Extrusion Increases the Mechanical Properties of 3D-Printable Nanocomposite Biomaterials

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Introduction

- Critically-sized segmental bone defects (CSBDs) are too large for a patient's own body to heal [1].
- Repair and reconstruction of CSBDs requires grafts with excellent mechanical properties to restore function and provide durability [2].
- Nanocomposites of functional biopolymer matrices reinforced with bioactive nanoparticles have potential for CSBD repair [3].
- Extrusion-based direct ink writing (DIW) is a fast and versatile 3D printing technique that involves extruding continuous "ink" filaments through a nozzle in a layer-by-layer scheme to fabricate complex 3D multi-scale objects with design-specific features [4].
- We studied the tensile mechanical properties of nanocomposites composed of nanohydroxyapatite (nHA), acrylated epoxidized soybean oil (AESO) and polyethylene glycol diacrylate (PEGDA).
- **Hypothesis:** Nanocomposite filaments extruded through smaller diameter needles would display greater strengths, consistent with Griffith's theory of brittle fracture [5].
- The **Objectives** of this study were:
  a) To evaluate the change of tensile mechanical properties of our nanocomposites when varying the extrusion diameter, and
  b) To evaluate how shear-induce extrusion affects the micro-scale and smaller structure of the nanocomposites.

Materials & Methods

- nHA (rod-shaped 120 x 40 nm, MKnano Inc. Canada) particles were dispersed in ethanol by ultrasonic homogenization for 15 min.
- AESO and PEGDA (Sigma Aldrich Co.) were added to the mixture and dispersed for another 5 min. 30 vol% of nHA with 49 vol% AESO and 21 vol% PEGDA. Irgacure 819 photoinitiator was used for UV curing. The mixture was kept under reduced pressure to remove the ethanol.
- The nanocomposite 'ink' was cast into molds and cured using UV light (385nm, Dymax, USA) to prepare dog-bone shaped tensile test specimens as control. The nanocomposite filaments were extruded using a metal syringe extruder on a Hyrel 30M (Hyrel Inc., USA) 3D printer and UV cured instantly. Single filaments were prepared by extruding through 0.84, 0.6, 0.41, 0.26 and 0.21 mm diameter needles.
- Enthalpy of melting was measured by conducting DSC using a TA Q2000 (TA instruments Inc., New Castle, DE). As prepared filaments were weighed (8 ± 1 mg) and heated from −20 °C to 300 °C at 5 °C/min. Enthalpy of melting was calculated as the area under the melting endotherm region of heat flow versus temperature curves.
- Tensile testing was performed using a Psylotech µTS (Psylotech Inc., USA) and strain was measured using microscope-enabled digital image correlation.Toughness was measured by calculating the area under the stress-strain curve. Fracture surfaces were imaged using scanning electron microscope (SEM) (FEI Quanta FEG250)
- Data are presented as mean ± SD, analyzed using GraphPad Prism 6.0 (GraphPad Software Inc., CA, USA). Means were compared using one-way ANOVA followed by Tukey's multiple comparison test. Differences between means were considered statistically significant at $p < 0.05$ and indicted with different lower case letters

Results and Discussion

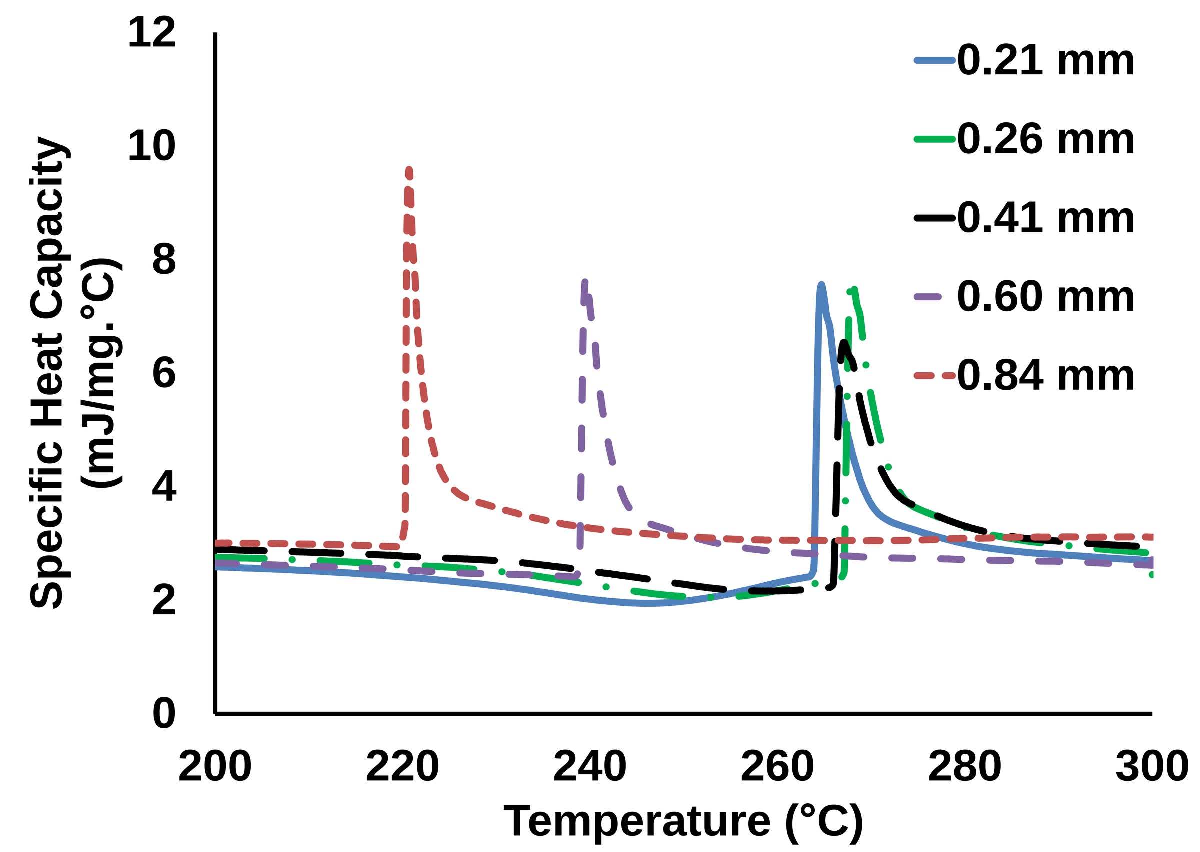

Fig. 1A: Specific heat capacity of extruded filaments analyzed using DSC. Note the increasing of melting temperatures with decreasing needle diameters.

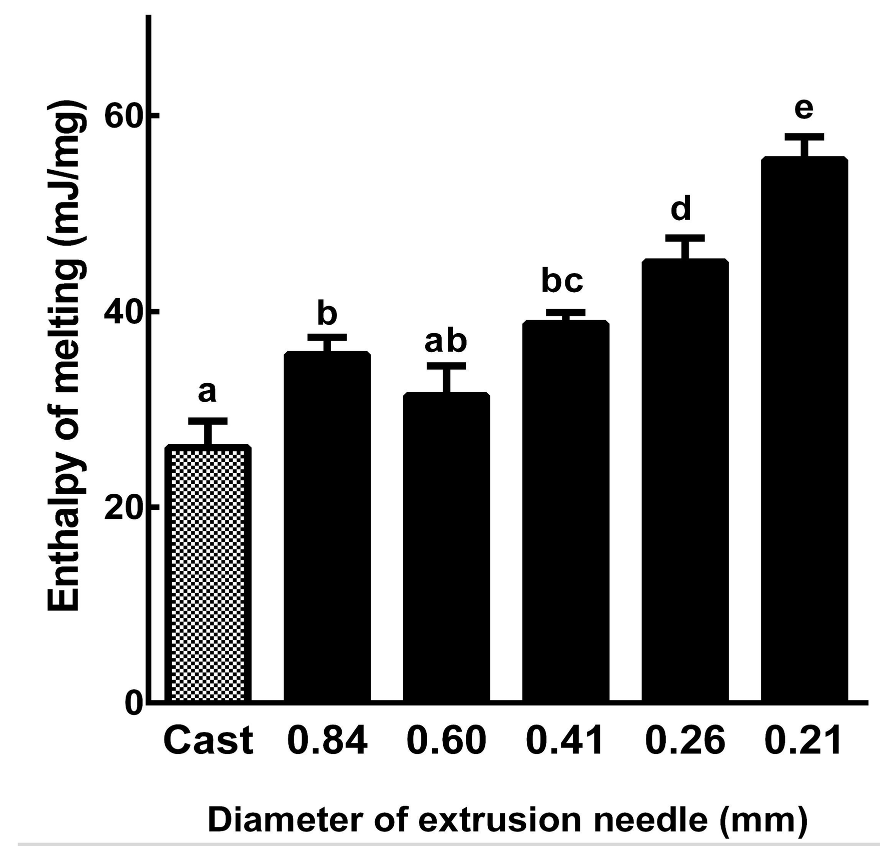

Fig. 1B: Enthalpy of melting of extruded filaments analyzed using DSC. Enthalpy values increased as filament diameters decreased.

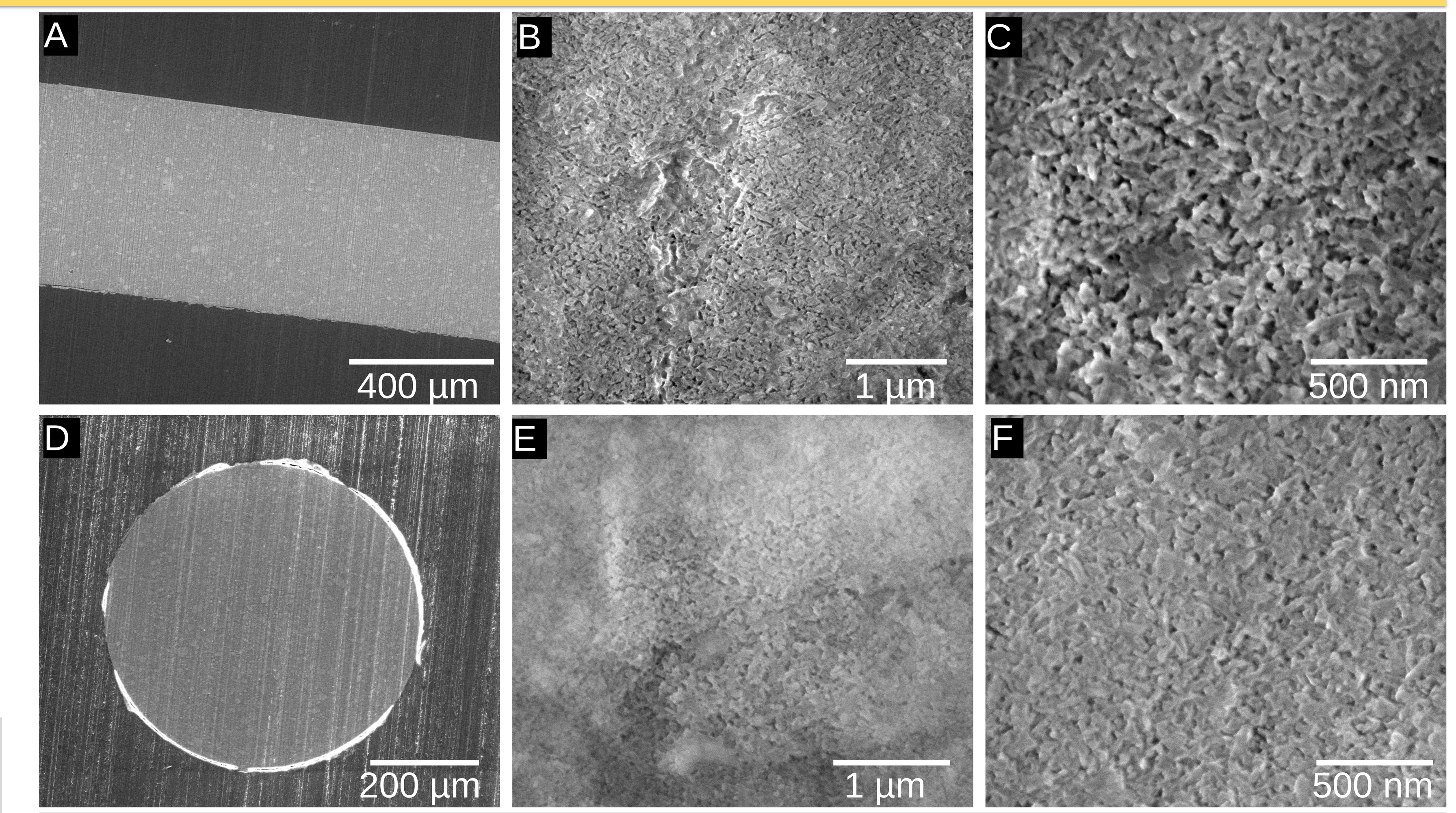

Fig. 2: Representative SEM images of extruded filaments indicated homogenous dispersion of nHA. A-C) longitudinal cross-sections; D-F) transverse cross-sections.

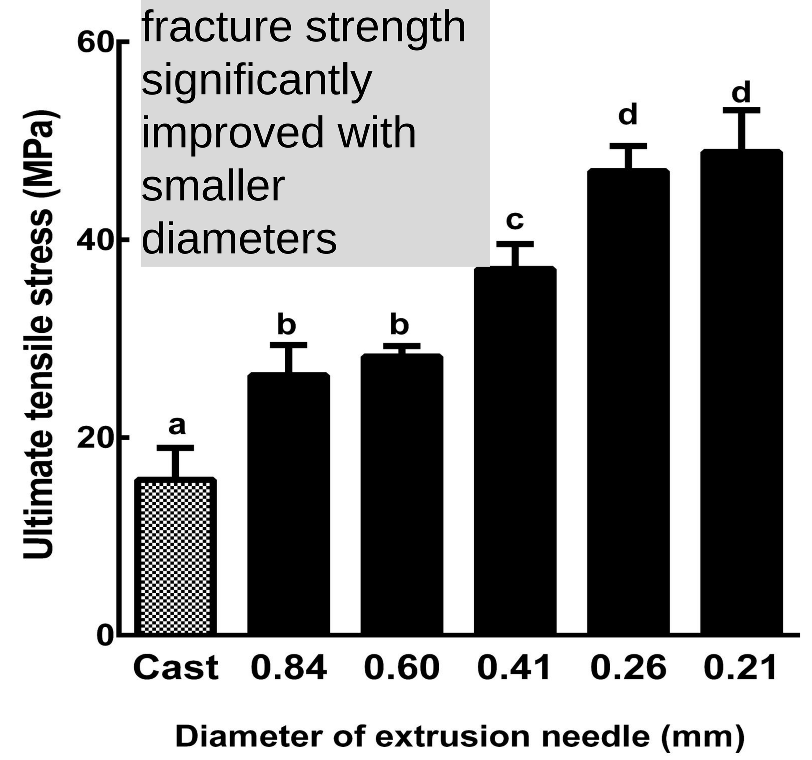

Fig. 3A: Tensile fracture strength significantly improved with smaller diameters

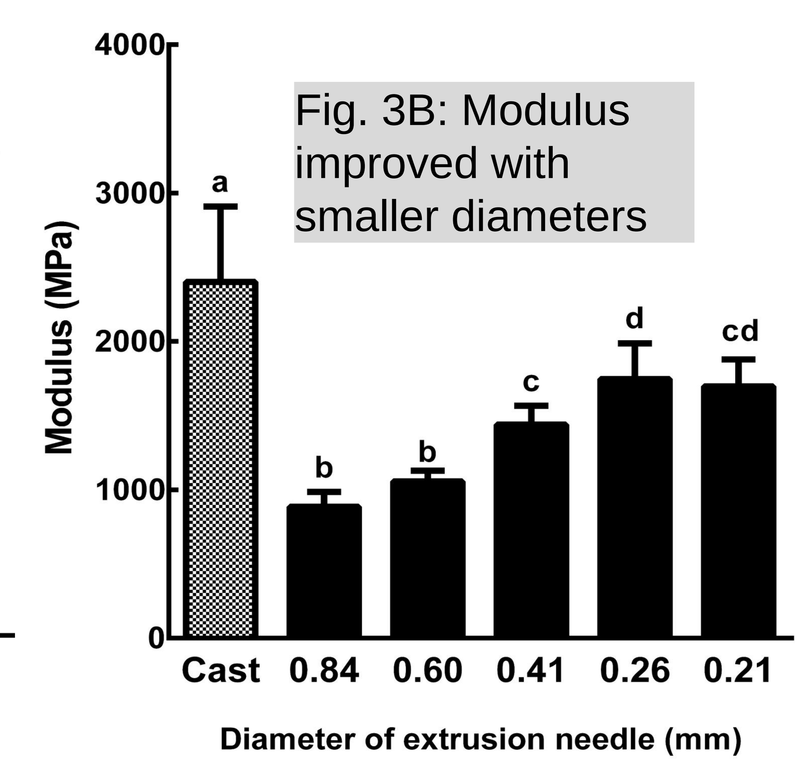

Fig. 3B: Modulus improved with smaller diameters

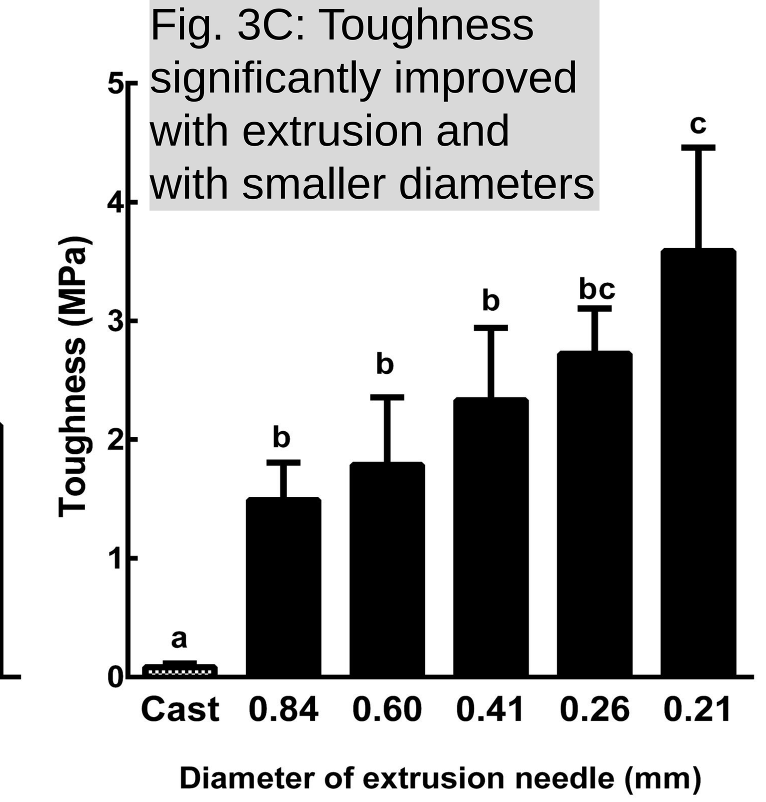

Fig. 3C: Toughness significantly improved with extrusion and with smaller diameters

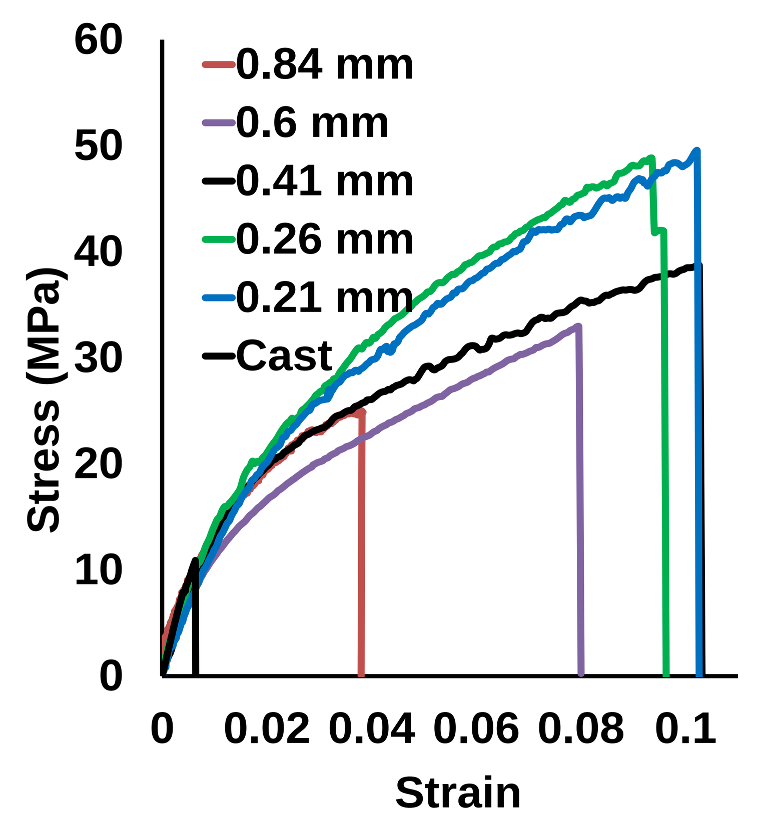

Fig. 3D: Representative Stress-Strain Curves

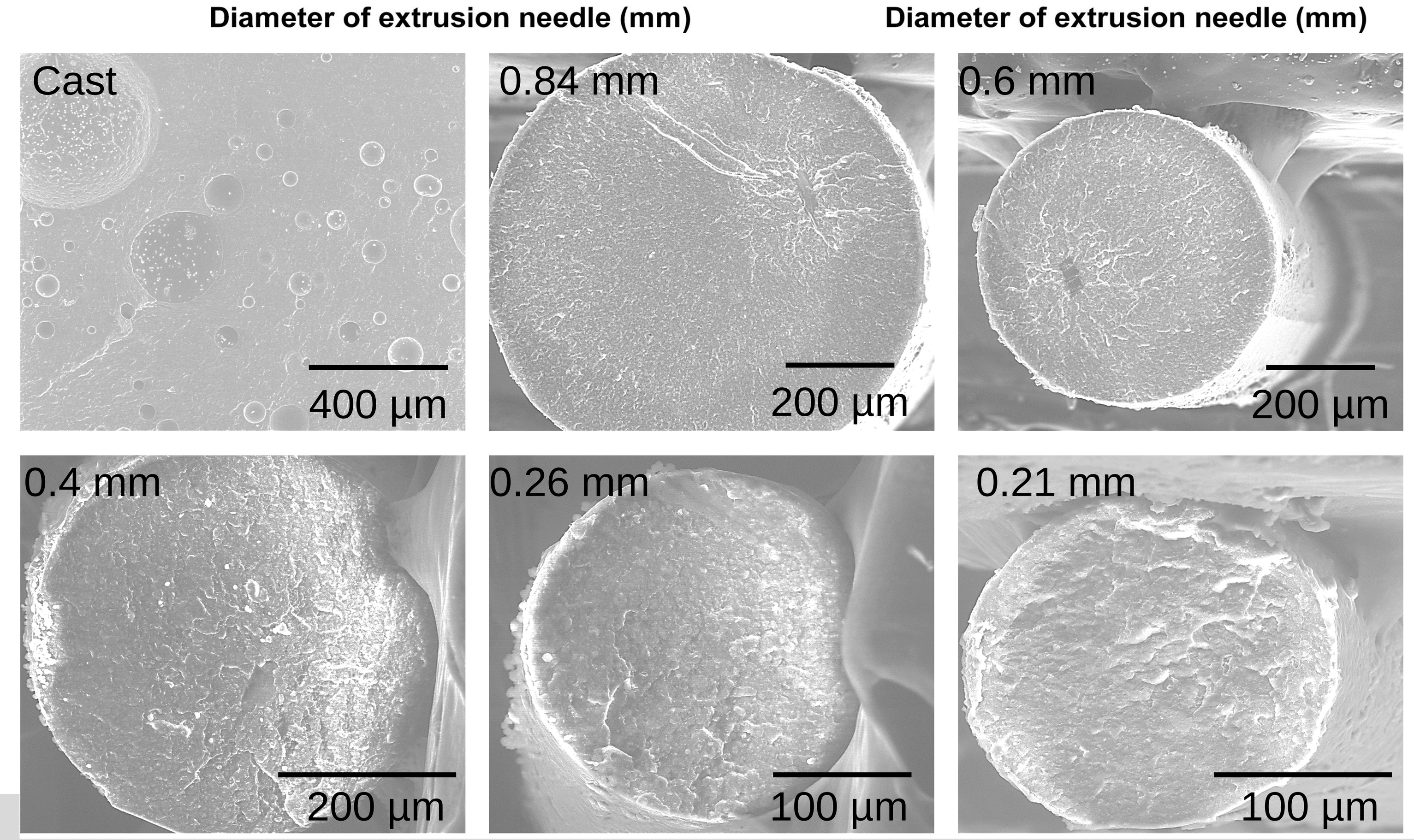

Fig. 4: Representative SEM images of fracture surfaces. Note the presence of spherical defects in the cast specimen, which are absent in the filaments

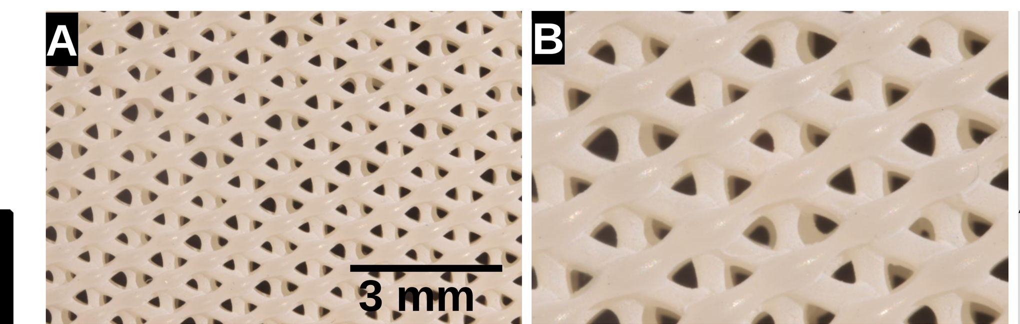

Fig. 5: Extrusion-based 3D printing of scaffolds for bone regeneration: A) low and B) high magnification

Summary & Conclusion

- This study demonstrates a novel 3D printable nanocomposite biomaterial and the possibility of achieving greater mechanical properties by extruding the uncured nanocomposite biomaterial through small diameter nozzles during DIW.
- The increase of tensile strength from decreasing extrusion diameter is a result of reducing the number of defects in the material and inducing semi-crystallinity in the polymer matrix.
- Higher tensile strength and toughness values may be the result of crystallite formation due to the shear applied during extrusion.
- The ultimate tensile stress values were increased 2-fold when the extrusion needle diameter was reduced by a factor of 4.

References

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CIHR IRSC Canadian Institutes of Health Research / Instituts de recherche en santé du Canada
NSERC CRSNG

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