Preparation of biodegradable PLA/PCL composite filaments: effect of PLA content on strength

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Abstract: As one of the predominant 3D additive manufacturing technology, fused deposition modeling (FDM) suffers from the rich printable filaments. The goal of this paper is to produce a fully biodegradable polymeric composite filament by blending polylactic acid (PLA) with polycaprolactone (PCL). The effect of PCL content on the geometry, size, roughness and ultimate tensile stress of PLA/PCL composite filaments was investigated, and mechanical properties of the printed components were tested. The results indicate that, with the increase of PCL content, the diameter and ultimate tensile stress gradually decreased, while the surface roughness gradually increased. Due to the toughing effect, with an increase in PCL content, the tensile strength of parts decreased, while the elongation at break and the impact strength kept rising. It was found the parts printed with the addition of 20% of PCL composite filament exhibits the optimal comprehensive performance.

1. Introduction
Among available 3D additive manufacturing technologies, the fused deposition modeling (FDM) has attracted increasing attention from industry and researchers [1, 2]. However, the lack of rich printable materials is a bottleneck restricting its development [3]. Many efforts have been devoted to develop new printable filaments for the FDM technology based on the polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS), which are the two most important printing wires at present. For instance, Carmen et al [4] used styrene ethylene butadiene styrene (SEBS) and ultrahigh-molecular-weight polyethylene (UHMWPE) to produce ABS-based binary and ternary polymer blends for 3D printing platforms. Castles et al [5] prepared BaTiO₃/ABS composite wires and investigated the microwave dielectric characterization of the printed parts. Carbon nanotubes and metal nanoparticles were also used to fabricate composite filaments with tailored mechanical properties [6, 7].

In this work, biodegradable polycaprolactone (PCL) was used to modify PLA and produce polymer composite filaments, which could be completely degradable. Although there some reports regarding the modification of PLA with PCL, these works were not extended to filament manufacturing for 3D printing. While PCL itself was already widely explored and used in printing wires, its low melting temperature limited its application in the 3D printing field. Blending PCL with PLA, however, can combine the excellent processing fluidity and toughness of PCL with the good mechanical properties of PLA, and seems to have brilliant prospects in biomedical applications. In this paper, the effect of PCL content on the geometry, size, roughness, and ultimate tensile stress (UTS) of PCL/PLA composite...
filaments was studied. The mechanical properties of printed parts made from PLA/PCL composite filaments were investigated and discussed in detail.

2. Experimental

2.1. Preparation of PLA/PCL blends
PLA (4032D type) was purchased from Nature Works, US. PCL (6800 type) was purchased from Solvay, US. Pellets were first dried at 45 °C for 24h. Then, PLA/PCL blends were prepared using a SJ20 single-screw extruder (Wuhan Yiyang Company, China). A series of PLA/PCL blends with various PCL ratios (0, 10, 20, 30, and 40%) were obtained.

2.2. Fabrication of PLA/PCL composite filaments
A Wellzoom-B desktop extruder (Shenzhen Misida Technology Company, China) was used to fabricate filaments with PLA/PCL blends obtained above. To obtain qualified filaments with a diameter of 1.75±0.1 mm, different extrusion parameters were determined for each PLA/PCL blend.

Table 1. 3D print parameters used for parts with PLA/PCL composite filaments

| Sample (PCL%) | T_e(°C) | B(mm) | S(mm/s) | F(%) |
|---------------|---------|-------|---------|------|
| 0             | 220     | 0.1   | 60      | 100  |
| 10            | 220     | 0.1   | 60      | 100  |
| 20            | 210     | 0.1   | 60      | 100  |
| 30            | 210     | 0.1   | 60      | 100  |
| 40            | 200     | 0.1   | 60      | 100  |

2.3. Printing of testing parts
Test samples were printed by a Makerpi-M2030 FDM 3D printer (Shenzhen Long River Technology Company, China), with PLA/PCL composite filaments. The printing parameters used are shown in table 1, where T_e, B, S, and F are the extruder temperature, build layer, extruding and filling rates, respectively.

2.4. Measurements and characterization
A digital vernier calipers (MNT, China) was used to measure the diameter of the monofilament. Five filaments were measured and their results were averaged as the final diameter of the sample. Surface roughness of the filaments was measured by a SJ-201 SurfTest (Mitutoyo, Japan). The ultimate tensile stress testing was conducted with a Sansi stretcher at room temperature with a 2mm/s stretching speed. The ultimate tensile stress was calculated based on the following equation: \( \sigma = \frac{F}{S} \), where F is the ultimate tensile force and S is the fractured filament cross-sectional area. The morphology of PLA/PCL was observed using a S-4800 type field-emission scanning electron microscope (FESEM, Hitachi Co., Japan) with a 15 KV accelerating voltage. Mechanical properties of printed parts were tested via a 4466-type universal testing machine (Instron, US) and a B5113-type Izod impact testing machine (Zwick/Roell, Germany).

3. Results and discussion

3.1. Effect of PCL content on the diameter of PLA/PCL composite filaments
During the fabrication, it was found that with an increase in PCL content, the diameter of PLA/PCL composite filaments decreases gradually, while the uniformity becomes worse (as shown in Figure 1). This is because the PCL addition reduces the melt point of the blending system [8], leading to a lower melt viscosity and better melt fluidity, which finally results in the decreased diameter and higher
dimension error after cooling down. In addition, the dilution and structural effects also contribute to the decrease of melting point of the PLA / PCL blending system. [9,10]

![Figure 1. Diameters of obtained filaments](image1.png)

![Figure 2. The surface roughness of filaments](image2.png)

![Figure 3. SEM micrographs of fracture surfaces of filaments with various PCL contents](image3.png)
3.2. Effect of PCL content on the surface roughness of PLA/PCL composite filaments

As shown in Figure 2, the surface roughness of PLA/PCL composite filaments gradually increases with the PCL content. This may result from the microphase separation of the blending system, which gradually increases with the PCL content. As seen in Figure 3b-e, PLA/PCL mixtures exhibit a typical “sea-island” structure, and the PCL phase is dispersed in the PLA matrix as micrometer-sized spheres. With an increase in PCL content, the PCL particle size also increases, and the two-phase interface becomes more pronounced. Similar results were observed by Han et al. for PLA/TPU blends [11]. The effect of coalescence of the droplet agglomeration during melt mixing also resulted in a slight ruggedness of the filament surface [12].

3.3 Effect of PCL content on UTS of PLA/PCL composite filament

The ultimate tensile strength (UTS) of filaments is crucial for its applications. Considering the continuity of printing, the filament should not be too fragile, otherwise it is vulnerable to fracture during printing. As shown in Figure 4, the UTS of PLA/PCL composite filaments gradually drops with the PCL content. A possible reason is the reduction of the crystallinity of PLA/PCL blends, resulting from the addition of PCL, which affects the strength of PLA/PCL composite filaments [13,14].

![Figure 4. The UTS of filaments with different PCL contents.](image)

3.4 Effect of PCL content on mechanical properties of 3D-printed parts

The mechanical properties of printed parts are very important for their practical application. Figure 5a shows the tensile strength of printed parts. As can be seen, the tensile strength gradually drops with the PCL content, probably due to crystallinity reduction of PLA/PCL blends, which reduces the strength of blends. Figure 5(b, c) shows the elongation at break and the corresponding impact strength of PLA/PCL blends. It can be seen that, both the elongation at break and impact strength of PLA/PCL blends gradually increase with the PCL content. This is due to the toughing effect of dispersed PCL particles.

![Figure 5. Effect of PCL content on mechanical properties of parts printed with various contents of PCL.](image)
in PLA matrix, which can improve the plastic deformation of blends, leading to an improvement of stretching and impact processes.

The toughing effect of PLA by addition of PCL can be seen in Figure 6. The impact section of neat PLA is very smooth and exhibits a typical brittle fracture. With an increase in PCL content, it can be seen in Figure 6(b-e) that the impact section of blends starts to exhibit numerous wrinkled protrusions, which number gradually increases with the PCL content. Therefore, PLA toughness has been effectively improved with the addition of PCL.

Figure 6. SEM micrographs of the impact section of parts printed with various PCL contents: a)0; b)10%; c) 20%; d) 30%; e) 40%
4. Conclusions
Biodegradable polymeric composite filaments of PLA/PCL were fabricated in this study. The effect of PCL content on the geometry, size, surface roughness, and ultimate tensile stress of the obtained composite filaments were examined, and the mechanical properties of parts printed by the FDM technology were investigated. It was found that the diameter and ultimate tensile stress gradually decreased and the surface roughness gradually increased with the PCL content. Due to the toughing effect, the tensile strength of printed parts deteriorated, while the elongation at break and the impact strength kept increasing with the PCL content. It was found the parts printed with the addition of 20% of PCL composite filament had excellent comprehensive performance. The developed PLA/PCL composite filaments have potential applications in biomedical fields, especially tissue engineering.

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