Solvent-cast 3D Printing with Different Molecular Weight Polymers

Tyler R. French[1], John W. Tolbert[1], Lesley W. Chow[1,2]

[1]Department of Materials Science and Engineering, [2]Department of Bioengineering
Lehigh University, Bethlehem, PA 18015, USA

Introduction

- Solvent cast 3D printing (SCP) is a novel printing technique that uses "inks" containing a polymer dissolved in a volatile solvent
- Printing with different molecular weight (MW) polymers enables us to modify mechanical properties without changing polymer type or scaffold architecture
- This project centers on characterizing how printing polymer molecular weight affects the mechanical properties of SCP scaffolds

Methods

- **Ink Formulation:** 370 mg/mL poly(caprolactone) (PCL) total dissolved in hexafluoroisopropanol (HFIP) at three ratios of 80 kDa:25 kDa by weight: 100:0, 90:10, and 80:20
- **Printing:** Inks 3D-printed with a customized Nordson EV printer with 32-gauge needle (inner diameter = 100 µm) at 70 psi or 56 psi depending on ink viscosity and line speeds of 0.4 mm/s for the first layer and 0.2 mm/s for subsequent layers
- **Rheology:** Inks were tested at room temperature at shear rates of 5 s^{-1} and 9 s^{-1} using a TA Instruments Discovery Hybrid Rheometer-2 with a modified parallel plate
- **Fiber Diameter:** Scaffolds were sputter-coated with iridium and imaged using a Hitachi 3500 scanning electron microscope (SEM). Fiber diameter were measured using the open-source program ImageJ.
- **Tensile Testing:** Arrays with 25 filaments (length = 60 mm) were printed and mounted on paper guides before testing on a Zwick/Roell Tensile Tester with a crosshead speed of 25 mm/min and 100 N load cell.

Rheological Characterization of Ink Viscosity

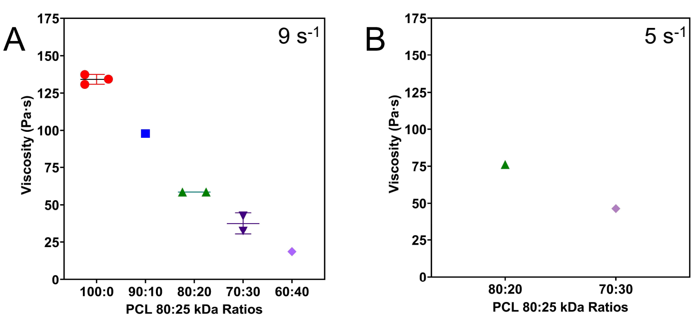
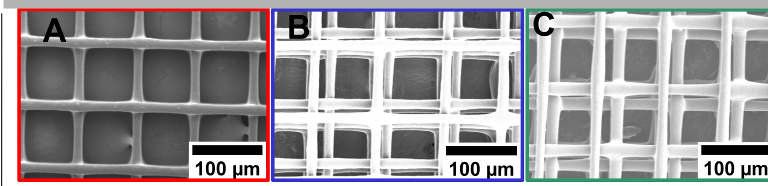


Figure 1: Viscosity (Pa·s) of inks containing different ratios of 80 and 25 kDa PCL at shear rates of (A) 9 s^{-1} and (B) 5 s^{-1} (N=1-3)

- Ink viscosity was matched to a predetermined set of print pressure and print speed to ensure consistent scaffold morphology across groups[1]
- Shear rates 5 s^{-1} and 9 s^{-1} correspond to print pressures 56 psi and 70 psi, respectively
- The viscosity of the 90:10 and 80:20 inks at 5 s^{-1} showed a lower viscosity and were therefore printed at a lower pressure based on prior work
- Viscosity of inks with 70:30 and 60:40 ratios were too low for printing and were not included in subsequent experiments

Scaffold Architecture and Filament Diameter



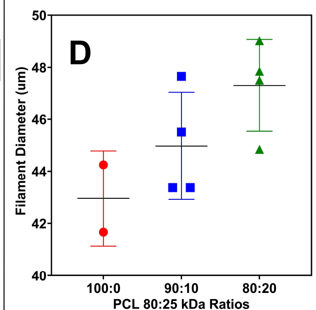


Figure 2: SEM images of (A) 100:0 (B) 90:10, and (C) 80:20 scaffolds. (D) Filament diameters measured for 100:0, 90:10, and 80:20 scaffolds (N=2-4).

- Overall scaffold architecture similar between groups with small differences likely due to deformation during SEM sample preparation
- Filament morphology was similar across the different scaffold groups
- The filament diameter increased as the viscosity of the inks decreased

Filament Stiffness

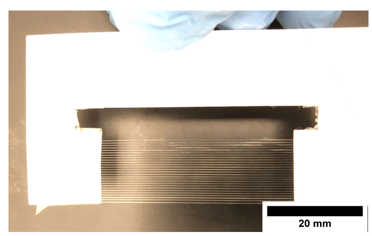


Figure 3: Macroscopic image of filament arrays in a paper guide for tensile testing.

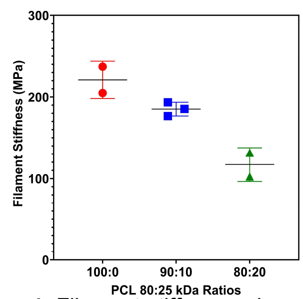


Figure 4: Filament stiffness values (MPa) for 100:0, 90:10, and 80:20 ratios (N=2-3)

- Increasing 25 kDa PCL content in the ink decreased filament stiffness
- Data shows that blending higher and lower MW species affects mechanical properties

Conclusions and Future Work

- 80 kDa and 25 kDa PCL blends can be successfully printed using SCP
- Ink viscosity was used to identify optimal print parameters
- Filament morphology and diameter did not significantly change across different ink formulations
- Increasing amount of lower MW PCL reduced filament stiffness overall
- **Future work:**
  - Increase sample size for all experiments
  - Perform microindentation of bulk scaffolds
  - Blend with other MWs to expand range of mechanical properties

References: (1) J. W. Tolbert, D. E. Hammerstone, N. Yuchimiuk, J. E. Seppala, L. W. Chow, *Macromol Materials Engineering,* 2100442, 2021

Acknowledgement(s):

David and Lorraine Freed Undergraduate Research Symposium as well as Lehigh's Electron Microscopy and Nanofabrication Facility and Polymer Characterization Facilities. Polymers were generously provided by Polyscienced, Inc. This work was supported by the National Science Foundation (NSF) through a Faculty Early Career Development (CAREER) award (DMR 1944914 to LWC) and start-up funds from Lehigh University awarded to LWC

LEHIGH UNIVERSITY | P.C. ROSSIN COLLEGE OF ENGINEERING AND APPLIED SCIENCE