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A New Biocomposite Material Based on Wheat Waste and Suitable for 3D Printing Applications

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Biopolymers, such as poly(lactic) acid (PLA), which is obtained through green synthesis pathways from renewable resources, has attracted considerable interest in recent years because of the increasing need to reduce petroleum-based plastic pollution and bringing their prices comparable with conventional thermoplastic commodities' price (e.g., polyethylene, polypropylene, and polystyrene). The present work investigates the employment of 10% wt of natural materials, deriving from wheat milling process, as biofiller of PLA to develop a biocomposite filament suitable for 3D-printing technique. The inclusion of a cost-free natural material leads to a strong reduction of the whole material cost. Implementing this new class of composite material to additive manufacturing technique allows to dramatically reduce the environmental impact of 3D printed products.

1. Introduction

Additive manufacturing (AM) technologies, also known as 3D printing, are able to create three-dimensional objects by a layer-by-layer process. In the last decade, AM technologies have extended toward aerospace, automotive, sport, medical, architecture, education, and fashion industries. Fused deposition modeling (FDM) is the most used 3D printing methodology for its cost-effectiveness, affordability, simplicity, reliability, minimal waste, and wide material availability. Among them, poly(lactic) acid (PLA) is one of the most widely used materials thanks to its cost-effectiveness, good mechanical properties, and biodegradability,[1–4] thus also reducing fossil-based plastic pollution. Furthermore, PLA also obtained from renewable resources, it is produced commercially on a large scale at a reasonable price, though still not comparable with conventional thermoplastic commodities' one (e.g., polyethylene, polypropylene, and polystyrene). The employment of natural materials as biofiller of PLA allowed to develop a new class of green composite materials, also known as biocomposite, bringing several advantages, such as full circularity of the resources, biodegradability, low specific gravity, high specific strength, and reduction of whole material cost. Implementing this new class of composite material to AM technique would allow to dramatically reduce the environmental impact of 3D printed products.[5–7] In the last decade, a lot of efforts were spent for the study of 3D printing biopolymers reinforced with lignocellulosic materials (wood in the form of short fibers, or powder[1,6,8]) to produce green composite materials or biocomposites. Nowadays, wood-reinforced PLA materials are commercially available, paving the way for the use of other natural fillers. Among a wide variety of natural materials, there are several examples of biocomposites in FDM applications: cassava and pineapple flours, coconut waste, hemp fibers, lemongrass fibers, flax fibers, rice straw powder and Kraft lignin, organosolv lignin, and lignosulfonate.

In the present paper, wastes deriving from wheat milling process are investigated as biofillers in a PLA-based 3D printing filament. Initially, preliminary tests are performed on biomass to define its water absorbance and morphological aspect. Then a 10% wt biofiller loaded PLA filament and the reference material, for example, neat PLA filament, are manufactured by double extrusion. Thermal properties of both filaments were studied by DSC, thermogravimetric analysis (TGA), and specific heat capacity (C_P) measurements. The thermo-mechanical response of the biocomposites was assessed by dynamic mechanical analysis (DMA) made on 3D printing filaments.

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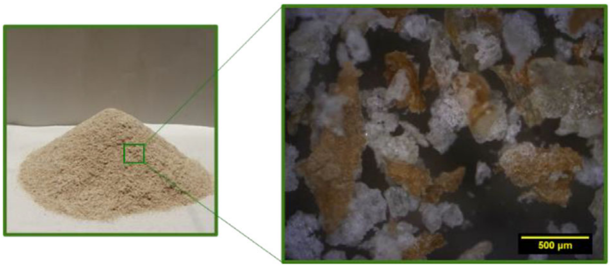

Figure 1. Image of grain of wheat waste as received and its optical microscope observation. The scale bar indicates 500 μm (nozzle diameter of the 3D printer).

2. Results and Discussion

Initially two fractions of wheat wastes, obtained from the wheat flour production process, were selected as potential biofillers for PLA matrix. The coarser one, the so-called fine bran, in constituted of particle with size over 500 μm. The incorporation of an excessively coarse filler in 3D printing materials could lead to several troubles, such as the lack of adhesion among layers during printing, elevated voids content, and finally, nozzle clogging throughout 3D printing. Consequently, the use of fine bran fraction in 3D printing application was excluded.

The finer fraction, that is, middlings, was thus investigated. Moisture content and morphological aspects of biofiller were defined, prior its thermal processes with PLA, to prevent the degradation of the matrix via hydrolysis.[2–4] The biofiller is composed of sub-millimetric irregular particles (**Figure 1**) most of which are below 500 μm, that is, nozzle diameter.

Grain of wheat wastes, as most of carbohydrate materials, are inclined to absorb moisture from the surrounding atmosphere. Since middlings have to be mixed with PLA, which is strongly affected by hydrolysis during thermal processing, it is fundamental to process the materials in dried state. So, the biofiller was dried in muffle at 115°C for 1 h under nitrogen flow. The treatment efficiency was established by TGA on middling samples before and after drying treatment. In **Figure 2**a, the effect of drying process is highlighted with the decrease of water content from 11.7% wt (before drying) to 1.6% wt (after drying).

After drying both PLA pellets and wheat waste in oven at 115°C for 1 h, they were kept in vacuum bag until compounding. The first extrusion was performed to mix efficiently the materials and to collect a pelletized extrudate composed by 90% wt of PLA and 10% wt of biofiller. The pelletized material was dried again in oven at 80°C for 1 h before the next extrusion. The second extrusion was performed for a further homogenization of the biofiller inside the filament and, mostly, to obtain a controlled diameter (≈1.75 mm) for the 3D-printable filament, thanks to an optical equipment installed at the die end.

Table 1. Thermal-degradative properties of poly(lactic) acid (PLA), biofiller, and biocomposite filaments.

Sample	T_o [°C]	$T_{max, deg}$ [°C]
PLA	351.6 ± 0.3	368.1 ± 0.3
Biofiller	206.0 ± 0.5	228.0 ± 0.5
	288.0 ± 0.5	315.0 ± 0.5
Biocomposite	336.9 ± 0.5	362.2 ± 0.8

First, it was worth to investigate the effect of middlings to PLA matrix in terms of thermal stability of the whole material. As shown in **Table 1**, the biocomposite filament showed a lower thermal stability than the pure PLA filament with onset of degradation temperatures of 337 versus 352°C. Similar results were obtained in analogous studies about PLA-biocomposite with several lignocellulosic biofillers, such as coconut waste,[9] kenaf, and rice husk.[10] The main reason of this thermal stability reduction in the biocomposite is the presence of the biofiller, which, as most of natural materials, degrades at relatively low temperatures. The principal constituents of wheat grain wastes are, beside starch, lignin, hemicellulose, and cellulose, and their onset thermal decomposition temperatures (T_o) are established at 160, 220, and 315°C, respectively.[11] It is worth to note that a small amount of water contained in middlings, about 1.5% wt, could anticipate the hydrolytic degradation of polymeric matrix as shown in Figure 2b. On the other hand, such a decrease in thermal stability did not compromise the use in 3D printing application since thermal degradation did not occur at processing temperatures (up to 220–230°C).

With the aim to assess the printability of produced filaments, it was important to investigate some properties, such as the crystallinity (χ) and the C_P, and the effect of the biofiller on them. As shown in Figure S1 (Supplementary Information), DSC thermogram of PLA pellets showed just a stepwise transition, ascribed to

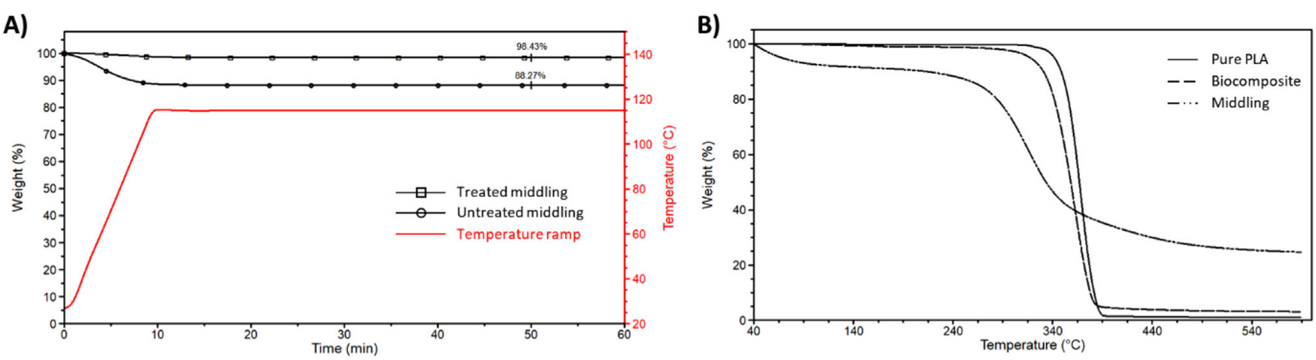

Figure 2. a) TGA thermograms of middling samples before (○) and after (□) drying treatment. b) TGA analysis of biocomposite filament (— • • —) and reference materials: pure PLA filament (——) and biofiller powder (— —). PLA, poly(lactic) acid; TGA, thermogravimetric analysis.

Table 2. Thermal properties of poly(lactic) acid (PLA) pellet and 3D printing filaments.

Sample	T_g [°C]	T_{cc} [°C]	ΔH_{cc} [J g^{-1}]$^{a)}$	T_m [°C]	ΔH_m [J g^{-1}]$^{a)}$	χ [%]	$C_{P,\,30°C}$ [J°C^{-1} g^{-1}]
PLA pellet	60	–	–	–	–	0	–
PLA filament	58	129	6.2 ± 0.2	153	7.0 ± 0.5	1	1.40 ± 0.07
Biocomposite	58	113	29.3 ± 1.3	148/155	31.2 ± 1.0	2	1.23 ± 0.14

a) Cold crystallization and melting enthalpy (ΔH_{cc} and ΔH_m) are normalized with the real polymer content in the composite material.

Table 3. DMA results of 3D printable filaments.

Filament	$E^I_{30°C}$ [GPa]	T_{onset} [°C]	$T_{\tan\delta}$ [°C]
PLA	3.1 ± 0.4	56 ± 1	65 ± 1
Biocomposite	3.2 ± 0.1	62 ± 1	72 ± 1

DMA, dynamic mechanical analysis; PLA, poly(lactic) acid.

the glass transition (T_g), located at around 60°C which kept unaffected by the biofiller addition in PLA matrix. Neat PLA filament, instead, showed, in addition to the T_g, a broad exothermic transition of low intensity at about 130°C, which can be ascribed to the phenomenon of cold crystallization, which is typical of semicrystalline polymers characterized by a low crystallization rate.

This phenomenon is more evident when the biofiller is added: the cold crystallization enthalpy (ΔH_{cc}) increased from 6.2 J g^{-1} for PLA filament to over 29.3 J g^{-1} for biocomposite filament (see **Table 2**). Such a behavior can be ascribed to the nucleating effect of the biofiller. Moreover, such a boost in crystallization process was noticeable also by the decrease of cold crystallization temperature (T_{cc}). Anyway, despite the nucleation effect of the biofiller, all the analyzed materials resulted essentially amorphous in the filament with crystallinity values around 1%.

Moreover, in Table 2 the specific heat coefficients (C_P) of manufactured filament were reported and compared with the reference material. The efficiency of heat dissipation was an important property in 3D printing materials because the presence of a temperature gradient in the 3D printed part during printing process could lead to an inhomogeneous contraction of the material and so, to the warping of the object. As reported in Table 2, specific heat coefficient of biocomposite is lower than pure PLA filament, 1.23 and 1.40 J°C^{-1} g^{-1}, respectively. The addition of the biofiller led to an enhanced thermal conductivity of the composite. Hence, during a printing process the material can cool down in a more homogeneous manner, so that thermal gradients are diminished throughout the specimen. Such a result is very promising for 3D printing process because higher thermal conductivity tends to minimize the warping during the printing process.

The thermo-mechanical performance of the designed material was assessed by DMA on 3D printing filament. At first glance, when wheat grain waste was added to PLA, an upward shift of all thermal signals (i.e., T_{onset} and $T_{\tan\delta}$) at higher temperatures is observed. Indeed reference PLA filament showed a lower T_{onset} and $T_{\tan\delta}$ than the biocomposite (see **Table 3**). Together with a slight increase of the glass transition, a concomitant slight increase of the storage modulus at room temperature ($E^I_{30°C}$) is also observed upon wheat waste load.

3. Conclusions

The present work demonstrates the suitability of wastes deriving from wheat milling process as biofiller in 3D printing materials. Upon the design and optimization of the whole production process, a 3D printable biocomposite filament was obtained and characterized. The designed material showed some variations in terms of thermal properties when compared to the reference material: that is, a slight decrease in thermal stability, a reduction of C_P value, and a strong nucleating effect of the wheat grain waste. Besides these results, the main properties of pure PLA are preserved and, so, the significance of these biocomposites was confirmed with the prosecution of further studies, such as 3D printing tests and designing of new biocomposite formulations.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data will be made available upon request.

Keywords

additive manufacturing, biomaterials, composites, poly(lactic) acid, wheat wastes

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