Hierarchisch strukturiertes Siliziumdioxid und seine mechanischen Eigenschaften

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In cooperation with the Institute of Materials Chemistry, TU Vienna, Austria

Sol-gel derived hierarchically structured SiO\textsubscript{2}

Nature’s strategies: hierarchical buildup, cellular structures, anisotropy, nanocomposites

Aims:
- study the evolution of meso- and macrostructure
- test mechanical properties
- additional level through macroscopic templating
**Synthesis of the Inorganic Network**

**Motivation**

**Material Synthesis**

**Structural properties**

**Mechanical properties**

**Macroscopic templating**

**Conclusion**

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**sol-gel principle:**

- **Hydrolysis:** $\text{Si-OR} + \text{H}_2\text{O} \rightarrow \text{Si-OH} + \text{ROH}$
- **Condensation:** $\text{Si-OH} + \text{HO-Si} \rightarrow \text{Si-O-Si} + \text{H}_2\text{O}$
  $\text{Si-OH} + \text{RO-Si} \rightarrow \text{Si-O-Si} + \text{ROH}$

**Si-precursor**

- *ethylene glycol modified silane*
- *phenylene bridged ethylene glycol modified silane*

**Advantage of the modified precursor:**
- high water solubility
- no catalyst needed
- high compatibility with lyotropic liquid crystal phases
- easy formation of monolithic material

Brandhuber et al., Chemistry of Materials (2005), 17(16), p. 4262-4271

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**Supramolecular Self Assembly-Templating**

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**Typical experimental procedure:**
- homogenisation
- gelation at 313 K
- ageing for 1 week at 313 K
  $\rightarrow$ wet mesostructured gel

**Non-ionic block copolymer surfactant**

**Pluronic P123,**

**PEO$_{20}$PPO$_{70}$PEO$_{20}$

**$+ \text{HCl}$**

**mesopores:** liquid crystalline templating

**macropores:** phase separation (spinodal decomposition)
In-situ synchrotron Small Angle X-ray Scattering (ESRF, ID2):

**Evolution of the periodic mesostructure during gel-formation**

**q-region overlap**
**SAXS**

*In-situ* synchrotron Small Angle X-ray Scattering (ESRF, ID2):

1. I: growth of silica/surfactant rich agglomerates (> 100 nm)
2. II: formation of spherical particles (R~10 nm)
3. III: formation of periodic mesostructure

**Influence of Dilution**

- **SEM morphology with smaller curvature**
- **time of phase separation and mesostructure formation**

Motivation
Material Synthesis
Structural properties
Mechanical properties
Macroscopic templating
Conclusion
Samples for Mechanical Testing

Motivation
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Conclusion

*In-situ* synchrotron Small Angle X-ray Scattering (Elettra, SAXS-Beamline):

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<tr>
<td>50</td>
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ordered silica-surfactant phase forms

Fitting of the data

Drying of the Monoliths

wet monolith (as synthesized) - dry monolith

- Problem: capillary forces
- Solution: supercritical drying

low temperature (LT) with CO₂, high temperature (HT) with MeOH

<table>
<thead>
<tr>
<th>Supercritical fluid</th>
<th>Pcrit / bar</th>
<th>Tcrit / K</th>
<th>shrinkage</th>
<th>d_{100} / nm</th>
<th>g_{SBET} / m²/g</th>
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<tbody>
<tr>
<td>CO₂ LT</td>
<td>73.8</td>
<td>304.4</td>
<td>10.4 %</td>
<td>11.64</td>
<td>891</td>
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<tr>
<td>MeOH HT</td>
<td>80.9</td>
<td>512.6</td>
<td>19.2 %</td>
<td>11.22</td>
<td>462</td>
</tr>
</tbody>
</table>

SEM
Young's Modulus

compression test:

LT: 72.3 ± 4 MPa
HT: 338.5 ± 52 MPa

correlation between porosity and modulus

Instrumented indentation testing

LT-samples:
- more easily penetrated
- network relaxes after unloading

HT-samples:
- rigid
- higher degree of irreversible damage

Puchegger et al., Journal of Non-Crystalline Solids (2006), 352, p. 5251-5256
**Complex Macroscopic 3D-Shape**

**Aim:**
- macroscopical 3d-shape of the mesostructured SiO₂ (e.g., high geometric complexity and heavily undercut features)

**Why?**
- widens the application possibilities of mesostructures materials (e.g., fluidic devices)

**How?**
- templating by using sacrificial molds

**Problem with conventional methods:**
- often involve high temperatures to remove the mold (not possible for organically modified gels)
- or are not compatible with the sol-gel process (e.g., water-soluble molds)
- shrinking of the SiO₂-network → cracking before removal of the mold

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**Mold Processing of Sol-Gel Materials**

**proposed approach:**

- Computer aided design
- Digital light processing (DLP)
- light sensitive resin based on branched dialkylacrylamides and a cleavable crosslinker
- sacrificial organosoluble photopolymer-mold

Inführ et al., RadTech, Conference Proc. (2005), 2, 489-494
Mold Process

- mesostructured SiO₂: inorganic polymer
- Digital light processing (DLP): sacrificial organosoluble photopolymer-mold
  → additional hierarchical level

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Drying with Supercritical MeOH

Hierarchically structured monoliths with 3 structure levels:
  nanometer – sub-micron - macrostructure

Summary

- Synchrotron x-ray scattering with variable camera length (up to 10m) is a suitable method to study the structure on the nanometer and sub-micrometer scale of hierarchical materials.

- The structure formation can be followed in-situ. The mesostructure and sub-micrometer structure evolution takes place in parallel for a mesostructured silica system based on organically modified EGMS as precursor.

- Compression tests and instrumented indentation measurements give values for the Young’s modulus that are in accordance with literature and are correlated to the porosity/density of the material.

- By templating mesostructured silica with Rapid Prototyping-molds made from an organo-soluble resin, an additional 3D structure on the macro-scale can be induced → 3 levels of structural hierarchy (nano-micro-millimeter).
Thanks to R. Liska and R. Inführ (Institute of Applied Synthetic Chemistry, TU Vienna) for developing the organosoluble photopolymers, also special thanks to H. Peterlik and S. Puchegger (Institute of Materials Physics, University of Vienna) for help and fruitful SAXS-discussions and the ICMAB and MATGRAS (Anna Roig, Elena and Raul) in Barcelona for the possibility to dry my samples supercritically.

Thank you for your attention!