



# Processing Method for an Alumina-Toughened Zirconia (ATZ) Composite Ink used in Dental Prostheses



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## Introduction/Objective

Conventional methods for producing ceramic restorations, such as powder-liquid condensation and heat pressing, present major drawbacks, such as the reliance on manual production. With the advent of CAD/CAM and intraoral scanning technologies, an automated production process has been introduced in oral rehabilitation that allows for a customized treatment with reduced production costs and improved time efficiency. However, despite the high efficiency of such systems, the CAM manufacturing process still presents some limitations concerning equipment costs and the dimension of the tools associated with the equipment, affecting the designing of complex geometries. Moreover, even with optimal block/disc capacity, the material consumption is high since non-milled parts might result in up to 80% waste.<sup>1</sup>

To overcome problems associated with CAM processing, additive manufacturing technologies (AM) have been introduced to manufacture indirect restorations. The layer-by-layer approach reduces the overall material waste and allows for the construction of highly complex structures. Different AM procedures have been investigated regarding their suitability for manufacturing ceramics components, such as selective laser sintering (SLS), fused deposition modeling (FDM), direct ink writing (robocasting), and stereolithography (SLA). Direct ink printing is a promising AM technology for polycrystalline ceramics, with post-processed zirconia samples reaching a high density (96.9%) and high flexural strength (763-843 MPa), all similar to values reported for milled zirconia samples<sup>2,3</sup>. However, irrespective of the AM method, developing a ceramic ink with a high solid loading, low viscosity, and homogeneous dispersion, which favor additional post-processing steps, such as sintering, to create a dense structure, is critical and still requires extensive investigations, especially for polycrystalline ceramic composites that have been scarcely investigated<sup>4</sup>. Therefore, the current study aimed to evaluate the physical and mechanical properties of an ATZ composite processed through 3D printing (Direct ink printing, robocasting).

## Methods

### 3D-Printed group:

- A colloidal gel suspension (40% ceramic volume) was obtained using ATZ powder (TZ-3Y20A, Tosoh Corporation) mixed with distilled water and a dispersive polymer, ammonium polyacrylate (Darvan 821A). Subsequently, a viscocifier, hydroxypropylmethylcellulose (F4M), and a flocculant, polyethyleneimine (PEI), were added and mixed (Table 1).

**Table 1.** Colloidal gel composition (%w - g) of the 3D-printed ATZ.

|                  |       |
|------------------|-------|
| H <sub>2</sub> O | 0.45  |
| Darvan           | 28.14 |
| ATZ              | 68.12 |
| F4M              | 2.57  |
| PEI              | 0.72  |

- Disc-shaped specimens were 3D-printed via direct ink printing, robocasting (robocasting (3D Inks LLC, Tulsa, OK), at a print velocity of 2 mm/s and deposition rate of 0.1 mm<sup>3</sup>/sec. Layer height was set to 196 µm, with a spacing of 240 µm between the printed rods (Figure 1).



**Figure 1.** ATZ ink synthesis and 3D printing via direct ink printing, robocasting.

### Control group:

- ATZ discs were obtained by uniaxially pressing the ceramic powder at 3,500 Kg/cm<sup>2</sup> for 30 seconds using a metallic matrix (Figure 2).

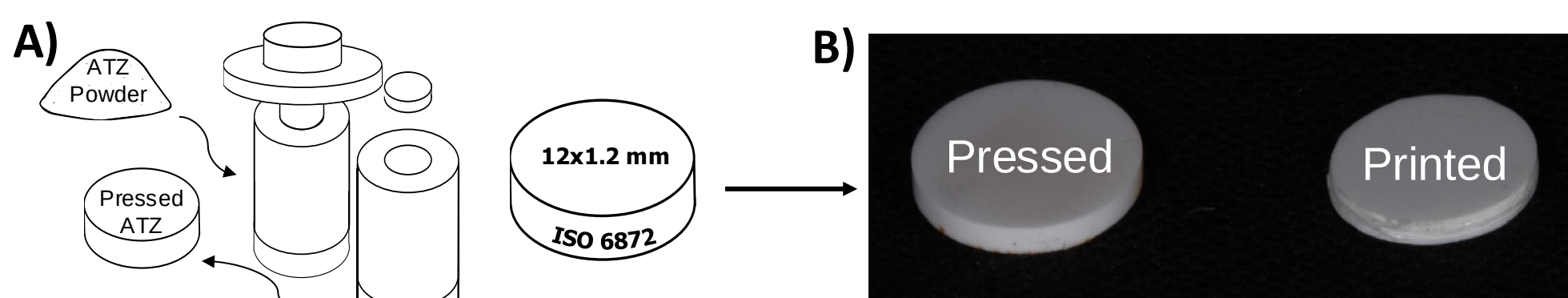


**Figure 2.** Pressed ATZ control group processing (A). Comparison between as-processed pressed and printed ATZ (B)

- Sintering:** all discs were pre-sintered at 1000C/1h and sintered at 1550C/2h.

- Physical and mechanical characterization** before and after hydrothermal aging in an autoclave for 20h, at 134°C and 2.2 bar, the following tests were performed:

- ATZ ink flow properties, viscosity and shear rate, using a **Rheometer** (Figure 3);
- Density using the **Archimedes' Principle** (Table 2);
- Crystalline content using an **X-ray Diffraction (XRD)** (Figure 4);
- Microstructure of the surface using a **Scanning Electron Microscope (SEM)** (Figure 5);
- Optical properties, contrast ratio and translucency parameter, using a **Spectrophotometer** (n:10/group) (Figure 6);
- Elastic modulus and hardness using a **Nanoindentation** (n:5/group) (Figure 7);
- Weibull statistics – Weibull modulus, characteristic strength, and probability of survival using the failure distribution after **Biaxial Flexural Strength Testing** (n:30/group) – ISO 6872:2015 (Table 3 & 4, Figure 8 & 9)

## Results

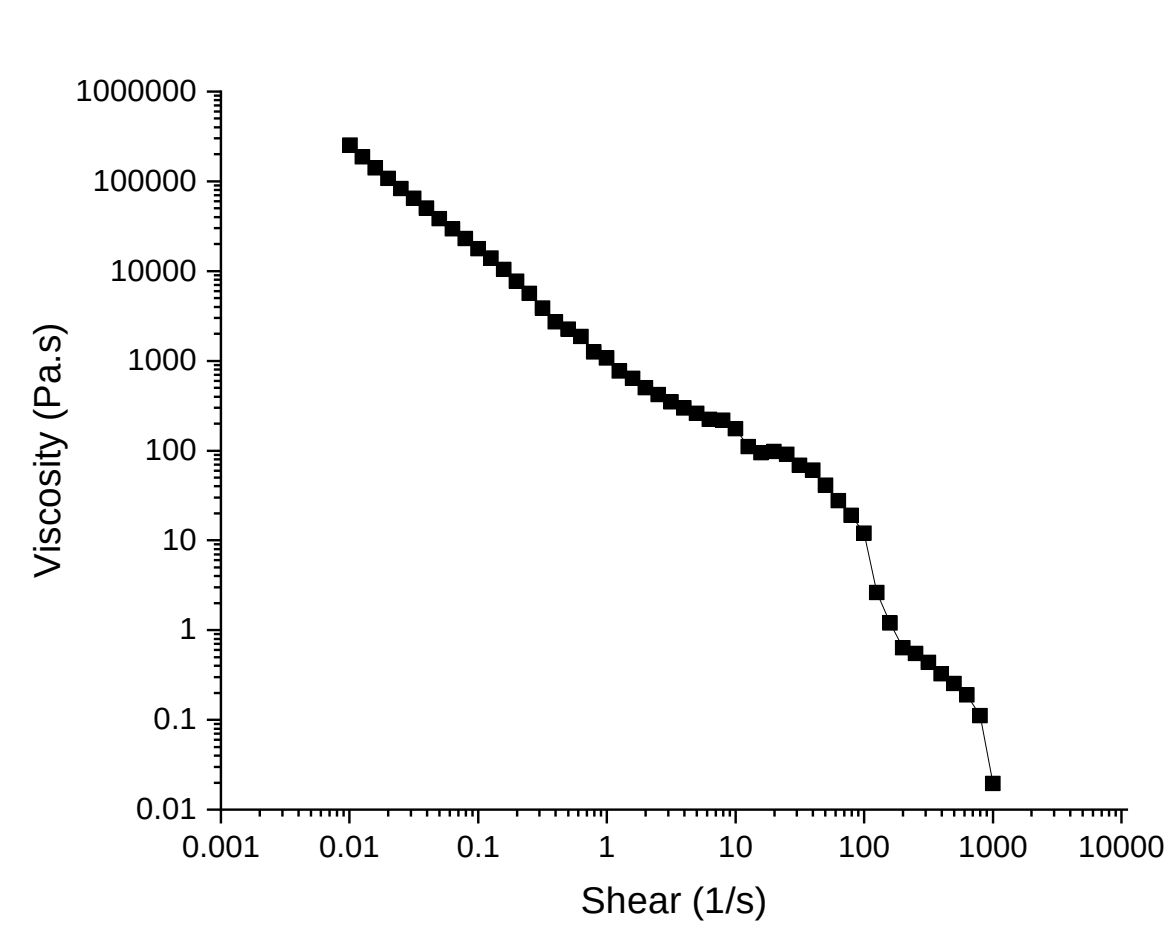


**Figure 3.** Viscosity versus shear rate of the printed ATZ ceramic composite ink. The outcome of the flow sweep test demonstrates the steady state values of the viscosity against the shear rate, where a strong shear thinning behavior can be observed on the analyzed range of shear rates, indicating the favorable printability of the material.

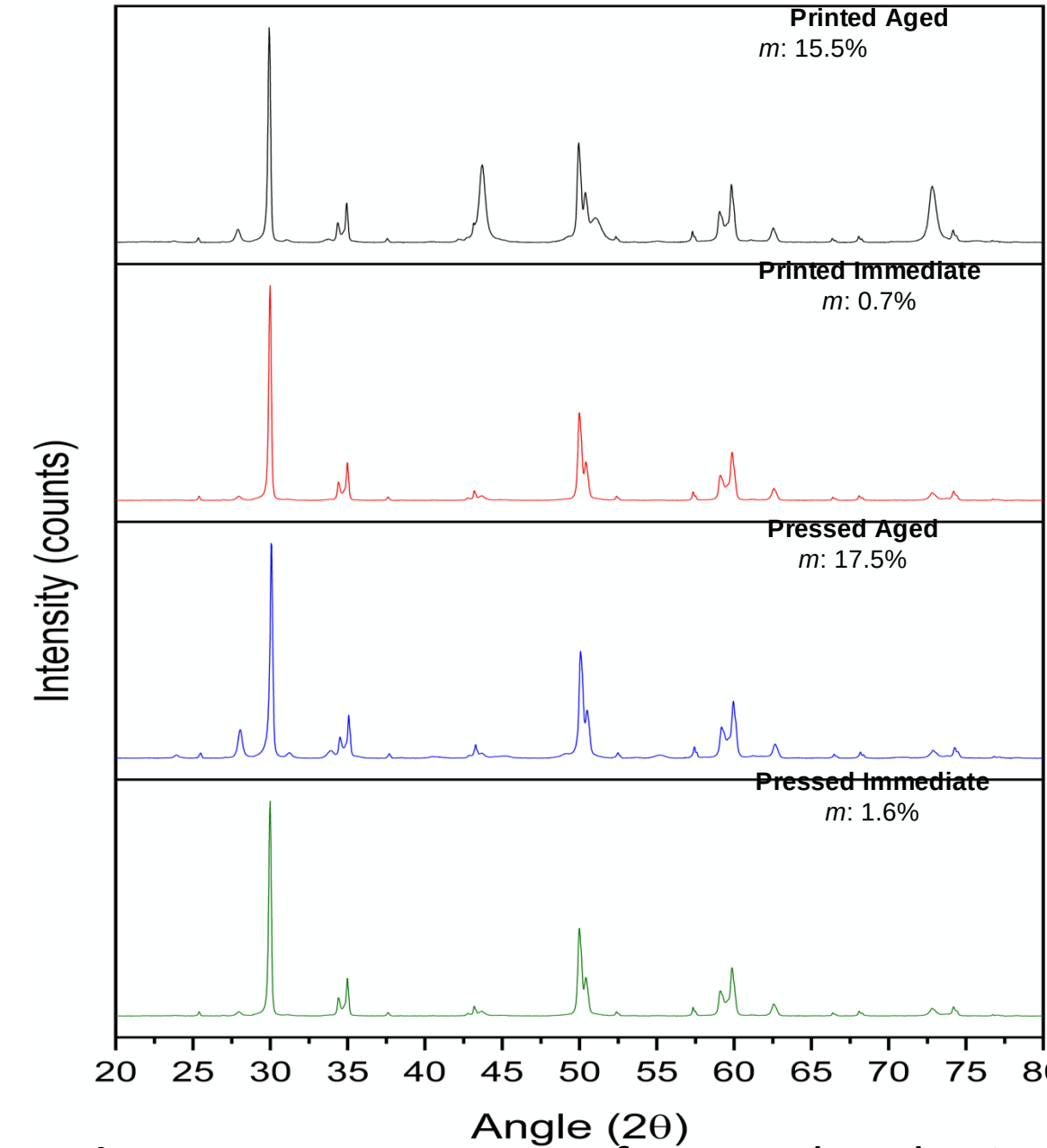


**Figure 4.** XRD spectra of pressed and printed ATZ before and after aging. While no significant monoclinic (m) content can be observed in the as-processed ATZ systems, aging triggers tetragonal-to-monoclinic (t-m) phase transformation for both ATZ systems.

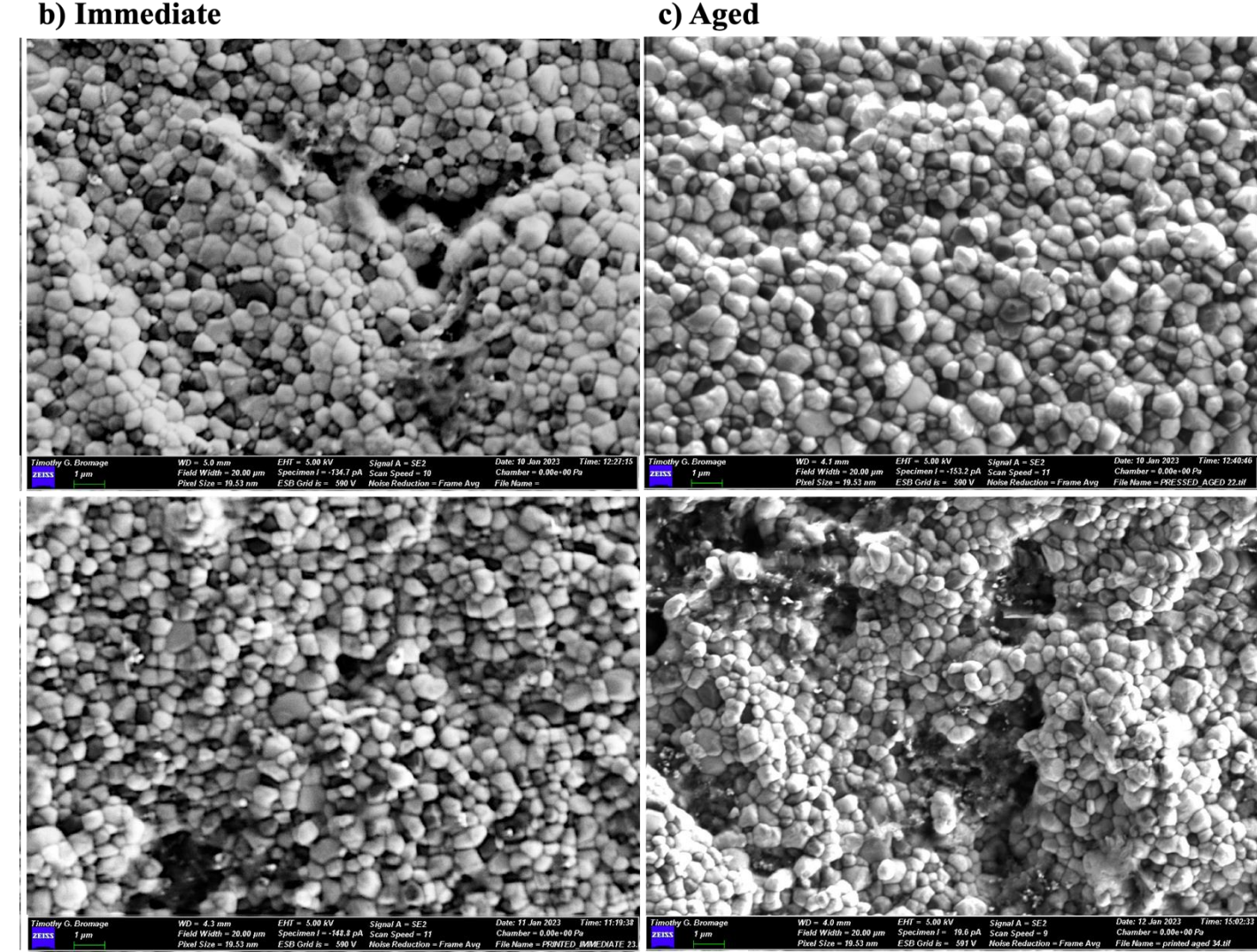


**Figure 5.** SEM micrographs of pressed and printed ATZ before and after hydrothermal aging. SEM images show a dense fully crystalline ceramic matrix, with the presence of spherical grains and few intergranular defects on the surface, especially after aging.

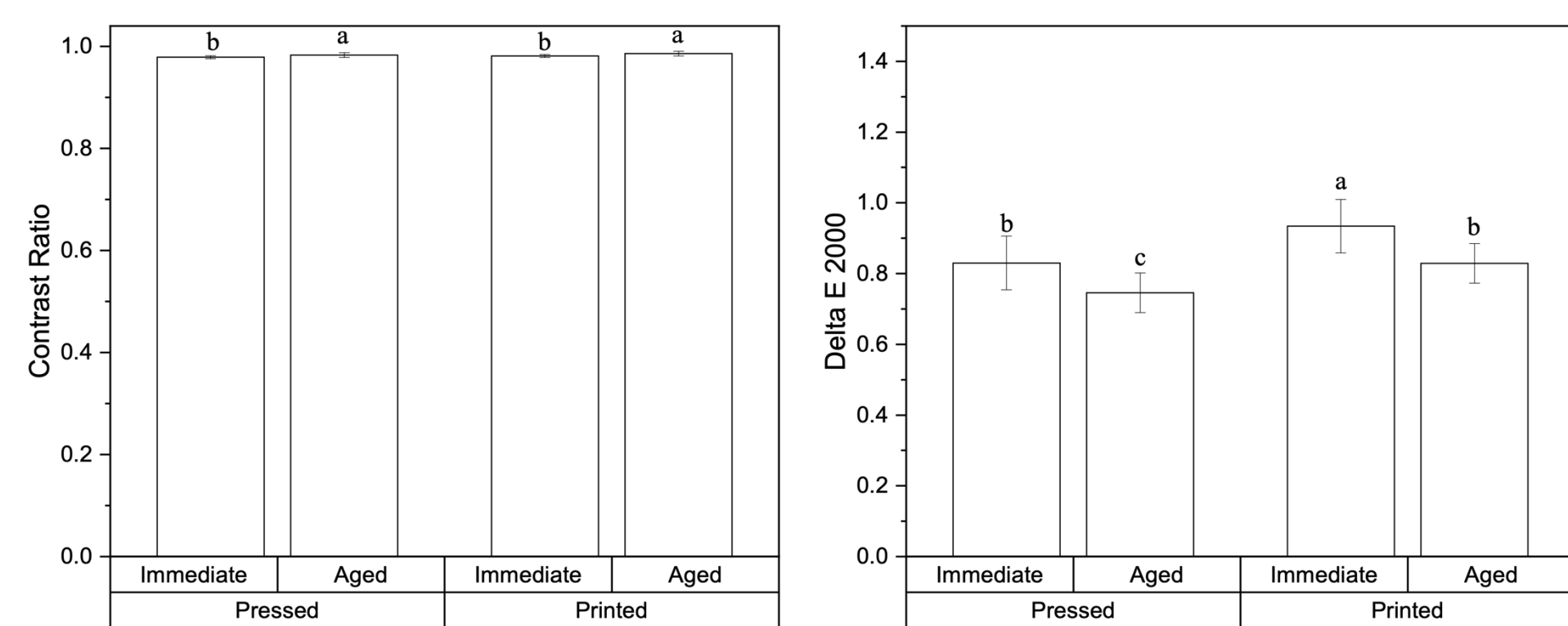


**Figure 6.** Contrast Ratio (CR) and Translucency Parameter (TP, Delta E 2000) of pressed and printed ATZ before and after aging. Irrespective of the processing method, ATZ systems demonstrate high CR and low TP, which determines the opacity of the material. The opacity significantly increased after the aging process.

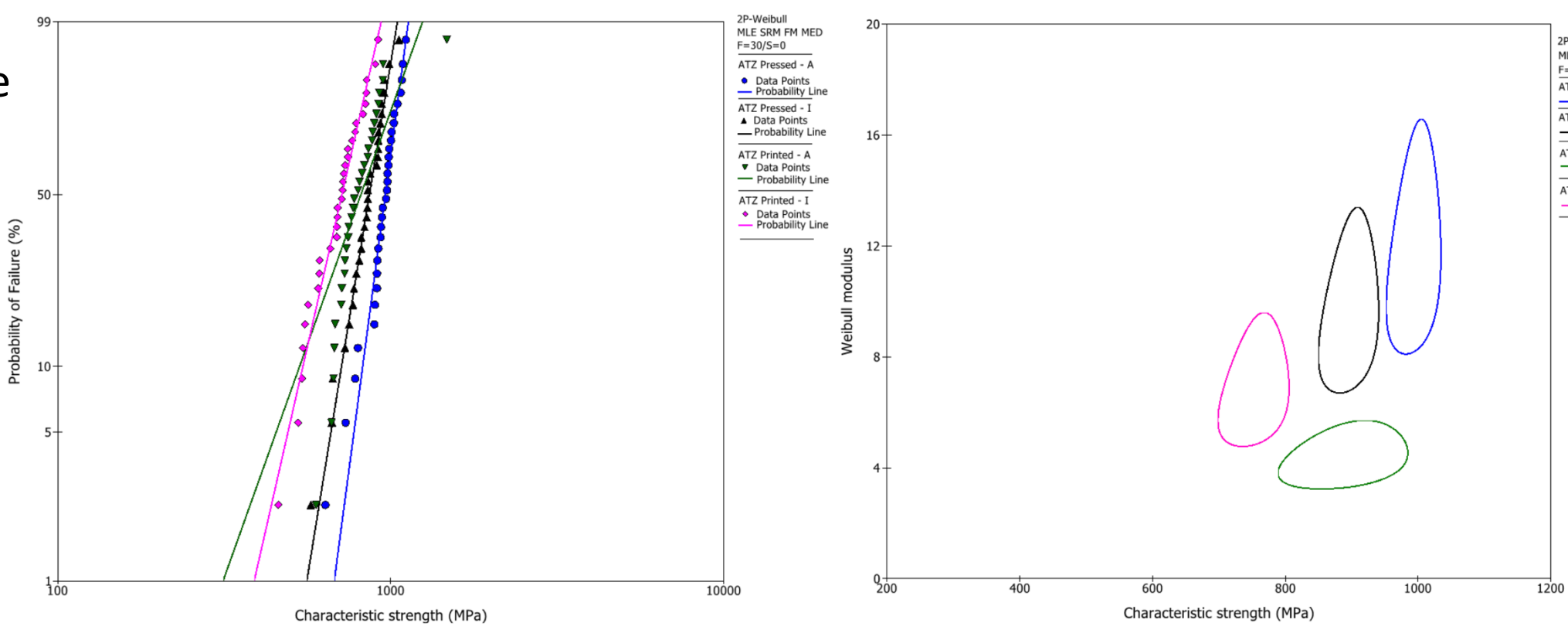


**Figure 8.** Probability of Failure versus characteristic strength (MPa) and Weibull Modulus and Characteristic Strength (MPa) (b) of printed and pressed ATZ before and after aging.

|         |           | Weibull Modulus (m) | Characteristic strength (MPa) |
|---------|-----------|---------------------|-------------------------------|
| Pressed | Immediate | 9.7 (7.4-12.8) A    | 895 (861-930) B               |
|         | Aged      | 11.9 (9-15.8) A     | 993 (962-1024) A              |
| Printed | Immediate | 6.9 (5.2-9.2) AB    | 751 (712-793) C               |
|         | Aged      | 4.4 (3.5-5.5) B     | 883 (810-962) B               |

**Table 3.** Weibull modulus and Characteristic Strength (MPa) of pressed and printed ATZ before and after aging. \*Different uppercase letters indicate statistical differences between groups. The pressed processing method resulted in significantly higher characteristic strength than the printed processing method, either for as-processed or aged storage conditions, with approximately 140 MPa difference. Both processing methods significantly increased the characteristic strength values after hydrothermal aging, with approximately a 110 MPa difference.

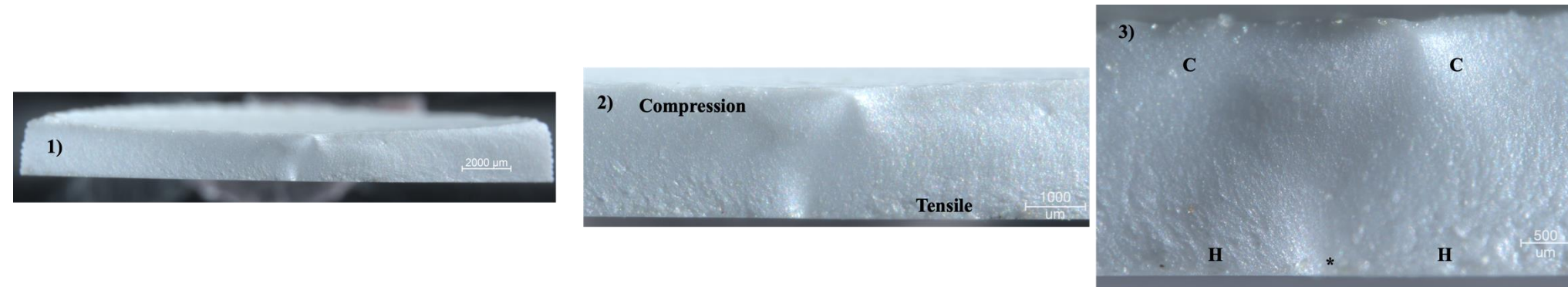


**Figure 9.** Stereomicroscope images of a representative fractured ATZ (1-3). Images show marks such as compression curl (CC) opposite to the fracture origin (\*) and hackle lines (H), indicating the direction of crack propagation.

## Conclusion

The physical and mechanical properties of the 3D-printed ATZ ceramic composite support its applicability in dentistry.

## References

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