LA-UR- 04- 2102

Approved for public release; distribution is unlimited.

Title: Surface Modification of Low Density Silica and Bridged Polysilsesquioxane Aerogels

Author(s): Kimberly A. DeFriend, Douglas A. Loy, Kenneth V. Salazar, and Kennard V. Wilson

Submitted to: 227th American Chemical Society National Meeting; Anaheim, CA

Los Alamos
NATIONAL LABORATORY

SURFACE MODIFICATION OF LOW DENSITY SILICA AND BRIDGED POLYSILSESQUIOXANE AEROGELS

Kimberly A. DeFriend, Douglas A. Loy, Kenneth V. Salazar and Kennard V. Wilson

Los Alamos National Laboratory

Coatings and Polymers MST-7

Materials Science and Technology Division

Los Alamos, NM 87532

Silica and bridged polysilsesquioxane aerogels are low density materials that are attractive for applications such as, thermal insulation, porous separation media or catalyst supports, adsorbents. However, aerogels are notoriously weak and brittle making it difficult to handle and machine monoliths into desired forms. This prevents the development of many applications that would otherwise benefit from the use of the low density materials. We will describe our efforts to chemically modify and mechanically enhance silica-based aerogels using chemical vapor techniques without sacrificing their characteristic low densities. Monolithic silica and organically bridged polysilsesquioxane aerogels were prepared by sol-gel polymerization of the respective methoxysilane monomers followed by supercritical carbon dioxide drying of the gels. Reactive modification of the gels with volatile silylating compounds during and after the drying process and these effects on the mechanical properties and density of the aerogels will be described.

Surface Modification of Low Density Silica and Bridged Polysilsesquioxane Aerogels

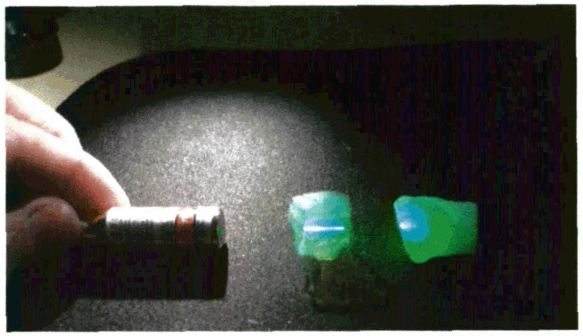
Los Alamos
NATIONAL LABORATORY

Kimberly A. DeFriend, *Douglas A. Loy*,
Kenneth V. Salazar and Kennard V. Wilson
Materials Science & Technology Division
Los Alamos National Laboratory, Los Alamos, NM 87545

LA-UR#

What are Aerogels?

Silica aerogels were first prepared by S. S. Kistler is 1931



Laser light penetrating a silica aerogel

Low densities (0.003 - 0.7 g/ cc)
High transparency
High porosity (>95%)
Low thermal conductivity (0.012 W/ mK)
Large surface area (1600 m^2/g)
Small pore sizes (<100 nm)
Open pore structure
Silica, alumina, carbon, RF organic systems
Transition metals, mixed metal oxide systems
Brittle

Applications

- **Thermal insulation**
- **Cherenkov particle detection and counters**
- **Catalyst supports**
- **Dielectric films**
- **Energy storage**
- **Filters, membranes and absorbing media**
- **Encapsulating media for waste management**
- **Cometary dust encapsulant**
- **Hydrogen fuel storage**
- **Energetic materials**
- **ICF targets for thermonuclear fusion**
- **Shock absorbing material**

Monomers Used for Silica Aerogel Processing

Generation I

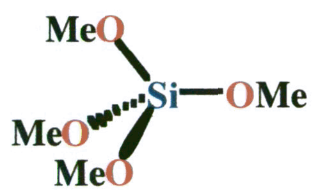
Water Glass

$SiO_2 : Na_2O$

- First used to make silica aerogels
- Inexpensive
- Alkaline

Generation II

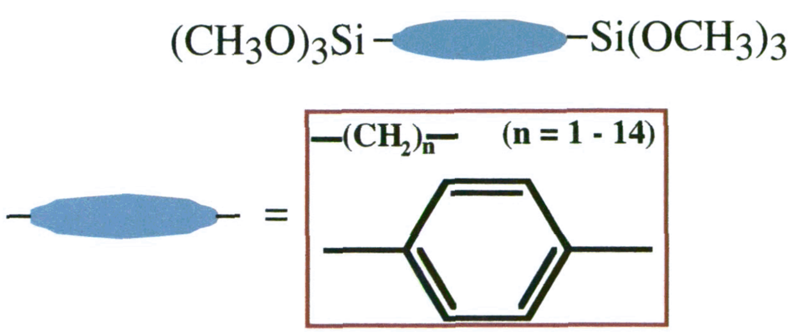
Silicon Alkoxides



- Examples: TMOS, TEOS
- Traditionally used to make aerogels
- Relatively inexpensive

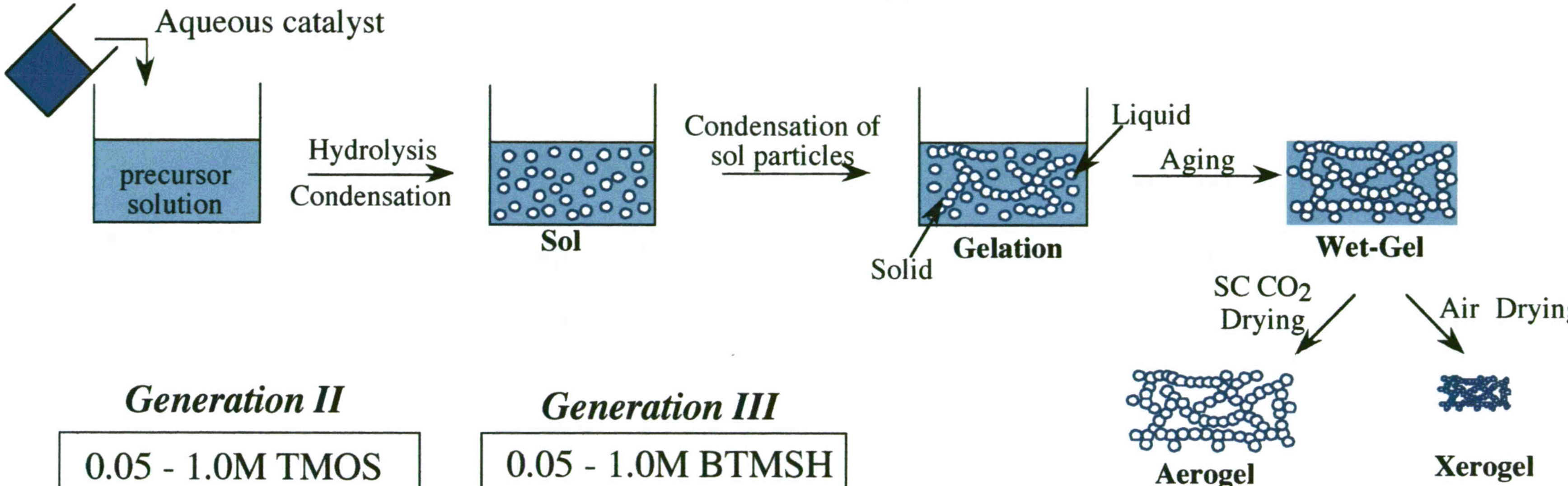
Generation III

Polysilsesquioxanes

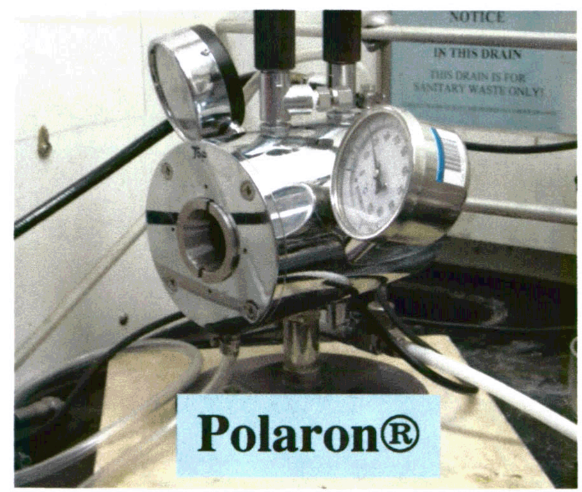


- Ex: 1,6-Bis(trimethoxysilyl)hexane ⇒ BTMSH
- Increased chemical functionality
- Posses both inorganic & organic characteristic
  - inorganic stability
  - organic flexibility & robustness
- Tailor gel architecture through organic spacer

Preparation of Aerogels by Sol-Gel Processing



Generation II	*Generation III*
0.05 - 1.0M TMOS MeOH 4 or 8 eq. H_2O 7 mole% NH_4OH	0.05 - 1.0M BTMSH MeOH 6 or 12 eq. H_2O 10 mole% NaOH



Hydrolysis

$$\text{Si-OR} + H_2O \rightleftharpoons \text{Si-OH} + \text{ROH}$$

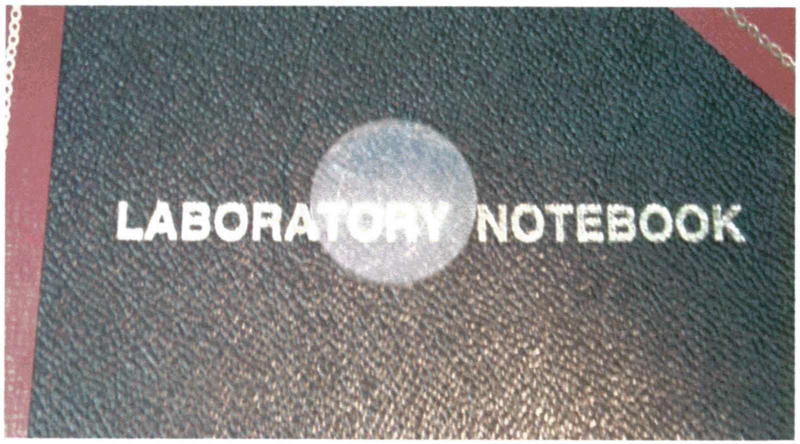
Condensation

$$\text{Si-OR} + \text{HO-Si} \rightleftharpoons \text{Si-O-Si} + \text{ROH}$$

$$\text{Si-OH} + \text{HO-Si} \rightleftharpoons \text{Si-O-Si} + H_2O$$

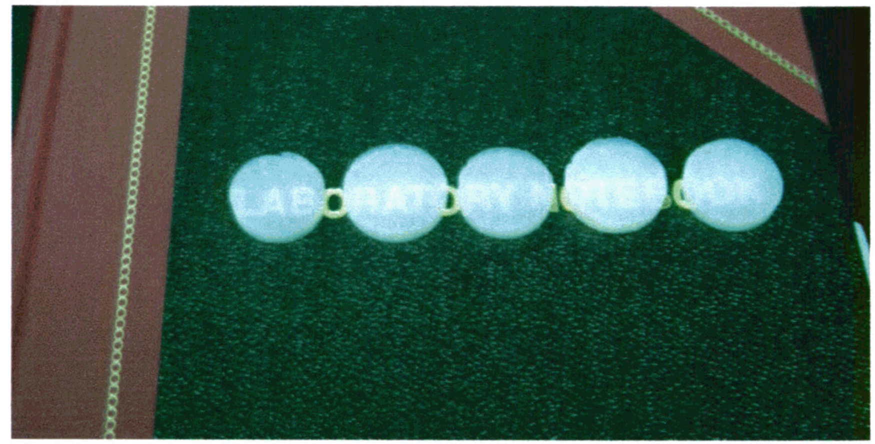
TMOS & 1,6-Bis(trimethoxysilyl)hexane Derived Silica Aerogels

TMOS Aerogel



- **Transparent**
- **Densities: 0.03 - 0.09 g/cc**
- **Surface Areas: 800 m^2/g**

BTMSH Aerogel



- **Translucent/transparent**
- **Densities: 0.09 - 0.29 g/cc**
- **Surface Areas: >700 m^2/g**

Brittle

Modifying to Strengthening Aerogels

- **Ostwald Coarsening** ⇒ extended aging time
  - M. -A. Einarsrud *et al.*, J. Non-Cryst. Solids, 285, 2001, 1-7
  - G. W. Scherer *et al.*, J. Non-Cryst. Solids, 121, 1990, 202-205

- **Composite Formation** ⇒ addition of particles, fibers or organics
  - E. Molins *et al.*, Applied Physics A., 74, 2002, 119-122
  - F. Milstein *et al.*, J. Non-Cryst. Solids, 223, 1998, 179-189
  - P. Norris *et al.*, J. Non-Cryst. Solids, 285, 2001, 222-229

- **Solution Silylation** ⇒ hydrophobic, monolayer surfaces & control shrinkage
  - D. Smith *et al.*, Langmuir, 8, 1992, 2753-2757
  - G. Scherer *et al.*, J. Non-Cryst. Solids, 188, 1995, 191-206
  - A. Rao *et al.*, Applied Surface Science, 206, 2003, 262-270

- **Post-Process Chemical Vapor Deposition** ⇒ composites
  - A. Hunt *et al.*, J. Non-Cryst. Solids, 185, 1995, 227-232

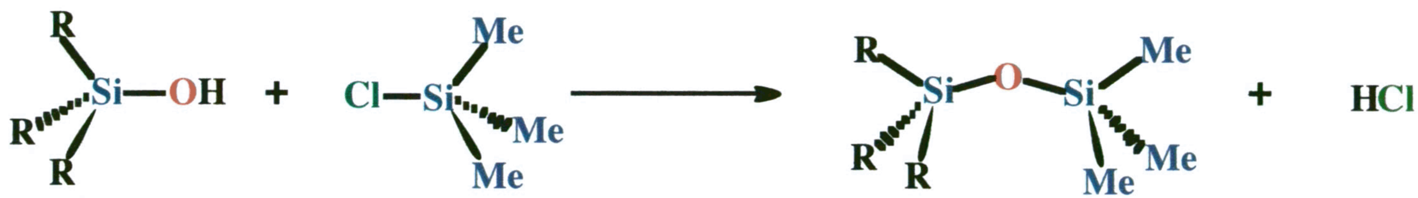
Post-Process Gas Phase Chemical Modification

Known silylating agents: trimethylchlorosilane, hexamethyldisilazane

Aerogel + gas phase silylating agent → Si-O-Si(CH_3)$_3$

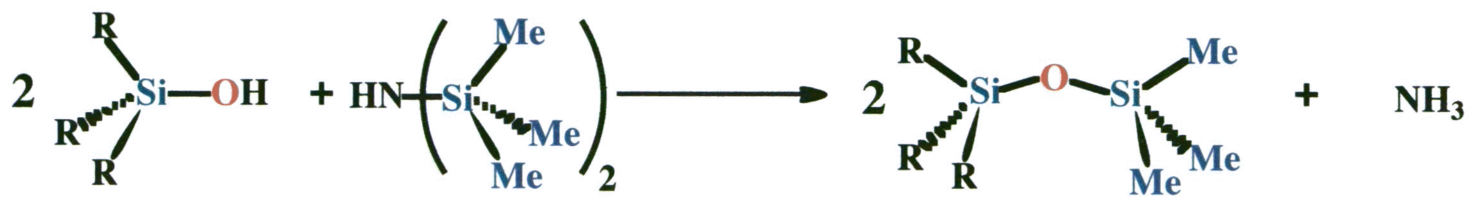
Silylating Agents

Trimethylchlorosilane



- TMS-Cl
- B_p: 56-57 °C
- VP: 187.5 mmHg @ 20 °C
- 1 functional group

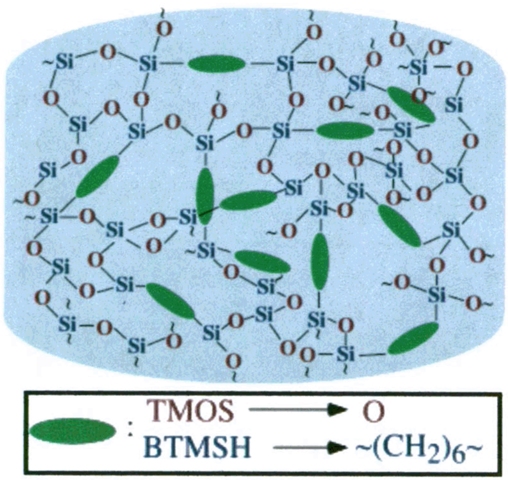
Hexamethyldisilazane



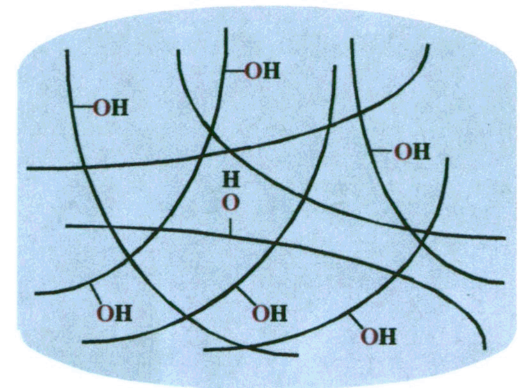
- HN-$(TMS)_2$
- B_p: 124-127 °C
- VP: 15 mmHg @ 20 °C
- 2 functional groups

Aerogel Gas Phase Silylation Scheme

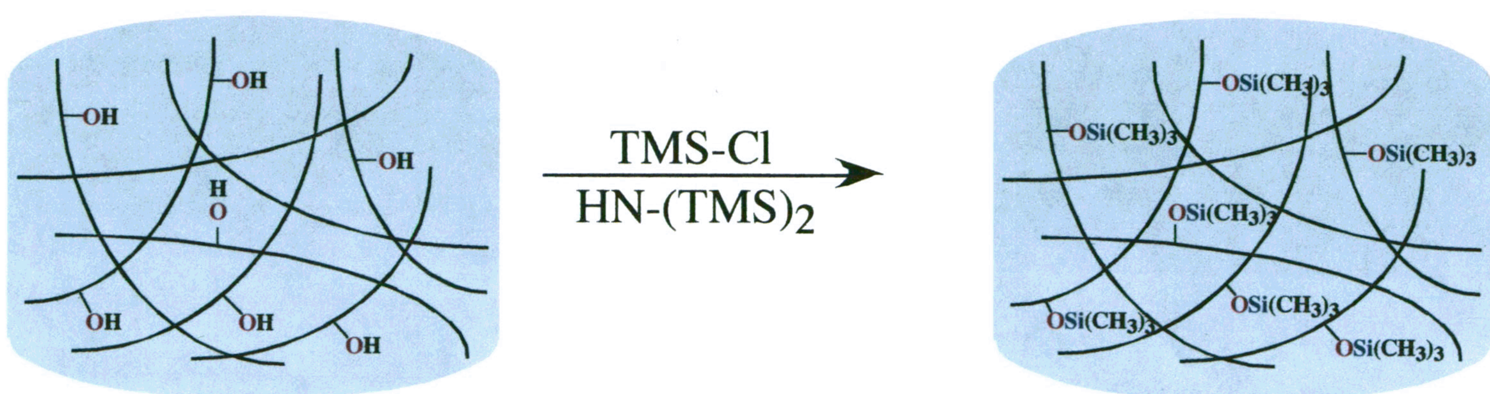
Aerogel



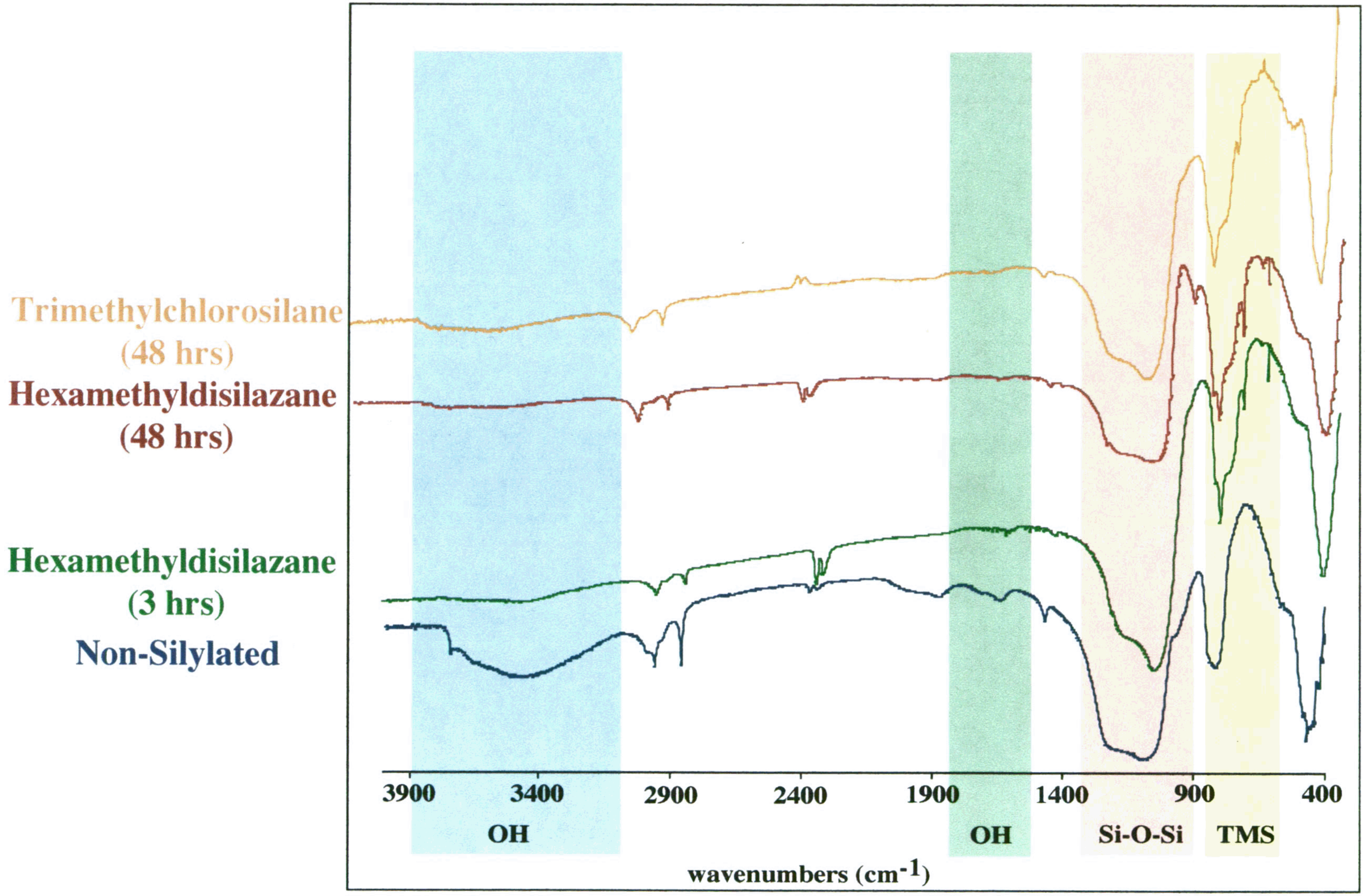
Aerogel showing surface hydroxyls



Formation of TMS Monolayer

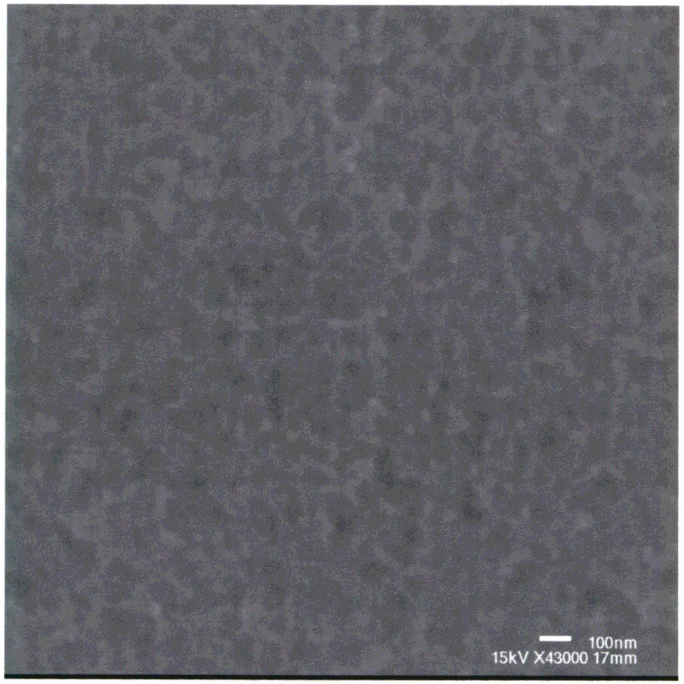


Following Reactive Modification of Aerogel by IR Spectroscopy



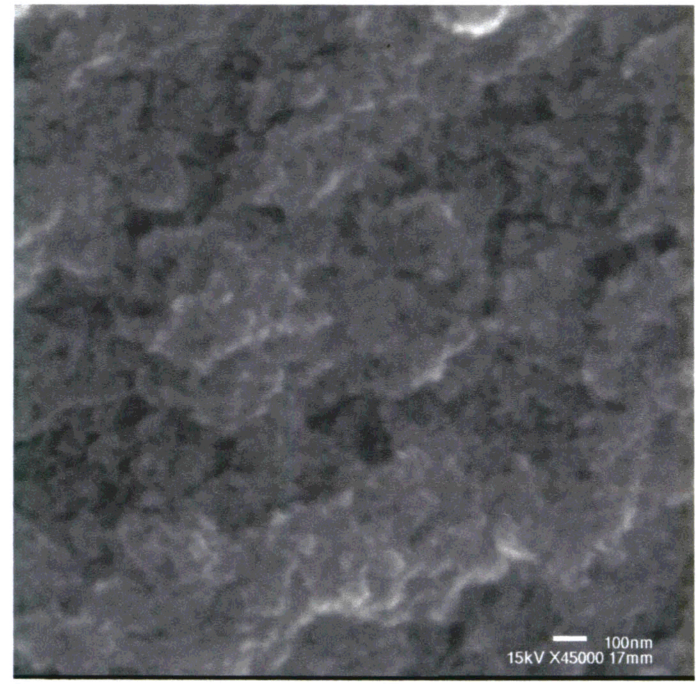
Aerogel Microstructure Resulting from Silylations

Unmodified Aerogel



- Web-like microstructure
- Small and large pore present
- Surface Area: 800 m^2/g
- Pore Volume: 1.58 cc/g
- Pore Diameter: 79 Å

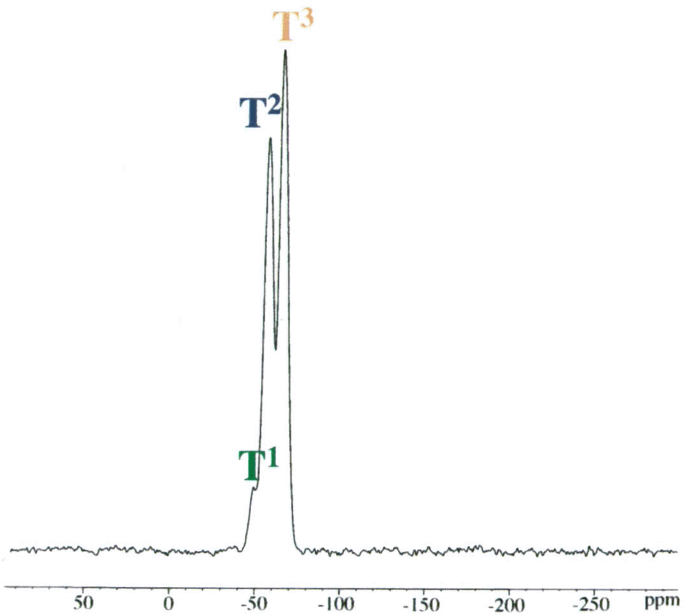
Modified Aerogel

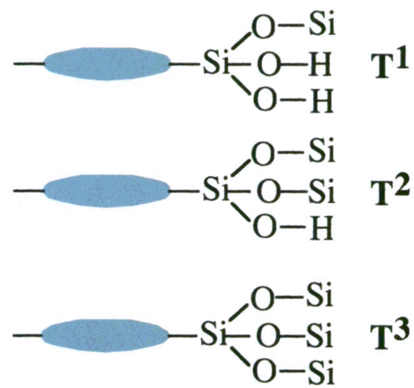


- Thickening of the pores
- Decrease in amount of smaller pores
- Surface Area: 770 m^2/cc
- Pore Volume: 1.64 cc/g
- Pore Diameter: 85 Å

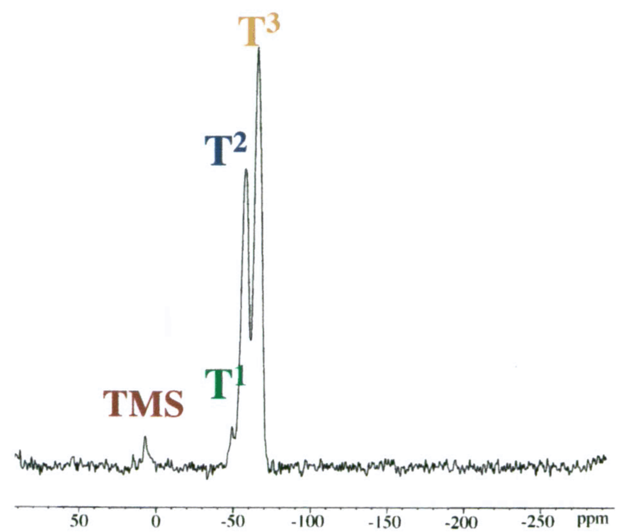
^{29}Si CPMAS NMR on the BTMSH Unmodified and Modified Aerogels

Unmodified aerogel





Modified aerogel

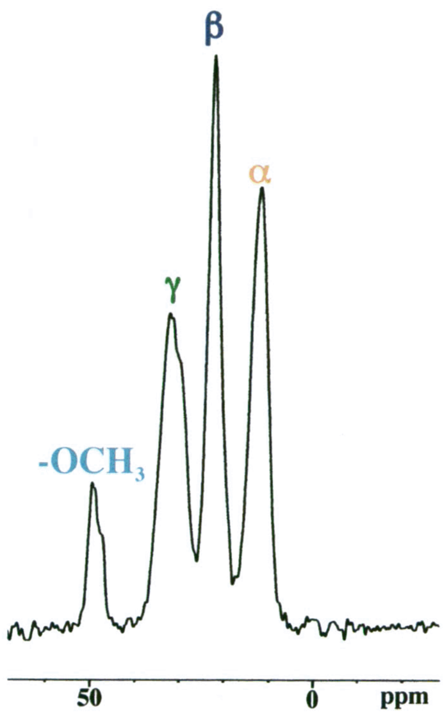


	Unmodified Area	Modified Area
T^1	5%	7%
T^2	45%	41%
T^3	50%	50%
TMS		2%

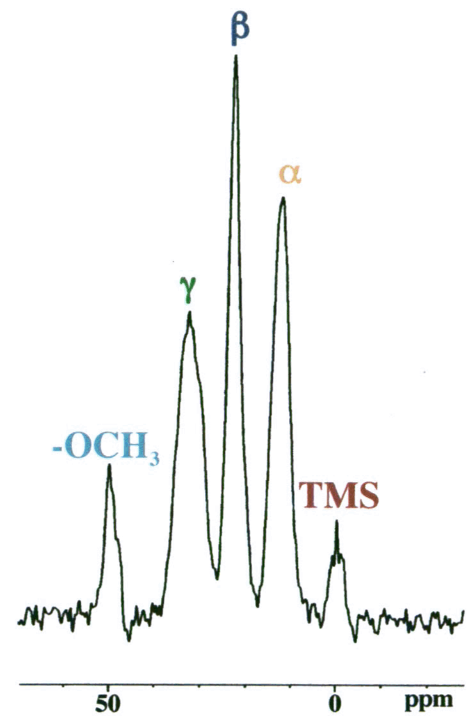
82% degree of condensation

^{13}C CPMAS NMR on BTMSH Unmodified and Modified Aerogels

Unmodified aerogel



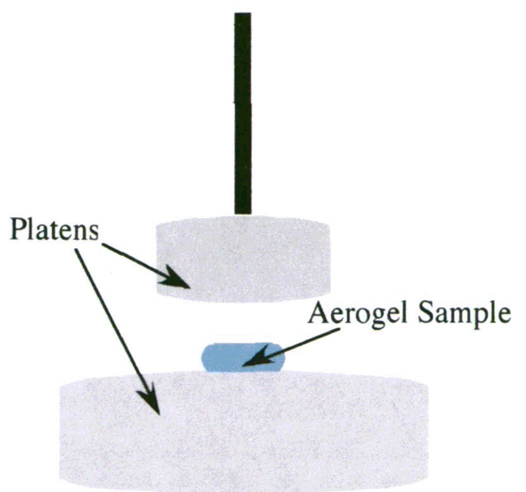
Modified aerogel

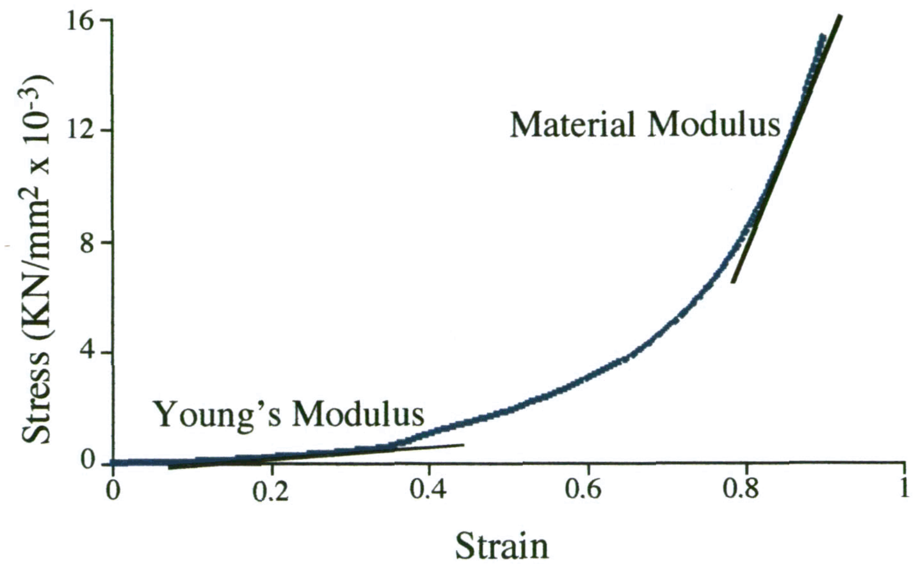


- Aerogel was silylated with TMS
- The BTMSH linkage is not affected
- TMS peak ⇒ 0.6 mmol/g of TMS added

Compression of the Aerogels

- Instron 4483
- Cross-head speed: 2.5 mm/min.
- Sample Load: 10 KN
- 3-5 samples were measured
- Young's Modulus and Material Modulus
- Sample Thickness: 8 mm ± 2 mm



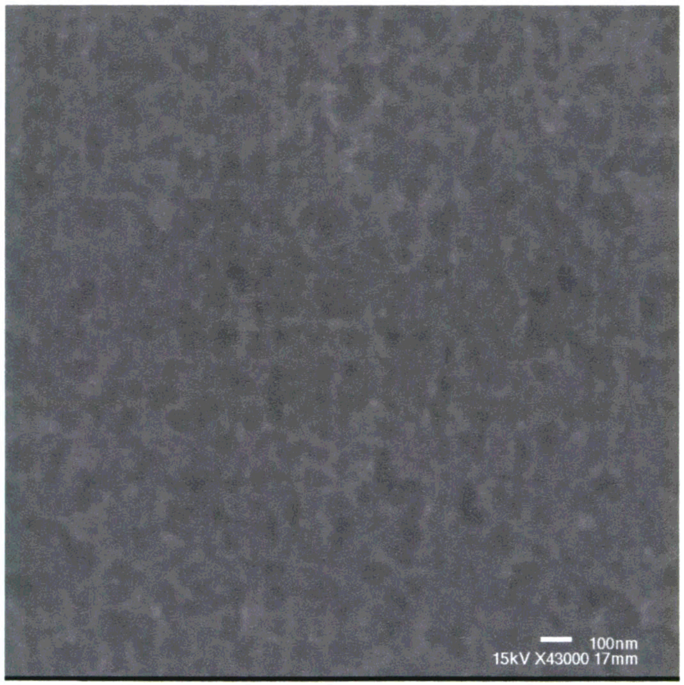


Young's Modulus: polymeric network

Material Modulus: densification of the material

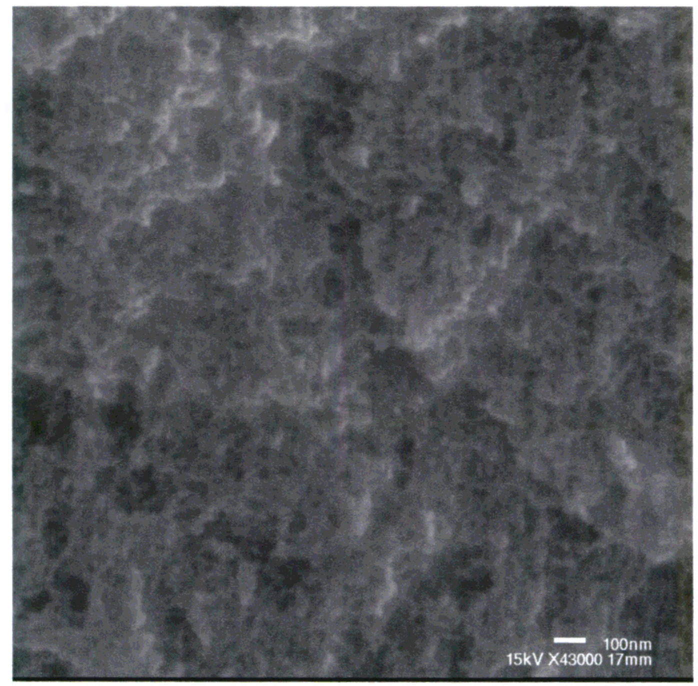
Effect of Compression on Aerogel Microstructure

BTMSH Derived Aerogel



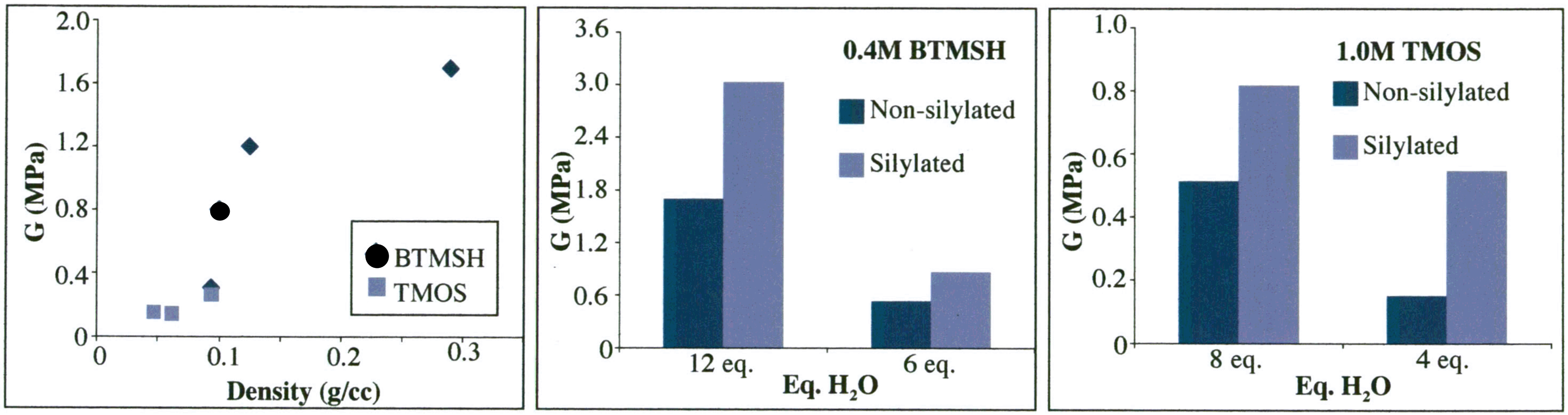
- Web-like microstructure
- Surface Area: 800 m^2/g
- Pore Volume: 1.58 cc/g
- Pore Diameter: 79 Å

Post-Compression



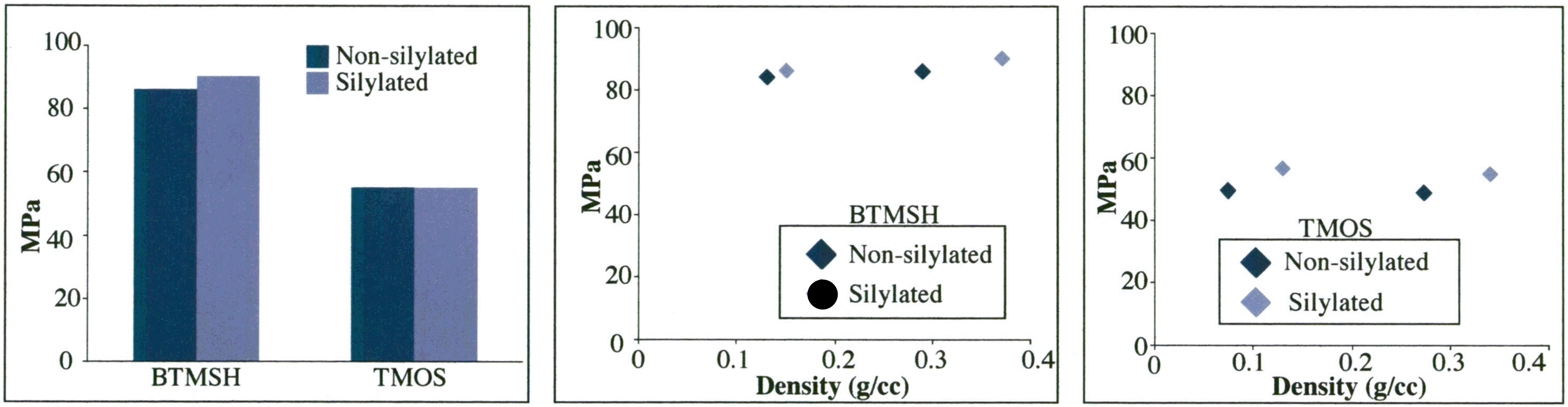
- Collapse of the network and pores
- Surface Area: 735 m^2/g
- Pore Volume: 1.20 cc/g
- Pore Diameter: 65 Å

Young's Modulus of the Aerogels



- *Density and modulus are related*
- *Strength of TMOS aerogels are < 0.4 MPa*
- *Strength of BTMSH aerogels approach 2 MPa*
- *Silylation increases the strength of the aerogels*
    - *-addition of the TMS monolayer*
    - *-steric repulsion between the TMS and Si-O-Si*
- *Water equivalents affects the aerogel strength*
    - *- increase in the hydrolysis with a larger H_2O equivalent*

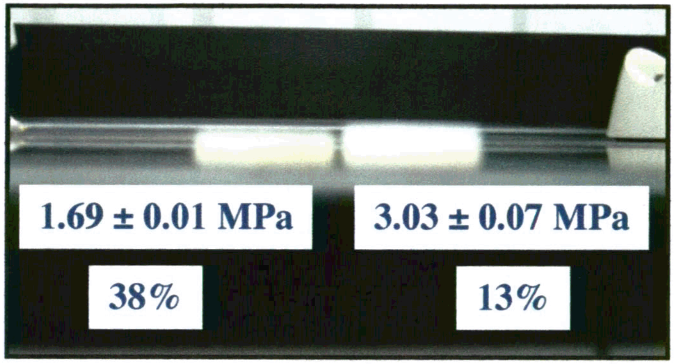
Material Modulus of TMOS and 1,6-Bis(trimethoxysilyl)hexane Aerogels



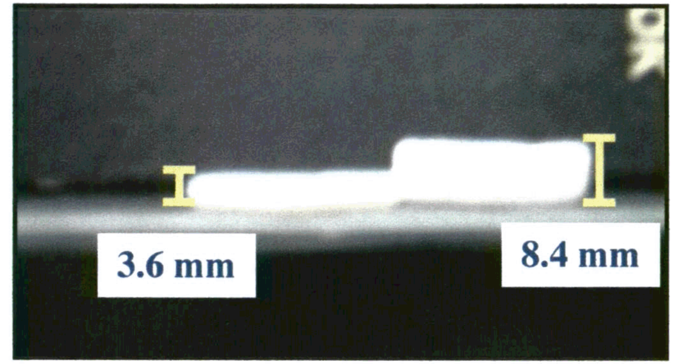
- *BTMSH aerogels have a higher material modulus than TMOS*
- *Silylated Material Moduli is comparable to Non-silylated Material Moduli*
- *Material Modulus is not dependent with density*

Physical Appearance of the Aerogels after Compression

Unreacted & Reacted Aerogels



Compressed & Monolithic Aerogels



57% Δ in thickness

Compressed & Monolithic Aerogel

Unreacted aerogels compress easier than reacted aerogels
-Lower Young's Modulus
Silylating the aerogel increases the Young's Modulus
-strengthens the network
Unlike traditional O-Si-O bridging, TMS inhibits compression
- steric repulsion from the bulky TMS monolayer
Compressed aerogel exhibits a translucent appearance
- decrease in pore size (from 79 Å to 65 Å)

Conclusions

- Bridged polysilsesquioxane aerogels posses a higher Young's Modulus than TMOS aerogels.
- Material Modulus is higher for the bridged polysilsesquioxane aerogels than the TMOS aerogels.
- Lower density aerogels are weaker than higher density aerogels.
- The variance in water content has an effect on the strength of the aerogels.
- The lower density aerogels can be strengthened by employing gas phase silylation techniques.
- TMS hinders total collapse of the aerogel.

Future Work

- Investigate other bridged polysilsequioxane monomers
  - 1,4-Bis(trimethoxysilyl)benzene
- Use hexachlorodisilane to increase the number of Si-O-Si linkages
  - Compare the strength between the TMS modified aerogel and the Si-O-Si modified aerogel
- Investigate in using other volatile inorganics to strengthen the aerogel
  - Ex: Al, Ga, Ti
- What are the effects of catalysts on the strength of the aerogels?
  - Different gel times associated with the monomer and the catalyst
- Altering the aerogel architecture
- Synthesizing BTMSH aerogels with densities lower than 0.09 g/cc
  - Ideally below 0.003 g/cc

Acknowledgements

- Eric Brown
- E. Bruce Orler
- Jim Small
- Warren Steckle
- Jonathan Stoddard

Funding

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36