Tunable FDM 3D printing of flexible poly(butylene adipate terephthalate)-based biocomposite filaments

TUNABLE FDM 3D PRINTING OF FLEXIBLE POLY(BUTYLENE ADIPATE TEREPHTHALATE)-BASED BIOCOMPOSITE FILAMENTS

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Introduction

Poly(butylene adipate-co-terephthalate), PBAT, is a synthetic and 100% biodegradable polymer based on fossil resources, with high elongation at break and high flexibility[1]. These properties are comparable to low-density polyethylene, making PBAT a very promising biodegradable material that could replace it in some industrial applications[2]. However, its lower mechanical properties have limited its application range. The reinforcement of PBAT with rigid filler, such as zein-TiO_2 (ZTC) complex microparticles, has the purpose to expand its application field, especially in the food and agricultural packaging sector.
This study reports on the development of bio-based composite filaments at high ZTC content (5 to 40 wt%), where zein was used to raise the interaction between the filler and the matrix and improve the structural properties of the final composite. These flexible filaments were then 3D printed to produce complex and completely bio-based solid systems, with remarkable bio-compatibility properties, according to the carried-out cytotoxicity tests. The advantages of these eco-friendly materials can thus be combined with the production of customizable design objects by additive manufacturing, with numerous potential applications in biomedical and healthcare research[3].

Results and discussion

ZTC complex was compounded with the polymer at the increasing concentration by solvent casting: 0, 5, 10, 20, and 40 wt% (Figure 1). The biocomposite pellets were injection-molded to obtain model 1BA specimens, according to standard UNI EN ISO 527, for subsequent characterization (Figure 2).

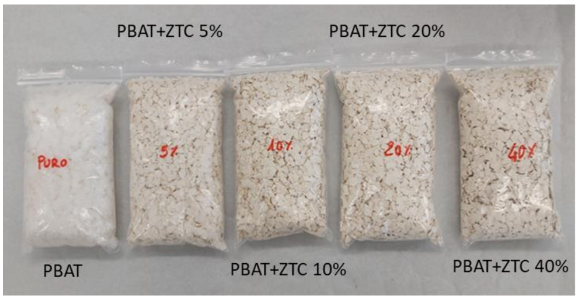


Figure 1. PBAT-based composite pellets at different ZTC content, after solvent casting preparation.

Figure 2. Injection-molded specimens at different ZTC content: from left to right the ZTC wt% varies from 0 to 40% (the dimensional marker is equal to 1 cm).

The PBAT-ZTC pellets were also employed to produce composite filaments for 3D printing through a single screw extrusion system, equipped with a cooling fan array, to cool down the polymer melt, and a spooler, equipped with an optical sensor, to collect the produced filament with a constant diameter (Figure 3). The extruded filaments of pure and loaded PBAT were used for the FDM 3D printing of two types of objects: a scaffold as an example of complex geometry and a ring to macroscopically highlight the possible variations and customization of the mechanical behavior due to the different composite material composition.

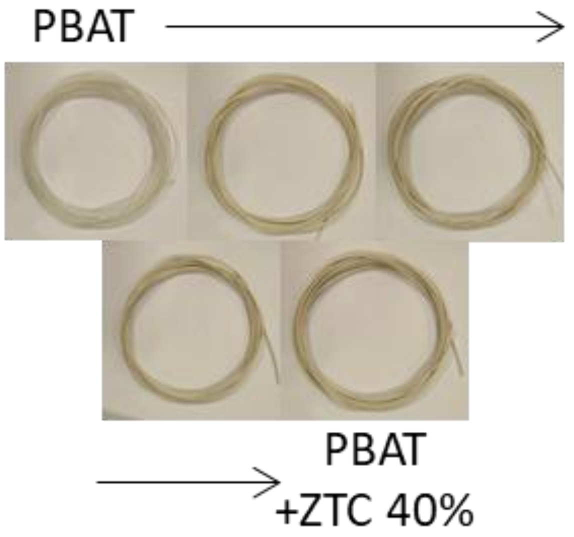
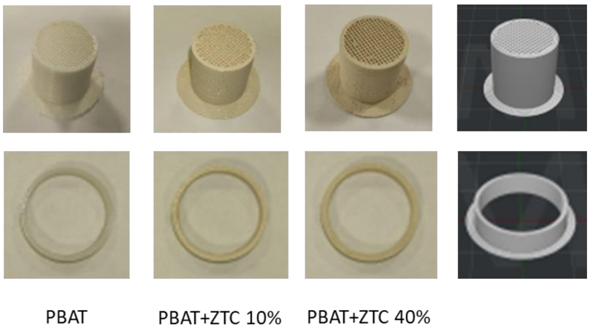


Figure 3. Filaments of pure and ZTC-loaded PBAT (according to the arrow direction, from 5 to 40 wt%).

Results reveal that storage modulus increased with increasing the ZTC content, leading to a slight increase in the glass transition temperature. The creep compliance varies with the ZTC concentration, denoting a better resistance to deformation under constant stress conditions for composites with higher complex content. Scanning electron microscopy was used to assess the quality of interphase adhesion between PBAT and ZTC, showing good dispersion and distribution of complex microparticles in the polymer matrix. Infrared spectroscopy confirmed the formation of a valid interface due to the formation of hydrogen bonds between filler and polymer matrix. Ring structures and cylindrical scaffolds, with the filling pattern obtained by alternating the direction of filament deposition between 0 and 90°, were printed for each composite formulation (Figure 4). The 3D model is also shown on the right of Figure 4.
The printed scaffolds correspond to the designed model from the dimensional and geometric point of view, with similar performances in terms of the filament consistency for the pure PBAT and the PBAT-based composites at different ZTC content. Preliminary tests on the biocompatibility of these materials were also performed, showing no cytotoxic effects on cell viability.



F*igure 4. 3D printed ring structures and cylindrical scaffolds for representative composite formulation (on the right the 3D printed models).*

Conclusions

A successful method for preparing FDM 3D printed PBAT-based biocomposite filaments is described. Different formulations, with reinforcing content up to 40 wt% of ZTC complex, were obtained via the solvent casting approach. The procedure allowed for the effective enhancement of viscoelastic and thermo-mechanical properties of pristine PBAT.
IR spectra revealed the formation of hydrogen bonds between the polymer chains and presumably the protein structures of the ZTC complex, underlining the coupling effect assumed by the zein in increasing the affinity between the PBAT matrix and inorganic filler in the developed composite system. The spectroscopy results confirmed the thermo-mechanical and structural characterizations.
From these composite materials, constant size filaments were experimentally obtained and used for FDM 3D printing of different solid structures.
Preliminary cytotoxicity assay did not show any detrimental effects of PBAT-based composites after direct contact with in vitro cultured HDFs, according to transmitted light microscopy observations and cell viability assay.
Obtained data support the idea that PBAT-based composites with different ZTC content combine the tunable mechanical properties, sustainable eco-designs, and the potential of additive manufacturing properties with short time, direct-contact biocompatibility, paving the way towards wide possibilities of advanced biomedical applications.

References

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