

DI-ISOCYANATE CROSSLINKED AEROGELS WITH 1, 6-BIS (TRIMETHOXYSYLYL) HEXANE INCORPORATED IN SILICA BACKBONE

Stephanie L. Vivod, Mary Ann B. Meador, Baochau N. Nguyen, Derek Quade, Jason Randall, Renee Perry

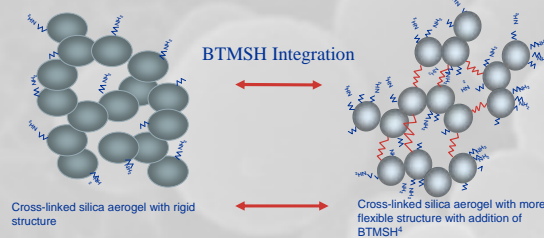
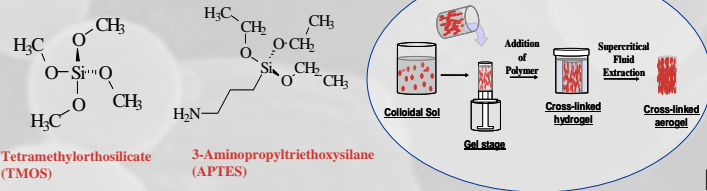
NASA Glenn Research Center, Cleveland OH 44135



Abstract

Silica aerogels are desirable materials for many applications that take advantage of their light weight and low thermal conductivity. Addition of a conformal polymer coating which bonds with the amine decorated surface of the silica network improves the strength of the aerogels by as much as 200 times. Even with vast improvement in strength they still tend to undergo brittle failure due to the rigid silica backbone. We hope to increase the flexibility and elastic recovery of the silica based aerogel by altering the silica back-bone by incorporation of more flexible hexane links. To this end, we investigated the use of 1,6-bis(trimethoxysilyl)hexane (BTMSH), a polysilsesquioxane precursor³, as an additional co-reactant to prepare silica gels which were subsequently cross-linked with di-isocyanate. Previously, this approach of adding flexibility by BTMSH incorporation was demonstrated with styrene cross-linked aerogels.⁴ In our study, we varied silane concentration, mol % of silicon from BTMSH and di-isocyanate concentration by weight percent to attempt to optimize both the flexibility and the strength of the aerogels.

Precursors & Procedure



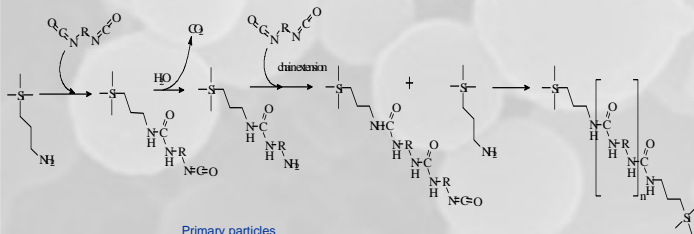
Preliminary Results

Incorporation of the hexane linked precursor exhibits flexibility upon extraction. Cross-linked wet gel can be bent and re-bent with out fracturing.

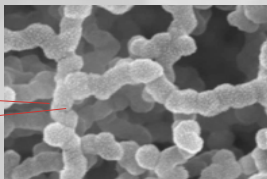


Di-isocyanate Cross-linking

Polymer cross-linking of the porous secondary particles strengthens the neck region which increases overall strength by 2 orders of magnitude, while only doubling the density^{1,2}.



Primary particles bond through surface chemistry to form secondary porous particles

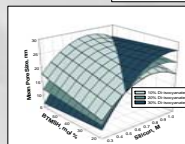
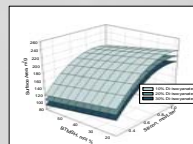


Empirical models

Data was collected and modeled using statistical design software and graphed with sigma plot 10. Figure to the right shows experimental runs in study in which silicon concentration, mol % of silicon from BTMSH and di-isocyanate concentration by weight percent were varied.

Bulk density and skeletal density derived from helium pycnometry was used to calculate porosity. Pore size and surface area were measured by BET nitrogen adsorption-desorption.

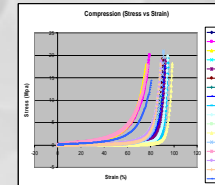
Total Si concentration has the greatest affect on density and porosity since it controls both amount of Si and amount of APTES available for cross-linking. BTMSH mol % only slight effect.



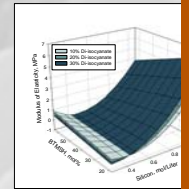
Surface area shows slight decrease with increased BTMSH while pore size increases with increasing BTMSH especially at lower polymer concentrations.

Mechanical Testing

COMPRESSION

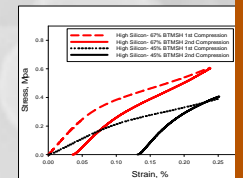


Modulus is calculated from the initial slope of the stress/strain curve. Results show that Si concentration has the greatest affect on modulus. Modulus also decreases with increasing BTMSH especially at high total Si concentration.

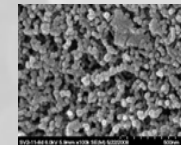


LOAD / UNLOAD

Samples were compressed to 25 % strain, twice. In graph at right, red curves from sample with 67 mol% BTMSH show more elastic recovery compared to 45 mol% BTMSH (black curves). Both samples had similar ranges of silicon concentration, density and morphology as shown below with the scanning electron micrographs. Lower density samples (low total Si concentration) exhibit much less elastic recovery.



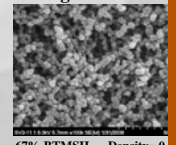
Low BTMSH



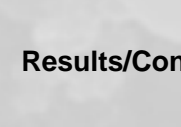
45% BTMSH Density = 0.157 g/cc
Porosity = 88.27%
Surface Area = 202m²/g
Modulus of Elasticity = 3.7Mpa



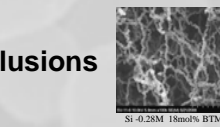
High BTMSH



67% BTMSH Density = 0.187 g/cc
Porosity = 85.17%
Surface Area = 166m²/g
Modulus of Elasticity = 4.27Mpa



Si - 0.28M 18mol% BTMSH



Si - 0.38M 67 mol% BTMSH

Results/Conclusions

- Preliminary results show that BTMSH imparts flexibility to the aerogels
- Dry aerogels show greater recovery after compression
- Wet gels bend instead of breaking—should improve manufacturability
- Greater recovery at higher Si concentrations
- Density and porosity are unaffected by BTMSH concentration

Further Study

Current research is investigating the use of a more cost efficient silica precursor (tetraethylorthosilicate-TEOS) in place of TMOS, and extending model to include higher silicon concentration and different concentrations of APTES.

Acknowledgement: We thank Linda McCorkle (OAI) for SEM photos and Dan Scheiman (QSS) for running thermal analysis. We also thank Bayer Corporation for supplying Desmodur N3200. We gratefully acknowledge funding from the Fundamental Aeronautics Program.

REFERENCES

- (1) Meador, M.A.B.; Capadona, L. A.; McCorkle, L.; Papadopoulos, D. S.; Leventis, N. *Chem. Mater.* **2007**, *19*, 2247.
- (2) Meador, M.A.B.; Fabrizio, E.F.; Ihan, F.; Dass, A.; Zhang, G.; Vassiliaras, P.; Johnston, J.C.; Leventis, N. *Chem. Mater.*, **2005**, *17*.
- (3) Shea, K. J.; Loy, D. A. *Chem. Mater.* **2001**, *13*, 3306
- (4) Nguyen B.N., Meador, M. A. B., Tousey M.E., and Shonkwiler B. *Polymer Preprints*, **2008**, *49*