Pore Morphology Tailoring in Polymer-Derived Ceramics Generated through Photopolymerization-Assisted Solidification Templating

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A new processing approach combining solidification templating of initially liquid preceramic polymers with a low-temperature, photoinduced cross-linking step based on a thiol-ene click reaction was recently introduced, allowing for the generation of porous polysilazane-derived ceramics with directionally aligned pore channels. In this work, the focus is set on investigating the roles of the type of structure-directing solvent, the addition of nucleating agents, and the initial precursor content on the resulting porosity, pore morphology, and properties of ceramics generated through this technique. The variation of the structure-directing solvent facilitates the generation of various pore channel morphologies, ranging from dendritic to lamellar and columnar structures. The generated materials are evaluated with regard to gas permeability and compressive strength. Depending on the processing parameters, porosity between 40% and 78% is achieved, with median pore opening sizes ranging from 7 to 70 μm. Consequently, a large range of gas permeability (3 \cdot 10^{-13} \text{ m}^2 \text{ to } 1 \cdot 10^{-10} \text{ m}^2) and compressive strength values (0.7 to 51 MPa) are observed. The results show that photopolymerization-assisted solidification templating of preceramic polymers is indeed a robust technique for a wide parameter range, allowing for the generation of well-tailored pore structures for various prospective fields of application.

1. Introduction

Porous ceramics have found entry into numerous technological and industrial fields, including filtration and separation, as support structures in membrane science or catalysis, or as biomaterials by combining beneficial properties intrinsic to ceramics, that is, high thermal and chemical stability and unique mechanical characteristics, with defined pore structures, further improving thermal shock resistance or allowing for the permeation of liquid media. Depending on the specific application, the amount, shape, and size of porosity is of essential importance. As a result, suitable processing techniques have to be applied which allow for a fulfillment of the requirements set forth by the application scenario. Techniques employed range from the replication of reticulated polymer sponges to direct foaming or sacrificial templating approaches.[1-3]

Solidification templating, also known as freeze-casting, has been studied extensively for the generation of directionally aligned porosity in ceramic materials in the recent past.[4-6] In its classic, colloidal approach, a dispersion containing ceramic particles in a liquid medium is directionally solidified by freezing, resulting in the formation of solvent crystals, leading to phase separation. The solidified solvent is then removed by sublimation before the residual structured ceramic particles are consolidated by sintering, the voids left by the removed solvent comprising the pore structure. A distinct benefit of this technique lies in its versatility in terms of tailoring of pore morphology; parameters affecting the resulting pore structure include the content of solids in the initial mixture, solidification parameters such as freezing rate, or the choice of solvent acting as structure-directing agent.

Recently, solidification templating has been combined with non-traditional ceramic consolidation techniques involving the use of preceramic polymers, also known as polymer precursor route or, with regard to the materials generated, polymer-derived ceramics (PDC). Here, a mostly organosilicon-based polymer acts as starting material which can be converted into a ceramic by a controlled thermal decomposition treatment (pyrolysis) at temperatures between 800 and 1400 °C. Numerous precursor
systems are available, including polysiloxanes, polycarboxilanes, or polysilazanes. Advantages of the PDC technique include the polymer nature of the starting materials facilitating new processing approaches, low requirements in terms of processing temperatures, as well as access to material systems with highly interesting properties, including polycarboxilane-derived silicon carbide or polysiloxane-derived silicon oxycarides.[7]

With regard to solidification templating, both polycarboxilane,[8,9] and polysiloxane-derived systems[10–15] have successfully been generated, using both particulate- and solution-based approaches. Advanced pore tailoring techniques successfully applied to solidification-templated PDCs involve the introduction of additional particulate fillers[16] or the development of a two-stage freeze-casting procedure,[17] leading to improved performance of the resulting materials due to increased specific surface areas or improved mechanical properties.

In solidification templating, the choice of structure-directing solvent strongly affects the resulting pore structure.[4] As a result, numerous solvents have been employed for solidification templating of PDCs, including camphene, tert-buty alcohol, cyclooctane, cyclohexane, dioxane, dimethyl carbonate, or water.[8,10,12,13] Naviroj et al.[12] showed for four different solvent systems that pore morphologies in freeze-cast PDCs can be correlated with the so-called Jackson α-factor,[18,19] a factor largely determined by a solvent’s enthalpy of fusion. The α-factor gives an indication on the type of crystal growth behavior, which in turn is responsible for the morphology of solvent crystals formed during solidification and, consequently, the definition of the resulting pore structure in freeze-cast PDCs.

A main challenge in solidification templating of liquid preceramic compounds is the preservation of the structural integrity after removal of the solvent template. This is generally achieved by partial cross-linking treatments in the liquid starting mixture.[12] However, for non-oxide compounds such as polysilazanes, in most instances, this approach is not viable: commercially available polysilazane precursors are generally cross-linked via vinyl side groups, often involving radical initiators. In this case, elevated process temperatures and difficult control over the degree of polymerization effectively render the precuring approach unsuitable.

Recently, we introduced a new concept of solidification templating of preceramic polymers by employing a photo-induced thiol-ene “click” reaction in order to cross-link a liquid poly(vinyl)silazane compound within a solidified solvent template at temperatures well below –10°C, using a quaternary thiol compound and a photoinitiator.[20] In our original introduction of the photopolymerization-assisted solidification templating (PASST) technique, the use of camphene as structure-directing solvent resulted in Si-C-N-(O)-based materials with dendritic pore structures.

Based on this initial work, the question arises whether other structure-directing solvents can be applied to PASST as well, eventually leading to a higher variability in the pore morphologies achievable and thus potentially increasing the applicability of the respective materials. Therefore, the main objective of this study is the investigation of the roles of the type of structure-directing solvent, the addition of nucleating agents, and the initial precursor content on the resulting porosity, pore morphology, and properties of ceramics prepared through the PASST technique. In addition, small modifications to the initially developed technique are presented, e.g., in order to increase reactivity during photopolymerization.

2. Experimental Section
2.1. Starting Materials
Poly(vinyl)silazane (PVS, Durazane® 1800, durXtreme GmbH, Germany) was used as a preceramic polymer compound, which can be converted into a silicon carbonitride-based ceramic upon pyrolytic conversion at 800 to 1000 °C. Pentacyclosiloxane tetrakis-(3-mercaptopropionate) (TT, Aldrich, Germany) was used as a crosslinking agent by utilizing a thiol-ene “click” reaction, based on work by Reddy et al.[21] (+)-Camphene (Merck, Germany), p-xylene (Lancaster, USA), dimethyl carbonate (Lancaster, USA), and L-(-)-bornyl acetate (Alfa Aesar, Germany) were used as pore structure-directing solvents. Ethyl (2,4,6-trimethylbenzoyl)phenylphosphinate (ETPP, Speedcure TPO-L, Lambson, United Kingdom) was used as photoinitiator. Silicon nitride (Si3N4 SN-E10, UBE Industries, Japan) was used as nucleating agent.

2.2. Solidification Templating and Thermal Treatment
The preparation procedure was based on a recently published methodology developed in our group.[20] The reaction mixture consisted of two compounds, 1) the precursor compound, composed of PVS and TT, and 2) the solvent mixture, containing one of the four studied pore structure-directing solvents (camphene, p-xylene, dimethyl carbonate, bornyl acetate), the photoinitiator ETPP, and optionally the nucleating agent Si3N4. The ratio of PVS to TT was kept constant at 73:27 wt%. Three general reaction paths were investigated, involving different variations of starting mixtures: a) mixtures of structure-directing solvents with 25 wt% of the precursor compound and 0.6 wt% ETPP, without nucleating agent; b) mixtures of structure-directing solvents with 25 wt% of the precursor compound, 0.8 wt% ETPP, and 0.1 wt% Si3N4 as nucleating agent (no nucleating agent was added to the camphene-based samples due to fabrication issues); c) mixture of bornyl acetate with 15 to 40 wt% of the precursor compound, 0.8 wt% ETPP, and 0.2 wt% Si3N4.

For the precursor compound, PVS was degassed, followed by mixing with TT and stirring under a reduced pressure of 6 mbar for 30 to 40 min. The next step depends on the solvent used: in case of using p-xylene, dimethyl carbonate or bornyl acetate, the respective solvent was added to the precursor compound, followed by the addition of nucleating agent (if applicable). After ultrasonication for 5 min, the mixture was stirred for 2 min, ETPP was added, and the mixture was again stirred for 2 min. In case of using camphene, ETPP was added to camphene at 55 °C and stirred for 5 min. The ETPP/camphene mixture was then added to the precursor compound and stirred vigorously at 55 °C for 2 min.

2.3. Directional Solidification and Photo-Curing
The reaction mixture was introduced into a tubular PMMA (for camphene, p-xylene, and bornyl acetate) or glass mold (for
dimethyl carbonate) with inner diameters of 19 mm and a height of 30 mm, which had been placed on an aluminum base plate. In a typical experiment, the mold was filled to a liquid level of 22 mm. Directional solidification was started at a base plate temperature of 55 °C for camphene, 23 °C for p-xylene and dimethyl carbonate, and 10 °C for bornyl acetate. In case of bornyl acetate, a thin layer of solidified solvent was provided prior to the addition of the reaction mixture. Complete sublimation of the solvents was carried out at prior to any further investigations. Sublimation of the solvents was achieved by lowering the base plate temperature at a cooling rate of 8 K min⁻¹. After solidification, the base plate temperature was raised to −30 °C to −25 °C. After 5 min at this temperature, the photo-crosslinking reaction was started by light exposure, using six high power LEDs emitting at 400 nm (each operating at a nominal power density of 130 mW cm⁻²). Photocuring times were 5 min (route (a)) or 15 min (routes (b) & (c)). Figure 1 shows the experimental setup used for solidification and photo-polymerization of specimens.

After the curing step, the samples were demolded, and 2−3 mm of the top and bottom parts of the samples were cut off prior to any further investigations. Sublimation of the solvents camphene, p-xylene, and dimethyl carbonate was carried out at room temperature and a pressure of 0.1 mbar. Bornyl acetate was removed by using a freeze-drier operating at −0.1 mbar. Bornyl acetate was weighed into aluminum crucibles (11 ± 1 mg) which were covered with glass lids. Samples were cooled to −10 °C at a ramp of 2 K min⁻¹. After the temperature had been kept constant for 4 min, photocuring was conducted with an irradiation power of 10 mW cm⁻² at the surface of the sample, a wavelength of 400 nm (Exfo OmniCure LX400UV LED spot curing system), and a curing time of 5 min. The photocuring step was repeated to ensure completeness of the curing process.

Bulk density and apparent porosity were determined by using the water immersion test method after EN 623−2.[22] Pore morphology and microstructure were examined by scanning electron microscopy (SEM, Quanta 200, FEI, the Netherlands), observing fracture surfaces parallel to the freezing direction as well as perpendicular to the freezing direction.

Pore opening diameters and pore size distributions were evaluated by mercury intrusion porosimetry (Pascal 140/440, POROTEC, Germany) with a maximum applied intrusion pressure of 400 MPa.

Gas permeability measurements were performed on a test rig using filtered compressed air as the permeating fluid. Shrinking tubes were used to laterally seal the cylinders. The stationary permeating gas flow Q through the sample along the freezing direction was recorded as a function of the pressure drop Δp between upstream (p1) and downstream (p2) side of the specimen. The permeated area A and the sample height l were calculated from the dimensions of the pyrolyzed samples. Δp was varied between 0.2 and 2 bar. Permeability coefficients were determined using Forchheimer’s equation for compressible fluids (Equation (1)), employing a quadratic fit to (ṗ − ṗ0)²/(2ρ0l) using the least-squares method[23] (assuming an air viscosity η of 1.85 · 10⁻⁵ Pa s and an air density ρ of 1.17 kg m⁻³):

\[
\frac{p_1^2 - p_2^2}{2 \rho_0 l} = \frac{\eta Q}{k_1 A} + \frac{\rho}{k_2} \left( \frac{Q}{A} \right)^2
\]  

2.4. Characterization

The effect of the structure-directing solvent on the photopolymerization reaction was studied by performing differential photocalorimetry measurements (DSC 204 F1, NETZSCH, Germany). The reaction mixtures were prepared along reaction path (a) with an addition of 0.25 wt% Si₃N₄ for p-xylene, dimethyl carbonate, and bornyl acetate. The prepared mixtures were weighed into aluminum crucibles (11 ± 1 mg) which were covered with glass lids. Samples were cooled to −10 °C at a ramp of 2 K min⁻¹. After the temperature had been kept constant for 4 min, photocuring was conducted with an irradiation power of 10 mW cm⁻² at the surface of the sample, a wavelength of 400 nm (Exfo OmniCure LX400UV LED spot curing system), and a curing time of 5 min. The photocuring step was repeated to ensure completeness of the curing process.

After a thermal post-curing step at 200 °C for 4 h under a nitrogen flow of 0.3 l min⁻¹, pyrolytic conversion to the ceramic was carried out in an alumina tube furnace at 1000 °C for 2 h under a nitrogen flow of 0.5 l min⁻¹. A heating ramp of 1 K min⁻¹ and a cooling ramp of 2 K min⁻¹ were used. From the cured to the pyrolyzed state, the specimens exhibited an overall linear dimensional shrinkage of around 30%.

![Figure 1. Experimental setup: a) tubular mold placed on aluminum base plate; b) photopolymerization chamber placed on top of the solidified sample; c) top-side view of the photopolymerization chamber showing LED positions.](image-url)
Compressive strength testing was conducted for samples fabricated along reaction path (b), using a universal testing machine (Zwick 1474, Germany). Cylinders with plane-parallel faces and a height between 7 and 10 mm were prepared by grinding the top and bottom planes of the specimens. The compression axis was aligned with the axis of freezing direction, and the testing conducted with a crosshead speed of 0.5 mm min\(^{-1}\). The maximum force was used to calculate the compressive strength, averaging the results of a minimum of three individual samples per composition. In spite of the limited number of samples, the results were used to screen for significant effects of the sample composition on mechanical properties.

3. Results and Discussion

The pore structuring of polysilazane-based samples was successfully accomplished by employing the recently developed photopolymerization-assisted solidification templating (PASST) technique. Some minor modifications were implemented, including the use of ethyl(2,4,6-trimethylbenzoyl)phenylphosphinite (ETPP) instead of camphorquinone as photoinitiator, resulting in a significantly accelerated photopolymerization reaction.

3.1. Role of Structure-Directing Solvents

In addition to camphene, three alternative structure-directing solvents (bornyl acetate, dimethyl carbonate, and p-xylene) were introduced in order to control the pore structure in general and the pore channel morphology in particular. The solvents were chosen based on 1) their melting point range, allowing for directional solidification within a reasonable and experimentally accessible temperature interval, 2) a high vapor pressure facilitating rapid solvent removal by sublimation, and 3) a compatibility with the other components present in the reaction mixture, including polysilazane, thiol, and photoinitiator.

In case of camphene, the reaction mixture was opaque, while the use of the other solvents resulted in clear solutions. The difference in appearance did not seem to affect the solidification. However, the determination of freeze front velocities was easier when clear solutions were used due to the distinct identifiability of the freeze front. In the latter case, freeze front velocities in the range of 15 μm s\(^{-1}\) were observed for the chosen base plate cooling rate of 8 K min\(^{-1}\).

In a first step, the performance of the photopolymerization reaction was evaluated for all four solvents using Photo-DSC investigations (Figure 2). In order to simulate the low-temperature conditions present during photopolymerization after solidification templating, Photo-DSC investigations were carried out at -10 °C. For all four solvents, the major portion of the photopolymerization reaction is completed within 20 s after the start of the irradiation. Parameters describing the reaction progress are listed in Table 1. Differences in photopolymerization behavior of the cross-linking reaction can be observed for different structure-directing solvents. While the time of the peak maximum (t\(_{\text{max}}\)) is comparable for all four solvents (between 1.6 s and 2 s after starting the irradiation), the \(t_{95}\) value, corresponding to the time when 95% of the reaction are finished, varies from 22 s (bornyl acetate) up to 107 s for camphene. In combination with the peak areas observed, it can be concluded that the photopolymerization reaction in the presence of camphene is both slower and less exothermic than for the three other solvents. A possible explanation for this behavior is the presence of a terminal C=C double bond in the camphene molecule, which may interfere with the thiol-ene click reaction between the thiol group and the ene-functionality of the poly(vinyl)silazane. Furthermore, reactions within the reaction mixture between camphene and/or PVS and the thiol compound may have already occurred during preparation of the sample.

Table 1. Results of Photo-DSC investigations of starting mixtures containing four different structure-directing solvents.

| Structure-directing solvent | \(t_{\text{max}}\) [s] | \(t_{95}\) [s] | Peak height [mW mg\(^{-1}\)] | Peak area \([\Delta H]\) [J g\(^{-1}\)] |
|-----------------------------|-----------------|----------------|-----------------------------|-----------------------------|
| Camphene                    | 1.6 ± 0.2       | 107 ± 29       | 3.00 ± 0.26                 | 22.6 ± 1.6                  |
| Bornyl acetate              | 1.7 ± 0.2       | 22 ± 12        | 6.50 ± 1.06                 | 39.8 ± 2.0                  |
| Dimethyl carbonate          | 1.8 ± 0.2       | 54 ± 8         | 5.14 ± 0.53                 | 54.5 ± 6.7                  |
| p-Xylene                    | 2.0 ± 0.2       | 47 ± 1         | 5.86 ± 1.26                 | 55.8 ± 2.4                  |

Measurements were performed at a wavelength of 400 nm and at -10 °C (initial precursor content: 25 wt%).
mixtures carried out at 55°C before DSC investigations, potentially resulting in correspondingly decreased ΔH values.

As all four systems were shown to be curable by low-temperature photopolymerization, the effect of the structure-directing solvent on the resulting pore channel morphology was evaluated next by preparation of directionally solidified specimens following the PASST technique (Figure 3). In accordance with previously published data, the use of camphene results in a rather fine, dendritic structure. In contrast, the other solvents crystallize in coarse, lamellar structures.

Recently, Naviroj et al.[12] showed that the morphologies generated during solidification templating of preceramic polymers are related to the Jackson α-factor, which is determined, inter alia, by a solvent’s melting point Tm and enthalpy of fusion L.[18,19] The α-factor, describing the crystal growth regime, can consequently be used as a guide to predict the solidification microstructure of a given solvent and, in turn, the resulting pore morphology. When comparing the entropic terms of the Jackson α-factors calculated for the solvents used in this work (Table 2), it can be seen that the general observations described in previous works can indeed be retraced here. Camphene, having a rather low entropic term of around 3.5, shows dendritic growth, while an increase in the entropic term value goes along with an increase in faceted growth. The use of dimethyl carbonate (entropic factor of 5.0) results in lamellar-like structures. Lamellar structures are also observed for bornyl acetate (entropic factor of 6.0) and, even more pronounced, in case of p-xylene (entropic factor of 7.2). While this correlation acts as a general guide, the actual resulting pore structure and morphology is affected by several other factors as well. Also, potential reactivity within the solvent/precursor system is not taken into account. In this work, a pronounced tendency toward supercooling was observed for all solvents with the exception of camphene, which was shown to strongly affect the resulting pore structure in the final materials, leading toward irregular crystal growth and, depending on the solvent used, a significant coarsening of the pore structure.

### 3.2. Role of Nucleating Agents

In order to evaluate the possibility to mitigate the detrimental effects of supercooling during the solidification step, nucleating agents were introduced into the reaction mixtures. Si3N4 powder was chosen due to its chemical compatibility with the final polymer-derived ceramic materials in order to provide additional nucleation sites and to promote a more even and directed solidification of the structure-directing solvents.

Due to an increased turbidity after the introduction of Si3N4, the preparation conditions were slightly modified (increased initiator concentration, increased irradiation time) in order to ensure a homogeneous distribution as well as thorough cross-linking of the whole specimen.

In case of camphene, Si3N4 could not be dispersed homogeneously as a result of the increased viscosity of the reaction mixture. Additionally, photopolymerization was negatively affected for this material combination. As a consequence, the effect of Si3N4 on the resulting pore morphologies could not be investigated for camphene-containing reaction mixtures.

| Table 2. Physical properties of pore structure-directing solvents used in this work. |
|---------------------------------|-----------------|------------------|-----------------|
| Solvent                        | Density at 20°C | Melting point Tm | Enthalpy of fusion L | Entropic terms (L/RTm) of the Jackson α-factor |
| Camphene                       | 0.85 g cm⁻³     | 51 °C            | 9.44 kJ mol⁻¹      | 3.50                                                |
| Bornyl acetate                 | 0.98 g cm⁻³     | 27 °C            | 14.92 kJ mol⁻¹     | 5.98                                                |
| Dimethyl carbonate             | 1.07 g cm⁻³     | 5 °C             | 11.58 kJ mol⁻¹     | 5.01                                                |
| p-Xylene                       | 0.87 g cm⁻³     | 13 °C            | 17.11 kJ mol⁻¹     | 7.19                                                |

*[^1](#) data sheet values and [^2] values estimated according to ref. [26].

![Figure 3. Effect of structure-directing solvent on fracture surface morphologies of pyrolyzed materials structured by PASST; SEM images, top: transversal plane; bottom: longitudinal plane (precursor content: 25 wt%).](image-url)
For the remaining three structure-directing solvents, the effect of Si$_3$N$_4$ addition on the resulting pore morphologies showed significant differences depending on the choice of solvent (Figure 4). While a pronounced reduction of feature size was found for materials structured with bornyl acetate, no significant differences could be observed for dimethyl carbonate or p-xylene after addition of Si$_3$N$_4$. In addition to the smaller feature size, a distinct change in pore morphology was found for bornyl acetate-containing materials. In comparison to samples prepared without nucleating agents, columnar pore channels with spiral-like structures were now observed.

The effect of structure-directing solvent and nucleating agent on the morphological feature size was further investigated by mercury intrusion porosimetry studies (Figure 5). For samples prepared without the addition of nucleating agent, the median pore opening diameters were 6.9 $\mu$m (camphene), 43.8 $\mu$m (bornyl acetate), 40.2 $\mu$m (dimethyl carbonate), and 69.0 $\mu$m (p-xylene). Based on the histograms, a portion of pore openings in materials structured with p-xylene appear to be larger than 125 $\mu$m, which could not be accessed by the intrusion setup used; this has to be taken into account when interpreting the median pore opening diameter mentioned above. No significant differences in the pore opening size distribution were found for dimethyl carbonate or p-xylene after addition of Si$_3$N$_4$. In contrast, in the case of bornyl acetate, a significant reduction in pore size was found in the presence of the nucleating agent, resulting in a narrowing of the distribution as well as a decrease in median pore opening diameters to 26$\mu$m. No significant difference was found by increasing the Si$_3$N$_4$ content from 0.1 to 0.2 wt% (median pore opening diameters of 25.8 and 26.6 $\mu$m, respectively), indicating that even small amounts of nucleating agent are sufficient in avoiding supercooling.

The reason for the difference in effect of Si$_3$N$_4$ on the solidification of bornyl acetate (significant effect) and of dimethyl carbonate or p-xylene (no apparent effect) may be linked to differences in the interaction between the surface of the nucleating agent particles and the solvent molecules. Si$_3$N$_4$, which was chosen primarily due to its chemical compatibility with the resulting polysilazane-derived ceramic material, and which apparently provides interfacial properties effective for heterogeneous nucleation of bornyl acetate, may not be ideally suited for the crystallization of dimethyl carbonate or p-xylene. The degree of affinity between particle surface and solvent molecules may also affect the dispersibility of Si$_3$N$_4$ particulates in the reaction mixtures depending on the choice of solvent, promoting either dispersion or agglomeration, respectively, and thus leading to differences in the number of nucleation loci effectively available.

### 3.3. Role of Initial Precursor Content

Aside from the choice of structure-directing solvent and the addition of nucleating agents, the precursor content in the starting reaction mixture can be considered as one of the most straightforward factors determining the resulting porosity in the final materials. In order to evaluate the effects of a variation of the composition of the starting reaction mixture, the initial precursor content in bornyl acetate containing mixtures was varied between 15 and 40 wt%. As anticipated, both bulk density
and apparent porosity are directly affected by the starting composition (Figure 6). The addition of nucleating agent did not appear to significantly alter this behavior due to the very low amounts of Si₃N₄ added. For precursor contents exceeding 30 wt%, the crack formation tendency within the material was highly increased. Samples containing 40 wt% of precursor in the starting mixture contained macroscopic cracks and were thus excluded from further investigations.

Aside from the total porosity, the initial precursor content also affected the pore morphology when nucleating agents were present, as shown in Figure 7. Samples containing initial precursor contents of 25 wt% and below are composed of columnar as well as spiral-like pore structures, while at higher precursor contents, a transition toward columnar pore structures is observed. This is most likely caused by the higher solid content effectively constraining the lateral growth of bornyl acetate crystals during solidification, and thus defining the structure of the resulting porosity in the final ceramic material. The reduction in pore size can be clearly illustrated by mercury intrusion porosimetry investigations (Figure 8). An increase in precursor content in the initial reaction mixture results in a shift of the pore opening size distributions toward lower values, with a shift of the median pore opening diameter from 39 μm (15 wt% precursor content) to 27 μm (25 wt%) and finally 13 μm (35 wt%).

3.4. Permeability and Mechanical Properties

As shown in the previous sections, a wide variety of pore morphologies can be obtained through a variation of the structure-directing solvent in combination with the addition of nucleating agents promoting more uniform solidification through reducing the tendency toward supercooling and, as a result, spontaneous non-directional solidification.

With respect to prospective applications of the generated structures in the fields of separation or catalysis, their performance in terms of fluid permeability and strength are of major interest, and were thus investigated in detail. An overview of structural and mechanical properties of a selected range of materials prepared in this work is shown in Table 3.

Air permeability measurements, tested using a permeating flow parallel to the solidification direction, showed Darcian permeability values spanning three orders of magnitude, depending on the choice of structure-directing solvent (Figure 9a). While camphene-structured ceramics showing dendritic, small pore structures resulted in a Darcian permeability of 10⁻¹³ m², p-xylene-structured ceramics with large, lamellar pores exhibited values higher than 10⁻¹⁰ m² (based on initial precursor contents of 25 wt%). The permeability of accordingly prepared materials structured with bornyl acetate and dimethyl carbonate, both having intermediate pore sizes (Figure 5), was in the range of 10⁻¹¹ m².

The reduction in feature size after introducing Si₃N₄ as nucleating agent also affected the resulting permeability, albeit to a smaller degree. However, depending on the initial precursor content used, the difference in Darcian permeability between samples prepared without nucleating agent (thus undergoing supercooling and, consequently, spontaneous large-scale solidification) and samples containing 0.2 wt% Si₃N₄ can be as high as 250% (Figure 9b).

Large differences between samples prepared from different structure-directing agents can also be observed in terms of mechanical properties, showing a relation inverse to gas...
permeability characteristics. Camphene-structured materials show the highest compressive strength values of 50 MPa, while the strength of p-xylene-structured materials is well below 1 MPa.

The mechanism of failure appears to be comparable for all materials, showing progressing failure (corresponding to a failure of individual pore walls) after the maximum stress value had been reached following the initial elastic deformation region (Figure 10).

The difference in sample strength appears to be predominantly governed by total porosity and by pore opening size, as shown in Table 3. Furthermore, the shape of pore channels can be assumed to have a high impact on sample strength, as has been described in several earlier reports.

As shown by these results, the choice of the structure-directing solvent has a tremendous impact on the resulting ceramic material’s pore structure and, in extension, to its performance in prospective application fields.

With regard to the sample dimensions achievable through this process, two sets of limitations have to be considered. First, for reproducible freeze-casting results, a constant solidification front velocity has to be sustained throughout the whole solidification process, which is limited by several factors including the cooling capacity of the base plate, the thermal conductivity of the solidified material, and heat transport through the reactor walls. Second, the attainable depth of photopolymerization required for curing of the precursor phase is limited by absorption processes in the solidified reaction mixture, which can be affected by the opacity of the solidified mixture as well as by additional scattering effects caused by nucleating agent particles.

Table 3. Overview of structural and mechanical properties of pyrolyzed specimens obtained by PASST (initial precursor content: 25 wt%).

| Structure-directing solvent | Nucleating agent (Si₃N₄) [wt%] | Apparent porosity[a] [%] | Median pore opening diameter[b] [μm] | Darcian permeability $k_1$ [m²] | Non-Darcian permeability $k_2$ [m] | Compressive strength [MPa] |
|-----------------------------|--------------------------------|--------------------------|------------------------------------|-----------------------------|---------------------------------|---------------------------|
| Camphene                    | –                              | 43                       | 6.9                                | $2.6 \times 10^{-13}$       | $2.2 \times 10^{-8}$            | 50.8 ± 17.5                 |
| Bornyl acetate              | –                              | 64                       | 43.8                               | $1.0 \times 10^{-11}$       | $1.6 \times 10^{-5}$            | 0.23 ± 0.64                 |
|                            | 0.1                            | 64                       | 25.8                               | $8.2 \times 10^{-12}$       | $8.0 \times 10^{-6}$            | 8.23 ± 0.64                 |
| Dimethyl carbonate          | –                              | 69                       | 40.2                               | $2.5 \times 10^{-11}$       | $8.4 \times 10^{-6}$            | 3.21 ± 0.66                 |
|                            | 0.1                            | 68                       | 40.6                               | $1.5 \times 10^{-11}$       | $3.6 \times 10^{-5}$            | 3.21 ± 0.66                 |
| p-Xylene                    | –                              | 73                       | 69.0                               | $1.1 \times 10^{-10}$       | $1.1 \times 10^{-5}$            | 0.69 ± 0.01                 |
|                            | 0.1                            | 73                       | 72.1                               | $5.4 \times 10^{-11}$       | $1.5 \times 10^{-5}$            | 0.69 ± 0.01                 |

[a] determined by immersion method; and [b] determined by mercury intrusion porosimetry.
4. Conclusions

In this work, we introduced new approaches toward controlling porosity and pore structure in PDC, employing the recently reported photopolymerization-assisted solidification templating (PASST) technique. By careful selection of structure-directing solvents such as camphene, bornyl acetate, dimethyl carbonate, or p-xylene, the resulting pore channel morphologies can be controlled in a straightforward manner, ranging from dendritic to lamellar and columnar structures. For selected solvents, the addition of a nucleating agent (in the present case, Si3N4) significantly improved the robustness of the preparation technique by promoting controlled solidification and thus suppressing the tendency of the reaction mixture toward supercooling. By a combined variation of structure-directing solvent, precursor content, and nucleating agent in combination with the PASST technique, solidification-templated polysilazane-derived ceramics with a large range of porosity and pore morphologies are accessible for the first time. Consequently, this allows for a straightforward tailoring of material properties, in particular with regard to strength and permeability, thus being well-suited for creating novel materials applicable in prospective applications related to energy conversion or environment, examples including separation or catalysis.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

freeze-casting, polymer-derived ceramics, polysilazane, porosity

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