SUPPORTING INFORMATION

PLA–potato thermoplastic starch filament as a sustainable alternative to conventional PLA filament: processing, characterization and FFF 3D printing

Agnieszka Haryńska^{1*}, Helena Janik¹, Maciej Sienkiewicz¹, Barbara Mikolaszek², Justyna Kucińska-Lipka¹

¹ Department of Polymers Technology, Faculty of Chemistry, Gdansk University of Technology (GUT), Narutowicza Street 11/12, 80-233, Gdansk, Poland

² Department of Pharmaceutical Technology, Faculty of Pharmacy, Medical University of Gdansk, Al. Gen. J. Hallera 107, 80-416, Gdansk, Poland

* Correspondence: agnieszka.harynska@pg.edu.pl

Total number of pages: 7 (Page S1-S7) Total number of tables: 5 (Table S1-S5) Total number of figures: 6 (Figure S1-S6)

Contents

| 1. | Preparation of the samples for testing – 3D printing settings, dimentions of samples | 2 |
|----|--|---|
| | Preparation and description of the virtual models (vertebra C1, L3, cancellous bone, gyroid) | |
| 3. | SEM images of the samples during degradation studies in 0.1 M PBS | 4 |
| 4. | Laboratory compost – composition | 5 |
| | SEM images of the samples during laboratory-scale composting test | |
| 6. | Images of printed anatomical models and porous structures | 6 |
| | Description of challenges faced during 3D printing with the PLA/TPS filament | |

1. Preparation of the samples for testing – 3D printing settings, dimentions of samples

 Table S1 3D printing settings of the test samples used for the characterization of both tested materials.

| 3D printing parameter | FF | PLA/TPS | |
|--------------------------------------|--------|---------|--|
| Extrusion temperature (°C) | 215 | 180 | |
| Bed temperature (°C) | | 60 | |
| Cooling | Fan on | | |
| Printing speed (mm s ⁻¹) | | 20 | |
| Layer height (mm) | (|).2 | |
| Nozzle diameter (mm) | (|).4 | |
| Shell number | | 2 | |

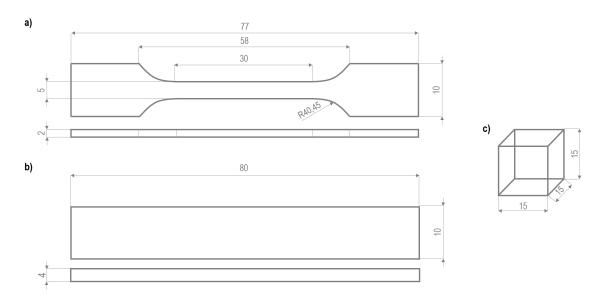


Figure S1 Dimentions of tested samples. a) dumbbell-shaped tensile specimen (ISO 527-2, 1BA), b) Charpy impact test specimen (ISO 179-1, unnotched), c) cubic compression test specimen

2. Preparation and description of the virtual models (vertebra C1, L3, cancellous bone, gyroid)

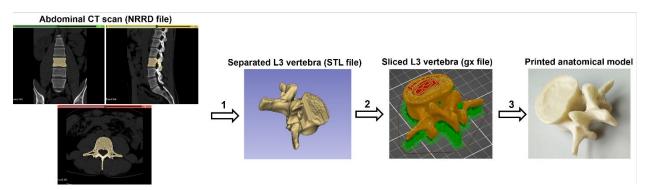


Figure S2 Scheme of the procedure used during the preparation of personalized anatomical models (vertebra C1, and L3). The scale of printouts 1:1

 $1 \rightarrow$ Conversion of CT scan into STL file (segmentation, slicing, modeling)

2 \rightarrow Conversion of STL file into gx code (optimization, assigning printing settings, supports

architecture, slicing)

 $3 \rightarrow 3D$ printing and post-processing/finishing (supports removal, polishing)

Table S2 View of models of porous structures. The gyroid structure was designed in Autodesk Inventor software. The cancellous bone STL file was downloaded from NIH 3D Print Exchange – an opensource community (https://3dprint.nih.gov/).

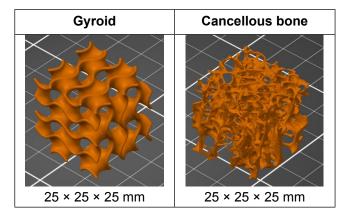
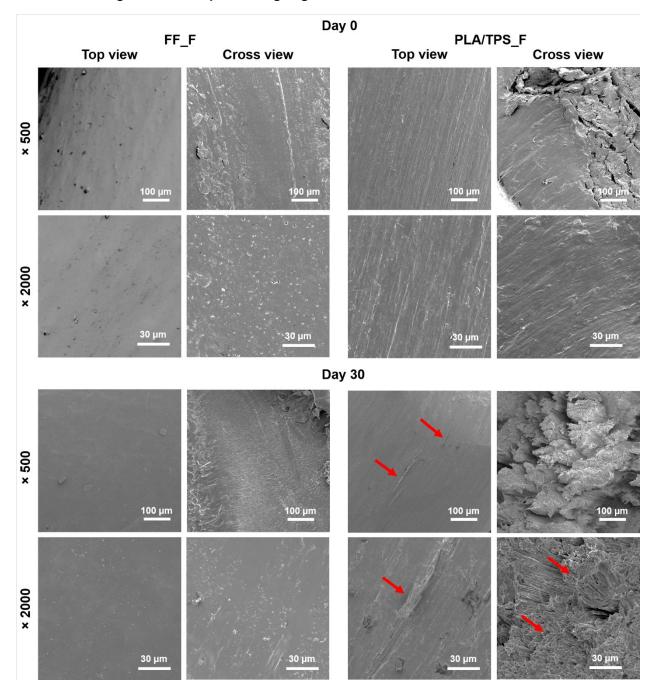


Table S3 3D printing settings of anatomical models and porous structures.

| 3D printing parameter | Vertebra L3 | Vertebra C1 (atlas) | Cancellous bone | Gyroid |
|--------------------------------------|------------------------------------|------------------------|--------------------|-----------|
| Print time | 5 h 30 min | 2 h | 1 h 12 min | 1 h 6 min |
| Used filament (m) | 12.62 | 4.35 | 0.95 | 1.42 |
| Extrusion temperature (°C) | 215(FF) / 185 (PLA/TPS) | | | |
| Bed temperature (°C) | 60 | | | |
| Cooling | Fan on | | | |
| Printing speed (mm s ⁻¹) | Contour 20, Infill 80, Supports 40 | | | |
| Layer height (mm) | 0.18 | | | |
| Nozzle diameter (mm) | | 0.4 | 1 | |



3. SEM images of the samples during degradation studies in 0.1 M PBS

Figure S3 SEM images taken before (day 0) and at the end (day 30) of the degradation studies in 0.1 M PBS solution of FF and PLA/TPS filaments. Top view – the surface of the filament, cross-view – side view of the filament. Red arrows point out the changes in filament morphology during the incubation time (cracks, fibre-like structure).

4. Laboratory compost - composition

| Component | Content (%) |
|---------------|-------------|
| Sawdust | 40 |
| Rabbit food | 30 |
| Compost | 10 |
| Potato starch | 10 |
| Sugar | 5 |
| Canola oil | 4 |
| Urea | 1 |
| All | 100 |
| + Water | 55 |

 Table S4 Composition of laboratory compost (EN ISO 20200:2015)

5. SEM images of the samples during laboratory-scale composting test

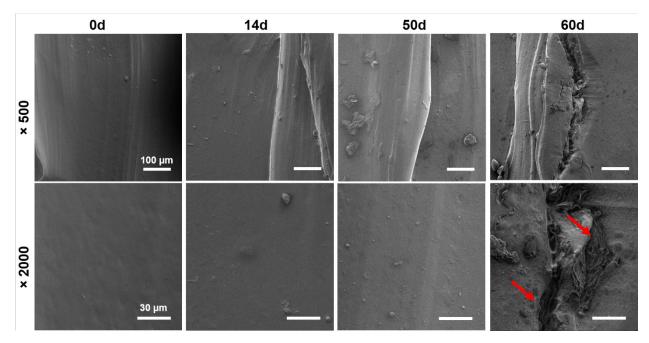


Figure S4 SEM images of the FF_P during a laboratory-scale composting test. The red arrows indicate cracks in the surface of the sample formed during the composting process.

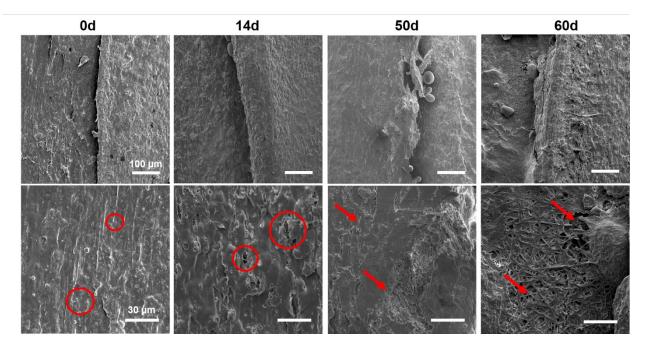


Figure S5 SEM images of the PLA/TPS_P during a laboratory-scale composting test. The red circles show the TPS granules distributed in the PLA matrix (0d) and the places of TPS cavities (14d). The red arrows represent changes in the morphology of the sample, which remained during the composting process (pinholes, cracks, cavities).

6. Images of printed anatomical models and porous structures

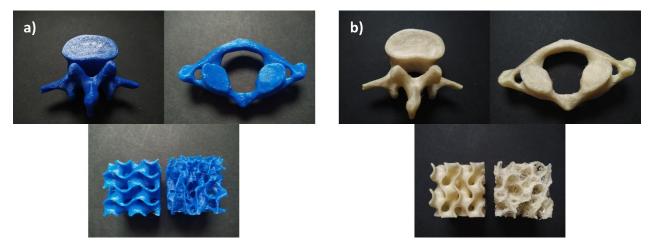


Figure S6 The view of printed with (a) FF_F and (b) PLA/TPS_F anatomical models and porous structures.

7. Description of challenges faced during 3D printing with the PLA/TPS filament

Table S5 Observations recorded during the optimization of 3D printing parameters of the PLA/TPS filament.

| Issue | Comment |
|-----------------------------|---|
| Printing temperature | The temperature range was set to 180-185°C which corresponds to a relatively narrow printing temperature range. This is due to the two-component nature of the PLA/TPS filament. Below the temperature of 180°C, the nozzle becomes clogged with insufficiently molten PLA, while above 185°C, the degradation of the TPS occurs (the glycerin contained in it begins to evaporate, the filament is destabilized, and thus deforming the printout). |
| Printing speed | The optimal printing speed was set to 5-40 mm s ⁻¹ . The underextrussion phenomenon (gaps between the layers of the printed object) take places at a higher print speed. The filament slips on the drive gear, resulting in the irregular feeding of the material. |
| Adhesion to the build plate | Printouts adhere well to the build plate – the use of glue is not necessary. However, when printing complex structures, it is recommended to heat the build plate to temperature of 60°C. |
| Shrinkage effect | High dimensional tolerance of the printed objects. Shrinkage effect negligible. |
| Cooling the printout | It is highly recommended to cool the printout during printing (fan on). |