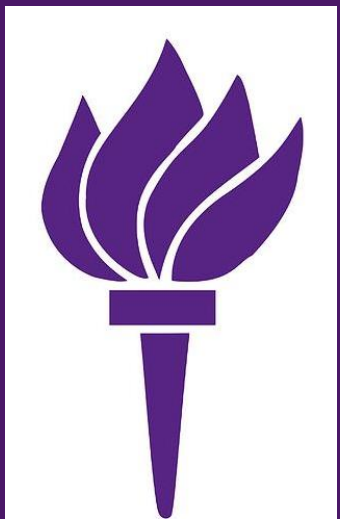




Synthesis and Processing of a 3D-Printed Ultra-Translucent Zirconia Ink for Dental Prosthesis

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Introduction/Purpose

Traditional methods of producing ceramic restorations have limitations due to manual production. The introduction of intraoral scanning and CAD/CAM technologies has revolutionized oral rehabilitation by allowing for automated production processes that are cost-effective and time-efficient. However, CAM manufacturing still faces challenges such as tool dimensions, which can impact the design of complex geometries, and material waste, with up to 80% waste from non-milled parts.¹

To address these issues, additive manufacturing technologies (AM) have currently been utilized to fabricate dental prostheses. Different AM procedures, including selective laser sintering (SLS), fused deposition modeling (FDM), direct ink writing (robocasting), and stereolithography (SLA) have been explored. Direct ink writing method stands out as a promising AM technology for dental ceramics, with 3Y-TZP zirconia samples achieving high density (96.9%) and high flexural strength (763-843 MPa), all similar to values reported for milled zirconia samples.^{2,3} The current group has also obtained favorable physical and mechanical (751-883 MPa) properties for AM produced high-strength zirconia-based samples, comparable to conventional pressed counterparts.⁴ However, there is a lack of literature data on AM processed high-translucency zirconia, 5Y-PSZ, which is currently in extensive use for esthetic cases due to its favorable optical properties.⁵

In fact, it is challenging to develop a ceramic ink with high solid content, low viscosity, and homogeneous particles dispersion which is crucial for favoring post-processing steps like sintering and for creating a dense ceramic structure. This is especially important for polycrystalline ceramics, such as ultra-translucent zirconia. Therefore, this study aimed to synthesize an ultra-translucent 5Y-PSZ colloidal gel for 3D printing (3DP – direct ink writing - robocasting), as well as to evaluate the physical and mechanical properties of samples printed with different layer thicknesses, 250 and 500 μm , and compare the results to a conventional pressed counterpart.

Methods

5Y-PSZ Ink Synthesis & 3DP Groups

• A colloidal gel suspension was fabricated using an ultra-translucent zirconia powder (5Y-PSZ, Zpex Smile, Tosoh Corporation) mixed with distilled water, dispersant polymer (ammonium polyacrylate), viscocifier (hydroxypropylmethylcellulose – F4M, and flocculant (polyethyleneimine - PEI) (Table 1).

Table 1. Colloidal gel composition (%w - g) of the 3DP 5Y-PSZ.	
H ₂ O	29.47
Ammonium Polyacrylate	1.71
5Y-PSZ Zirconia powder	107
Hydroxypropylmethylcellulose (F4M)	4.32
Polyethyleneimine (PEI)	1.85

• Disc-shaped specimens were designed and 3DP using direct-ink writing, robocasting (3D Inks LLC, Tulsa, OK), at a print velocity of 2 mm/s and deposition rate of $\sim 0.1 \text{ mm}^3/\text{s}$. The parameters were configured to print layers of 250 and 500 μm (Figure 1).

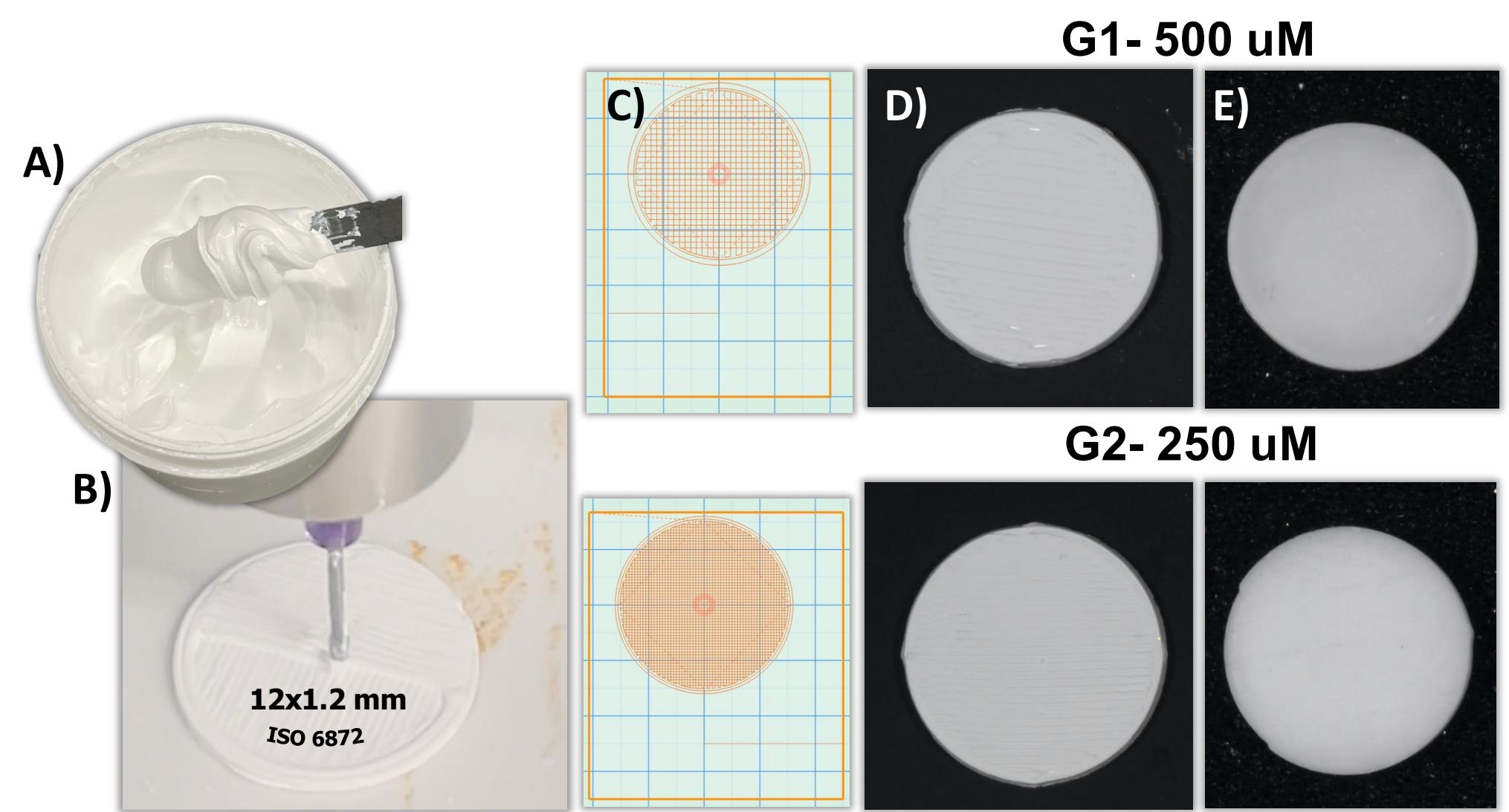


Figure 1. 5Y-PSZ colloidal gel (A) and 3DP process via robocasting (B). STL files with layer thicknesses of 250 and 500 μm (C). Representative printed samples of both groups, as-processed (D) and sintered (E).

5Y-PSZ Pressed Control Group

• 5Y-PSZ discs were obtained by uniaxially pressing the ceramic powder at 3,500 Kg/cm² for 30 seconds using a metallic matrix (Figure 2).

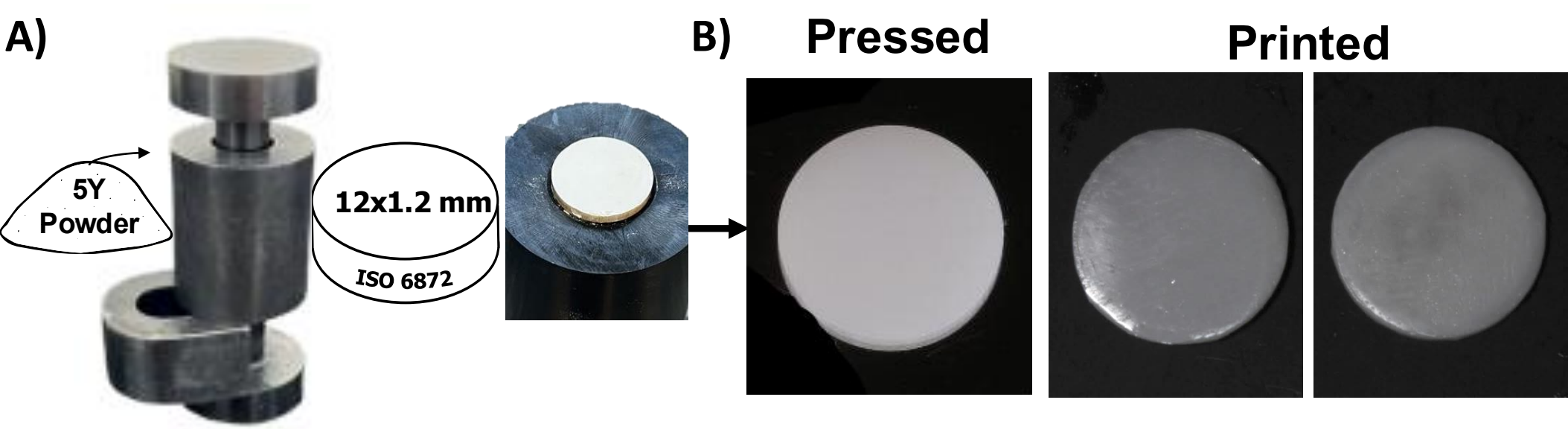


Figure 2. Pressed 5Y-PSZ control group (A). Comparison between pressed and printed 5Y-PSZ samples (B).

Sintering Process

- All discs were pre-sintered at 1000°C/1h and sintered at 1450°C/2h.

Physical & Mechanical Characterization

- 5Y-PSZ ink flow properties, viscosity and shear rate, using a Rheometer (Figure 3);
- **Microstructure** of the surface using a Scanning Electron Microscope (SEM) (Figure 4);
- **Crystalline content** using an X-ray Diffraction (XRD) (Figure 5);
- **Optical property:** translucency parameter (TP), using a Spectrophotometer. Data was analyzed using one-way Anova and Tukey Test ($p < 0.05$, n:6/group) (Figure 6);
- **Elastic modulus and hardness** using a Nanoindentation. Data was analyzed using one-way Anova and Tukey Test ($p < 0.05$, n:5/group) (Figure 7);
- **Weibull modulus, characteristic strength, and probability of survival** using the failure data after Biaxial Flexural Strength Testing. Data was analyzed using Weibull Distribution (n:20/group) – ISO 6872:2015 (Table 3 & 4, Figure 8 & 9)
- **Fractographic analysis** was performed using a stereomicroscope (Figure 10).

Viscosity

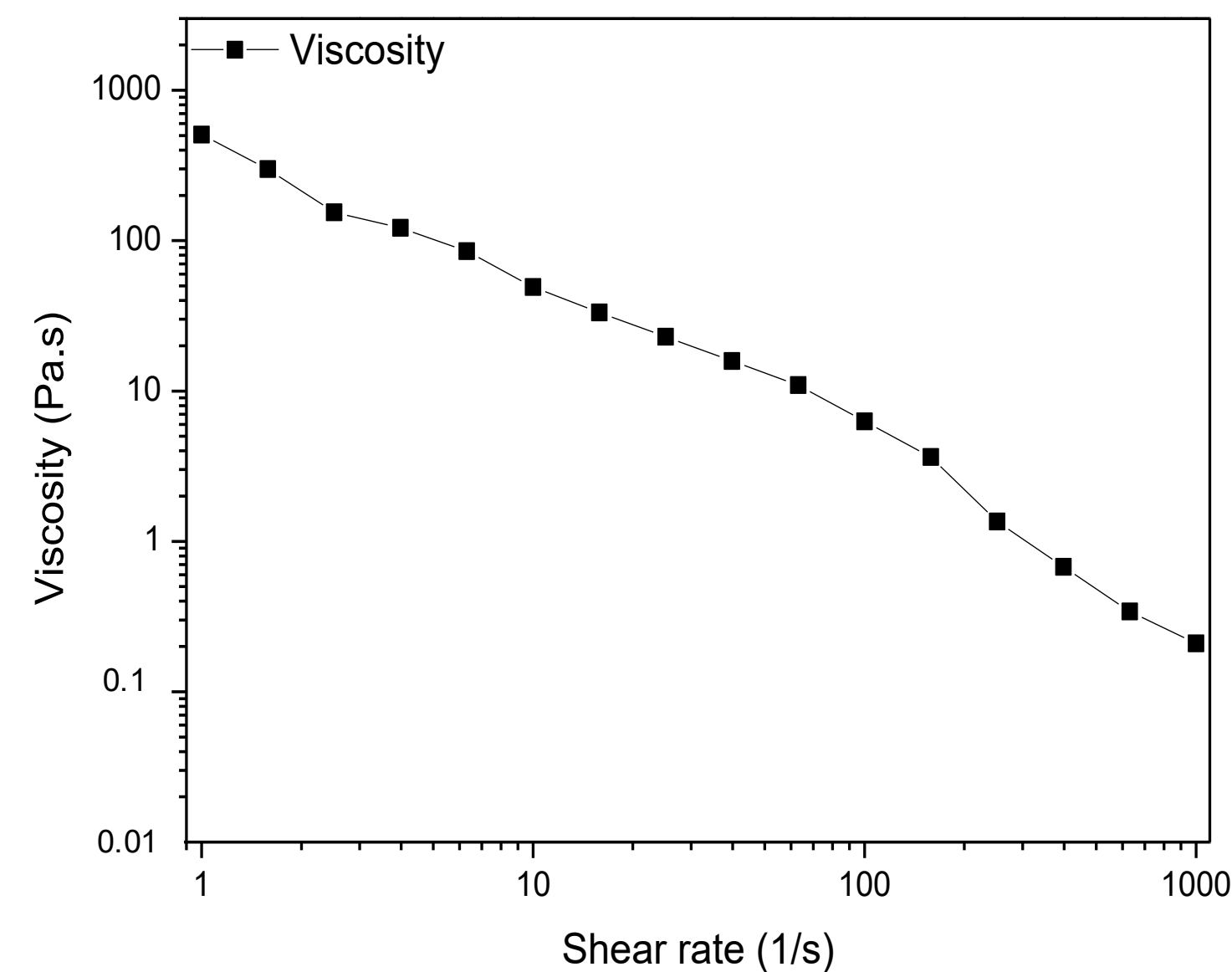


Figure 3. Viscosity versus shear rate of the 5Y-PSZ colloidal gel. The outcome of the flow sweep test demonstrates the steady state values of the viscosity against the shear rate, where a shear thinning behavior can be observed on the analyzed range of shear rates, indicating the favorable printability of the material.

Microstructure

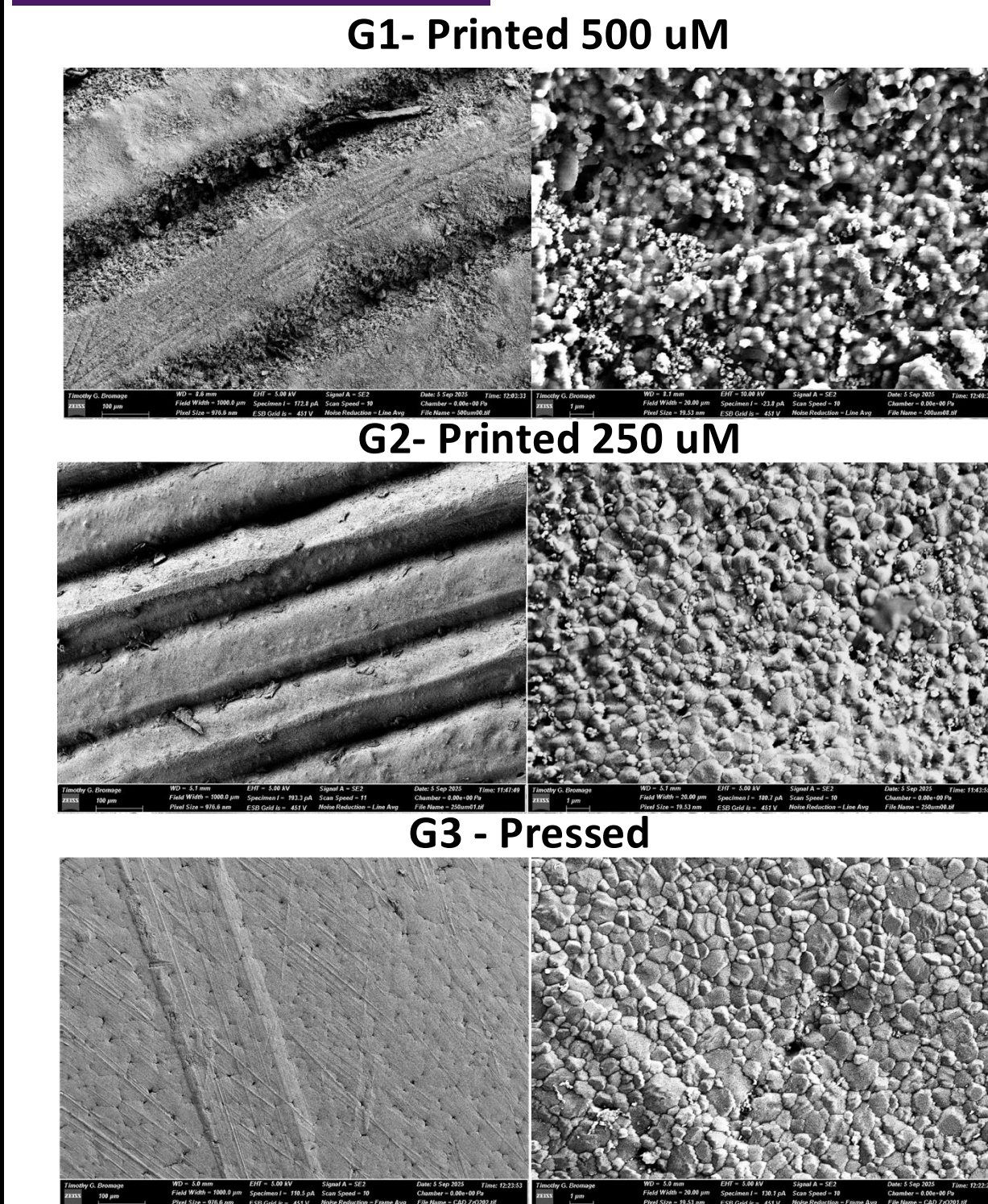


Figure 4. SEM micrographs of pressed and 3DP 5Y-PSZ. SEM micrographs exhibited the 3DP layers for both thicknesses designed. Also, a dense and homogeneous polycrystalline matrix can be observed for both processing methods; with pores/defects more prominent for 3DP 5Y-PSZ.

Fractography

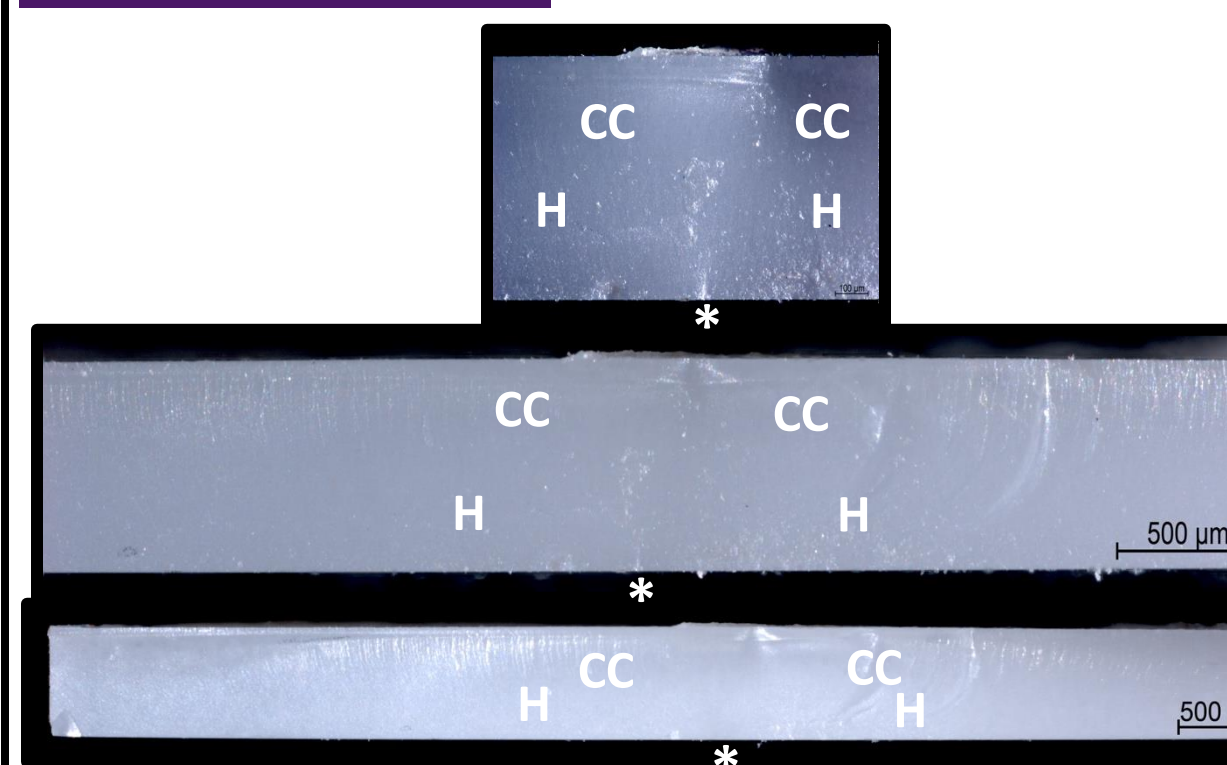


Figure 10. Stereomicroscope images of a representative fractured 5Y-PSZ disc. Images show marks such as compression curl (CC) opposite to the fracture origin (*) and hackle lines (H), indicating the direction of crack propagation.

Optical Properties

TP: 8.8 (± 1.6) TP: 8.6 (± 1.6) TP: 7.6 (± 1.6)

Figure 6. Translucency Parameter (TP) with the corresponding 95% CI for pressed and 3DP 5Y-PSZ groups. No significant difference was observed between groups. Literature findings report higher translucency for 5Y-PSZ.⁵

Results

Crystalline Content

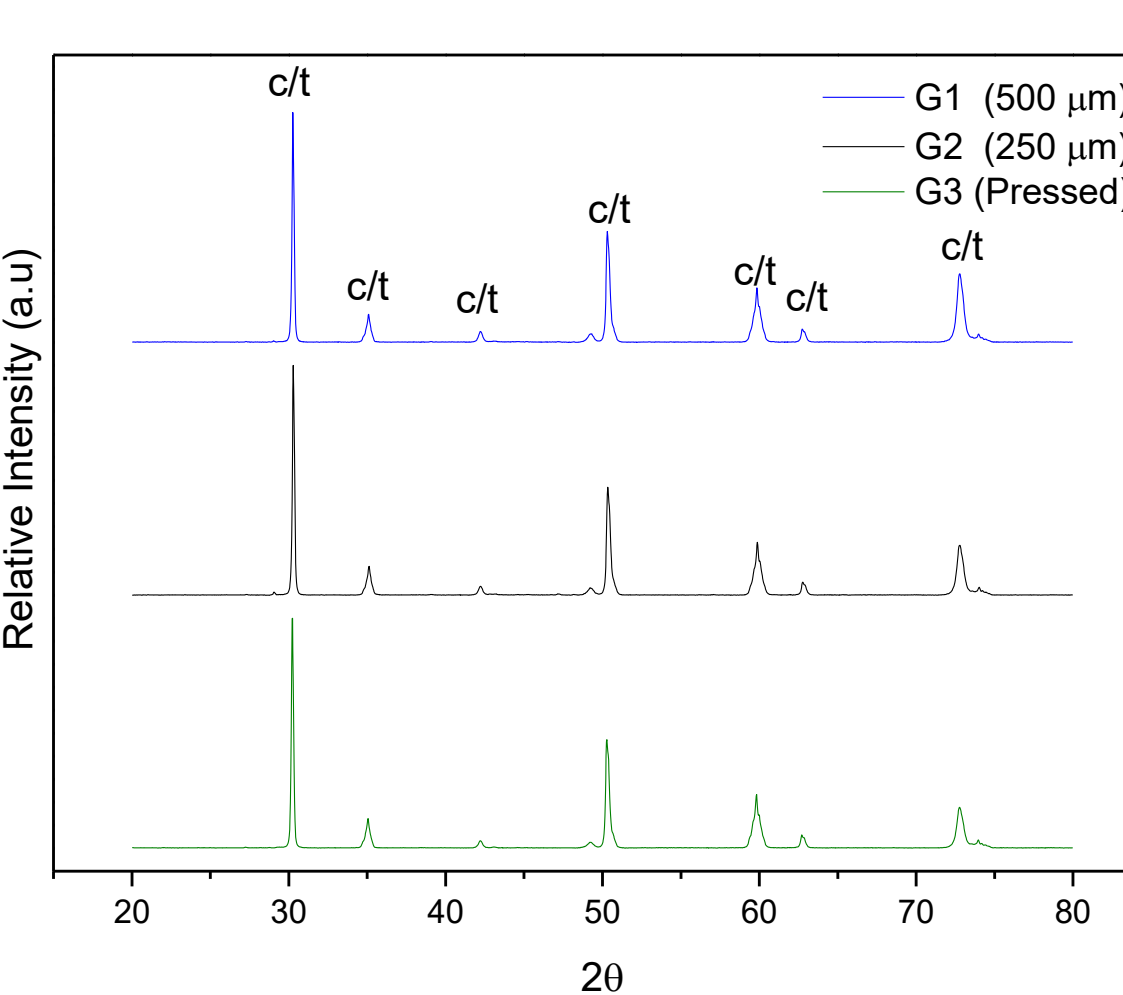
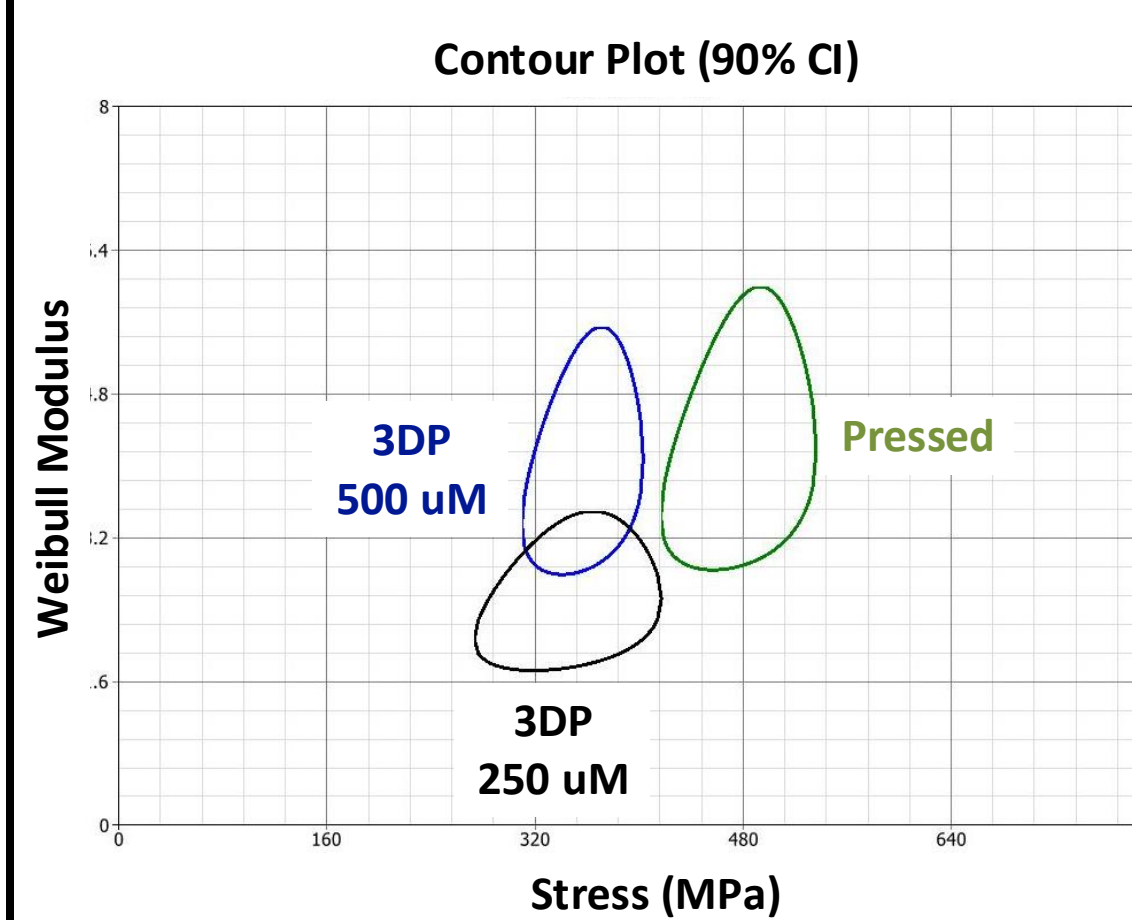


Figure 5. XRD spectra of pressed and 3DP 5Y-PSZ. Irrespective of group, Rietveld refinement indicated the presence of approximately 78% cubic (c) phase and 22% tetragonal (t) phase for all groups.

Weibull Modulus & Characteristic Strength

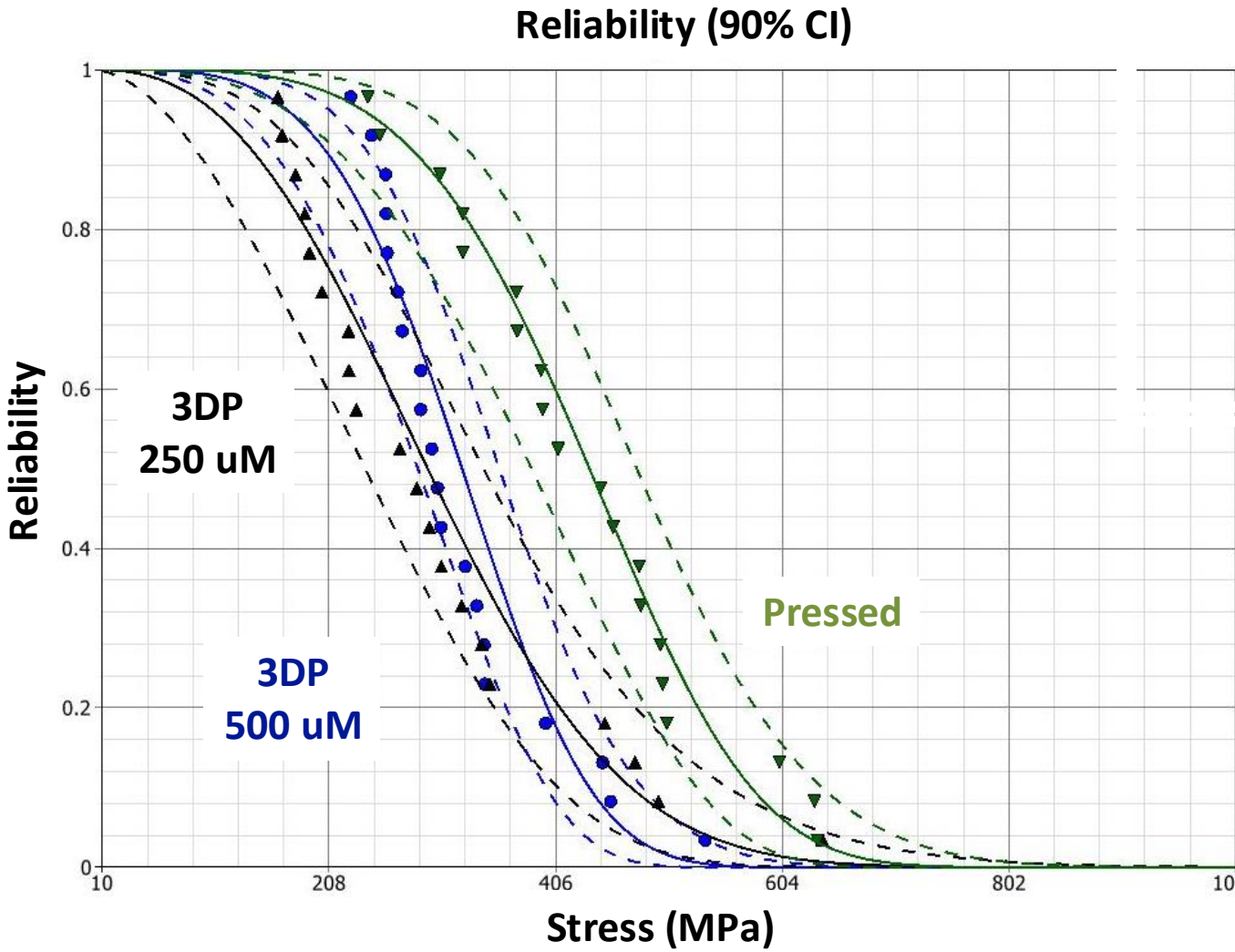


		Weibull Modulus (m)	Characteristic strength (MPa)
Pressed		4.3 (3.0-5.9) A	474 (426-529) A
	500 μm	4.0 (2.9-5.5) A	355 (316-398) B
Printed	250 μm	2.5 (1.8-3.5) A	340 (283-408) B

Figure 8 and Table 3. Weibull modulus (m) and Characteristic strength (MPa) with the corresponding 90% confidence interval (CI) for all groups. *Different uppercase letters indicate statistical differences between groups. Pressed 5Y-PSZ discs demonstrated significantly higher characteristic strength relative to 3DP 5Y-PSZ discs, with both 3DP-thickness discs showing no significant difference between them.

Probability of Survival

Figure 9 and Table 4. Probability of survival (%) with the corresponding 90% confidence interval for pressed and 3DP 5Y-PSZ with different thicknesses for missions of 50, 100, 300 and 500 MPa. *Different lowercase letters indicate statistical differences between groups. *Different uppercase letters indicate statistical differences between missions. Independent of processing method, 5Y-PSZ presented high probability of survival for missions up to 100 MPa (>96%), with no significant difference between groups, which is equivalent to the indication of single-unit prostheses, according to the ISO 6872.



Probability of Survival (Reliability %)		Pressed	Printed	
			500 μm	250 μm
50 MPa	Upper Reliability	99	99	99
	Lower Reliability	99 aA	99 aB	99 aA
100 MPa	Upper Reliability	99	99	99
	Lower Reliability	99 aA	99 aA	96 aA
300 MPa	Upper Reliability	94	75	64
	Lower Reliability	86 aB	60 abB	48 bB
500 MPa	Upper Reliability	45	9	20
	Lower Reliability	29 aC	2 bC	7 bC

Conclusion

The ultra-translucent zirconia colloidal gel obtained for 3D printing was successfully synthesized and processed with different layer thicknesses, being suitable for the fabrication of dental crowns.

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