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Title: Silylation of Low-Density Silica and Bridged Polysilsesquioxane Aerogels

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

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SILYLATION OF LOW-DENSITY SILICA AND BRIDGED POLYSILSESQUIOXANE AEROGELS

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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, and cometary dust capture agents. However, aerogels are notoriously weak and brittle making it difficult to handle and machine monoliths into desired forms. This complication prevents the development of many applications that would otherwise benefit from the use of the low-density materials. Here, 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 organic-bridged polysilsesquioxane aerogels were prepared by sol-gel polymerization of the respective methoxysilane monomers followed by supercritical carbon dioxide drying of the gels. Then the gels were reactively modified with silylating agents to demonstrate the viability of CVD modification of aerogels, and to determine the effects of silylation of surface silanols on the morphology, surface area, and mechanical properties of the resulting aerogels.

Silylation of Low Density Silica and Bridged Polysilsesquioxane Aerogels

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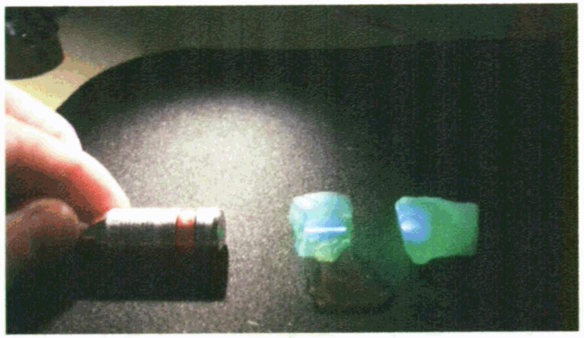
What are Aerogels?

Silica aerogels were first prepared by S. S. Kistler in the 1930's



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 areas (500- 2200 m^2/g)
Mesoporous materials (2 - 50 nm)
Open pore structure
Silica, alumina, carbon, RF organic systems
Transition metals, mixed metal oxide systems
Fragile & 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

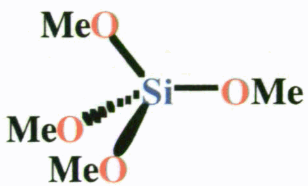
Water Glass

$SiO_2 : Na_2O$

- First used to make silica aerogels
- Inexpensive
- Low stability in alkaline environments

Generation II

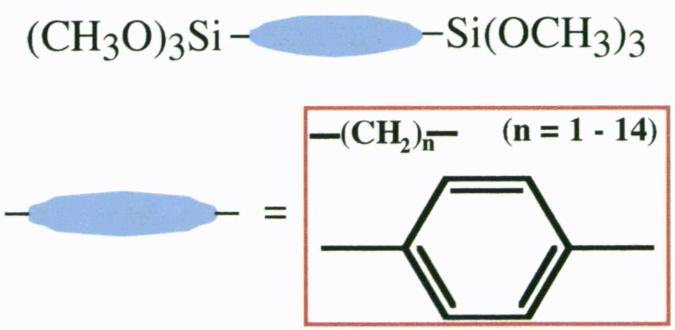
Silicon Alkoxides



- Examples: TMOS, TEOS
- Traditionally used to make aerogels
- Stabile in acidic and alkaline environments

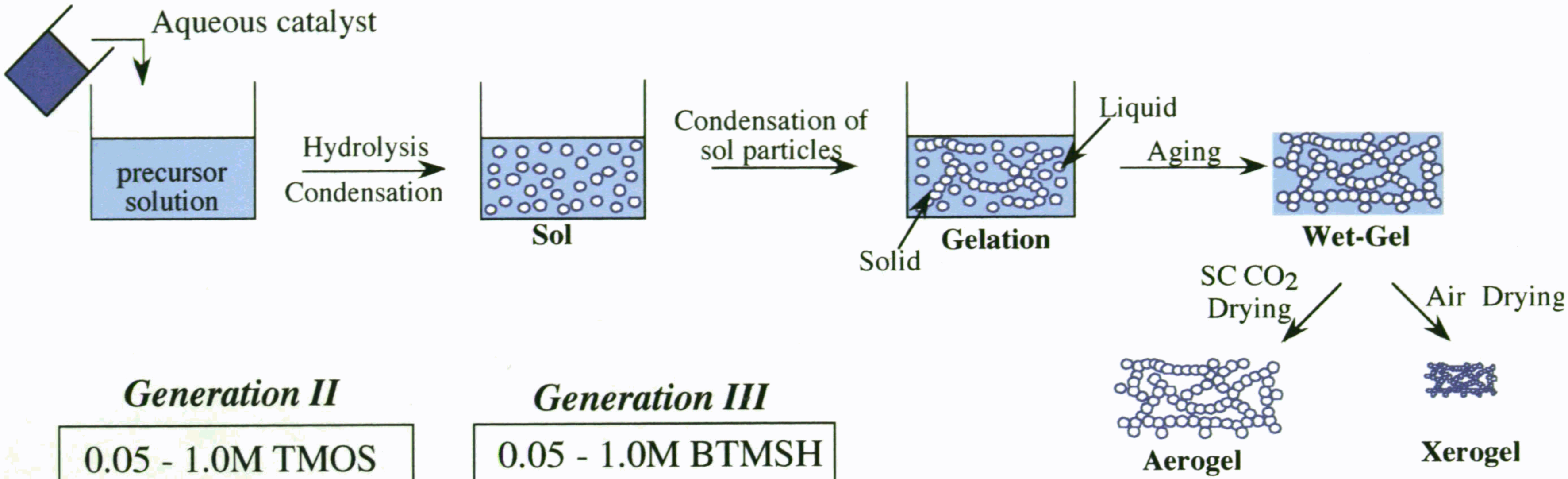
Generation III

Polysilsesquioxanes

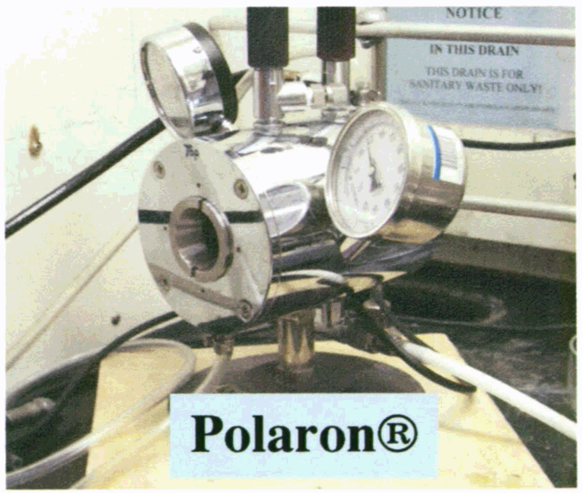


- Ex: 1,6-Bis(trimethoxysilyl)hexane ⇒ BTMSH
- Increased chemical functionality
- Posses both inorganic & organic characteristics
  - inorganic stability
  - organic flexibility & robustness
- Tailor gel architecture through organic spacer

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

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

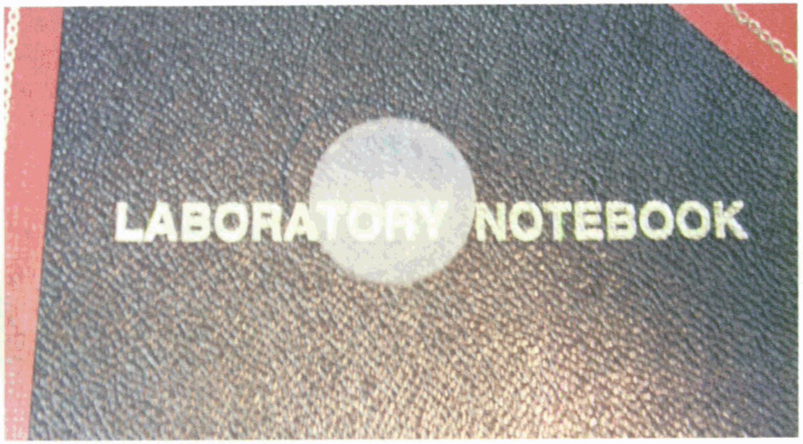
Condensation

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

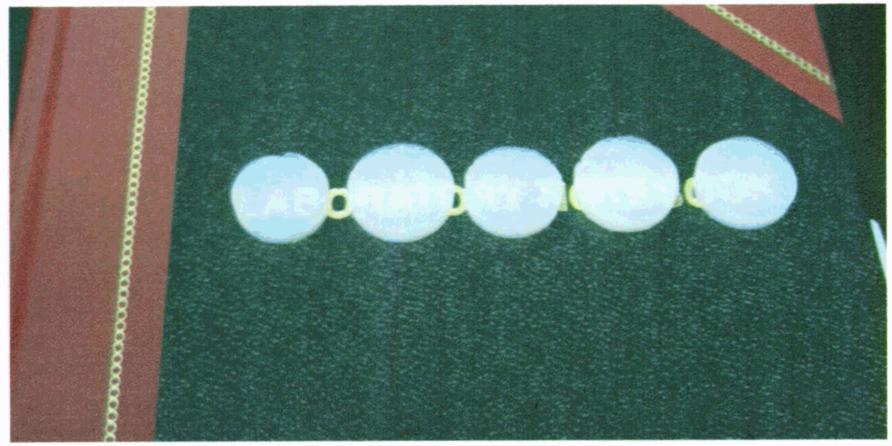
$$\text{Si-OH} + \text{HO-Si} \rightleftharpoons \text{Si-O-Si} + H_2O$$

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

TMOS Aerogel



BTMSH Aerogels



- **Transparent**
- **Densities: 0.03 - 0.09 g/cc**
- **Surface Areas: 800 m²/g**

- **Translucent/transparent**
- **Densities: 0.09 - 0.29 g/cc**
- **Surface Areas: >700 m²/g**

Fragile & Brittle

Modify to Strengthen 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

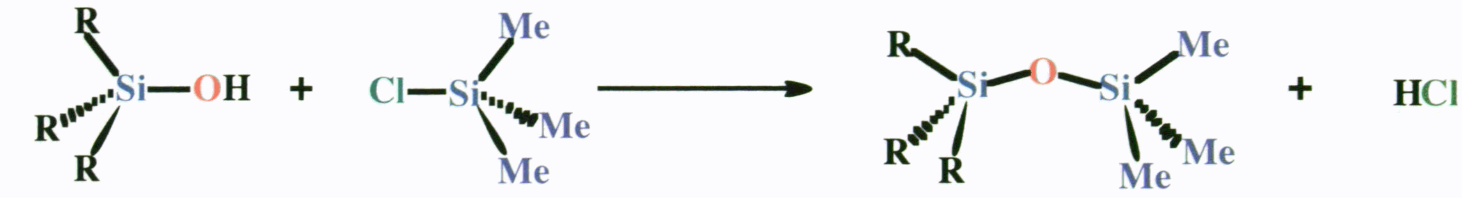
Post-Process Gas Phase Chemical Modification

Known silylating agents: trimethylchlorosilane, hexamethyldisilazane, hexachlorodisilane

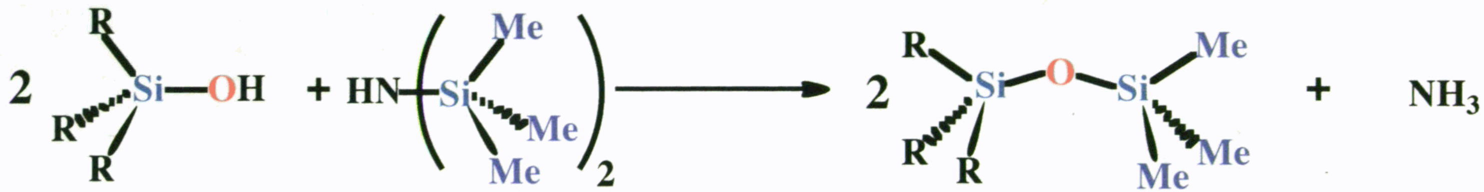
Aerogel + gas phase silylating agent → monolayer or multi-layer systems

Silylating Agents

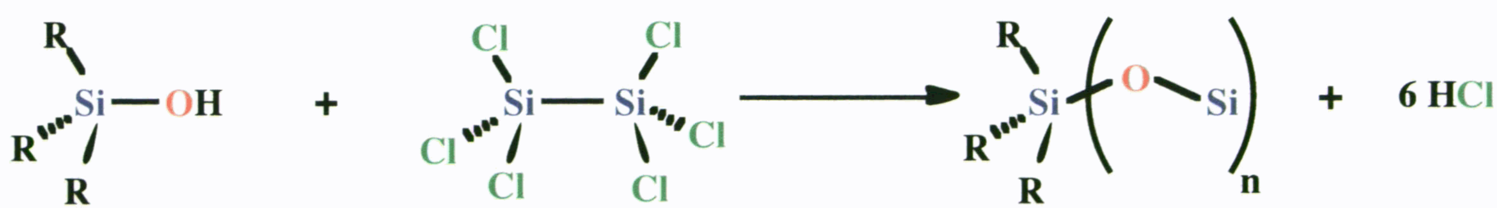
Trimethylchlorosilane



Hexamethyldisilazane



Hexachlorodisilane



Post-Process Gas Phase Chemical Modification

I. *Gas Phase Chemical Modification: TMS Monolayer*

- Initial study to explore the success of post-process gas phase chemical
  - -Modification through the addition of a TMS monolayer using trimethylchlorosilane and hexamethyldisilazane

Aerogel + gas phase silylating agent → $Si\text{-}O\text{-}Si(CH_3)_3$

- Effects of the TMS layer on the strength and morphology of the aerogel.

II. Gas Phase Chemical Modification: Forming a Multi-Layer System

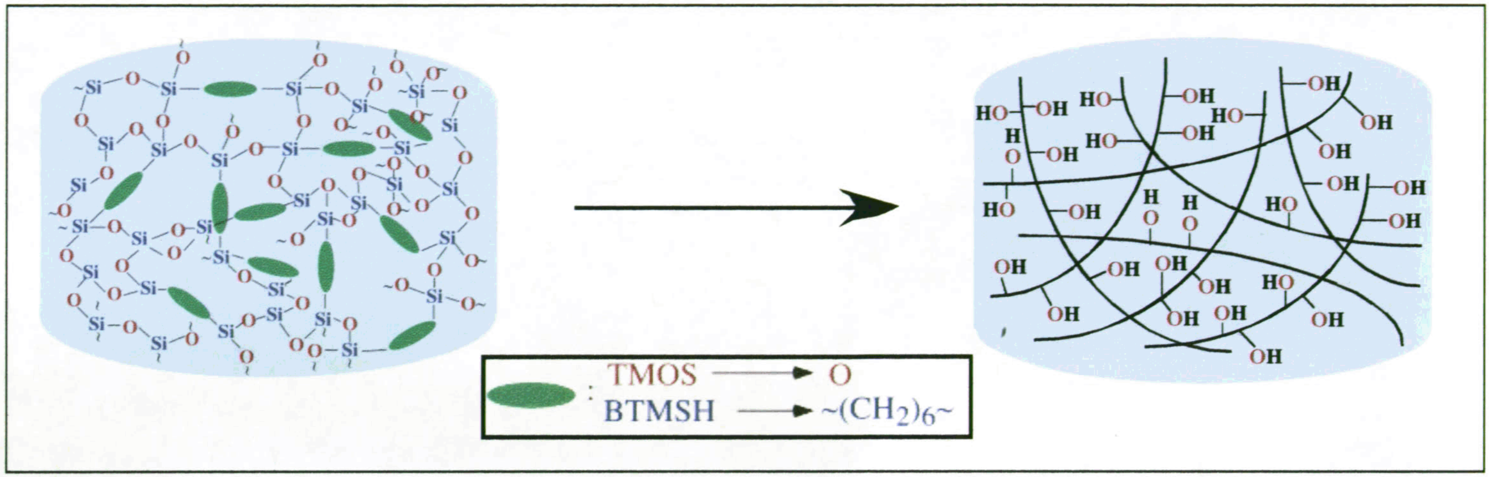
- Silylation to form multiple Si- layers
  - -Build up of silicon layers forming a multi-layer using hexachlorodisilane

Aerogel + gas phase silylating agent → Aerogel-O-Si-Si

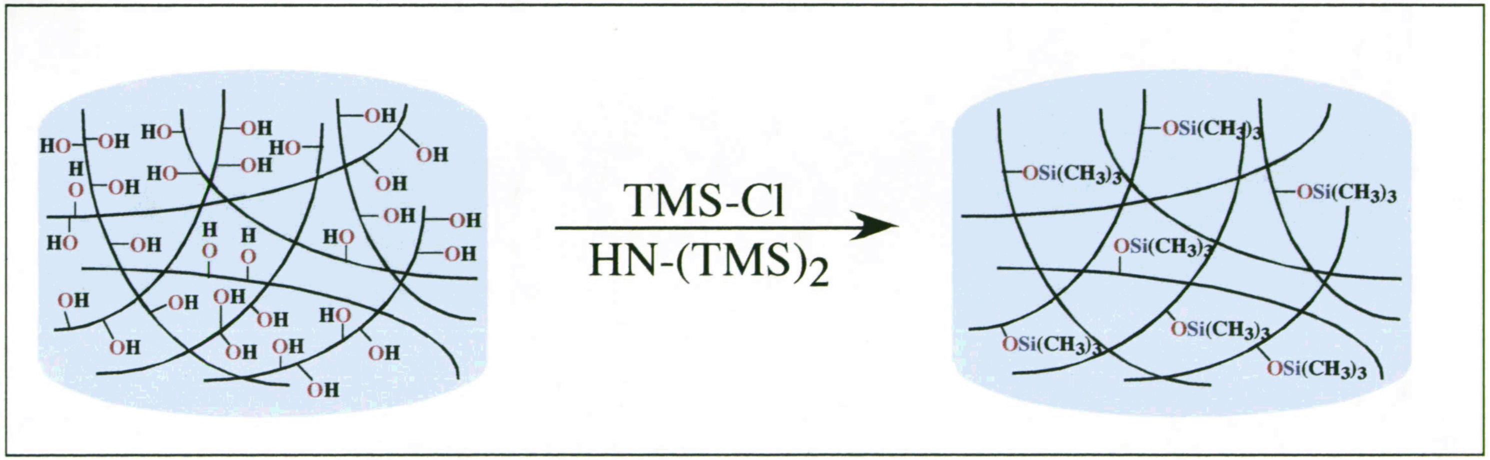
- Effects of silylation on the strength and morphology of the aerogel.

Gas Phase Modification Scheme: TMS Monolayer

Surface Hydroxyls on Aerogel



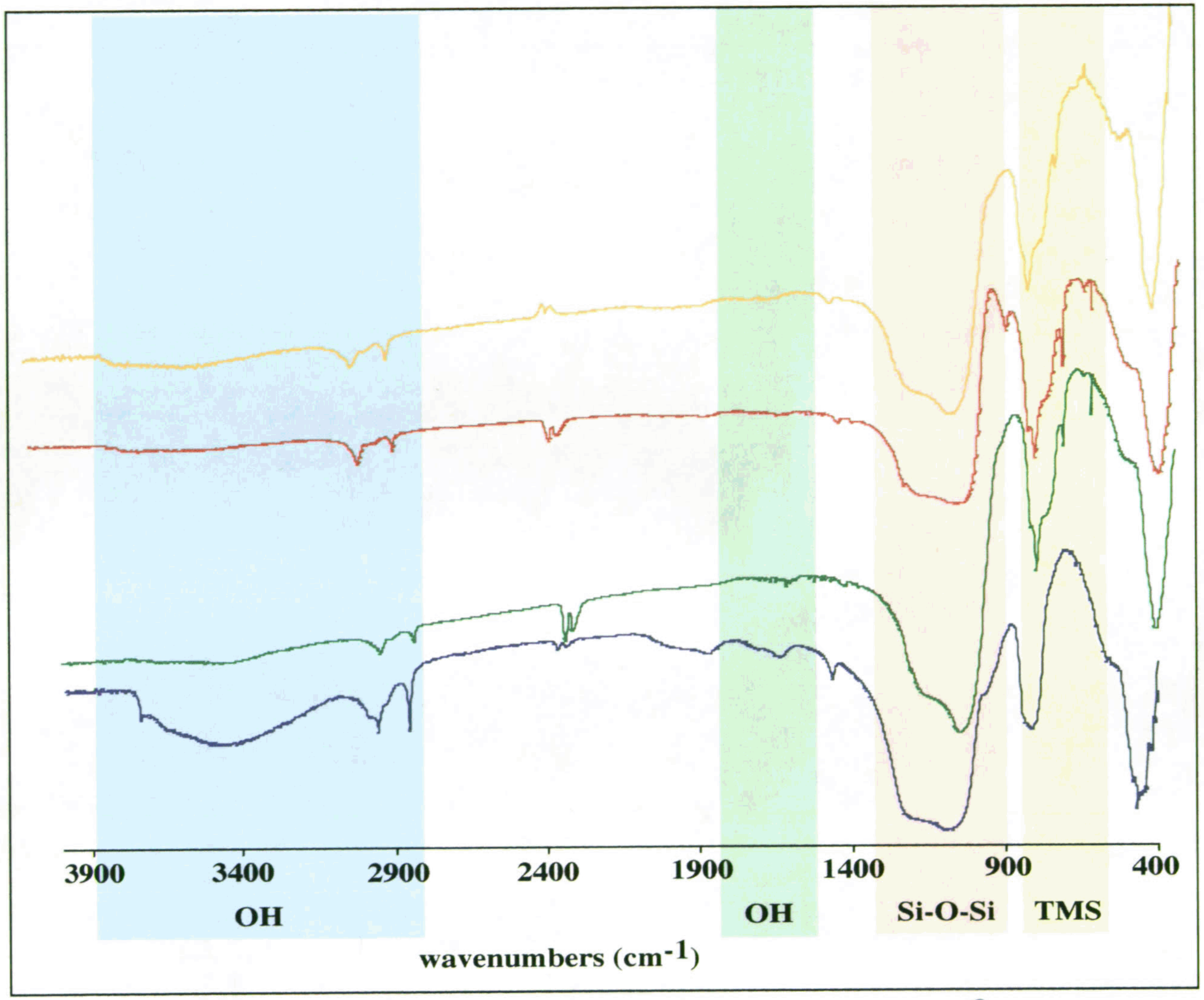
TMS Monolayer on Aerogel



Following Reactive Modification of Aerogels by IR Spectroscopy

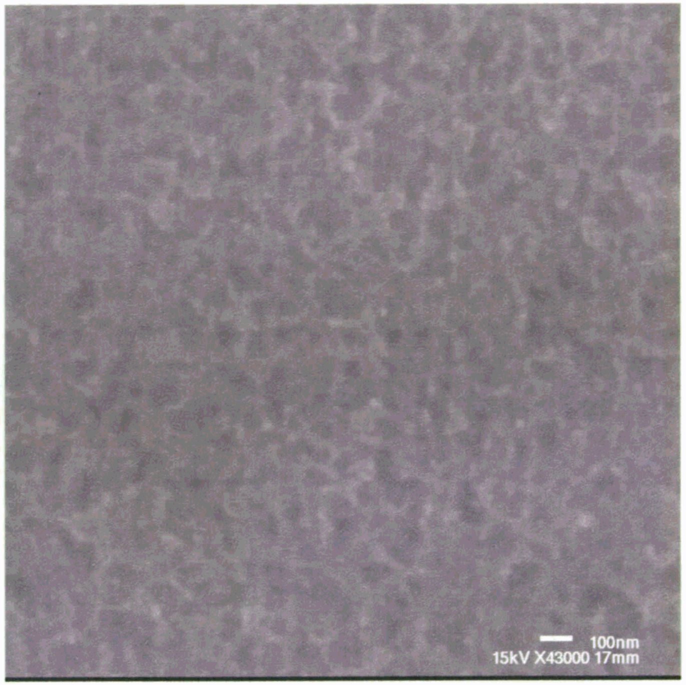
Trimethylchlorosilane
(48 hrs)
Hexamethyldisilazane
(48 hrs)

Hexamethyldisilazane
(3 hrs)
Non-Silylated



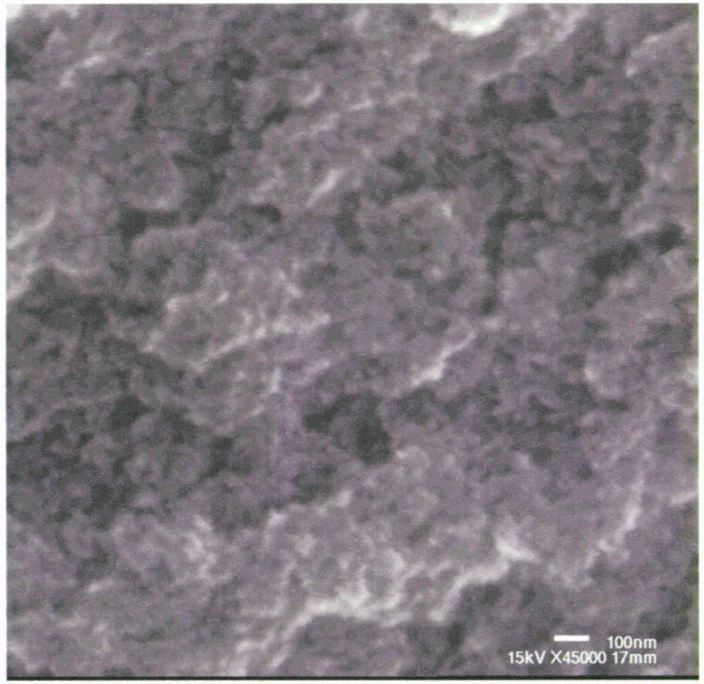
Aerogel Microstructure Resulting from TMS Modification

Unmodified Aerogel



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

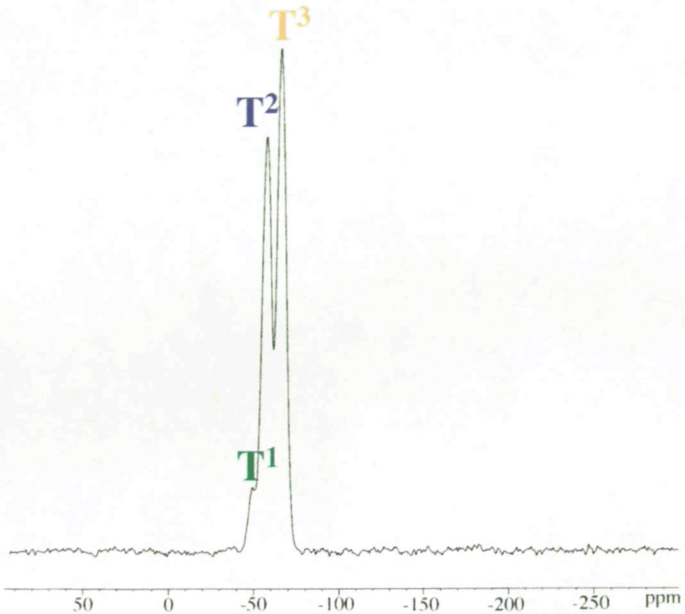
Modified Aerogel

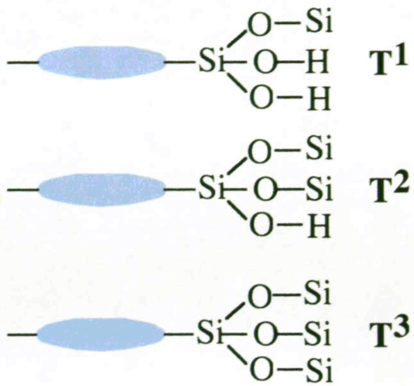


- Thickening of the pores
- Surface Area: 770 m^2/g
- Pore Volume: 1.64 cc/g
- Pore Diameter: 85 Å

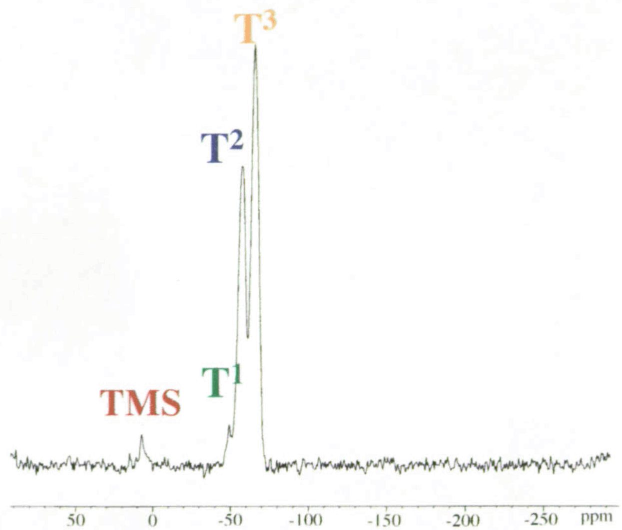
^{29}Si CPMAS NMR on the BTMSH Unmodified and TMS Modified Aerogels

Unmodified Aerogel





TMS Modified Aerogel

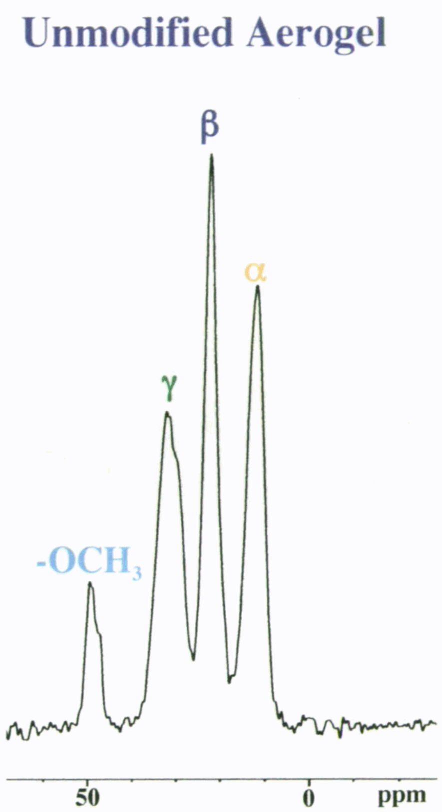


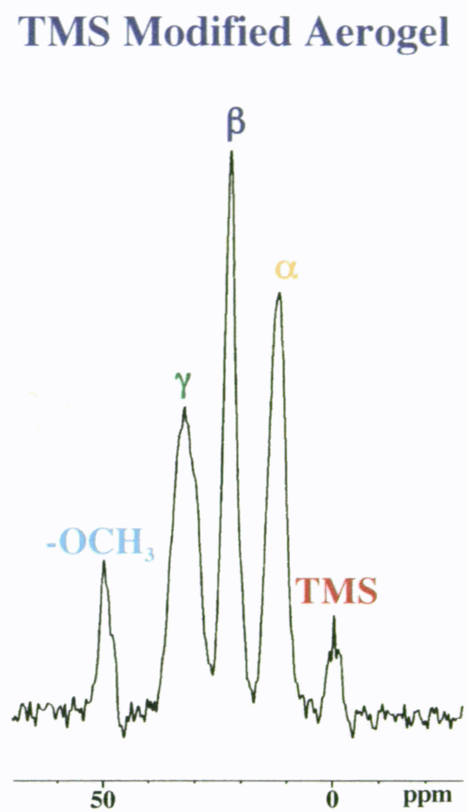
	Unmodified Area	Modified Area
T^1	5%	7%
T^2	45%	41%
T^3	50%	50%
TMS		2%

PUT in picture of TMS gel

82% degree of condensation

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

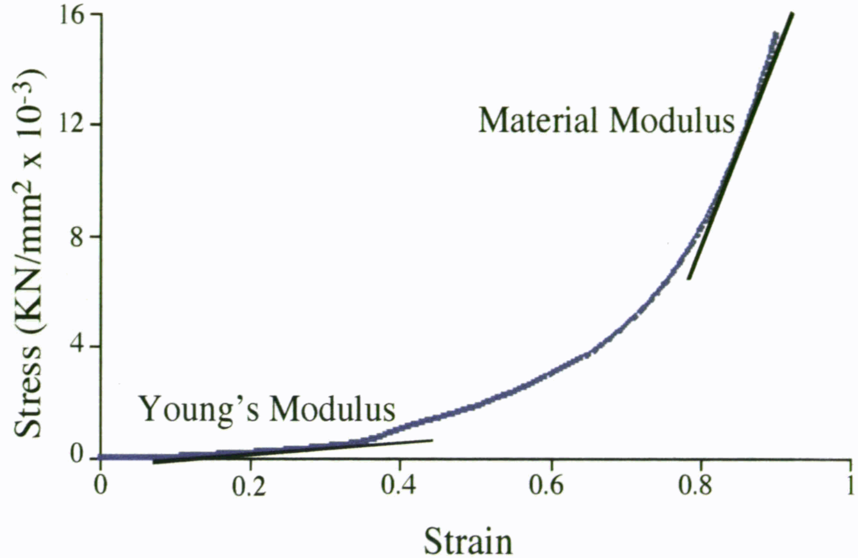




- Aerogel was silylated with TMS
- The hexylene linkage is not affected
- TMS peak ⇒ 0.6 mmol/g of TMS added

Compression of the Aerogels

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

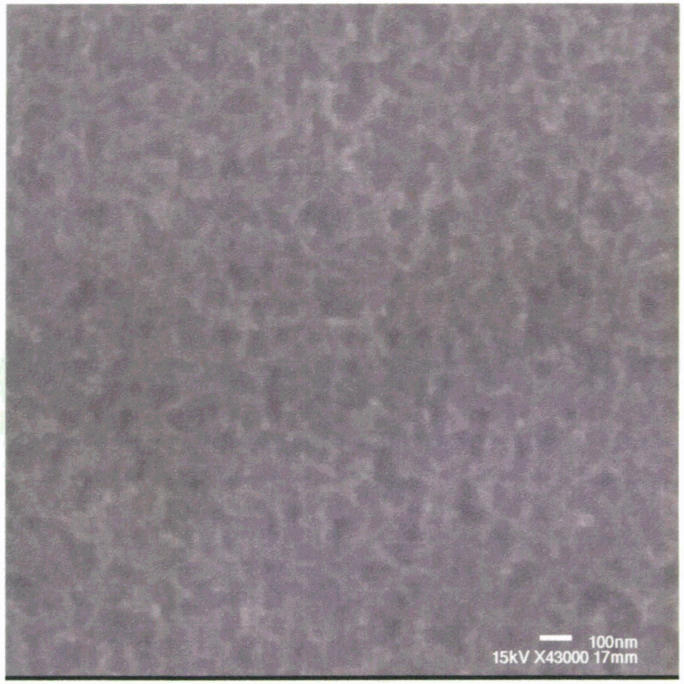


Young's Modulus: polymeric network

Material Modulus: densified material

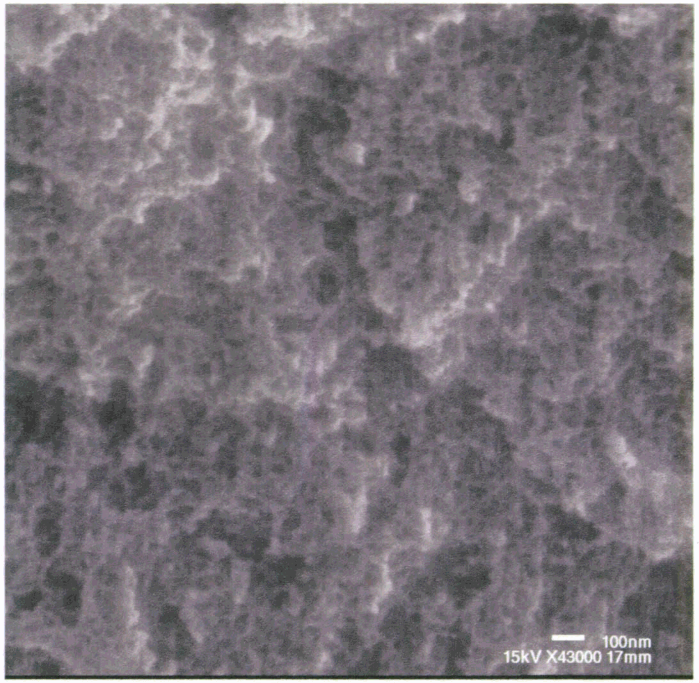
Aerogel Microstructure Resulting from Compression

BTMSH Derived Aerogel



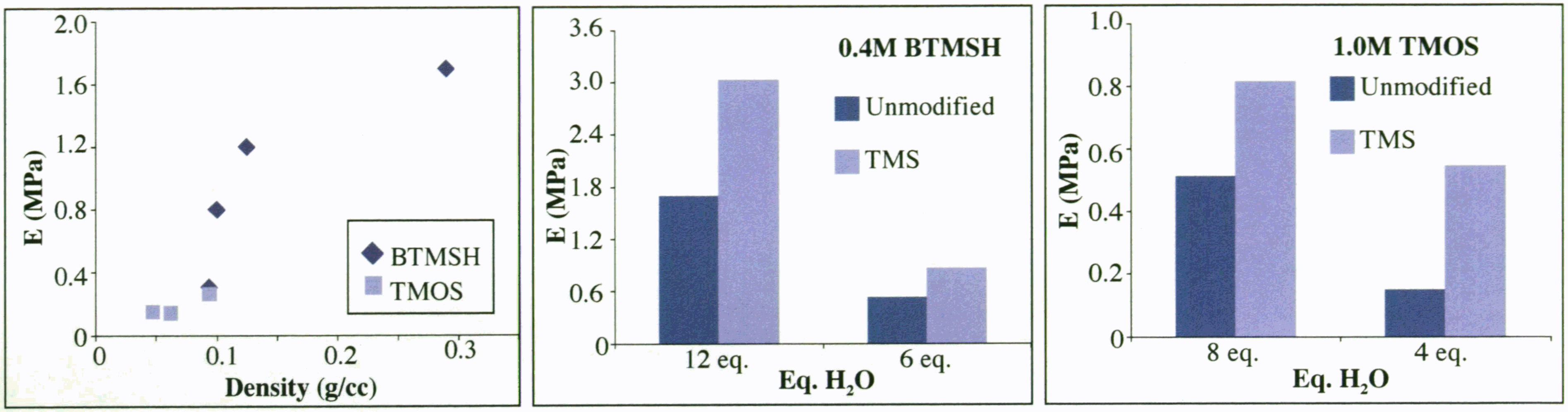
- Porous microstructure
- Surface Area: 800 m^2/g
- Pore Volume: 1.58 cc/g
- Pore Diameter: 79 Å

Post-Compression



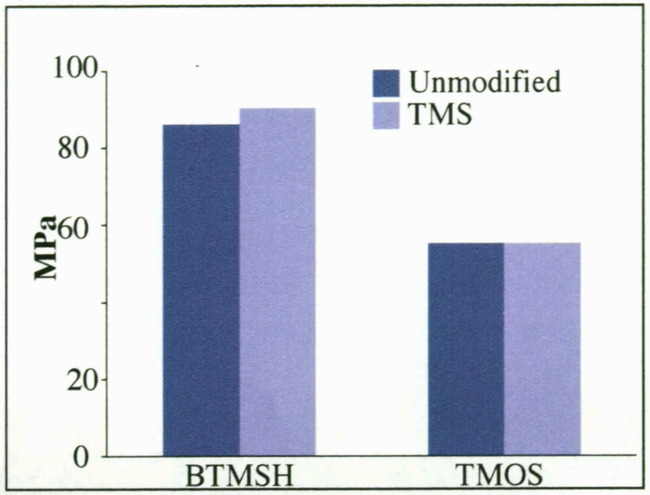
- Compression of porous network
- Surface Area: 735 m^2/g
- Pore Volume: 1.20 cc/g
- Pore Diameter: 65 Å

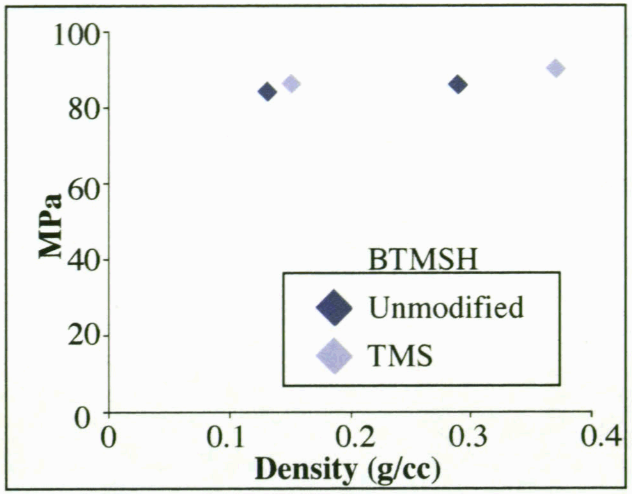
Young's Modulus: TMS Modified Aerogels

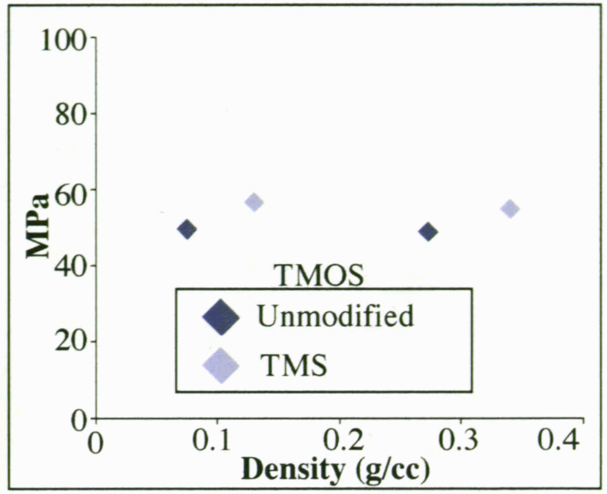


- *Density and modulus are related*
- *Strength of TMOS aerogels are < 0.4 MPa*
- *Strength of BTMSH aerogels approach 2 MPa*
- *TMS surface modification increases the strength of the aerogels*
  -addition of the TMS monolayer
  -steric repulsion between the TMS and Si-O-Si network
- *Water equivalents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

Material Modulus: TMS Modified Aerogels







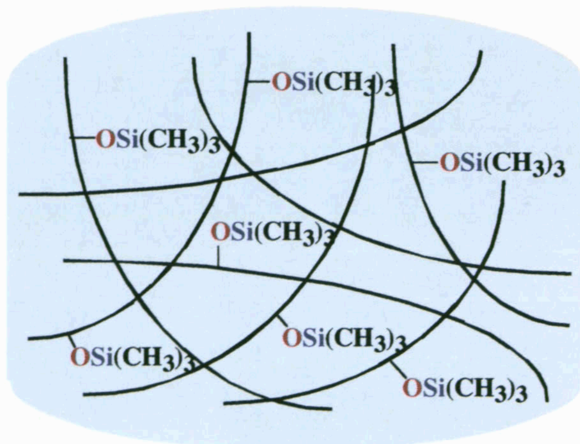
- *BTMSH derived aerogels have a higher Material Modulus than TMOS aerogels*
  - *organic bridging group strengthens the material*

- *TMS modified aerogel and unmodified aerogel Material Modulus are comparable*
  - *only a monolayer is added to the aerogel surface*

- *Material Modulus is not dependent with density*
  - *dependent on the material composition*

Summary of TMS Modified Aerogels

- Surface area decreases with TMS modification of the aerogel surface
  - TMS groups cover the aerogel surface
- The pore volume and pore diameter increases with TMS modification
  - TMS could be covering the surface of the smaller pores first
- Young's modulus of the aerogel increases with TMS silylation



Post-Process Gas Phase Chemical Modification

I. Gas Phase Chemical Modification: TMS Monolayer

- Initial study to explore the success of post-process gas phase chemical
  - -Modification through the addition of a TMS monolayer using trimethylchlorosilane and hexamethyldisilazane

$$\text{Aerogel + gas phase silylating agent} \rightarrow \text{Si-O-Si(CH}_3)_3$$

- Effects of the TMS layer on the strength and morphology of the aerogel.

II. *Gas Phase Chemical Modification: Forming a Multi-Layer System*

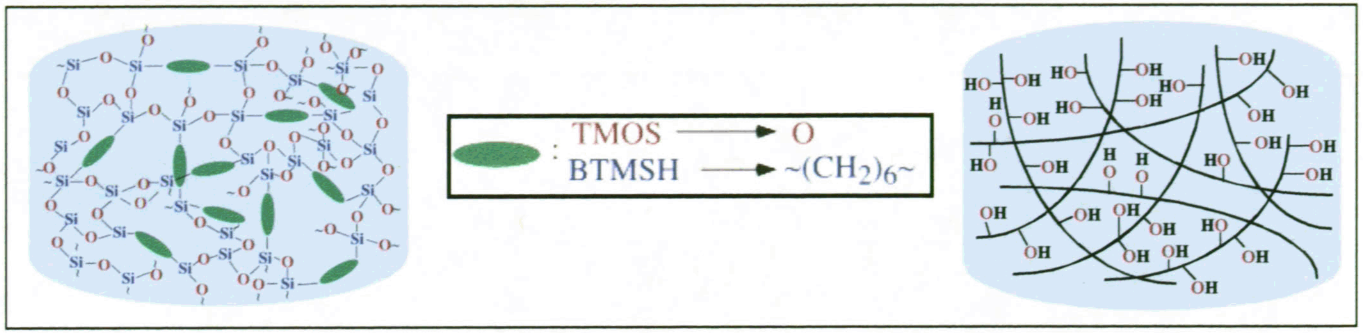
- Silylation to form multiple Si- layers
  - -Build up of silicon layers forming a multi-layer using hexachlorodisilane

$$\text{Aerogel + gas phase silylating agent} \rightarrow \text{Aerogel-O-Si-Si}$$

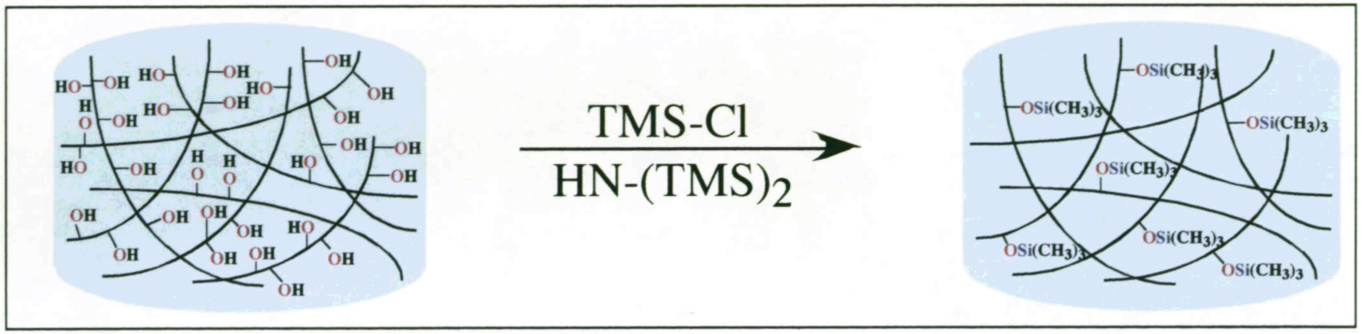
- Effects of silylation on the strength and morphology of the aerogel.

Aerogel Gas Phase Silylation Scheme

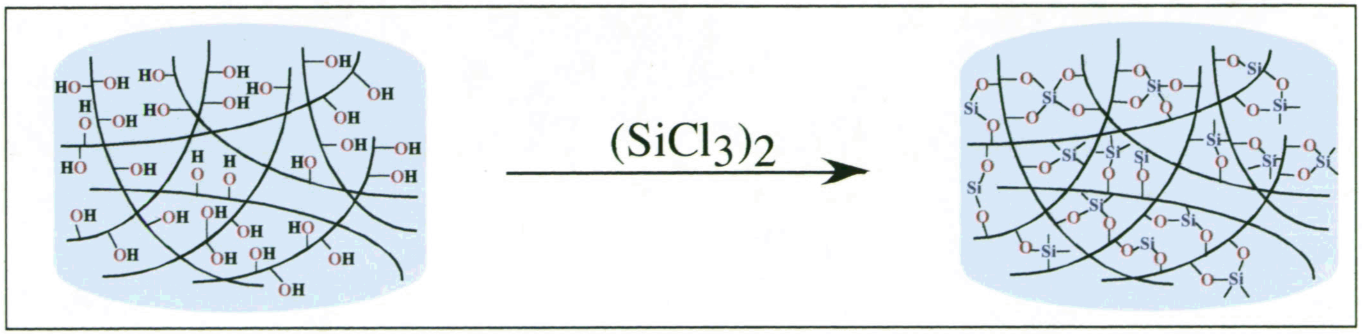
Surface Hydroxyls on Aerogel



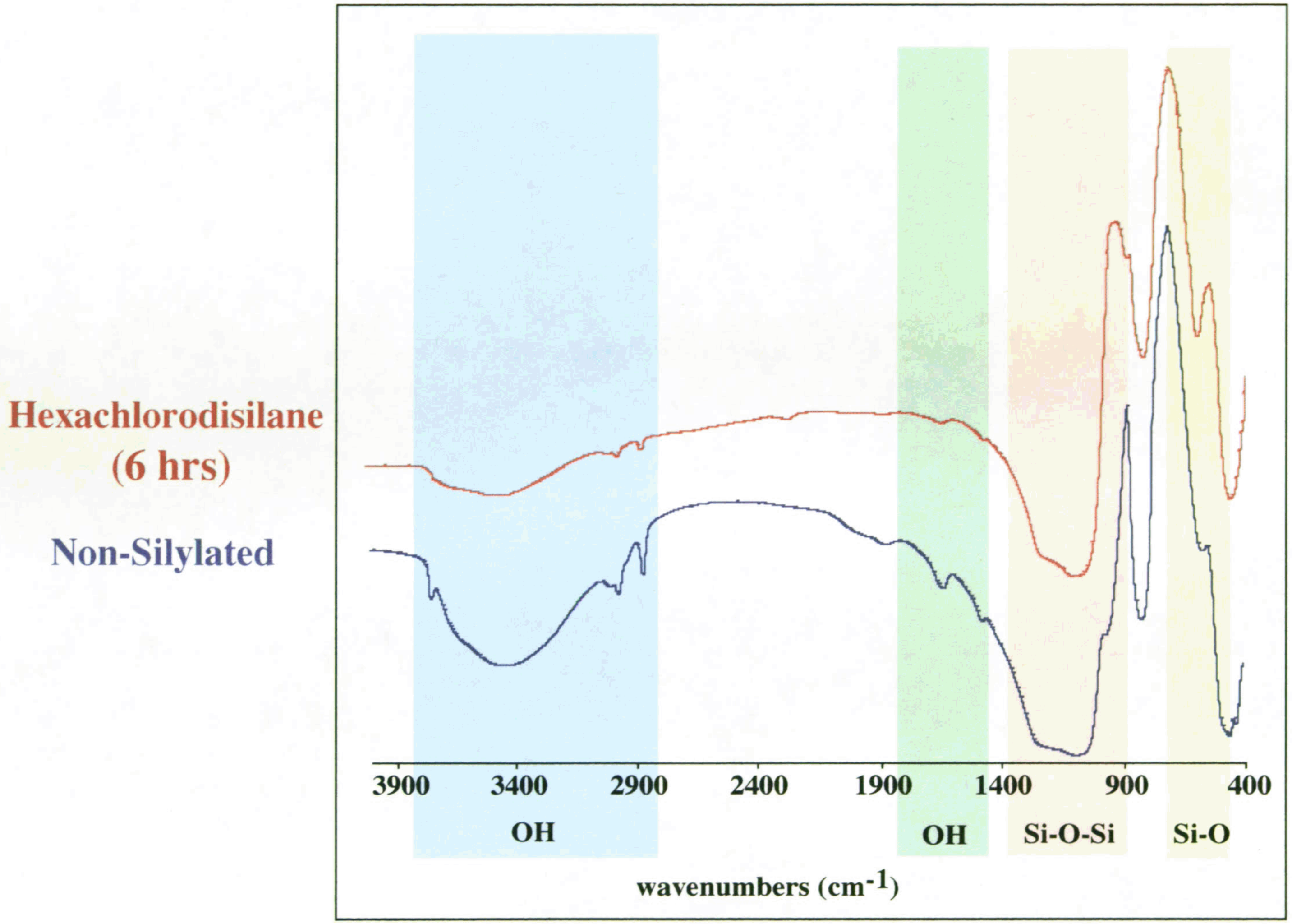
TMS Monolayer on Aerogel



Forming Multi-layers on Aerogel



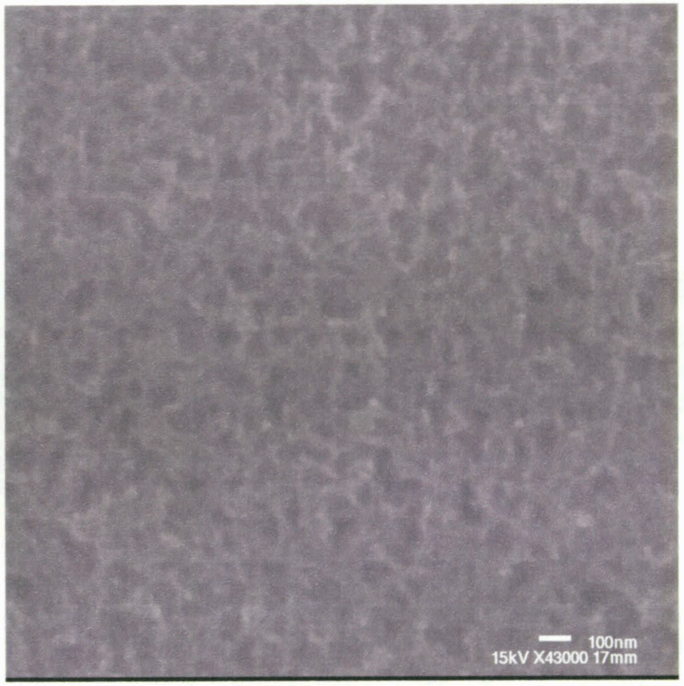
Following Silylation of Aerogels Through IR Spectroscopy



Longer Silylation Times Disintegrate the Aerogel Framework

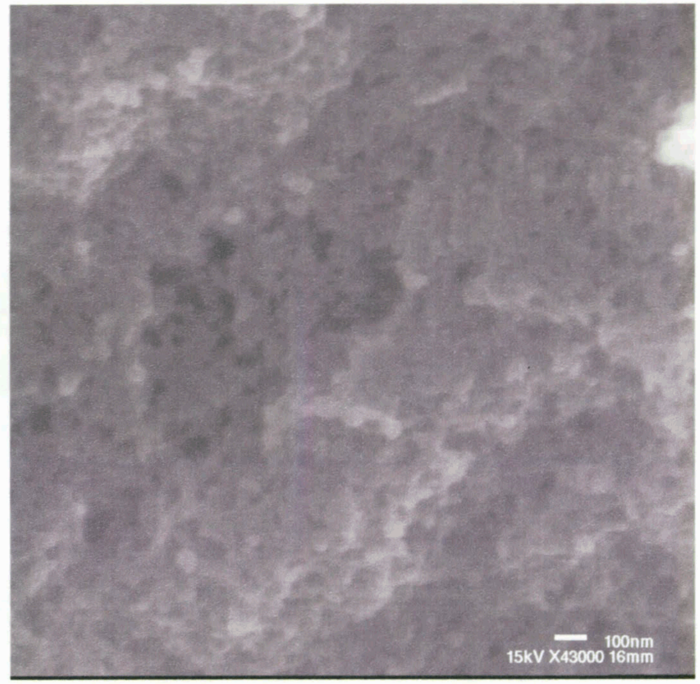
Aerogel Microstructure Resulting from Silylation Modification

Unmodified Aerogel



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

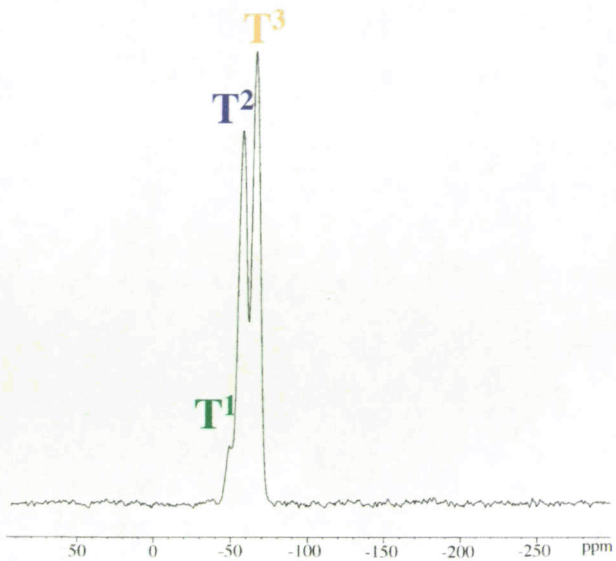
Silylated Aerogel



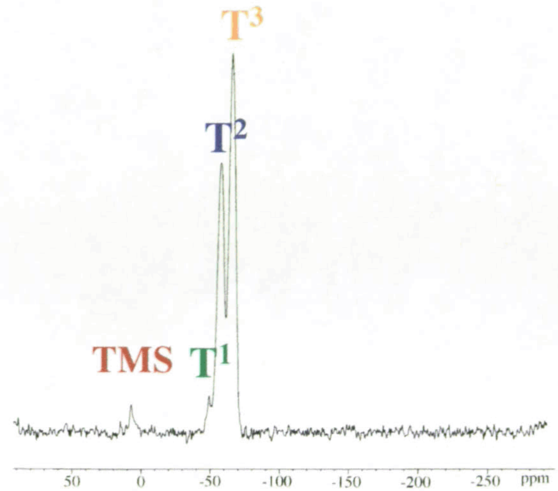
- Thickening of the pores
- Surface Area: 800 m^2/g
- Pore Volume: 1.5 cc/g
- Pore Diameter: 75 Å

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

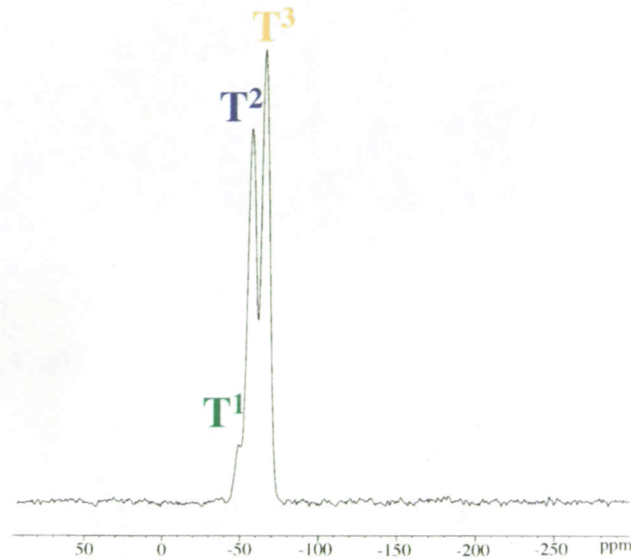
Unmodified Aerogel

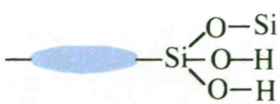


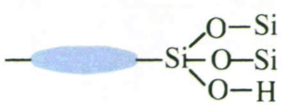
TMS Modified Aerogel

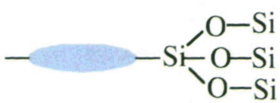


Silylated Aerogel




T^1


T^2

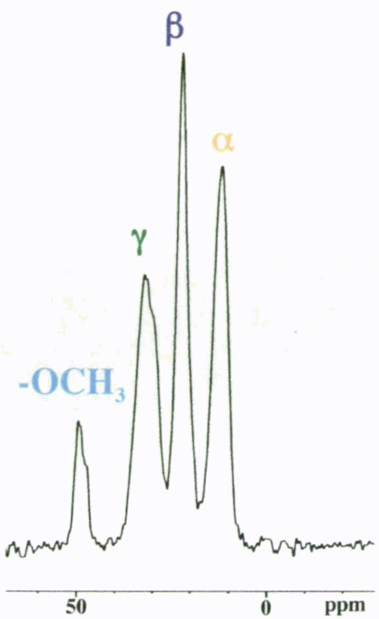

T^3

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

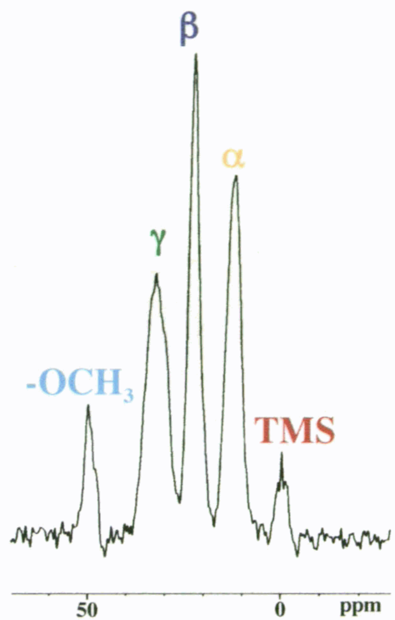
82% degree of condensation

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

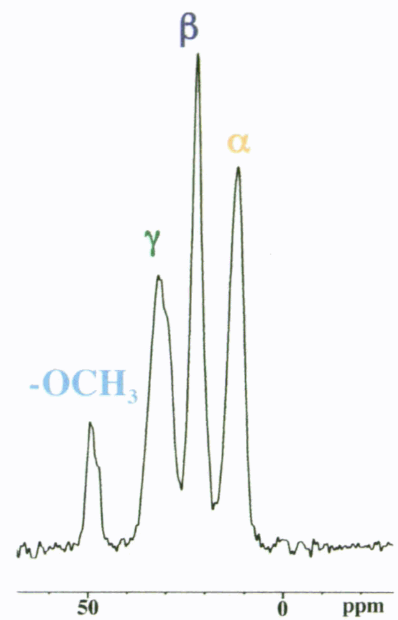
Unmodified Aerogel



TMS Modified Aerogel



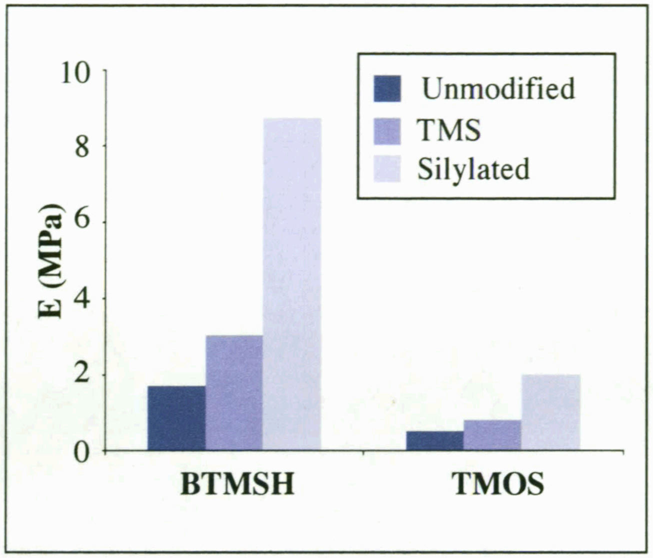
Silylated Aerogel



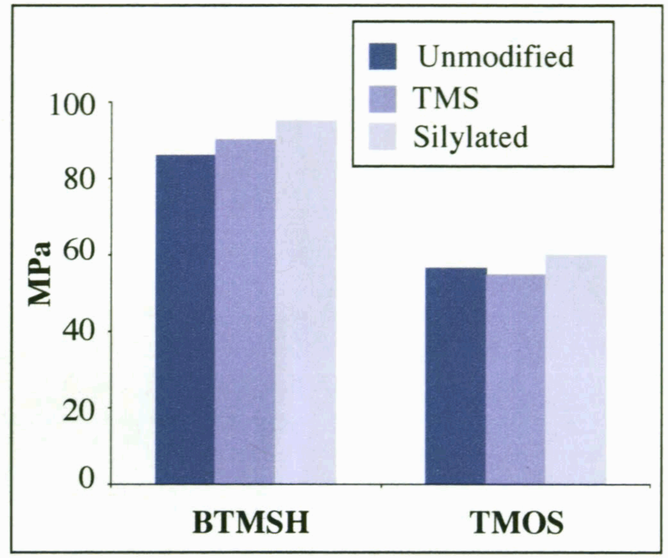
- Aerogel was silylated with TMS
- The BTMSH linkage is not affected from the silylations
- TMS peak ⇒ 0.6 mmol/g of TMS added

Young's Modulus & Material Modulus of Silylated Aerogels

Young's Modulus



Material Modulus



- Young's Modulus: Higher for silylated BTMSH and TMOS aerogels compared with TMS monolayer modification
  - increasing the Si-Si linkages compared to TMS monolayer
  - forming a multi-layer system
- Material Modulus: Slightly increases with silylation
  - increasing Si-Si linkages
  - not drastically changing the material composition

Conclusions

- Bridged polysilsesquioxane aerogels posses a higher Young's Modulus and Material Modulus than TMOS aerogels.
- Aerogel strength is dependent on density.
- 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.
- Silylating the aerogels increases the aerogel modulus
  - silylating to form multi-layers, has a greater impact on the modulus than forming the TMS monolayer
- Microstructure of the silylated aerogels:
  - densities of the aerogels are not greatly compromised
  - aerogels continue to posses high surface areas
  - aerogels remain mesoporous

Future Work

- Investigate other bridged polysilsequioxane monomers
  - 1,4-Bis(trimethoxysilyl)benzene
- Use hexachlorodisiloxane to investigate the success in increasing the number of Si-O-Si linkages
  - Compare the strength between the TMS modified aerogel and the hexachlorodisilane Si-O-Si modified aerogel
- Investigate in using other volatile inorganics to strengthen the aerogel
  - Ex: Al, Ga, Ti, V, Ta
- 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

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