DIRECT INK WRITING OF MICROSTRUCTURED BIOCERAMICS

P. DEE [1], S. TAN[1], H. LE FERRAND[1]

1 : School of Mechanical and Aerospace Engineering, 50 Nanyang Avenue, Nanyang Technological University, 639798, Singapore
hortense@ntu.edu.sg

Introduction

Biological ceramic materials have intricate microstructures giving outstanding mechanical properties. Current 3D printing techniques of bioactive ceramics do not provide microstructure control [1]. Here, we develop a water-based ink containing calcium phosphate (CaP) microplatelets and use direct ink writing (DIW) to build 3D structures with local microstructure. Although the CaP ink has a low storage modulus, extrusion onto a water-absorbent substrate enables shape retention and buildability. The shear stresses developed during extrusion align the CaP microplatelets to form filaments with a core-shell microstructure. Custom-shaped bioactive ceramics with complex microstructure obtained through our printing method has potential applications in orthopaedics.

Rheology and Direct Ink Writing (DIW) of inks composed of CaP microplatelets

Rheological properties of water-based inks with CaP microplatelets

Our inks consist of an anionic surfactant (Dolapix CE 64) as dispersant, synthesized CaP microplatelets ($CaHPO_4{\cdot}2H_2O$, length ~10 µm, thickness ~14 nm), and 7 wt% polyvinylpyrrolidone (MW ~360000) w.r.t. water as binder.

Unlike conventional inks used in DIW, all inks with 16 to 27 vol% CaP have $G' < G''$, with no crossover point (Fig. 1a). Yet, the inks displayed shear-thinning property. Their viscosities were fitted with the Herschel-Bulkley equation (Fig. 1b). Inks containing 21% CaP or more can be extruded into continuous lines and support additional layers (Fig. 1c).

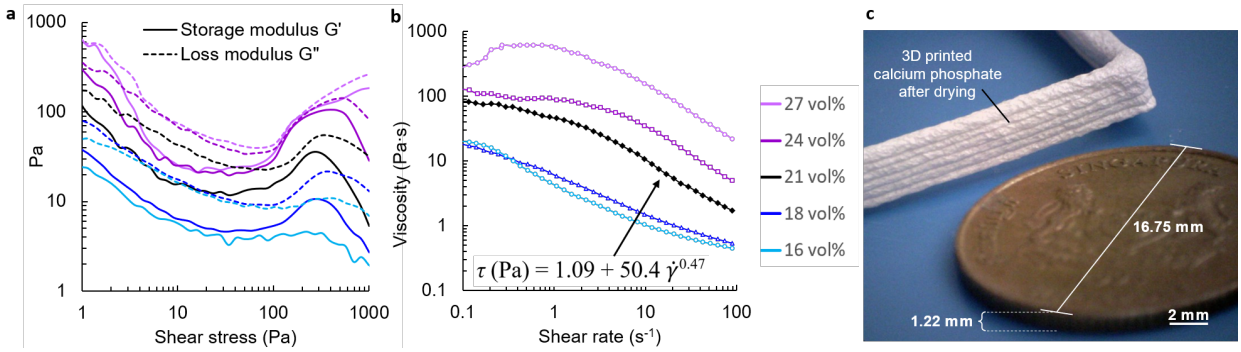

Fig. 1 – (a-b) Rheological curves of inks comprising 16 to 27 vol% CaP. In (b), the equation corresponds to the Herschel-Bulkley model for the ink with 21 vol% CaP. (c) Optical image of CaP printed from 21 vol% CaP ink, placed next to a Singapore 5-cent coin.

Direct ink writing of the ink containing 21 vol% CaP microplatelets

Tapered nozzles (Nordson) of inner diameter d = 0.41, 0.58, 0.84, 1.19 and 1.60 mm were used. A porous, flat piece of gypsum was used as the printing substrate. Upon extrusion (3D PotterBot Micro 8) onto the gypsum substrate, the water from the ink is rapidly absorbed, increasing the solid loading of the printed filament and maintaining its shape. After drying overnight, the 3D printed green parts were calcined at 900°C to yield a stiff, consolidated part.

The cross-section of filaments was examined (Fig. 2a, 2b). The filament size A was observed to increase linearly with nozzle diameter and flow rate multiplier (Fig. 2c). Since the post-calcination volume can be estimated, the desired print resolution may be achieved by choosing a reasonable nozzle and calculating the flow rate required.

Microstructure of printed CaP parts

The cross-section of the filaments revealed a core-shell microstructure (Fig. 3a). During extrusion, the shear stresses in the nozzle aligned the microplatelets tangentially [2,3], especially those close to the filament edge (Fig. 2b, 2d). At the core of the filaments, microplatelets under plug flow exhibited poor alignment. The relative core size remained constant with the printing speed (1 to 10 mm/s), the nozzle size [2], and the flow rate.

As a result of the gradient change in microplatelet orientation (Fig. 2b, 2d), the cracked surfaces of printed filaments would be either concave (Fig. 2a) or convex. In multi-layer prints, the gradient microstructure was maintained (Fig. 2e). Furthermore, bulk parts displayed good interlayer bonding. Designing the microstructure of calcium phosphate parts could enable control of the crack path as a toughening mechanism.

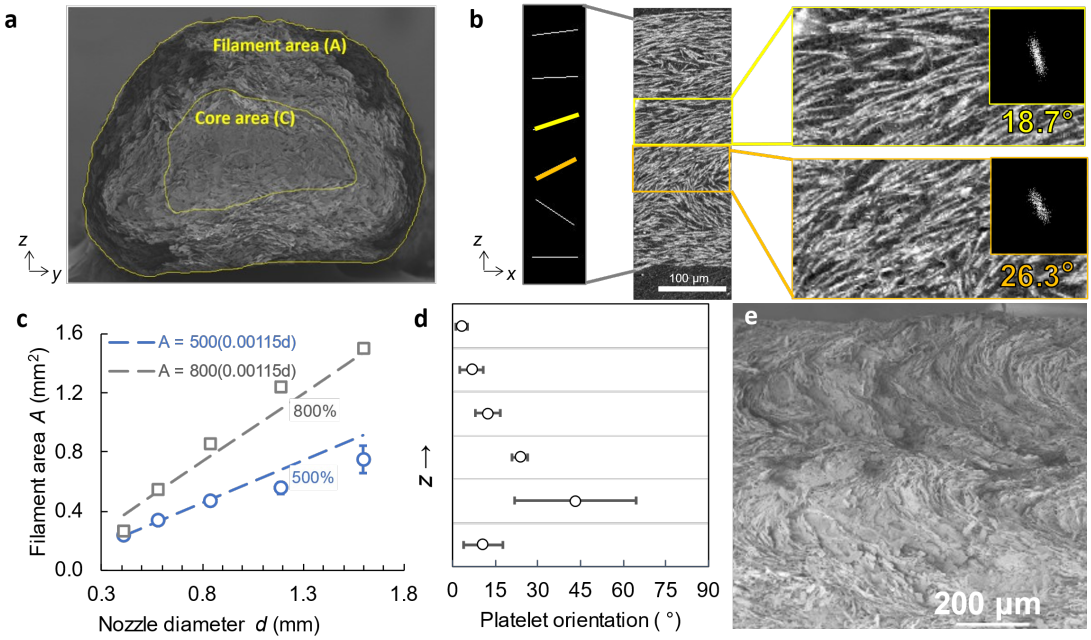

Fig. 2 (a) Filament cross-section showing concave fracture surface. (b) Gradient platelet orientation in filament. (c) Filament cross-section area at flow rate multiplier 500% and 800%. (d) Typical platelet orientation in a filament. (e) Gradient microstructure in multi-layer structure.

Conclusion

In this work, we developed a water-based ink containing at least 21 vol% in CaP microplalelets, which is printable by direct ink writing, despite its low storage modulus and low viscosity <100 Pa·s. Shear stresses during extrusion impart tangential alignment of the microplatelets in the filaments, leading to a core-shell microstructure. The print resolution can be tuned by the nozzle size and flow rate multiplier without affecting this microstructure. Multilayer constructs can be thus be 3D printed to yield microstructured bioactive ceramics similar to biological ceramic materials. This simple direct ink writing method could enable fabrication of new bioceramic materials designed to prevent brittle failure in biomedical applications.

References

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