Tubular ceramic structures from polymer precursors with controlled porosity, strength, and permeability characteristics

Thomas KONEGGER,† Thomas PROCHASKA and Richard OBMANN

TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-CT, 1060 Vienna, Austria

A processing technique for the preparation of porous, silicon carbonitride-based ceramics in tubular geometry derived from a liquid polysilazane precursor is presented. After casting of polysilazane/polymer-microbead dispersions, cross-linking, and subsequent pyrolytic conversion and selective removal of polymer templates, specimens with an inner and outer diameter of 6 and 10 mm, respectively, and a length of up to 65 mm were obtained. Porosity was controlled by sacrificial template content and reached values up to 48% after pyrolytic conversion, at average pore opening radii of 1 μm. The tubular specimens exhibited diametral compression strengths (C-ring test) between 24 ± 6 and 36 ± 4 MPa. Darcian permeability constants of up to 1.7·10⁻¹⁴ m² were found by gas permeability testing. The results demonstrate that this methodology facilitates the straightforward generation of complex-shaped porous specimens, further allowing for a control of strength and permeability in a specific range. Potential applications for the tubular, porous structures developed can be anticipated in the fields of separation or catalysis.

Key-words : Polysilazane, SiCN, Casting, Porosity, Tubular structures

1. Introduction

Current global challenges in the energy and environmental sectors have resulted in a rising awareness for more sustainable and efficient industrial processes. Increased process efficiency is often achieved by operation in more demanding environments, including high temperatures, often in the presence of reactive species. This, in turn, creates an increasing demand for the development of new, suitable, and cost-effective materials. Specific examples can be found in the fields of separation science or catalysis. In both cases, functionally relevant structures such as catalytically active centers or selective membrane layers are either only present in small quantities or do not offer sufficient mechanical strength for the prospective application. As a result, porous ceramics are often used as support structures. In addition to mechanical requirements, these materials have to exhibit chemical and thermal stability at the intended operating environments as well as high permeability for gaseous or liquid species. Due to their excellent performance in terms of corrosion stability, thermal and mechanical properties, ceramics such as Al₂O₃, SiC, or Si₃N₄ have been used for this purpose, as well as for conventional filtration, primarily for applications at increased temperatures. However, limitations in pore structure control during conventional ceramic processing techniques stemming from the requirement of using solid powders as starting materials, as well as highly demanding and thus cost-increasing sintering process requirements – in particular for non-oxide ceramic materials, often requiring sintering temperatures well beyond 1500°C – are commonly encountered disadvantages.

The preparation of ceramic materials from polymer precursors, the so-called polymer pyrolysis route, opens new paths towards generating ceramic structures. Here, polymer compounds such as polysiloxanes, polycarbosilanes, or polysilazanes act as precursors to amorphous or crystalline ceramic materials such as silicon oxycarbides, silicon carbide, or silicon carbonitrides, which are obtained through a controlled pyrolytic conversion process. Owing to the use of polymer educts, a wide variety of processing options are available, which can be used to create structures ranging from monolithic materials to fibers or coatings. This high flexibility in shaping options, in combination with comparably low thermal requirements for consolidation, are major advantages of this route, and have also led to an increased interest towards generating porous compounds. Pore formation strategies applied to polymer-derived ceramics include replica techniques, direct foaming, or the use of sacrificial templates. The latter technique, which employs the selective removal of organic or inorganic porogens by chemical or thermal means, has been shown to be of particular suitability due to its versatility and robustness.

Recently, we reported on a new methodology to create planar, porous, polymer-derived ceramic structures from polycarbosilane and polysilazane precursors in combination with polyethylene templates, with prospective applicability in the fields of separation or catalysis. However, for an anticipated use of these materials on a larger scale, up to the industrial application, planar geometries are less suitable due to a decreased functional surface. Generally, a tubular setup of supports with an increased surface-to-volume ratio is preferred. As a consequence, the objective of this work is the development and presentation of a casting-based approach to generate porous, polymer-derived ceramic structures in tubular geometry, to evaluate their applicability in terms of pore structure control, strength, and permeability characteristics, and to discuss benefits as well as limitations of the proposed approach.

2. Experimental procedure

2.1 Preparation of tubular specimens

A liquid poly(vinyl)silazane (Durazane 1800, durXtreme
GmbH, Germany) was used as precursor compound, which transforms into an amorphous Si–C–N–based material by pyrolytic conversion in the temperature range between 300 and 700°C in N₂ atmosphere. Due to its sensitivity towards hydrolytic decomposition, all processing steps up to cross-linking were conducted in protective nitrogen atmosphere. As sacrificial porogen compound, ultrahigh-molecular weight polyethylene microbeads (Mipelon PM 200, Mitsui Chemicals Europe, Germany; average particle size 10 µm, molecular weight 1.8 x 10⁶ g/mol) were used. The porogen particles were dried in a vacuum chamber at 60°C before application.

The porogen was dispersed in the precursor compound using a magnetic stirrer under vacuum, with a variation of porogen contents between 25 and 35 Vol.%. Subsequently, the flowable mixture was cast into molds defining the tubular shape, consisting of an elastomeric cup made of a condensation-curing polydimethylsiloxane compound (MoldMax XLS II, Smooth-On Inc., USA) in combination with a removable PTFE core. The core was centered by a cavity in the elastomeric mold and by an aluminum lid with a corresponding bore.

After initial problems resulting from bubble formation during the cross-linking step, specifically when casting larger specimens, two mitigation strategies were employed. First, the polysilazane/porogen mixture had to be thoroughly degassed, using a final vacuum of well below 1 mbar. Second, the elastomeric molds were preconditioned at 110°C before casting any residual moisture potentially contributing to hydrolytic decomposition of the polysilazane compound. Condensation-curing PDMS molds yielded superior results compared to addition-curing PDMS molds or rigid PTFE-based molds used in preliminary experiments, which were found to cause excessive adhesion to the cross-linked samples or crack formation due to cross-linking induced stresses, respectively.

The cast mixtures were cross-linked in flowing N₂ atmosphere at 105°C for 16 h before demolding. The material on the inner and outer surface of the tubular specimens in contact with the mold was removed by abrading/polishing before ceramization. Pyrolytic conversion was conducted in high-purity flowing N₂ (0.5 L/min) in an alumina tube furnace (HIZ 12/600, Carbolite, Germany) for 4 h at 800°C, using a heating rate of 1 K/min up to 300°C with an intermediate holding segment at 130°C for 2 h, and with a heating rate of 0.5 K/min between 300 and 800°C. After pyrolytic conversion, tubular specimens with outer and inner diameters of 10 and 6 mm, respectively, and lengths of up to 65 mm were obtained.

2.2 Characterization techniques

Microstructural features and pore morphology were evaluated by scanning electron microscopy (Quanta 200, FEI, the Netherlands).

The bulk density ρ₀ was determined by the Archimedes method. The skeletal density ρₛ was determined by helium pycnometry of crushed pyrolyzed samples (Ultrapycnometer 1000, Quantachrome, Germany). Total porosity Φ was calculated by Φ = 1 – (ρ₀/ρₛ). The distributions of pore opening radii of selected samples were determined by mercury intrusion porosimetry (Pascal 140/440, Porotec, Germany).

The strength of the specimens was determined using the C-ring setup for testing of tubular sections. Sections with a length of 5 mm were cut from the pyrolyzed specimens using a diamond cut-off wheel. An additional cut was placed in longitudinal direction, and the resulting ring segments were tested in diametral compression at a crosshead speed of 0.5 mm/min until failure (Model 1474, Zwick, Germany). The failure stress σₘ was calculated using Eqs. (1) and (2), rₒ: outer radius; rᵢ: inner radius; r: mean radius with r = (rₒ + rᵢ)/2:

\[ \sigma_m = \left[ \frac{(rₒ - 0.5 \cdot t) \cdot (rₒ - L)}{rₒ \cdot (r - L)} - 1 \right] \frac{F}{Bt} \]  \tag{1}

with

\[ L = \frac{t \ln \left( \frac{rₒ}{rᵢ} \right)}{\ln \left( \frac{rᵢ}{rₒ} \right)} \]  \tag{2}

For each composition, an average strength value was calculated from testing of 10 sections, taken from a minimum of three individual specimens.

Permeability testing was conducted at room temperature using pyrolyzed, tubular samples with a length of 25 to 30 mm, with filtered compressed air as fluid. Using a soap bubble flow meter, the stationary permeating gas flow Q through the tube wall was recorded as a function of differential pressure between upstream and downstream side of the specimen, varying Δp between 0.25 and 2 bar. 8 sets of pressure drop and Q values were recorded per sample, with a minimum of three samples tested per composition. Using Forchheimer’s equation for compressible fluids,

\[ \frac{p_1^2 - p_2^2}{2p_m \cdot l} = \frac{\eta \left( \frac{Q}{A} \right)}{k_1 A + \frac{Q}{k_2 A}} \]  \tag{3}


\[ \frac{p_1^2 - p_2^2}{2p_m \cdot l} = \frac{\eta \left( \frac{Q}{A} \right)}{k_1 A + \frac{Q}{k_2 A}} \]  \tag{3}

k₁ and k₂ were calculated by fitting of a quadratic function to \((p_1^2 - p_2^2)/2p_m \cdot l)\) versus \(Q/A\) using the least-squares method.

3. Results and discussion

3.1 Preparation of tubular specimens

Following the developed procedures resulted in the successful preparation of crack- and bubble-free tubular specimens (Fig. 1). The mold size was designed to accommodate linear shrinkage encountered during pyrolytic conversion, typically in the range of 23 to 25%, resulting in final lengths of > 60 mm and inner and outer diameters of 6 and 10 mm, respectively. The addition of polymeric templates was found to be an essential requirement for

![Fig. 1. Tubular precursor/porogen-derived specimens after cross-linking and demolding (left) and after pyrolytic conversion (right).](image-url)
the preparation of intact specimens – no template-free specimens were prepared owing to excessive cracking during pyrolytic conversion.

After cross-linking, abrading of the outer and inner surfaces of tubes was found to be necessary to avoid the presence of closed surfaces resulting from the wetting of the mold surfaces by the preceramic polymer during the casting process. If retained during pyrolytic conversion, these closed surfaces would lead to inferior permeability characteristics.

3.2 Microstructure and porosity

Samples exhibited a microstructure dominated by spherical pores with diameters of 7–8 μm defined by the microbead templates (Fig. 2). The type of interconnection between pores shifted from microcracks spanning several pores, predominating at lower template contents, to circular pore windows at higher template contents. A preferred orientation of microcracks in circumferential direction was observed, most likely a result of shrinkage-induced stresses during pyrolytic conversion.

As expected, a direct correlation between initial porogen contents and resulting total porosities was found (Table 1). The resulting porosities were significantly larger than anticipated from the porogen volume fractions, caused by the formation of porosity in the preceramic polymer backbone, as well as by the emergence of microcracks.

Information on the pore opening radii was obtained by mercury intrusion porosimetry. The size of pore openings, effectively corresponding to the pore windows, limits the intrusion of fluids such as mercury, and, consequently, has a significant effect on permeability characteristics. The results indicated differences in the pore opening size distribution depending on the initial porogen content, with a slight shift of the average pore radius from 1.1 to 0.8 μm at the highest template content (Fig. 3). This observation, confirmed by repeated porosimetry measurements, can be explained by the aforementioned differences in pore connectibility; larger microcracks, present in specimens with lower porosity, lead to a filling of primary pores at lower mercury pressures, resulting in larger apparent pore sizes and, subsequently, a widening of the pore radius distributions. Both the pore opening diameter and the total porosity can be anticipated to strongly affect the resulting material properties.

As shown from the results in Fig. 3, small amounts of porosity in the mesopore range (pore sizes < 50 nm) are present in the sample. The evolution of both micro- and mesoporosity during the pyrolytic conversion of preceramic polymers has been reported previously,23) with prospective uses in a wide variety of applications, including catalysis, gas separation, or gas storage.24) Hierarchical porosity as encountered in the present materials, consisting of porogen-derived macropores in combination with mesopores in the ceramic backbone structure, may lead the way to additional functionality, e.g. as catalyst carriers.

3.3 Strength

The strength of ring segments of tubular specimens was tested in diametral compression using a C-ring setup. In the used setup, the obtained strength values correspond to the failure stress on the outer diameter of the tube opposite of the applied sectioning cut, which experiences a tensile load regime. The possibility to test the as-fabricated tube surfaces is a major advantage of this test setup vs. common alternatives such as machined four-point-flexural bars, as the influence of machining damages is minimized.

![Fig. 2. Micrographs of fracture surfaces of pyrolyzed tubular specimens with initial porogen contents of 25% (a, b), 30% (c, d), and 35% (e, f).](image)

![Table 1. Density and porosity characteristics of pyrolyzed specimens](image)

<table>
<thead>
<tr>
<th>Template content / Vol. %</th>
<th>Bulk density / g/cm³</th>
<th>Total porosity* / %</th>
<th>Average pore opening radius / μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>1.31 ± 0.03</td>
<td>35.6 ± 0.7</td>
<td>1.1</td>
</tr>
<tr>
<td>27.5</td>
<td>1.26 ± 0.01</td>
<td>38.3 ± 0.4</td>
<td>—</td>
</tr>
<tr>
<td>30.0</td>
<td>1.18 ± 0.01</td>
<td>42.0 ± 0.5</td>
<td>1.1</td>
</tr>
<tr>
<td>32.8</td>
<td>1.10 ± 0.04</td>
<td>46.1 ± 1.5</td>
<td>—</td>
</tr>
<tr>
<td>35.0</td>
<td>1.06 ± 0.01</td>
<td>48.0 ± 0.6</td>
<td>0.8</td>
</tr>
</tbody>
</table>

*with respect to skeletal density of crushed samples determined by He-pycnometry (2.04 g/cm³).

†determined by mercury intrusion porosimetry.

![Fig. 3. Pore size distribution of pyrolyzed materials as a function of initial porogen content, determined by mercury intrusion porosimetry.](image)
present case, the correlation can be adequately described by a relationship between typical porosities and pore sizes (e.g., \(9.5 \times 10^{-12} \text{m}^2\)) and an average pore opening radius of 1 \(\mu\text{m}\). Non-Darcian contributions to the permeating fluid as well as pore windows interconnecting the spherical, template-defined pores, in addition to increased porosity, both of which contribute to increased permeabilities.

A major benefit of this preparation technique for tubular specimens is the versatility in shaping, which is not only limited to tubular specimens, but also suitable for more complex shaped porous structures, by being able to use economical mold materials with a high degree of freedom in terms of shapes accessible due to their own castability. Furthermore, as it can be seen from the results of strength and permeability tests, a straightforward control of these characteristics, albeit in a range confined by the processing parameters, is available to tailor these relevant materials to prospective applications. Further parameters for pore tuning which have not been explored in this work include the variation of porogen size or the use of multimodal porogen content.

Table 2. Mechanical properties and air permeability characteristics of pyrolyzed, tubular specimens

<table>
<thead>
<tr>
<th>Template content/Vol.%</th>
<th>Strength (C-ring) (\sigma_c/\text{MPa})</th>
<th>Darcian permeability (k_1/10^{-15} \text{m}^2)</th>
<th>Non-Darcian permeability (k_2/10^{-19} \text{m})</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>36.0 ± 3.6</td>
<td>6.9 ± 0.9</td>
<td>1.6 ± 0.5</td>
</tr>
<tr>
<td>27.5</td>
<td>30.9 ± 2.6</td>
<td>8.1 ± 0.9</td>
<td>2.5 ± 1.0</td>
</tr>
<tr>
<td>30.0</td>
<td>29.2 ± 4.5</td>
<td>10.0 ± 1.1</td>
<td>3.3 ± 0.3</td>
</tr>
<tr>
<td>32.8</td>
<td>22.5 ± 3.2</td>
<td>12.4 ± 0.5</td>
<td>5.6 ± 0.7</td>
</tr>
<tr>
<td>35.0</td>
<td>23.5 ± 6.4</td>
<td>16.5 ± 1.6</td>
<td>8.5 ± 6.3</td>
</tr>
</tbody>
</table>

Fig. 4. Strength of pyrolyzed, tubular specimens as a function of porosity (C-ring test of ring segments), showing an exponential fit to the mean values (solid line) and the corresponding 95% confidence interval (between dashed lines).

Strength decreases from 36 MPa for samples with an initial porogen volume content of 25% to 24 MPa for samples prepared with 35 Vol.% (Table 2). Owing to the domination of failure by surface flaws on the outer diameter of tubes, considerable scattering of strength data can be observed. The obtained strength values can be considered satisfactory over the whole parameter range.

The strength behavior can be described by commonly used models for strength/porosity correlations, e.g. the frequently observed exponential relationship \(\sigma_c = \sigma_0 \exp(-b\Phi)\). In the present case, the correlation can be adequately described by fitting parameters of \(\sigma_0 = 131 \text{MPa}\) and \(b = 3.7\) (Fig. 4).

3.4 Gas permeability

The permeability characteristics of tubular, pyrolyzed specimens showed deviations from the classical Darcian behavior of compressible fluids, where only viscous contributions are considered. Hence, both the compressibility of the fluid as well as inertial (Non-Darcian) contributions at higher flow velocities were taken into account to adequately describe the permeability characteristics, following the relationship between pressure drop and permeating flow for compressible fluids described by Forchheimer [Eq. (3)]. Based on sets of flow/pressure drop pairs recorded for multiple specimens (Fig. 5), Darcian- and Non-Darcian contributions to the permeating flow were calculated (Fig. 6).

Again, as expected, a clear correlation between permeability and porosity was observed. Darcian permeability constants were found to lie between 0.7 to 1.7 \(\times 10^{-12} \text{m}^2\), thus being in the range of permeabilities encountered for planar materials with comparable porosities and pore sizes (e.g., 9.5 \(\times 10^{-15} \text{m}^2\) at a porosity of 42% and an average pore opening radius of 1 \(\mu\text{m}\)). Non-Darcian permeability constants were distributed over a wider range, spanning nearly an order of magnitude up to \(10^{-6} \text{m}\), and showed a higher degree of scattering between individual samples. The sets of Darcian/Non-Darcian permeability constants observed for the materials investigated in this work are well within typical ratios observed for cellular ceramic materials.

Reduced pore opening diameters observed for specimens prepared with higher porogen contents did not have a diminishing effect on permeability; on the contrary, an increase in permeability going beyond the linear relationship observed for lower porogen contents was found. An explanation for this is a potentially decreased tortuosity due to an increased number of pore windows interconnecting the spherical, template-defined pores, in addition to increased porosity, both of which contribute to increased permeabilities.

Fig. 5. Typical air flow curves for pyrolyzed tubular specimens with varying porogen volume contents (as listed in the graph).

Fig. 6. Darcian and non-Darcian permeability constants of pyrolyzed, tubular specimens as a function of porosity (fluid: air).
compositions, both of which can be considered to significantly affect the strength/permeability characteristics.

A limitation lies in the requirement for a flowable starting mixture, which is constrained by the precursor/porogen ratio, and subsequently limits the porosity range accessible by this technique. Preliminary experiments have shown the precursor/porogen mixtures to be castable up to porogen contents of 45 Vol.% without the addition of further compounds such as solvents. At higher porogen contents, pressure-assisted techniques may have to be applied for shaping. Following this approach might also allow for a more direct control of the pore opening window size by pressure/temperature-induced viscous flow of the porogen microbeads. In this case, however, the structural integrity of the precursor network during porogen decomposition has to be warranted, e.g. by a tightly controlled porogen decomposition routine, in order to avoid excessive cracking during ceramization.

4. Conclusions

In this contribution, we present novel tubular, porous ceramic structures employing the casting of a preceramic polymer compound in combination with pore generation through the addition of sacrificial templates, followed by a subsequent thermal treatment responsible for both precursor ceramization and template decomposition.

This technique allows for a straightforward variation of tube dimensions using suitable molds, as well as control of the resulting porosity through the initial casting composition. Consequently, a control over the porosity also facilitates a control of strength as well as permeability of the generated materials, both of which were shown to be directly correlated to the initial composition parameters.

The chosen parameter range thus facilitates the production of tubular structures achieving both satisfactory mechanical properties as well as sufficiently high permeabilities for prospective applications in a variety of fields, including separation or catalysis.

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