Enabling Fast Debinding of Ceramic Vat Photopolymerization Prints with Supercritical Carbon Dioxide as a Solvent

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Introduction

Supercritical carbon dioxide ($scCO_2$) extraction was used to remove uncured substances from polymeric and ceramic vat photopolymerization (VPP) prints to create gas flow channels in form of nanosized porosity, to accelerate further thermal debinding. This is a successful demonstration of chemistry that is suitable for both $scCO_2$ extraction and VPP printing, and may lead to significant reduction of process time of VPP printed ceramic parts, that now may require 10 days.

Materials and methods

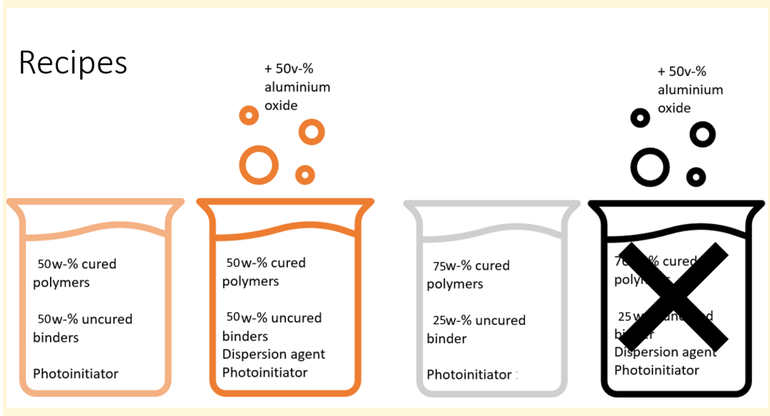

Figure 1: 2 polymeric resins and 2 ceramic slurries developed for this study.

2 polymeric resins (Figure 1) were printed with Prusa SL1S printer. 2 ceramic resins were printed with Lithoz CeraFab7500. The prints were extracted with $scCO_2$ with Thar RESS250 in varying pressure, temperature and time conditions (Figure 2). Changes in mass, dimensions, density, porosity, defects, and composition were studied to understand the effects of $scCO_2$ extraction. Mercury porosimetry, optical and electron microscopy, thermogravimetric analysis, Fourier-infrared spectroscopy, and measuring masses and dimensions were used as methods.

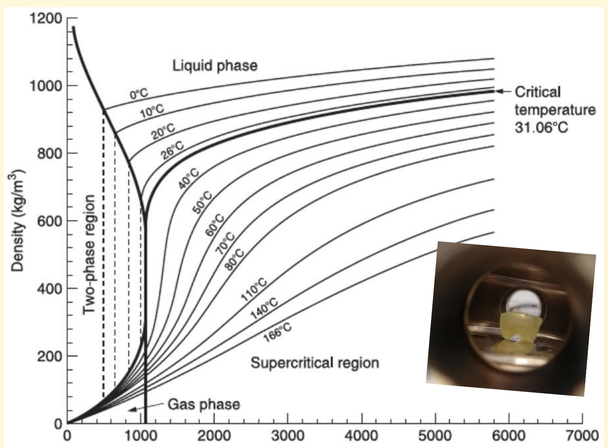

Figure 2: Density of carbon dioxide as a function of pressure. From J. M. DeSimone and W. Tumas, Green Chemistry Using Liquid and Supercritical Carbon Dioxide. Oxford, UNITED STATES: Oxford University Press, Incorporated, 2003.

Results

Porosity

The creation of porosity was present only in $scCO_2$ extracted samples, and not in the as-printed samples (Figure 3). The most frequent pore diameter in ceramic samples was 30 nm and 84 nm in polymeric samples.

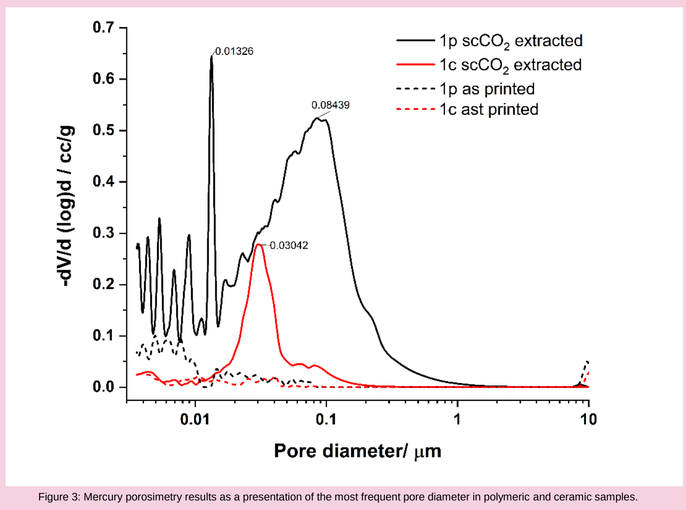

Figure 3: Mercury porosimetry results as a presentation of the most frequent pore diameter in polymeric and ceramic samples.

Defects

Both the $scCO_2$ extraction conditions and the chemical composition of used resin/slurry were found to have an impact on the cracking and delamination of samples. Slurry 2 was found incompatible with $scCO_2$ extraction in the conditions used, as the samples were badly delaminated after extraction in all conditions (Figure 4a). However, slurry 1 did not present major defects after $scCO_2$ extraction (Figure 4b), and was suitable for both VPP printing and $scCO_2$ extraction.

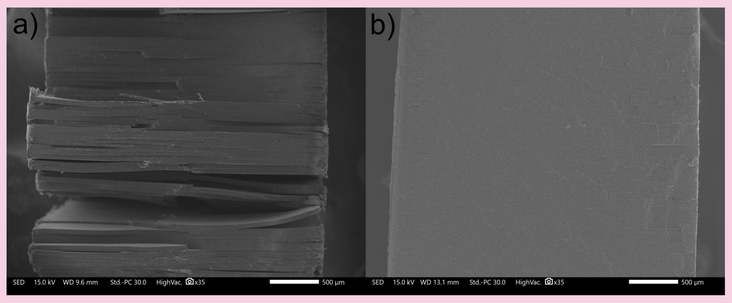

Figure 4: Secondary electron images of a) Slurry 2 after scCO2 extraction and b) slurry 1 after scCO2 extraction.

Mass removal

Mass removal as a result of $scCO_2$ extraction was studied with thermogravimetric analysis (Figure 5). The thermal degradation of the $scCO_2$ extracted samples became closer to the average degradation curve of cured monomer content with increasing extraction time and carbon dioxide density. Similar can be seen in the weighed mass change study in Figure 6, where the mass removal is presented as a function of carbon dioxide density. The extraction was more efficient in ceramic samples, and 90 wt.% of uncured monomer content was removed in 2 h when using high-density scCO2 chamber conditions.

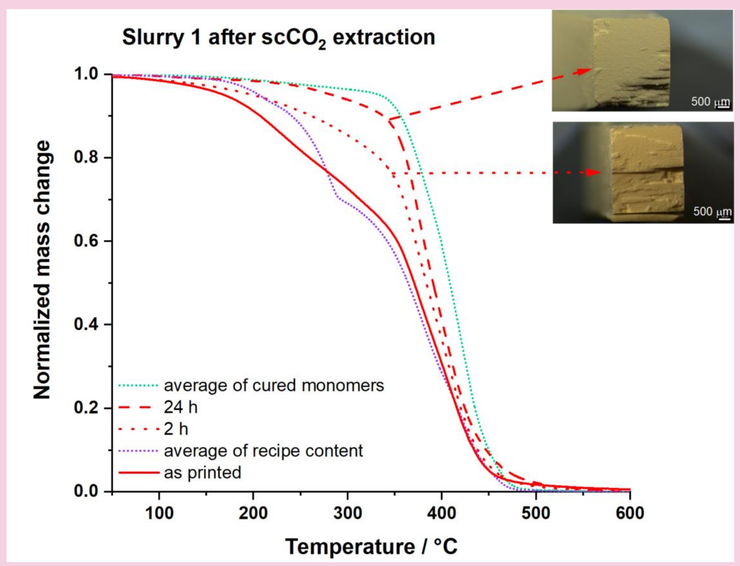

Figure 5: Thermal degradation curves of slurry 1 after scCO2 extraction for 2 and 24 h.

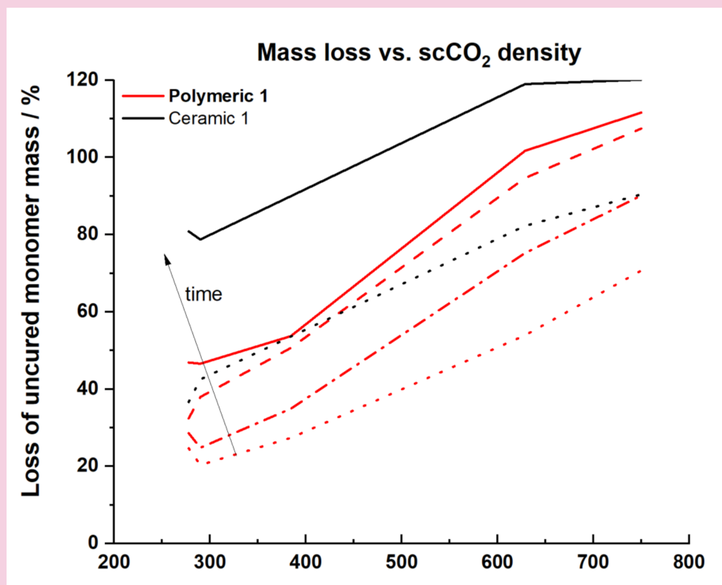

Figure 6: Mass loss out of uncured monomer content vs. carbon dioxide density, for polymeric and ceramic recipes.

Acknowledgements

The funding for this research was provided by Business Finland co-innovation project cerAM Ceramic 3D Printing (DNO 6333/31/2021). The study has used Tampere University premises for study purposes. The company Arkema Sartomer Europe is acknowledged for providing monomers used in this study. We acknowledge the following people from the Research Group of Ceramic Materials, Tampere University, Tampere, Finland: Stella Zakeri for the support in ceramic VPP, Arnold Ismailov for the support in electron microscopy, and Aaretti Kaleva for the support in $scCO_2$ studies. Dominique Hautcoeur (Belgian Ceramic Research Centre, Mons, Belgium) is acknowledged for the support in conceptualization.

Conclusions

- $scCO_2$
  - Uncured monomers successfully extracted, 90 wt-% in 2h for ceramic samples
  - No major delamination of certain prints
- porosity
  - Nanosized porosity created during $scCO_2$ extraction, in both polymeric and ceramic samples
  - Channels can act as flow channels during debinding
- time
  - Sample pre-conditioning/drying can be reduced significantly
  - Further investigation on the effect on thermal debinding time