles (more than 20% in weight) from agricultural waste, making our products as particulate bio-composite materials.

In particular, the by-product particles used as filler have been standardized, by controlling the respective humidity values, spherical shape and caliber as indicated in Table 1.

Table 1. Main characteristics of the particles used as filler phase from agricultural waste

Material	Relative humidity	Shape	Particle Size [µM]
HEMP	6%	spherical-like	130
WEED	4%	spherical-like	150

The choice of industrial plant by-products, selected according to their chemical properties and particle size, is the first stage for the production process. In detail, the standardized particles, illustrated in Table 1, are joined to the thermoplastic PLA matrix in a two-screw extruder (Fig. 1) which has the role of mixer/compounder in the temperature range of PLA melting point. Furthermore, the organic by-products are treated before to be added into the hopper, by using a micronizer and a dehumidifier in order to increase the compatibility between the matrix and the filler. In Table 2 the injection parameters used into the two-screw extruder are reported. The final product is a biodegradable thermoplastic polymer; upon leaving the mixer/compounder, the compound is placed in a granulator for the production of granules or in an extruder in order to produce filaments for 3D printing.

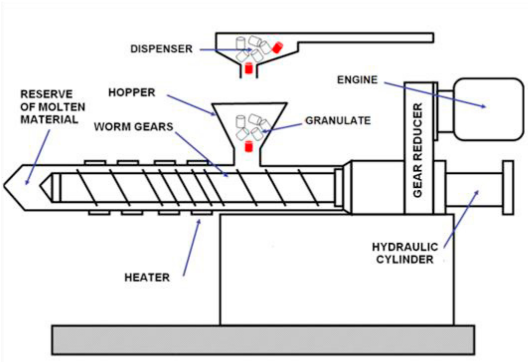

Fig. 1. Workflow to produce bio-composites particulate based on PLA and natural waste.

Table 2. Injection parameters

Parameter	Value
Drying granules	10 hours in a vacuum oven at 90 °
Barrel temperature	160 ÷ 170 °C
Mould temperature	30 °C
Screw speed	300 rpm
Injection speed	Slow

The two different bio-plastic compounds filaments, obtained by varying the organic by-product fillers used, are:

- HEMP (Fig. 2a): filament of natural and compostable origin containing exclusively hemp (ranging from 15% to 25%);
- WEED (Fig. 2b): filament of natural and compostable origin, containing exclusively waste powder from hemp inflorescences (ranging from 10% to 15%). In this latter case, the presence of cannabinoids, that is lipids, play a role of emulsifier inside the polymeric matrix.

The diameter of the produced filaments described here is 1.75 mm.

(a) (b)

Fig. 2. Thermoplastic bio-composite filaments: (a) HEMP; (b) WEED.

3. Performance evaluation and mechanical characterizations

In order to evaluate the performance of our materials, we tested the following properties on the new bio-plastic filaments:

- Manufacturing capability: this property was evaluated considering melting temperatures, filament surface roughness, density, and retraction behaviour, intended as longitudinal moulding shrinkage. In all the bio-composite materials, the melting temperature was evaluated by DSC according to standard ISO 11357; the density was estimated at 23°C according to standard ISO 1183; the longitudinal moulding shrinkage was measured at 23°C according to standard ASTM D 995;
- Roughness: the average value of this characteristic was measured for object printed with these new bio-composites materials and compared with that of object printed with pristine PLA.
- Mechanical properties: the elastic modulus, the yield strength, the yield elongation, the ultimate stress, and the ultimate elongation were evaluated. The elastic modulus was evaluated at 23°C by using a dynamic mechanical analyzer (DMA Q800, TA Instruments) according to standard ISO 527. The yield and elongation strength together with the ultimate stress and elongation were estimated by a static mechanical machine (Instron 5569), setting a displacement rate equal to 10 mm/min. All mechanical properties were tested at 23°C according to standard ISO 527.

All experimental tests were carried out at SUPERLAB S.r.l. Salvaterra (RE) using the equipment described here: “http://www.superlab.it/laboratorio/”

4. Manufacturing capability, Roughness and Mechanical properties

Bio-plastic compounds filaments are as printable as PLA, since they can be extruded at even lower temperatures. Extruding at up about -13% temperatures implies significant energy savings. In addition, filled PLA has generally shown a shrinkage which makes printing more accurate, without the need for further processing [23, 24]. Table 3 summarizes the main manufacturing capability properties of the new bio-plastic compounds filaments.

The roughness was examined by using a NANOVEA Optical Profilometer mod. PS50 (Sensibility 2 µm, height range 25 mm, sampling length 2.5 mm, measuring speed of 0.5 mm/s). The experimental measurements were carried out to evaluate medium roughness (Ra) of bio-plastic compounds.

The medium roughness of bio-plastic compounds was evaluated in flat surfaces (without taking into account "staircase" or "stair-stepping" problems) printed parallel (par) to the printing area and in flat surfaces printed orthogonal (ort) to the printing area. The printing parameters used are shown in Table 4. Moreover, bio-plastic compounds result in better surface finishing compared both to ABS and PLA (Fig. 3).

Table 3. Main manufacturing capability of new bio-plastic compounds in comparison with pristine PLA filament.

Materials	Density [g/cm^3]	Melting temperature [°C]	Filament surface roughness [μm]	Molding shrinkage [%]	Melt Vol. Rate [cm^3/10’]	Melt Flow Rate [g/10’]	Flexural modulus [MPa]
PLA	1.350	172.5	3.0	0.32	18.2	21.0	3200
HEMP	1.256	145.0	3.5	0.23	21.3	24.0	3833
WEED	1.265	150.5	3.2	0.28	76.0	86.9	3455

Table 4. Printing parameters

Parameter	Value
Layer height [mm]	0.25
Infill ratio [%]	50
Nozzle diameter [mm]	0.6
Printing speed [mm/s]	60
Printing temperature [°C]	200

Table 5. Main mechanical properties of new composites in comparison with pristine PLA

Materials	Colour	Elastic Modulus [MPa]	Yield Stress [MPa]	Yield Elongation [%]	Ultimate Stress [MPa]	Ultimate Elongation [%]
PLA		1900	35.9	2.0	26.4	3.8
HEMP	Wood	4420	41.8	1.5	33.6	3.5
WEED	Green	3887	32.0	1.3	19.5	8.8

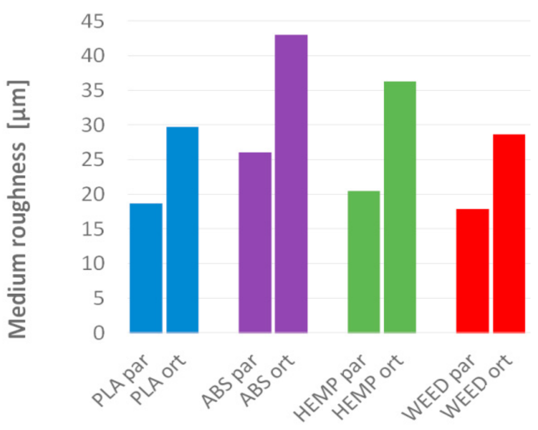

Fig. 3. R_a of new composites in comparison with pristine PLA and ABS.

Each filler produces some specific benefits from the point of view of the mechanical properties. The evaluations of the mechanical properties (Table 5) were carried out following the rules reported in section 3 and using the printing parameters reported in Table 4.

More details are given in the following:

- HEMP (powder from hemp canapule fillers 20%): this material has excellent tensile strength, thanks to the high presence of silicon contained in the hemp canapule. This is a result not obtainable even with hemp fiber or wood sawdust. The elastic modulus is more than double if compared to PLA (+133%) and also the yield strength increases significantly (+16%) (see Table 5);
- WEED (powder from hemp inflorescences fillers 20%): again results in a relevant increment of the elastic modulus; however, both yield stress and ultimate stress are slightly smaller than PLA. In addition, this material undergoes a very high plastic deformation; this is due to cannabinoids which give much plasticity to the material: the starting PLA has a percentage of elongation at rupture equal to about 3% [23]. Adding 20% of hemp flower powder, this percentage reaches 9%.

5. Applications to a Biomedical Device

Hemp shivers exhibit interesting antibacterial properties [25] which along with good aesthetics breathability, stiffness and touch pleasant, make HEMP bio-plastic composite a suitable material for biomedical prototypes. In this study, a neck orthosis (Fig. 4) was manufactured through the Printer D300 Technology® equipped with a 0.6 mm nozzle. The device combine specification of breathability, lightness, stiffness good aesthetics, all characteristics exceptionally appropriate for the qualities of the HEMP material. In addition, this is an object-large enough to significantly benefit from the shrinkage of the HEMP bio-plastic compound. The printing parameters applied to produce the prototype are listed in Table 4. It is noteworthy that the process parameters remain the most important matter final characteristics of a manufactured part [26].

The customized orthosis was designed starting from the Computer Tomography (CT) scan of the neck of a volunteer subject (Fig. 4). The first step was the manufacturing of a "full" neck collar prototype; subsequently a honeycomb pattern of voids was designed in order to improve the breathability and decrease the overall weight (Figs. 4a-b). More detailed description about the design process and printing characteristics through the FDM technique printing are available in [16].

(a) (b)

Fig. 4. 3D printed neck orthosis from Hemp filament with a pattern of voids.

6. Conclusions

The proposed filaments constitute a fascinating perspective to connect primary and secondary industries through the integration between sustainable PLA and agricultural wastes. This idea could appear somehow trivial or innate from a physical and chemical point of view. However, as demonstrated by the above-described application, the final product is appropriate for end use and can undoubtedly represent a valid alternative to reduce the additive toxicity. Besides, it has been demonstrated that bio-composites here described exibit superior mechanical properties, better manufacturing capability, and lightweight. Further researches are ongoing in order to employ other by-product fillers, developing as well, models able to predict their performances in terms of mechanical properties, manufacturing capability, and, visual/outer appearance.

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