

**WHAT:** ECerS 2023, oral presentation. 1st prize at the Shen-Kosmač speech contest in 'Clinical Applications of Ceramics and Technologies in Dentistry' Satellite Symposium

**WHEN:** 2.-6.7.2023

**WHERE:** Lyon Convention Center, Lyon, France

### Supercritical Carbon Dioxide as a Solvent in Debinding Stereolithography Prints

Nonna Nurmi\*, Erkkka Frankberg, Antonia Ressler, Piie Konnunaho, Erkki Levänen

Ceramic debinding with possible pre-conditioning can require a week of time, but it is an essential and carefully controlled processing step necessary to prevent part deformation and cracks caused by pressure gradients from evaporating substances. The use of ceramics in dental applications, which require unique characteristics from ceramic forming, has been limited due to the difficulty of manufacturing parts with minor deviation in properties. Nowadays, ceramic dental replacements are mostly milled into final shape from ceramic blocks, which is cost effective, but the material waste percentage can be even 95 %. Additive manufacturing (AM) methods, such as stereolithography, have become an alternative to milling providing better user safety, lower waste production, and increasingly lower price range due to increasing popularity of AM methods.

The thermal debinding of dental restorations could be made more economical by extracting some of the slurry substances prior to thermal debinding, creating flow channels for gases to exit. Supercritical carbon dioxide (scCO<sub>2</sub>) extraction was used for different polymeric and ceramic stereolithography prints to find out which substances dissolve from the stereolithographically printed part without cracking and part deformation. The scCO<sub>2</sub> extracted samples were characterized with thermogravimetric analysis, optical microscopy, and the sample mass and dimensions were measured before and after the extraction test. The scCO<sub>2</sub> extraction testing time, pressure, temperature, and monomer fractions and slurry contents in recipes were varied. PEG400, PEG200 difunctional methacrylate, uncured 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, and uncured 1,10-decanediol diacrylate were successfully extracted. Increase of pressure in extraction parameters resulted in faster extraction rate and increase in temperature resulted in decrease of extraction rate and part deformation in polymeric prints. The same was studied with ceramic alumina samples.



Photo: Sébastien Ferraro

**WHAT:** BioCAM Workshop, poster presentation

**WHEN:** 6.-7.12.2023

**WHERE:** Van Der Valk Conference Center, Mons, Belgium

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

Nonna Nurmi\*, Erkka J. Frankberg, Milla Rinne, Teemu Sandblom, Piie Konnunaho, Erkki Levänen

Thermal debinding of ceramic parts, with a possible pre-conditioning step, can require a week of time. However, it is an essential and carefully controlled processing step that is necessary to prevent part deformation and cracks caused by pressure gradients from evaporating substances. The use of ceramics in e.g., dental applications, which require unique characteristics from ceramic forming, has been challenging due to the difficulty of manufacturing parts with minor deviation in properties. Nowadays, ceramic dental restorations are mostly milled into final shape from ceramic blocks, which is cost effective, but the material waste percentage can be even 95 %. Additive manufacturing (AM) methods, such as vat photopolymerization, have become an alternative to milling providing better user safety, lower waste generation, and increasingly lower price range due to increasing popularity of AM methods.

The thermal debinding of ceramic 3D printed parts could be made more economical by extracting some of the slurry substances prior to thermal debinding, creating flow channels for gases to exit the structure. Supercritical carbon dioxide (scCO<sub>2</sub>) extraction was used for different polymeric and ceramic vat photopolymerization prints to find out which substances dissolve from the part without cracking and part deformation. The scCO<sub>2</sub> extracted samples were characterized with mercury porosimetry, thermogravimetric analysis, optical microscopy, and the sample mass and dimensions were measured

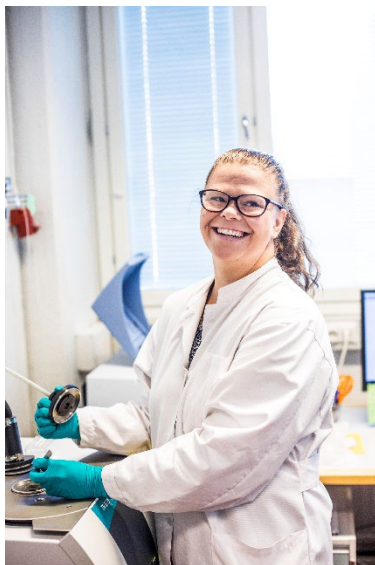
before and after the extraction test. The scCO<sub>2</sub> extraction time, pressure, temperature, and monomer fractions in slurry recipes were varied. Various uncured monomers were successfully extracted. Extraction in conditions with high scCO<sub>2</sub> density resulted in the most efficient mass removal in the printed samples.

**WHAT:** FinTAC seminar “Applications of thermoanalytical methods in 3D printing”, invited speaker

**WHEN:** 10.4.2024

**WHERE:** Messukeskus, ChemBio Finland

10:15-10:40  (20+5min)	Resin content characterization of supercritical carbon dioxide extracted vat photopolymerization prints  Nonna Nurmi, Doctoral Researcher, Tampere University
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*Photo: Jonne Renvall.*

Resin Content Characterization of Supercritical Carbon Dioxide Extracted Vat Photopolymerization Prints

Nonna Nurmi, Erkka Frankberg, Milla Rinne, Teemu Sandblom, Piie Konnunaho, Erkki Levänen

Thermal debinding is the processing bottleneck of ceramic vat photopolymerization based printing technologies. The challenge of long processing time has been studied by i.e., microwave-assisted debinding, but ways to shorten the debinding time are limited due to large binder content in slurry recipes. A way to enable faster thermal debinding of vat photopolymerization (VPP) printed parts is to create gas flow channels within the ceramic part structure, so that polymerized binders can exit through them in gaseous form without causing flaws. These channels can be created by extraction of certain substances prior to thermal debinding. I am currently working on development of ceramic slurries suitable for both VPP printing and pre-debinding with supercritical carbon dioxide extraction. The aim is to be able to extract enough chemicals to create interconnected porosity and thus enable faster heating rates and shorter dwell times in thermal debinding programs.

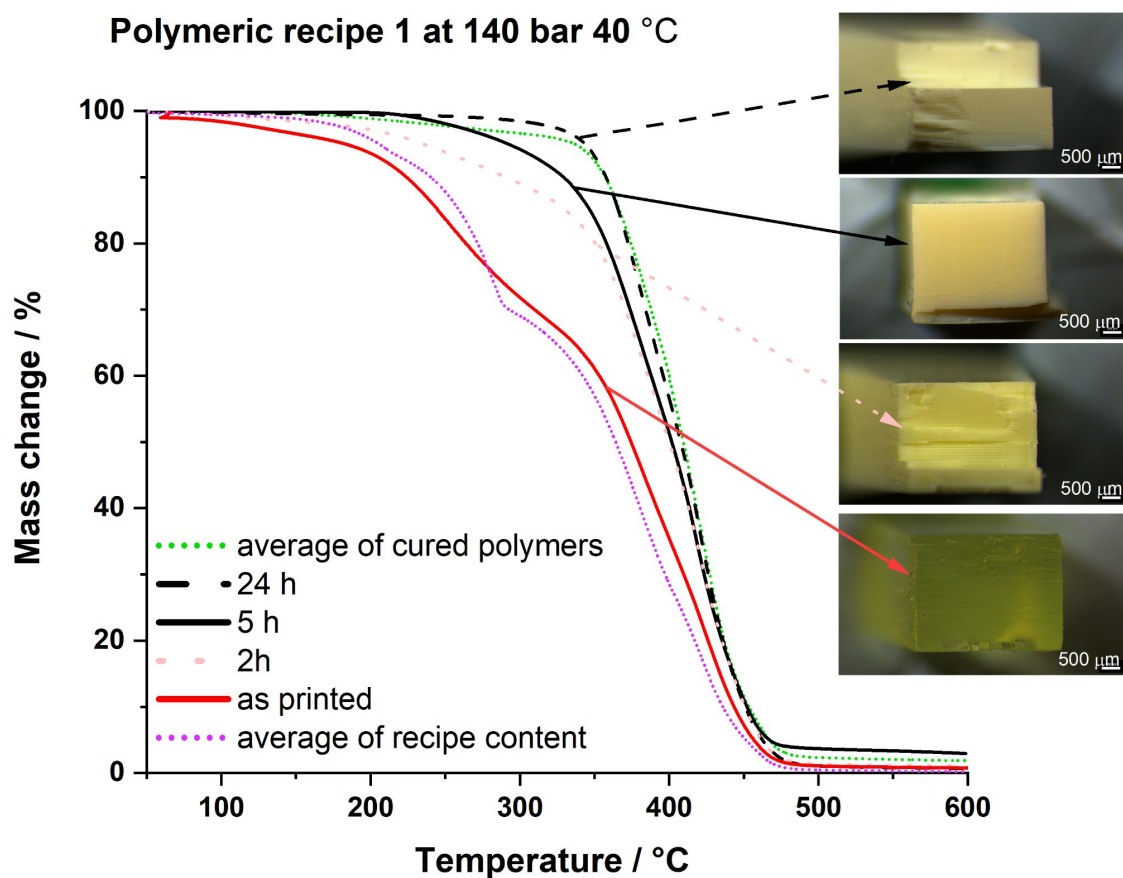


Figure 1. Thermogravimetric analysis of VPP prints before and after different  $scCO_2$  extraction times.

**WHAT:** yCAM forum 2024, oral presentation

**WHEN:** 6.-8.5.2024

**WHERE:** Tampere University

## Effects Of Debinding Conditions On Mechanical Properties And Porosity Of Ceramic Vat Photopolymerization Prints

Nonna Nurmi\*, Dominique Hautcoeur, Erkka J. Frankberg, Arnold Ismailov, Stella Zakeri, Erkki Levänen

Thermal debinding of ceramic parts, with a possible pre-conditioning step, can require a week of time. However, it is an essential and carefully controlled processing step that is necessary to prevent part deformation and cracks caused by pressure gradients from evaporating substances. The use of ceramics in e.g., dental applications, which require unique characteristics from ceramic forming, has been challenging due to the difficulty of manufacturing parts with minor deviation in properties. Nowadays, ceramic dental restorations are mostly milled into final shape from ceramic blocks, which is cost effective, but the material waste percentage can be even 95 %. Additive manufacturing (AM) methods, such as vat photopolymerization, have become an alternative to milling providing better user safety, lower waste generation, and increasingly lower price range due to increasing popularity of AM methods. Supercritical carbon dioxide (scCO<sub>2</sub>) extraction was used to study if by extracting some of the slurry substances prior to thermal debinding and creating flow channels for gases to exit the structure, the thermal debinding of ceramic 3D printed parts could be made faster. Samples were postprocessed in differing debinding conditions, varying gas atmosphere, heating rate and dwell times. Samples were characterized before and after postprocessing steps by thermogravimetric analysis, dilatometry, and optical microscopy. Sample mass and dimensions were measured to observe changes in sample density and size. Mechanical properties were studied by 3-point bending and Knoop hardness testing. The effect of scCO<sub>2</sub> pre-debinding and shorter thermal debinding on mechanical properties are presented.

**WHAT:** YCN Newsletter 18 - Research in Spot

**WHEN:** 4.10.2023

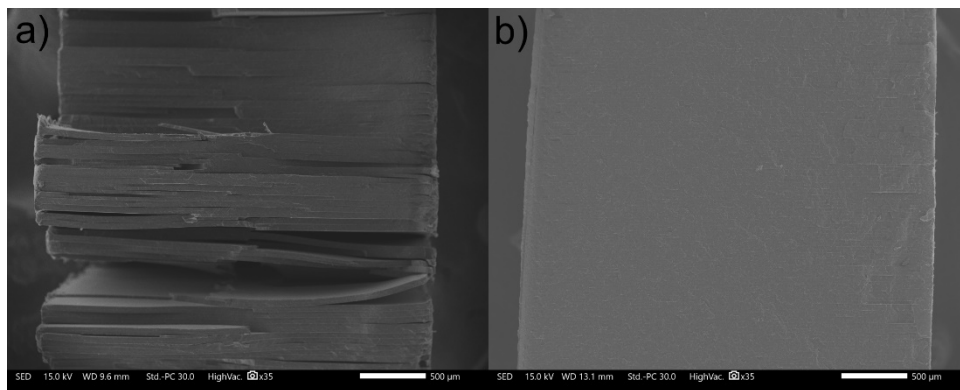
**WHERE:** <https://ecers.org/ycn-research-in-spot>

### **Towards faster debinding with the help of supercritical fluids**

Thermal debinding is the processing bottleneck of ceramic stereolithography based printing technologies. The challenge of long processing time has been studied by i.e., microwave-assisted debinding, solvent extraction and optimizing the debinding program, but ways to shorten the debinding time are limited due to large binder content in slurry recipes.

A way to enable faster thermal debinding of stereolithography (SLA) printed parts is to create gas flow channels within the ceramic part structure, so that polymerized binders can exit through them in gaseous form without causing flaws. These channels can be created by extraction of certain substances prior to thermal debinding. I am currently working on development of ceramic slurries suitable for both SLA printing and pre-debinding with supercritical carbon dioxide extraction. The aim is to be able to extract enough chemicals to create interconnected porosity and thus enable faster heating rates and shorter dwell times in thermal debinding programs.

This might lead us to significantly shorter processing times of i.e., SLA printed dental prostheses. This research topic got positive feedback at the ECerS 2023 conference, where I was granted the 1<sup>st</sup> prize at the Shen-Kosmač speech contest in ‘Clinical Applications of Ceramics and Technologies in Dentistry’ Satellite Symposium.



*Figure 1. Secondary electron images of alumina SLA print fracture surfaces with recipes a) unsuitable and b) suitable for supercritical carbon dioxide extraction. Image: Milla Rinne.*