FUNDAMENTAL STUDIES ON POLYMER AND ORGANIC-INORGANIC HYBRID NANOPARTICLES REINFORCED SILICA AEROGELS

A Dissertation

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

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May, 2012
FUNDAMENTAL STUDIES ON POLYMER AND ORGANIC-INORGANIC HYBRID
NANOPARTICLES REINFORCED SILICA AEROGELS

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ABSTRACT

The objective of this research was to reinforce silica aerogels using functional organic-inorganic hybrid nanoparticles, silane end-capped polyurethane oligomer and chain extended polymer, and self-crosslinkable multi-functional polyurethane-urea such that aerogel articles with negligible changes in density and porosity could be produced. The reinforcing entities used in the study were expected to reinforce the aerogel structures by (a) bridging the neighboring secondary particles at the neck region, (b) by forming conformal coatings on several secondary particles, or (c) by forming coating layers on all secondary particles.

The baseline aerogels were synthesized from tetraethoxy silane (TEOS) or a mixture of TEOS and aminopropyltriethoxy silane (APTES). The aerogels were prepared using two-step sol-gel process followed by supercritical drying in liquid carbon dioxide.

Polyhedral oligomeric silsesquioxanes (POSS) with different organic side groups and Si-OH or epoxide functionalities were used. Four types of POSS with silanol groups but with different side groups, tri-POSS, cyclo-POSS, i-butyl POSS, and tetra-POSS, were utilized to modify the silica aerogels before the gelation step. Silanol groups from POSS nanoparticles participated in condensation reactions with other silanes, while epoxy-POSS grafted on to the aerogel structures via the reactions with amine groups of APTES after the formation of gel network. The gels were also surface modified with dimethoxy-methyl (3,3,3-trifluoropropyl) silane to render them super-hydrophobic and to compare
the performance of such surface modification with those of POSS molecules containing hydrocarbon side groups. The morphology, and mechanical and surface properties of the resultant aerogels were investigated respectively using scanning electron microscopy (SEM), Instron tensile tester, contact angle goniometry, and BET surface area and porosity analyzer. Solid state $^{13}\text{C}$ and $^{29}\text{Si}$ NMR spectra were used to investigate the chemical reactions between the silane monomers and POSS molecules. Small angle X-ray scattering (SAXS) was used to investigate the change of fractal dimension. It was observed that small amounts of POSS significantly enhanced the hydrophobicity and the compressive strength and modulus of the resultant aerogels, with small changes of density. It was found that silanol POSS reacted with other silanols and became part of aerogel structures.

Silica aerogels with polymeric reinforcement such as pre-modified polyurethanes and prepolymerers, with functionality greater than or equal to 2, were produced by one-step sol-gel process. The morphology and mechanical and surface properties of the resultant aerogels were investigated respectively using scanning electron microscopy (SEM), Instron tensile tester, contact angle measurement and BET surface area and porosity analyzer. The chemical structures of aerogels were studied by solid state $^{13}\text{C}$ NMR and $^{29}\text{Si}$ NMR. The fractal dimension was studied by SAXS. It was found that the addition of pre-modified polymer alleviated the issues of brittleness and moisture adsorption by either coating the surface of secondary particles or forming reinforced domains at the neck regions between the secondary particles.
Of all the reinforcement methods used, aerogels reinforced with POSS nanoparticles yielded the best results in that compressive modulus showed an improvement by a factor of six compared to TEOS-based aerogels with less than 10% change in density.
ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisor, Dr. Sadhan C. Jana, for his invaluable guidance, support, and encouragement to complete this dissertation. The participation to committee of Professors, Dr. Avraam I. Isayev and Dr. Kevin A. Cavicchi from Department of Polymer Engineering, Dr. Li Jia from Department of Polymer Science, and Dr. Edward A. Evans from Department of Chemical Engineering, and Dr. Mary Ann B. Meador from NASA Glenn Research Center, are also gratefully acknowledged. I would like also recognize everyone in Dr. Jana’s research group for their enlightening discussions and feedback in this work, especially Dr. Jason Randall for the valuable suggestions. Additionally, I am grateful to Dr. Anna M. Pischera, Bimala Lama, and Dr. Mathew P. Espe for solid state NMR studies. I would like to express special thanks to Dr. Robert A. Weiss and Dr. Stephen Z.D. Cheng for allowing us using the contact angle goniometer and SAXS equipment.
TABLE OF CONTENTS

Page

LIST OF TABLES.................................................................................................................. xi
LIST OF FIGURES.................................................................................................................. xiii

CHAPTER

I. INTRODUCTION .................................................................................................................. 1
II. BACKGROUND AND LITERATURE REVIEW ................................................................. 4

2.1 What is an aerogel? ....................................................................................................... 4

2.2 Discovery and developments ....................................................................................... 5

2.2.1 Discovery .................................................................................................................. 5

2.2.2 Developments .......................................................................................................... 7

2.3 Synthesis of silica aerogels via sol-gel process ............................................................ 9

2.3.1 Silica sol-gel process ............................................................................................. 10

2.3.2 Structures under acid/base-catalyzed conditions .................................................... 12

2.3.3 Supercritical drying ............................................................................................... 14

2.4 Polymer reinforcement and surface modification of silica aerogels ........................... 18

2.4.1 Polymer reinforcement ............................................................................................ 18

2.4.2 Hydrophobic silica aerogels via surface modification ............................................ 26

2.4.3 Summary .................................................................................................................. 28

2.5 Polyhedral oligomeric silsesquioxanes (POSS) ......................................................... 30

2.5.1 POSS cages ............................................................................................................. 31
5.1 Research Objectives .......................................................... 136
5.2 Results and discussion ....................................................... 137
  5.2.1 Density, shrinkage, and mechanical properties ................. 137
  5.2.2 Morphology ............................................................... 140
  5.2.3 Surface properties ...................................................... 142
  5.2.4 Comparison with POSS reinforced silica aerogels .............. 151
5.3 Summary ........................................................................... 151

VI. SILANE END-CAPPED POLYURETHANE AND ITS PREPOLYMER FOR REINFORCEMENT OF SILICA AEROGELS VIA PRE-GELATION MODIFICATIONS ........................................... 152
6.1 Research objectives ........................................................... 152
6.2 Results and Discussion ....................................................... 153
  6.2.1 Synthesis and structure of polymers ................................ 153
  6.2.2 Structure of aerogels .................................................... 156
  6.2.3 Properties of aerogels ................................................... 163
  6.2.4 Mechanical properties .................................................. 185
6.3 Discussion .......................................................................... 189
6.4 Conclusions ........................................................................ 190

VII. SELF-CROSSLINKABLE POLYURETHANE-UREA REINFORCED SILICA AEROGELS VIA PRE-GELATION MODIFICATIONS ..................................................... 191
7.1 Research Objectives ........................................................... 191
7.2 Results and Discussion ....................................................... 191
  7.2.1 Structure of self-crosslinkable polyurethane-urea from FT-IR 191
  7.2.2 Density, shrinkage, and compressive modulus ................. 193
  7.2.3 Morphology and surface properties ............................... 195
  7.2.3 Compositions and Thermal properties ........................... 199
7.2.4 Fractal dimension from SAXS .................................................. 202

7.3 Summary .................................................................................. 205

VIII. CONCLUSIONS ................................................................. 206

REFERENCES .............................................................................. 210

APPENDICES ............................................................................... 226

APPENDIX A. SOLID STATE NMR RESULTS AND COMPOSITIONS OF SIF3 MODIFIED TEOS-BASED SILICA AEROGELS ........................................ 227

APPENDIX B. SOLID STATE NMR RESULTS OF SELF-CROSSLINKABLE POLYURETHANE-UREA REINFORCED SILICA AEROGELS ................. 231
<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Critical constant for some solvents (data adapted from Ref. 89)</td>
</tr>
<tr>
<td>2.</td>
<td>Composition of silica aerogels in conjunction with different types of POSS</td>
</tr>
<tr>
<td>3.</td>
<td>Composition of silica aerogels modified with SiF3 solution</td>
</tr>
<tr>
<td>4.</td>
<td>Composition of silica aerogels with end-capped polyurethane/end-capped prepolymer</td>
</tr>
<tr>
<td>5.</td>
<td>Composition of silica aerogels reinforced with self-crosslinkable polyurethane-urea</td>
</tr>
<tr>
<td>6.</td>
<td>Density, shrinkage and compressive modulus of tri-POSS, cyclo-POSS, tetra-POSS and i-butyl-POSS reinforced TEOS based aerogels and epoxy-POSS reinforced TEOS/APTES based aerogels</td>
</tr>
<tr>
<td>7.</td>
<td>Values of contact angles and surface energy components of TEOS-based aerogels reinforced with different types of POSS</td>
</tr>
<tr>
<td>8.</td>
<td>Surface area, average pore size and dominant pore size of aerogel samples</td>
</tr>
<tr>
<td>9.</td>
<td>Compositions of TEOS-based aerogels reinforced with POSS nanoparticles</td>
</tr>
<tr>
<td>10.</td>
<td>Slopes from Porod’s plots and fractal dimension for different types of POSS-reinforced silica aerogels</td>
</tr>
<tr>
<td>11.</td>
<td>Batch to batch variation of compressive modulus of T-tri-POSS-5 aerogels</td>
</tr>
<tr>
<td>12.</td>
<td>Density and shrinkage data of SiF3 modified TEOS aerogels</td>
</tr>
<tr>
<td>13.</td>
<td>BET surface area, average pore size, and dominant pore size from gas adsorption method of TEOS aerogels without and with modification by SiF3</td>
</tr>
<tr>
<td>14.</td>
<td>Composition and contact angles data of TEOS-based aerogels as function of different modification steps</td>
</tr>
<tr>
<td>15.</td>
<td>Contact angle data of compressed TEOS based aerogel discs with SiF3/EtOH solution for post-modification</td>
</tr>
</tbody>
</table>
16. Surface energy data of compressed TEOS based aerogel discs with SiF3/EtOH solution for post-modification ................................................................. 150
17. Weight loss of TEOS/APTES-based silica aerogels reinforced with APTES end-capped polyurethane at 600 °C ................................................................. 162
18. Weight loss of TEOS/APTES based silica aerogels with APTES end-capped prepolymer at 600°C ................................................................. 163
19. Slopes and fractal dimension of TEOS/APTES aerogels reinforced with APTES end-capped polyurethane via Porod’s plot and Rg from Guinier’s law .......... 175
20. Values of contact angles and surface energy components of TEOS/APTES-based aerogels reinforced with APTES-PU and APTES-prePU ................................. 179
21. BET surface area, micropore surface area, average pore diameter, and the dominant pore size of APTES-PU and APTES-prePU reinforced silica aerogel samples ........................................................................ 185
22. Surface area, average pore size and pore size distribution of sPU reinforced silica aerogels from gas adsorption method .......................................................... 199
23. Weight loss of TEOS/APTES aerogels with sPU at 650 °C ............................... 200
24. Slopes and fractal dimension of TEOS/APTES aerogels reinforced with sPU via Porod’s Plot and Rg from Guinier’s law ............................................................ 204
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>General sol-gel reaction scheme. Here, R is the alkyl group, e.g., ethyl and methyl. M is the metal</td>
</tr>
<tr>
<td>2.</td>
<td>Hydrolysis mechanism of alkoxy silanes under acid/base catalyzed conditions</td>
</tr>
<tr>
<td>3.</td>
<td>Condensation mechanisms of alkoxy silanes under acid or base catalyzed conditions</td>
</tr>
<tr>
<td>4.</td>
<td>Gel structure for acid and base catalyzed reactions (adapted from Ref. 86)</td>
</tr>
<tr>
<td>5.</td>
<td>Representation of the contracting surface forces in pores of different size during drying. At the same pressure, the curvature of all menisci in the pores is the same. For this reason the larger pores empty first.</td>
</tr>
<tr>
<td>6.</td>
<td>Schematic representation of the principle of supercritical drying. At the critical point ( (T_c, p_c) ) the densities of the liquid and the gas are equal.</td>
</tr>
<tr>
<td>7.</td>
<td>Schematic representation of the pearl-necklace like structure of silica aerogel (adapted from Ref. 2)</td>
</tr>
<tr>
<td>8.</td>
<td>Overview of polymer crosslinking chemistry (adapted from Ref. 5)</td>
</tr>
<tr>
<td>9.</td>
<td>Structures of silsesquioxanes</td>
</tr>
<tr>
<td>10.</td>
<td>Scheme of completely condensed polyhedral oligo silsesquioxanes synthesis by hydrolytic condensation of trichloro- or trialkoxysilanes</td>
</tr>
<tr>
<td>11.</td>
<td>Scheme of incompletely condensed polyhedral oligo silsesquioxanes synthesis by slow hydrolytic condensation</td>
</tr>
<tr>
<td>12.</td>
<td>Scheme of incompletely condensed polyhedral oligo silsesquioxanes synthesis by acid- and base-mediated cleavage of completely condensed POSS</td>
</tr>
<tr>
<td>13.</td>
<td>Structures of tetraethoxysilane (TEOS), aminopropytriethoxysilane (APTES), trisilanol phenyl POSS (tri-POSS), glycidyl POSS© Cage Mixture (epoxy-POSS), trisilanol cyclopentyl POSS© (cyclo-POSS), trisilanolisobutyl POSS© (i-butyl-POSS), and tetrasilanol phenyl POSS© (tetra-POSS)</td>
</tr>
<tr>
<td>14.</td>
<td>Schematic illustration of synthesis of tri-POSS-reinforced TEOS-based aerogels</td>
</tr>
<tr>
<td></td>
<td>Illustration</td>
</tr>
<tr>
<td>---</td>
<td>--------------</td>
</tr>
<tr>
<td>15.</td>
<td>Illustration of reaction TEOS and <em>tri</em>-POSS after silane network formation</td>
</tr>
<tr>
<td>16.</td>
<td>Schematic illustration of synthesis of <em>epoxy</em>-POSS reinforced TEOS/APTES-based aerogels</td>
</tr>
<tr>
<td>17.</td>
<td>Illustration of reaction between TEOS/APTES and <em>epoxy</em>-POSS</td>
</tr>
<tr>
<td>18.</td>
<td>Structure of dimethoxy-methyl(3,3,3-trifluoropropyl)silane</td>
</tr>
<tr>
<td>19.</td>
<td>Structure of SiF3 modified silica aerogels</td>
</tr>
<tr>
<td>20.</td>
<td>Structures of 4, 4’-diphenylmethane diisocyanate, 1, 4-butanediol, and poly-tetramethylene glycol</td>
</tr>
<tr>
<td>21.</td>
<td>Structure of dibutyltin dilaurate (DABCO T120)</td>
</tr>
<tr>
<td>22.</td>
<td>Synthesis of prepolymer and APTES end-capped prepolymer</td>
</tr>
<tr>
<td>23.</td>
<td>Experimental set-up for synthesis of chain extended polyurethane via a two-step route</td>
</tr>
<tr>
<td>24.</td>
<td>Synthesis of chain extended polyurethanes via a two-step synthesis route and APTES end-capped polyurethanes</td>
</tr>
<tr>
<td>25.</td>
<td>Synthesis of APTES end-capped polyurethane reinforced aerogels</td>
</tr>
<tr>
<td>26.</td>
<td>Structure of amino ethyl aminopropyl trimethoxysilane (AEAPS)</td>
</tr>
</tbody>
</table>
27. Synthetic route of self-crosslinkable polyurethane-urea (sPU) .......................66
29. IUPAC classification of sorption isotherms\textsuperscript{171} (adapted from Ref. 171) .........76
30. Typical adsorption and desorption isotherms for mesoporous materials ..............76
31. BET plot to determine slope and intercept.........................................................77
32. t-plot of materials with micropores and mesopores ........................................82
33. The appearance of POSS nanoparticles reinforced silica aerogels (noting that the sample ID is listed in Table 2) .................................................................85
34. Density, shrinkage and compressive modulus of silica aerogels reinforced with tri-POSS nanoparticles ..........................................................86
35. Density, shrinkage and compressive modulus of epoxy-POSS nanoparticles reinforced TEOS/APTES aerogels ......................................................89
36. SEM images of aerogels without/with POSS (a) TEOS-based aerogel without POSS reinforcement, (b) TEOS-based aerogel with 5 wt\% tri-POSS, (c) TEOS-based aerogel with 5 wt\% cyclo-POSS, (d) TEOS-based aerogel with 5 wt\% tetra-POSS, (e) TEOS-based aerogel with 5 wt\% i-butyl-POSS (f) TEOS-based aerogel with 10 wt\% i-butyl-POSS, (g) TEOS/APTES-based aerogel without POSS reinforcement, (h) TEOS/APTES-based aerogel with 5 wt\% epoxy-POSS.93
37. Contact angle by static sessile drop method for T-tri-POSS-2 ...............................94
38. Optical microscopy image of one of compressed aerogel discs (T-tri-POSS-5) .95
39. AFM height image of one of compressed aerogel dics (T-tri-POSS-5)..............96
40. Contact angle trend of TEOS-based aerogels with i-butyl POSS .....................100
41. Images of TEOS-based aerogels with and without \(i\)-butyl POSS when exposed to deionized water: (a). deionized water absorbed in TEOS-based aerogels without POSS nanoparticles, (b). a deionized water droplet on top of the TEOS-based aerogels reinforced with 10 wt% \(i\)-butyl POSS, (c). a piece of TEOS-based aerogels reinforced with 10 wt% \(i\)-butyl POSS floats on top of deionized water.

42. Adsorption and desorption isotherms of TEOS-based aerogels without POSS and \(T-i\)-butyl-POSS-10.

43. Pore size distribution of TEOS-based aerogels with \(tri\)-POSS.

44. Pore size distribution of TEOS-based aerogels with \(tetra\)-POSS.

45. Pore size distribution of TEOS-based aerogels with \(i\)-butyl-POSS.

46. Pore size distribution of TEOS-based aerogels with \(cyclo\)-POSS.

47. Pore size distribution of TEOS-based aerogels with \(epoxy\)-POSS.

48. Solid-state \(^{13}\)C NMR spectra of (A) TEOS, (B) TEOS/5\% \(tri\)-POSS, (C) TEOS/APTES and (D) TEOS/APTES/5\% \(epoxy\)-POSS.

49. Solid-state \(^{29}\)Si NMR spectra of (A) \(tri\)-POSS, (B) TEOS, (C) TEOS/5\% \(tri\)-POSS, (D) TEOS/APTES and (E) TEOS/APTES/5\% \(epoxy\) POSS.

50. Solid-state \(^{13}\)C NMR spectra of (a) \(tetra\)-POSS (scans=2400), (b) \(T-tetra\)-POSS-2 (scans=28160) and (c) \(T-tetra\)-POSS-5 (scans=14376).

51. Solid-state \(^{29}\)Si NMR spectra of (a) \(tetra\)-POSS (scans=3032), (b) \(T-tetra\)-POSS-2 (scans=12128) and (c) \(T-tetra\)-POSS-5 (scans=26364).

52. Solid-state \(^{13}\)C NMR spectra of (a) \(cyclo\)-POSS (scans=2000), (b) \(T-cyclo\)-POSS-1 (scans=42804).

53. Solid-state \(^{29}\)Si NMR spectra of (a) \(cyclo\)-POSS (scans=2716) and (b) \(T-cyclo\)-POSS-1 (scans=26908).
54. Solid-state $^{13}$C NMR spectra of (a) $i$-butyl-POSS (scans=1000) (b) T-$i$-butyl-POSS-1 (scans=42228), (c) T-$i$-butyl-POSS-5 (scans=28160) and (d) T-$i$-butyl-POSS-10 (scans=13040) .................................................................117

55. Solid-state $^{29}$Si NMR spectra of (a) $i$-butyl-POSS (scans=840) (b) T-$i$-butyl-POSS-1 (scans=13184), (c) T-$i$-butyl-POSS-5 (scans=8536) and (d) T-$i$-butyl-POSS-10 (scans=27892) .................................................................119

56. SAXS intensity as a function of the modulus of the scattering vector ..........123

57. SAXS intensity as a function of the modulus of the scattering vector ..........124

58. Porod’s plot of SAXS intensity as a function of $q$ on a log-log scale ..........124

59. Porod’s plot of SAXS intensity as a function of $q$ on a log-log scale ..........125

60. Illustration of the reaction mechanism of TEOS-based aerogels reinforced with tri-POSS, $i$-butyl POSS, and cyclo-POSS .................................................................129

61. Illustration of the reaction of TEOS-based aerogels reinforced with different content of POSS (a) TEOS-based native silica aerogels without reinforcement of POSS, (b) TEOS-based silica aerogels reinforced with low content of POSS (1 wt% and 3 wt%), (c) TEOS-based silica aerogels reinforced with low content of POSS (5 wt% and 10 wt%) .................................................................130

62. Illustration of the reaction between TEOS/APTES and epoxy-POSS ..........131

63. Comparison of different types of POSS as reinforcement and surface modification agents for silica aerogels .................................................................134

64. Silylation reaction of chlorosilanes or silazanes with active hydrogen ..........137

65. Silylation reaction of TEOS-based aerogels with SiF3 ..................................137

66. Appearance of SiF3 modified TEOS-based aerogels with average diameters (a) TEOS-based aerogels without SiF3 modification, (b) TEOS-based aerogels modified with 5 wt% SiF3, (c) TEOS-based aerogels modified with 15 wt% SiF3, (d) TEOS-based aerogels modified with 25 wt% SiF3 .........................................................138

67. Density, shrinkage, and compressive modulus data of SiF3 modified TEOS-based silica aerogels .................................................................................140

68. SEM images of TEOS aerogels without/with modification of SiF3 (a) TEOS-based aerogels without SiF3 modification, (b) TEOS-based aerogels modified with 5 wt% SiF3, (c) TEOS-based aerogels modified with 10 wt% SiF3, (d) TEOS-based aerogels modified with 15 wt% SiF3, (e) TEOS-based aerogels modified with 20 wt% SiF3, (f) TEOS-based aerogels modified with 25 wt% SiF3 .................................................................................141
69. Adsorption and desorption isotherms of TEOS aerogels without/with modification of SiF₃ .................................................................143
70. Pore size distribution of TEOS aerogels without/with modification of SiF₃ from desorption isotherm determined by BJH method .............................................144
71. Contact angle images of SiF₃ modified TEOS based aerogels with water ........150
72. Pictures of hydrophobic TEOS-based aerogels modified with 15wt% SiF₃/EtOH solution (a) one water droplet on top of the aerogels (b) a monolithic aerogel floating on the top of water .................................................................150
73. FT-IR spectra of PTMG1000, MDI end-capped prepolymer and APTES end-capped prepolymer ...........................................................155
74. FT-IR of MDI end-capped polyurethane and APTES end-capped polyurethane 155
75. ¹H NMR of PTMG based polyurethane ................................................................156
76. ¹³C CP/MAS SSNMR spectra of (a) APTES end-capped polyurethane, (b) TEOS/APTES based aerogel, (c) TEOS/APTES/0.5 wt % APTES end-capped polyurethane, and (d) TEOS/APTES/15 wt % APTES end-capped polyurethane 158
77. ²⁹Si CP/MAS SSNMR spectra of of (a) APTES end-capped polyurethane, (b) TEOS/APTES based aerogel, (c) TEOS/APTES/0.5 wt % APTES end-capped polyurethane, (d) TEOS/APTES/10 wt % APTES end-capped polyurethane, and (e) TEOS/APTES/15 wt % APTES end-capped polyurethane .................159
78. Weight loss of TEOS/APTES aerogels with APTES end-capped polyurethane 161
79. Weight loss of TEOS/APTES aerogels with APTES end-capped prepolymer ..161
80. DSC scans of TEOS/APTES aerogels with APTES end-capped prepolymer ...162
81. Appearance of TEOS/APTES aerogels (a) without reinforcement, (b) with APTES end-capped prepolymer, and (c) with APTES end-capped polyurethane 164
82. Density and shrinkage of TEOS/APTES based aerogels reinforced with APTES end-capped polyurethane (APTES-PU) and APTES end-capped polyurethane prepolymer (APTES-prePU) ..............................................................................165
83. SEM image of TEOS/APTES-based silica aerogels reinforced without and with APTES end-capped prepolymer (a) TA-0, (b) TA-prePU-3, (c) TA-prePU-7, (d) TA-prePU-10. Compositions are presented in Table 4, page 69 .................................168
84. SEM image of TEOS/APTES based aerogels reinforced with APTES end-capped polyurethane (a) TA-0, (b) TA-PU-3, (c) TA-PU-5, (d) TA-PU-15, (e) and (f)
TA-PU-50 at different magnifications. Compositions are presented in Table 4, page 69. .................................................................170
85. SAXS intensity of TA-PU samples as a function of the scattering vector ..........172
86. SAXS intensity of TA-prePU samples as a function of the scattering vector....172
87. Porod’s plot of SAXS intensity as a function of $q$ on a log-log scale (TA-PU) 173
88. Porod’s plot of SAXS intensity as a function of $q$ on a log-log scale (TA-prePU)173
89. Guinier’s plots of TEOS/APTES-based aerogels reinforced with APTES end-
capped polyurethane ........................................................................174
90. Water contact angle images of APTES-end PU and MDI-end PU ..........178
91. Water contact angle images of TEOS/APTES/PU aerogels ......................178
92. Adsorption and desorption isotherms for TEOS/APTES aerogels with/without
silane end-capped polyurethane reinforcement ........................................182
93. Adsorption and desorption isotherms for TEOS/APTES aerogels with/without
silane end-capped polyurethane prepolymer reinforcement .......................183
94. The pore size distributions of TEOS/APTES aerogels reinforced with APTES
end-capped polyurethane determined by BJH method ...............................184
95. The pore size distributions of TEOS/APTES aerogels reinforced with APTES
end-capped polyurethane prepolymer determined by BJH method ..........184
96. Stress-strain curve of TEOS/APTES aerogels with APTES-end polyurethane.187
97. Stress-strain curve of TEOS/APTES aerogels with APTES-end prepolymer ...187
98. Compressive modulus vs. polymer wt% of TA-PU and TA-prePU aerogels ....188
99. Stress-strain curve of TA-PU-15 and TA-PU-50 .....................................188
100. FT-IR spectrum of self-crosslinkable polyurethane-urea, (a) PTMG1000, (b)
prepolymer with isocyante end-goups, (c) sPU ........................................193
101. Appearance of sPU gel and sPU-reinforced silica aerogels (a) TA-0, (b) TA-sPU-
5, (c) TA-sPU-10, (d) TA-sPU-15, (e) TA-sPU-20, (f) TA-sPU-25. Compositions
are listed in Table 5, page 70. (g) transparent sPU gel, (h) transparent sPU gel
compressed with fingers .........................................................................194
102. Density-shrinkage-modulus of sPU reinforced silica aerogels ............195
103. SEM images of sPU reinforced silica aerogels (a) TA-0, (b) TA-sPU-1, (c) TA-sPU-5, (d) TA-sPU-10, (e) TA-sPU-15, (f) TA-sPU-20. Compositions are listed in Table 5, page 70 ..................................................197

104. Adsorption and desorption isotherms of TEOS/APTES based silica aerogels without/with sPU reinforcement ..................................................198

105. Pore size distribution of sPU reinforced TEOS/APTES based silica aerogels ................................198

106. DSC curves of TEOS/APTES aerogels with/without sPU reinforcement ...............201

107. TGA curves of TEOS/APTES-based aerogels reinforced with/without sPU ....201

108. SAXS intensity as a function of the scattering vector.................................202

109. Porod’s plot of SAXS intensity as a function of q on a log-log scale............203

110. Guinier's plots of TEOS/APTES with sPU ........................................204

111. Solid-state $^{13}$C NMR spectra of (a) TEOS (CP time= 3ms, scans=13800) (b) TEOS/ SiF$_3$ 5% (scans=32768), (c) TEOS/ SiF$_3$ 10% (scans=26760) and (d) TEOS/ SiF$_3$ 20% (scans=28756) ..................................................227

112. Solid-state $^{29}$Si NMR spectra of (a) TEOS (scans=4908) (b) TEOS/ SiF$_3$ 5% (scans=27268), (c) TEOS/ SiF$_3$ 10% (scans=12964) and (d) TEOS/ SiF$_3$ 20% (scans=9596) ..................................................228

113. $^{13}$C CP/MAS SSNMR spectra of (a) TA-0 (scans=11976), (b) TA-sPU-5 (scans=31532) (c) TA-sPU-10 (scans=13012) and (c) TA-sPU-20 (scans=28604). ........................................................................231

114. $^{29}$Si CP/MAS SSNMR spectra of (a) TA-0 (scans=5532), (b) TA-sPU-5 (scans=27816) (c) TA-sPU-10 (scans=27848) and (c) TA-sPU-20 (scans=9596).233
Aerogel is a highly porous solid-state material derived from a wet gel in which the liquid component is replaced by air under supercritical conditions, compared to xerogels, which are dried under ambient conditions. This replacement is carefully carried out so as to keep the solid network from collapsing due to capillary action during removal of the liquid. This results in an extremely low-density solid material with several remarkable properties, particularly their effectiveness as a storage matrix from high surface area and extremely low density. However, the applications of aerogels are limited due to the inherent fragility of the silica networks and moisture absorbing nature. For example, a native silica aerogel structure derived from tetramethoxysilane (TMOS) with a density of about 120 mg/cm$^3$ can be easily destroyed under a stress of 31 kPa.\textsuperscript{1} This failure at relatively low stress is the direct result of the “pearl necklace” structure. It is believed that the “necks” where the secondary spherical silica particles join each other are only held by a few Si-O-Si bonds.\textsuperscript{2} The strength of aerogels can be greatly enhanced by reinforcing the silica particles with short or long chain reactive organic molecules.

The primary focus of current research on aerogels is to improve the strength of silica networks and to obtain strong mechanical properties from aerogel structures, while retaining low density and high surface area at the same level of native aerogels. Progress has been made to increase the strength and to make the aerogel surface hydrophobic.
Effective reinforcements were achieved by crosslinking the skeletal structures with different polymers, oligomers, and short chain molecules including isocyanates, epoxies, or styrene by introducing functional groups such as amine or vinyl into silane precursors, thus onto the surface of the silica network. In these cases, the functional groups were first incorporated into the skeletal structures of aerogels followed by crosslinking reactions.

The main goal for this research was to study the surface modification and mechanical reinforcement of silica aerogels and to elucidate their compositional and structural-morphological relationships. Several new approaches were studied in this work. First, several polyhedral oligomeric silsesquioxanes (POSS) molecules with different functional groups were selected as reinforcement of silica aerogels. POSS nanoparticles are a class of fillers widely used to modify the properties of polymers. The main feature of POSS is the presence of at least one non-silicate, organic group on the silicon atoms. The cage-shaped hybrid molecules composed of silicon and oxygen have similarities with both silica and silicone. The typical diameter of the POSS cage is about 1.5 nm with a molecular weight around 1000 g/mol. When mixed with polymers, the organic groups interact with the polymer chains, which results in a nanostructured organic-inorganic hybrid polymer. The POSS chains act as nano-scale reinforcing fillers and have the potential to offer better mechanical properties and extraordinary gains in thermal resistance. In our study, POSS molecules containing silanol groups, Si-OH, was used as a source of silanes in conjunction with tetraethoxy silanes (TEOS) to prepare stronger aerogels with negligible changes in density. In addition, functional POSS molecules such as POSS nanoparticles with eight epoxy groups were used to reinforce the aerogel
networks by reacting with the amine functionality residing in the gel. Due to the structural and chemical similarity of POSS molecules with conventional organic silanes such as TMOS, the issues of aggregation and phase separation during sol-gel preparation could be avoided.

Second, dimethoxy-methyl (3,3,3-trifluoropropyl) silane was utilized as a silylating agent and introduced into the pore structure after the alcogels were formed. This provided comparison with the method of surface modification using POSS. It was expected that this silylating agent would diffuse into the small pores of silica alcogels, eliminate the residual –OH groups by silylating reactions, and turn the surface hydrophobic. Since the silica network was formed first, no significant effects on morphology and structures were anticipated.

In previous efforts on reinforcement of silica aerogel networks by polymers such as isocyanates, epoxies, and polystyrene, the polymer was introduced into the network after the gel was formed. In this work, silane-modified polymers with multiple reacting functional groups were used and allowed to undergo hydrolysis and condensation reactions with other silane precursors. This avoided post-gelation crosslinking reactions. In this manner, the amount of polymers introduced in the aerogel structures could be controlled and the chain length between two crosslink points could be tailored. It was expected that long chain polymer molecules would introduce a certain degree of flexibility in the hybrid aerogel structures, thus improving the surface hydrophobicity.
2.1 What is an aerogel?

An aerogel is a highly porous solid material derived from a gel in which the liquid component is replaced by air under supercritical conditions. A xerogel in comparison is obtained when the gel is dried at ambient conditions. This replacement of liquid in the gel with air is carefully carried out so as to keep the solid network from collapsing due to capillary action during removal of the liquid. The replacement of the liquid component with a gas results in an extremely low-density solid material with several remarkable properties, particularly their effectiveness as a thermal insulator and extremely low density. The aerogels have been synthesized from a metal or metalloid element surrounded by various reactive ligands. However, the most common aerogel is silica aerogel. It is also the most extensively studied and widely used among the aerogels. Silica aerogels are a unique class of highly porous materials (porosity>95%) which received significant attention due to their remarkable properties, such as extremely low density (3-350 mg/cm$^3$), large surface area (500-1200 m$^2$/g), low thermal conductivity (ranging from 0.004 to 0.03 W/m·K), low dielectric constant (1.1-2.2), low index of refraction (~1.05), different morphologies (monoliths or powders) and optical properties (transparent, opaque or translucent). Due to these interesting properties, silica aerogels initially found applications in high-energy particle physics (Cherenkov
emitters), where they were used to generate Cherenkov radiation by passing charged particles through the aerogel at speeds faster than the speed of light within the aerogel. Second, aerogels are good convection inhibitors as air cannot circulate through the lattice. As a result, they offer excellent thermal insulation. Monolithic silica aerogels are well suited to deal with the energy savings coupled with alleviating some of the environmental concerns, e.g., their transparency may aid construction and building industry well in the form of transparent and superinsulating double windows, or promising space science application. Additionally, silica aerogels can be used as adsorbent, e.g. for oils and organic liquids, or used as sensors, catalysts, storage media and templates. Furthermore, silica aerogel is applied in life sciences such as in dealing with biocatalysis with a lipase enzyme or in a process to detect a viral particle by immobilized bacteria.

However, despite offering low thermal conductivities and density, the applications of aerogels are limited due to the fragility of the silica networks. For example, a native silica aerogel structure derived from tetramethoxysilane (TMOS) with a density of about 120 mg/cm³ can be easily destroyed under a stress of 31 kPa.

2.2 Discovery and developments

The first aerogel was created by Kestler in 1931. Later, a lot of research has been done in this area.

2.2.1 Discovery

The first aerogel was created by Steven S. Kistler in 1931. He dispersed colloidal silica particles in water. Then a gel was formed when the particles connected with each other by condensation of the silanol groups. At that time, Kistler wanted to remove the liquid...
component from the wet gel without damaging the solid components, in order to prove a hypothesis that a dry "gel" contained a continuous solid network of the same size and shape as in the wet gel. However, a wet gel would not maintain its original size upon drying. Instead, these wet gels usually shrink often to a fraction of its original size, if it is simply allowed to dry on its own under ambient conditions, which results in xerogels. Severe cracking of the gels often accompanies shrinkage, which results from the surface tension of water pulling on the silica networks as the liquid meniscus recedes.

Then Kistler discovered the key aspect of aerogel production.\textsuperscript{69, 70} He used a supercritical drying process, which allowed the liquid to be slowly drawn off without collapse of the structure from the capillary force.

The first gels studied by Kistler were silica gels prepared by condensation of aqueous sodium silicate under acid condition. However, a preparation of aerogels by converting the water in the gels to a supercritical fluid failed since the supercritical water redissolved the silica. The redissolved silica then precipitated as the water was removed by venting. To circumvent this, Kistler tried exchanging water for alcohol by soaking and rinsing the gel in the alcohol many times over a period of two weeks.\textsuperscript{69} Thereafter, the gel was placed in an autoclave where the temperature and pressure were raised until the critical point of the alcohol was exceeded. Above the critical point, the alcohol becomes a gas where the surface tension disappears and the gas escapes without destroying the network. Therefore the first true aerogels were formed by converting the alcohol to a supercritical fluid and by allowing the gaseous alcohol to escape. Kistler's aerogels were very similar to silica aerogels prepared today. They were transparent, low density, and highly porous materials that stimulated considerable academic research interest.\textsuperscript{70}
2.2.2 Developments

Although interesting and promising materials, aerogels were largely forgotten until the late 1970s, when the study of aerogels drew attentions while seeking a porous material for storing oxygen and rocket fuels. In order to get enough materials for the study, one of Teichner’s students was strongly motivated to find a better synthetic process instead of following Kistler’s time-consuming and laborious method. This synthetic process directly led to one of the main advances in aerogel science, namely the application of sol-gel chemistry to silica aerogel preparation.\(^1\) This recipe replaced the sodium silicate used by Kistler with an alkoxy silane, (tetramethoxysilane, TMOS).\(^2\) Hydrolysis of TMOS in a solution of methanol resulted in a gel in one step (called an "alcogel"). This process eliminated two drawbacks in Kistler's procedure, the solvent exchange step and the required presence of inorganic salts in the gel. In the following years, Teichner's group and other researchers extended this approach to prepare a wide variety of metal oxide aerogels.\(^2\)

After this development, aerogel science and technology progressed rapidly as more researchers joined the field. Some of the more notable achievements are listed below.

In the early 1980s, particle physics researchers found an important application of silica aerogels as an ideal medium for the production and detection of Cherenkov radiation.\(^3,4\) These experiments required large transparent tiles of silica aerogel.\(^3\)

In the middle of 1980s, Tewari et al.\(^5\) found that the very toxic compound TMOS could be replaced by tetraethoxysilane (TEOS), a much safer reagent without lowering the quality of the aerogel products. At the same time, Hunt et al.\(^5\) also found that the alcohol could be replaced by liquid carbon dioxide before supercritical drying without harming
the aerogel. This was considered a breakthrough as the critical point of CO\(_2\) (31 °C and 7.4 MPa) occurs at lower temperature than that of methanol (240 °C and 6.3 MPa).\(^7\) Additionally, carbon dioxide does not create an explosion hazard at its critical conditions as alcohol does. This process was put to use in making transparent silica aerogel tiles from TEOS.

In the late 1980s, researchers at Lawrence Livermore National Laboratory (LLNL) led by L. Hrubesh prepared the world’s lowest density silica aerogel, which was also the lowest density solid material. This aerogel had a density of 3 mg/cm\(^3\), only three times that of air.\(^7\)

Shortly afterward, Scherer et al., also from LLNL, applied the techniques of preparation of inorganic aerogels to preparation of aerogels of organic polymers, which included resorcinol-formaldehyde and melamine-formaldehyde aerogels.\(^7\) This progress opened a completely new area in aerogel research.

Another development in the synthesis of aerogels was introduced by Hrubesh and coworkers.\(^9\) A two-step sol-gel process was adopted with an acid catalyst at the beginning of hydrolysis and a base catalyst in the finishing step of the reaction.\(^7\) It was found that these slightly different processing conditions impart subtle, but important changes to the final aerogel product. The microstructure of the aerogels obtained from this two-step method was found to be different from the bead-like structure proposed for a single-step, base-catalyzed aerogels obtained from TMOS. Single-step base catalyzed aerogels are typically mechanically stronger, but more brittle, than two-step aerogels. The aerogels obtained from two-step procedures have smaller and narrower pore size distribution and are often optically clearer than aerogels obtained from single-step.\(^7\)
Researchers\textsuperscript{80, 81} at the University of New Mexico, led by C. J. Brinker,\textsuperscript{82} were pioneers in eliminating the need for supercritical drying step, which led to the founding of a company called Nanopore for commercialization of lower-cost aerogels. In principle, their procedure involved a series of solvent-exchange processes and a modification of the pore surfaces. The water/alcohol mixture in the pores of the gel was first exchanged for a water-free solvent, and the Si-OH groups at the surface were silylated (e.g. with chlorotrimethylsilane), which made the surface more hydrophobic. They found that one of the prerequisites for this procedure was the strengthening of the network by exact control of the aging conditions. Their work helped the commercialization of low-cost aerogels. Einarsrud et al.\textsuperscript{83} obtained similar good results with another strategy. They increased the strength and stiffness of the network drastically by aging the wet gels in solutions of tetraalkoxysilanes in aqueous alcohols, and were thus able to completely avoid shrinkage during drying. The gels can also be dried at ambient pressure between 20 and 180\textdegree{}C because of the stiffer network.

Recently, Leventis et al.\textsuperscript{2} from NASA Glenn Research Center proposed an idea for enhancement of strength by crosslinking the silica aerogel network with different functional groups introduced into the network, using polymers such as epoxies and urethanes. For instance, using aminopropyltriethoxysilane (APTES) as a co-precursor of silica gel, amine-modified gels, which were crosslinked with epoxies, showed an increase of 2-3 times in density, but an increase of more than 2 orders of magnitude in strength.\textsuperscript{84}

2.3 Synthesis of silica aerogels via sol-gel process

Recently, silica aerogels are prepared by following a sol-gel process using multifunctional silanes as precursors.
2.3.1 Silica sol-gel process

Sol-gel chemistry dates back to the 1800’s. It produces a variety of inorganic networks from silicon or metal alkoxide monomer precursors. The sol-gel process involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel).\textsuperscript{10, 85} The precursors for synthesizing these colloids consist of a metal or metalloid element surrounded by various reactive ligands. The most widely used precursors for silica aerogels are the alkoxy silanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS).

At the functional group level, two reactions are generally used to describe the sol-gel process: hydrolysis and condensation, which is shown in Figure 1.

\begin{equation}
\text{Hydrolysis:}
\text{M—OR + H}_2\text{O} \rightarrow \text{M—OH + ROH}
\end{equation}

\begin{equation}
\text{Condensation:}
\text{M—OR + M—OH} \rightarrow \text{M—O—M + ROH}
\end{equation}

Figure 1. General sol-gel reaction scheme.\textsuperscript{10} Here, R is the alkyl group, e.g., ethyl and methyl. M is the metal.

2.3.1.1 Hydrolysis

Hydrolysis is the reaction of a metal alkoxide (M-OR) with water, forming a metal hydroxide (M-OH). It can be carried out under either acidic or basic condition. For acid-catalyzed reaction, the transition state is positively-charged. On the other hand, the
transition state is negatively-charged under basic condition. Several factors can affect the hydrolysis reaction. One such factor is the different substituent in silane structure, which can influence the hydrolysis rate. Since alkoxy groups are more electron-donating than hydroxyl groups, more alkoxy groups make the positively-charged transition state more stable. Conversely, the negatively-charged transition state is more stable and thus the hydrolysis is faster for base-catalyzed reactions. The schemes of hydrolysis reactions in acidic and basic conditions are shown in Figure 2.

Acid-catalyzed:

Base-catalyzed:

Figure 2. Hydrolysis mechanism of alkoxy silanes under acid/base catalyzed conditions

2.3.1.2 Condensation

A condensation reaction occurs when two metal hydroxide molecules (M-OH) combine to give a molecule of metal oxide species (M-O-M). The reaction yields one water molecule. Condensation reactions may be acid- or base- catalyzed, and in either case the reaction proceeds via a rapid formation of a charged intermediate by reaction with a proton or hydroxide ion, followed by slow attack of a second neutral silicon species on this intermediate. It is generally believed that the acid-catalyzed condensation reaction
mechanism involves a protonated silanol species. Protonation of the silanol makes the silicon more electrophilic and thus prone to nucleophilic attack. Therefore, condensation reactions between the neutral species and the protonated silanols with large side groups may be preferred. The most widely accepted mechanism for the base-catalyzed condensation reaction involves the attack of a nucleophilic deprotonated silanol on a neutral silicic acid. The base-catalyzed condensation mechanism may involve penta- or hexa-coordinated silicon intermediates or transition states. Figure 3 shows the mechanism of condensation reaction under both acidic and basic conditions.

Acid-catalyzed:

Base-catalyzed:

Figure 3. Condensation mechanisms of alkoxy silanes under acid or base catalyzed conditions

2.3.2 Structures under acid/base-catalyzed conditions

According to Iler, sol-gel polymerization occurs in three stages:

(a) Polymerization of monomers to form particles

(b) Growth of particles

(c) Linking of particles into chains. Then networks extend throughout the liquid medium, leading to thickening into a gel.
Within these stages, many factors affect the resulting silica network, such as pH, temperature, reaction time, monomer concentrations, catalyst nature and concentration, H₂O/Si molar ratio (R), aging temperature, and time. However, for acid catalyzed reaction, the first step of the hydrolysis is the fastest, and the product of this first step also undergoes the fastest condensation. Since the alkoxy groups are more electron-donating than hydroxyl groups, a silanol with more alkoxy groups can yield more stable positively-charged transition states. Hence an open network structure results initially, followed by further hydrolysis and cross-condensation reactions. Therefore, it can generally be said that sol-gel derived silicon oxide networks, under acid-catalyzed conditions, yield primarily linear or randomly branched polymers shown in Figure 4, which entangle and form additional branches resulting in gelation.

On the other hand, for the negatively-charged transition state of base-catalyzed reaction, more OH groups mean more stabilization of the transition state and faster reaction. The negatively-charged transition state becomes more stable as more hydroxyl groups are formed. Thus hydrolysis steps occur increasingly rapidly, and fully hydrolyzed species undergoes the faster condensation reactions. As a result, highly cross-linked large sol particles are initially obtained which link to form a gel with large pores between the interconnected particles. Thus, primary particles form and then aggregate into secondary particles. These secondary particles finally link together to form a pearl-necklace like morphology. That is, silicon oxide networks derived under base-catalyzed conditions have more highly branched clusters which do not interpenetrate before gelation and thus behave as discrete clusters shown in Figure 4.
One important aspect of the aerogel pore network is its “open” nature and interconnectivity. In open-pore structures, fluids can flow from pore to pore, with limited restriction, and eventually travel through the entire material.

- **Acid-catalyzed**
  - yield primarily linear or randomly branched polymer

- **Base-catalyzed**
  - yield highly branched clusters

Figure 4. Gel structure for acid and base catalyzed reactions (adapted from Ref. 86)

### 2.3.3 Supercritical drying

It is a complicated process to remove the liquid component from a wet gel by evaporation. This process can be distinguished as to occur in four main stages.\(^\text{10}\)

In the first stage, the gel shrinks by a volume equal to that of water or other liquid that needs to be removed. If the network is compliant, as for gels derived from alkoxides, the liquid can flow from the interior of the gel body to the surface. In this case, the network can adjust to a reduced volume, which gives a deformed gel. During shrinkage, OH groups at the inner surfaces approach each other and form hydrogen bonds. As drying proceeds, the pore radii become smaller, and the network becomes increasingly stiffer and the surface tension in the liquid rises correspondingly. A representation of the contracting surface forces in pores of different sizes during drying is shown in Figure 5.
Figure 5. Representation of the contracting surface forces in pores of different size during drying. At the same pressure, the curvature of all menisci in the pores is the same. For this reason the larger pores empty first.\textsuperscript{10,89}

The second stage of the drying process starts at the “critical point”. At this point, the gel body becomes sufficiently stiff to resist the deformation caused by the surface tension, so no further shrinkage occurs. However, due to the surface tension and the small pore size, very large pressures are generated across the curved interfaces of the liquid menisci in the pores.\textsuperscript{76} Therefore, there is a great chance that the network may crack at this point.

At the next stage of drying, the liquid recedes into the capillary pores. However, there is still a contiguous liquid thin film remaining on the pore walls, because of the hydrophilic nature of the pore walls and the capillary forces. Further drying occurs when the thin film flows and evaporates, in addition to the direct evaporation from the pore region. The meniscus of the liquid in larger pores drops faster in gels with different pore radii. Once the larger pores are emptied, the vapor pressure decreases and the smaller pores begin to empty. Therefore, the walls between pores of different sizes undergo uneven stress and consequently crack.
At the last stage of drying, this liquid film is ruptured as the meniscus recedes from the surface. Finally, the liquid only stays in isolated pockets, which leaves the network only by diffusion into the gas phase.

Strategies to avoid cracking have been studied by researchers. The following important parameters have been found to influence the capillary forces – pore size,\(^{90-92}\) aging (the network becomes stiffer with aging), or hydrophobic treatments leading to a reduction of the surface energy, which in turn leads to a decrease in the capillary forces, or chemical additives that control drying.\(^ {93, 94}\) Although crack free xerogels can be obtained by exact control of these parameters, large shrinkage can never be avoided. The xerogels are dried at ambient conditions, while aerogels are dried under supercritical conditions. Supercritical drying is the best way to eliminate all these issues.

![Figure 6. Schematic representation of the principle of supercritical drying. At the critical point \((T_c, p_c)\) the densities of the liquid and the gas are equal.\(^ {10, 89}\)](image)

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318x53

At the last stage of drying, this liquid film is ruptured as the meniscus recedes from the surface. Finally, the liquid only stays in isolated pockets, which leaves the network only by diffusion into the gas phase.

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![Figure 6. Schematic representation of the principle of supercritical drying. At the critical point \((T_c, p_c)\) the densities of the liquid and the gas are equal.\(^ {10, 89}\)](image)
In supercritical drying, the solvent is transferred into its supercritical state, shown in Figure 6, where the distinction between liquid and vapor no longer exists. This process requires high temperature, high pressure, and consequently the process are very expensive and potentially dangerous. In principle, different organic solvents can be used for drying. The critical constants of the most common drying fluids are listed in Table 1, where \( T_c \) and \( p_c \) are respectively the critical temperature and pressure of a certain solvent.

Table 1. Critical constant for some solvents\(^9\) (data adapted from Ref. 89)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( T_c ) (°C)</th>
<th>( p_c ) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>240</td>
<td>7.9</td>
</tr>
<tr>
<td>ethanol</td>
<td>243</td>
<td>6.3</td>
</tr>
<tr>
<td>acetone</td>
<td>235</td>
<td>4.7</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>374</td>
<td>22.1</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>31</td>
<td>7.3</td>
</tr>
</tbody>
</table>

The most popularly used solvent for supercritical drying is carbon dioxide,\(^75\) which has the advantage of a very low critical temperature at a moderate critical pressure. During the supercritical drying process, the network of the wet gel can be mostly conserved. However, a time-consuming solvent exchange from the original solvent to liquid \( \text{CO}_2 \) is necessary. The length of this period is dependent on the time of diffusion of carbon dioxide into the gel, which in turn is dependent on the dimensions of the gel. Another requirement is the miscibility of the pore liquid with carbon dioxide. For example, water and \( \text{CO}_2 \) are immiscible, and therefore an intermediate solvent exchange (e.g. water for acetone) is also unavoidable.
2.4 Polymer reinforcement and surface modification of silica aerogels

The low density and thermal conductivity make silica aerogels suitable for various potential applications. However, their inherent fragility, moisture absorbing nature, and poor mechanical properties limit their use. A lot of efforts have been devoted to reinforce these silica based aerogels. In the following sections, highlights of such efforts are summarized.

2.4.1 Polymer reinforcement

Although silica aerogels are recognized as promising materials and have been studied for more than fifty years, little attention has been focused on the improvement of its mechanical strength. The poor resistance to mechanical stress and the hydrophilic nature strongly restrict the applications of native silica aerogels. This failure at relatively low stress is the direct result of the “pearl necklace” structure, shown in Figure 7. It is believed that the “necks” where the secondary spherical silica particles join each other are only held by a few Si-O-Si bonds.
As early as 1990s, Kramer et al.\textsuperscript{100} first successfully reinforced tetraethoxysilane (TEOS) based silica aerogels by reacting with hydroxyl-terminated polydimethylsiloxane (PDMS) from both acid and two-step acid/base catalyzed processes. These organically modified silicate aerogels were nicknamed as “aeromosils”. These aerogels had excellent properties, such as optical transparency, surface area of up to 1200 m\textsuperscript{2}/g, flexibility and better strength than corresponding silica aerogels with elongations at break exceeding 5% in some cases.

Then in early 2000s, Leventis and coworkers\textsuperscript{2, 101, 102} proposed an idea to strengthen the silica aerogels by making use of the residual –OH groups on the surface to react with the isocyanates. This would yield a crosslinked polyurethane coating that widened the neck zone between the particles. Aerogels were prepared by two different methods: one-step base-catalyzed sol–gel process and a two-step process involving an acid-catalyzed sol
and a base-catalyzed gel. The polymerization reactions and related properties were studied, which have showed that reactions of isocyanate with –OH groups yield carbamate and with water yield an amine and carbon dioxide. This amine in turn can react with additional isocyanates, forming chain extended polymer, which form bridges between the silica particles. The resultant crosslinked aerogels required more than ~300 times the breaking force than that of native aerogels, which increased the density only up to ~3 times. Moreover, it has been found that the crosslinking reduces the hydrophilicity by a factor of 10 and increases the dielectric constant by only ~35% relative to the values reported in literature for native silica aerogels at about the same porosity.101 The study implied that organic molecules other than isocyanates can be used to crosslink aerogels. Following this, Meador et al.103, 104 at NASA Glenn Research Center modified the mesoporous surfaces of tetramethoxysilane (TMOS) derived silica aerogels with amine groups by incorporating aminopropyltriethoxysilane (APTES) as another precursor, based on the knowledge that the reaction of isocyanates with amines is generally faster than their reaction with hydroxyls105, 106 and the resulting polyureas are generally stronger than polyurethanes.107 They studied the chemical, physical, and mechanical properties of the new crosslinked silica aerogels. The results showed that the crosslinked aerogels are linearly elastic under small strains (<4%) and then exhibit yield behavior (until 40% strain) at room temperature. The compressive Young’s modulus and the strain at ultimate failure were determined to be ~129 MPa and ~ 77%, respectively. Also these aerogels had a thermal conductivity at ~0.041 W/m·K. All these properties qualify the crosslinked aerogels for potential applications as thermal insulators where weight savings is needed.
Meador’s group also studied the structure-property relationships of isocyanate cross-linked silica aerogels as a function of preparation conditions. They examined the effects of four parameters: (1) total silane concentrations, (2) di-isocyanate concentration, (3) water concentration, and (4) the number of washes after gelation. The result showed that a balanced amount of silane and water in the initial sol helped shorten the processing time by reducing the solvent exchange time. Statistical models were generated to predict the properties of these crosslinked aerogels in a wide range of densities by controlling this four processing parameters.

The elastic properties and/or flexibility of polymer reinforced silica aerogels having methyltrimethoxysilane (MTMS) and bis(trimethoxysilylpropyl)amine (BTMSPA) making up the silica structure were examined by Nguyen et al. The dipropylamine spacer from BTMSPA was used both to provide a flexible linking group in the silica structure, and as a reactive site via its secondary amine for reaction with a tri-isocyanate. The tri-isocyanate provides an extended degree of branching or reinforcement, resulting in increased compressive strength of the aerogel monoliths while the overall flexibility arising from the underlying silica structure was maintained. The compressive moduli of the reinforced aerogel monoliths ranged from 0.001 to 158 MPa. Interestingly, formulations across this entire range of modulus recover nearly all of their length after two compressions to 25% strain.

Furthermore, Meador et al. utilized epoxies in place of isocyanates to crosslink the amine-modified mesoporous silica surfaces, derived from the copolymerization of tetramethoxysilane (TMOS) with aminopropyltriethoxysilane (APTES). The di-, tri-, and tetra-functional epoxies were attached to the amine groups during crosslinking of the
silica backbone. The strength of final aerogels increased by more than 2 orders of magnitude, while density increased by a factor of 2-3. Various parameters, such as the amount of APTES, the epoxy type and concentration, and the cross-linking temperature and time, were studied according to a multivariable design-of-experiments (DOE) model. The structure-property relationship of epoxy-crosslinked silica aerogels derived from APTES and tetraethoxysilane (TEOS) by using ethanol as the solvent was then studied by the same researchers. An additive in the underlying silica structure, 1,6-bis-(trimethoxysilyl) hexane (BTMSH), was used to form flexible aerogels. It was shown that the inclusion of BTMSH achieved increases in mechanical properties, reduction of shrinkage and improvements in the ability of the aerogels to recover elastically when compressed up to 50% strain. Empirical models were generated for the prediction of the properties of the epoxy-cross-linked aerogels over a wide range of densities, which provides the understanding of relationship between the processing parameters and the final properties.

Meador et al. compared a synthetic scheme that the ethanol-soluble epoxy monomers were included in the initial step of the sol-gel process without interfering with gelation of the starting silanes. This scheme shortened the process to make epoxy reinforced aerogels by eliminating monomer diffusion and half of the solvent washes to the previously described diffusion-controlled process. Notably, properties of aerogels made using a low amount of amine reactive sites have properties similar to those previously reported that used the longer diffusion controlled process, whereas higher amounts of amine sites produce less desirable monoliths with much higher density and lower surface areas.
Based on the previous research, the use of BTMSH was extended into the underlying silica structure of a styrene cross-linked silica aerogel by Nguyen, et al.\textsuperscript{,4} In this case, vinyltrimethoxysilane (VTMS) was used to provide a reactive site on the silica backbone for styrene polymerization, showing an advantage of combination of both the strength and elasticity. By replacing most TEOS with BTMSH and VTMS, improvements on the elastic behavior have been shown by measurement of the recovered length after compression of samples to 25\% strain. The compressive modulus of these elastic monoliths ranged from 0.2 to 3 MPa.

Compared to Nguyen’s work,\textsuperscript{,4} which introduced double bonds at the initial gelation step, Ilhan et al.\textsuperscript{111} modified the surface with amines and then introduced double bonds after the gel was formed. Hydrophobic monolithic aerogels with a three-dimensional core-shell structure by forming polystyrene layer on amine-modified silica were obtained. First, the mesoporous surfaces of silica were modified with the amines by a precursor with amine groups. Then styrene was attached to the surface through the reaction of p-chloromethylstylene and amines. Next, the double bonds of styrene were crosslinked by a free-radical polymerization process. In this way, the final three-dimensional core–shell structure was formed. The core was the assembly of nanoparticles of the skeletal network of silica aerogel, while polystyrene formed the shell. The mechanical strength of the resultant aerogels was improved, but lower than the strength of aerogels crosslinked with isocyanates and epoxies. Further studies showed that these crosslinked aerogels had lightweight (0.41–0.77 g·cm\textsuperscript{−3}), high porosity (porosity of 63\%, with BET surface areas in the range of 213–393 m\textsuperscript{2}·g\textsuperscript{−1}), and a low thermal conductivity (0.041 W m\textsuperscript{−1} K\textsuperscript{−1}). In addition, the contact angles of water droplets on discs cut from larger monoliths were
larger than 120°. This showed that these aerogels were more hydrophobic than those derived from polyurea and epoxy crosslinked aerogels.

Since the polymer crosslink is the limiting factor when trying to increase thermal stability of the hybrid organic-inorganic aerogel, Vivod et al.\textsuperscript{112} incorporated a bismaleimide (BMI) as the organic crosslinker in order to increase the use temperature while structurally enhancing the fragile native silica backbone. In addition to the BMI, they used p-aminophenyltrimethoxysilane (APTMS) in place of APTES for reactive site for polymer cross-linking. The improved aerogel system was incorporated into a higher temperature resistant batting.

A polymer cross-linked aerogel could also be used for the first time as the starting material in the synthesis of another porous material.\textsuperscript{113} This report described the synthesis of monolithic highly porous SiC by carbothermal reduction of 3D sol-gel silica nanostructures (aerogels) conformally coated and cross-linked with polyacrylonitrile (PAN). Here, the cross-linking polymer (PAN) was the reagent, it did not melt and the 3D core-shell structure was retained through aromatization, carbonization, and carbothermal reduction. The method described is one of the most efficient in the synthesis of highly porous monolithic SiC.

Crosslinked silica aerogels were reported with amine decorated silica surface crosslinked by di-isocyanates,\textsuperscript{104, 108, 114, 115} styrenes,\textsuperscript{4, 111, 116} or epoxies.\textsuperscript{84, 110, 117} These approaches showed significant increase in the strength with only a small effect on density or porosity. To explore the study, Meador and coworkers\textsuperscript{118} studied the effect of including up to 5% (w/w) carbon nanofibers in the silica backbone before crosslinking. The compressive modulus was improved by 3 times with the addition of 5% carbon nanofibers to the
aerogels, and the tensile stress at break was increased by 5 times without increasing the density. The carbon fiber even improved the strength of the initial hydrogels before crosslinking. Aerogels with/without carbon nanofibers had little difference in density and porosity, and a slight reduction in the surface area with increasing fiber concentration. Thus, the improvements were achieved in modulus and tensile strength without sacrificing other important properties.

Following this work, Li et al. applied a novel hybrid film casting/electro-spinning process to produce continuous polymer nanofiber-reinforced aerogels/xerogels. They used silanol-terminated poly (dimethylsiloxane) (PDMS) oligomers for modification of silica aerogels by a two-stage sol-gel process. Polymer nanofibers were electrospun into the cast sol film prior to gelation of the silica-based gel in order to reinforce the structure and overcome the disadvantages such as high fragility and poor mechanical strength. The result showed that the mesoporous hybrid aerogels modified with PDMS were reinforced by polyurethane (PU)/poly (ethylene oxide) (PEO) nanofibers with high surface area and large pore volume.

Silica aerogels can also be crosslinked via ring opening metathesis polymerization (ROMP) by providing the surface of silica particles with the norbornene functionality by Leventis et al.. Ring opening metathesis polymerization (ROMP) is a quite versatile method that produces a wide range of linear and cyclic polymers with a large amount of double bonds. Polymerization, and hence crosslinking can be carried out at ambient temperature, thus simplifying processing tremendously. Polymerization of norbornene engages silica surface-bound norbornene moieties creating a conformal coating with
interparticle molecular tethers (crosslinks). Covalently bonded polymeric tethers significantly increase the mechanical strength of the underlying silica backbone.

New development showed treatment of low-density monolithic silica and hexylene-bridged poly-silsesquioxane aerogels were treated by chemical vapor deposition (CVD) technique with hexa-methyl disilazane or hexachloro-disilane silylating agents, which produced TMS (trimethylsilane) or Si layers on the aerogel. Reinforcing the weak aerogels by controlled deposition process improved their compressive strength and preserved their characteristic properties such as low-density, high surface areas, high porosity, and the transparency. Nanocomposite aerogels were prepared by CVD and polymerization of cyanoacrylate on the surface of bridged poly-silsesquioxane aerogels. Phenylene- and hexylene-bridged aerogels were prepared by sol–gel polymerizations and supercritical carbon dioxide drying. Densities increased by as much as 65% due to the addition of the organic polymer, but the nanocomposite aerogels remained highly porous with high surface areas. Both types of polycyanoacrylate–phenylene/hexylene-bridged aerogel composites showed high flexural strengths and were found to be stronger than the untreated phenylene-bridged aerogels.

2.4.2 Hydrophobic silica aerogels via surface modification

Even though polymer reinforced silica aerogels have shown significant improvements in mechanical properties with little sacrifice in density, porosity, surface area, and thermal conductivity, limited improvement in surface hydrophobicity was reported due to the upper limit resulting from polymer coatings used in each system. Another focus on surface modification of silica aerogels is to get hydrophobic silica aerogels, even super hydrophobicity. Recently, hydrophobic silica aerogels have been proved to be promising
materials in various fascinating applications such as absorption of organic liquids/oils, transportation of liquid on nanoscale in chemical and biotechnological applications and adsorption of toxic substances.\textsuperscript{125}

Work has been carried out using various silanes\textsuperscript{126} to modify the silica surface, both reducing the surface tension forces as the pore fluid evaporates and preventing adjacent silica surfaces from bonding during drying. Silica aerogels synthesized with tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) are inherently hydrophilic due to the presence of surface active hydroxyl (–OH) end groups. This can be overcome by modifying the aerogels surface, replacing the –OH group with the hydrophobic organic functional group, O–Si–(CH\textsubscript{3})\textsubscript{3}. The use of agents with organic end groups, such as trimethylchlorosilane (TMCS), hexamethyldisiloxane (HMDSO), hexamethyldisilazane (HMDZ), or methyltriethoxy-silane (MTES) leads to replacement of –OH with –CH\textsubscript{3}.\textsuperscript{127-130} In particular, trimethylchlorosilane (TMCS) has been shown to drastically reduce the shrinkage of silica aerogels derived from sodium silicate\textsuperscript{126} and tetraethylorthosilicate.\textsuperscript{131} Mahadik et al.\textsuperscript{132} have demonstrated that the surface free energy of aerogels can be tuned by modifying their surface using trimethylchlorosilane (TMCS) and hexamethyl-disilazane (HMDZ) silylating reagents. The alcogels were prepared by two step acid–base catalyzed process. To modify gel surfaces, TMCS and HMDZ concentration were varied from 3\% to 12\% and such alcogels were dried at ambient pressure. The results had shown that an increase in concentration of silylating reagent resulted in an increase in hydrophobicity. This led to increase in contact angle for water from 123° to 155°, but also led to a decrease in surface free energy.\textsuperscript{133}
Another widely accepted route to make hydrophobic silica aerogels by chemical modification is to use alkylalkoxy compounds as co-precursor in earlier stage of preparation i.e. in sol stage. Methyltrimethoxysilane (MTMS) is one of the popular co-precursors used in the preparation of silica aerogels using tetramethoxysilane (TMOS) as precursor chemical.\textsuperscript{127, 134, 135} Methyltriethoxysilane (MTES) is another alkylalkoxy compound used to chemically modify aerogel surface using tetraethoxy-silane (TEOS) as a precursor and ammonium hydroxide as a catalyst.\textsuperscript{129} The surface characterization by nitrogen adsorption–desorption technique of organically surface-modified silica aerogels synthesized from various Si(OR)\textsubscript{4} and R′Si(OR′)\textsubscript{3} precursors were lately reported.\textsuperscript{131, 132, 136-138} These solids were prepared through a sol–gel process from various combinations of silicon precursors and co-precursors with the aim of obtaining identically modified materials. The silicon precursors are based on four identical hydrolysable alkoxy groups (methoxy or ethoxy) whereas one of the alkoxy groups in the co-precursors is substituted by a non-hydrolysable alkyl group (methyl, ethyl, n-propyl, iso-butyl, n-octyl, vinyl or phenyl). Obtained alcogels were dried under carbon dioxide supercritical conditions and their specific surface area, pore volume, mesoporosity, and pore size distribution were investigated. Mesoporous materials exhibiting high specific surface areas and total pore volumes were obtained, revealing a decrease in porosity along with the use of co-precursors having larger side chains.

2.4.3 Summary

The survey of selected work presented above showed that significant progress has been made in literature for reinforcement and surface modification of silica aerogels. Researchers investigated various ways to increase the strength and to make the aerogel
surface hydrophobic. A number of variations in the sol-gel synthesis process were reported. In addition, the inclusion of diverse precursors, different catalysts used in the process, improvements in supercritical drying conditions and increase of strength by various modifications have resulted in stronger, acceptable aerogels. Effective reinforcements were also achieved by crosslinking the networks with different polymers, oligomers, and short chain molecules including isocyanates, epoxies, and styrene. In these cases, the functional groups were first incorporated into the skeletal structures of aerogels followed by crosslinking reactions. The functional groups such as amines, vinyls, and acrylates have been studied. The overview of the crosslinking chemistry is shown in Figure 8. A review of the process for preparing polymer reinforced silica aerogels is reported in US patent 8,067,478. The process comprised of a one-pot reaction of at least one alkoxy silane in the presence of effective amounts of a polymer precursor to obtain a silica reaction product, the reaction was gelled and subsequently subjected to conditions that promoted polymerization of the precursor and then supercritically dried to obtain the polymer-reinforced monolithic silica aerogels. Other improvement for silica aerogels is mainly focused on the surface modification to make hydrophobic silica aerogels. A lot of efforts have been devoted either on using silylating agents or alkyl-alkoxy compounds as co-precursor.
The proposed study will investigate a number of new reinforcement methods. These include introduction of hybrid organic-inorganic particles into silica networks, modification of amine functionalized silica surface by hybrid organic-inorganic nanoparticles, and modification of silane precursors by polymer chains, such as polyurethanes, such that post-gel crosslinking reactions are not needed.

In the following sections, we present a summary of research carried out on hybrid organic-inorganic nanoparticles. These particles will play an integral role in the proposed study.

2.5 Polyhedral oligomeric silsesquioxanes (POSS)

Polyhedral oligomeric silsesquioxanes (POSS), also known as polyhedral oligosilsesquioxanes, or simply silsesquioxanes, is the general IUPAC name for a family of polycyclic compounds consisting of silicon and oxygen. POSS materials have drawn great interest because of their rigid framework and the unique opportunity which they offer for preparing truly molecularly dispersed nanocomposites.
2.5.1 POSS cages

Silsesquioxanes are a part of a larger family of silicon-oxygen compounds. The main feature of silsesquioxanes is the presence of at least one non-silicate, organic group on the silicon atoms. The formula for the completely condensed silsesquioxanes $R_n(SiO_{1.5})_n$ reflects the ratio of silicon and oxygen, where $R$ may be any organofunctional groups, while $n$ is an even integer $\geq 4$. This kind of POSS molecules has a nanosized cage structure with sizes of $1–3$ nm, and can be considered as the smallest particles of silica. The variety of $R$ groups makes POSS molecules amenable to be compatible with different monomers or polymers. Silsesquioxanes exist in a variety of structures from random polymers to more ordered arrangements, which is shown in Figure 9. They are a unique class of materials that possess the feature of hybrid (inorganic-organic) chemical composites and three-dimensional nanosized structures with all types of functional groups attached. In fact, cage-like structured POSS molecules draw most interest since they can be considered as the smallest silica particles possible that can carry up to eight functional groups. These functional groups, in this research will be used to form chemical bonds with silica particles in the network as well as with the crosslinking polymers. Moreover, these POSS molecules may be used to exert additional features like adhesion, light sensitization, catalytic activity, and solubility with various side groups.
Figure 9. Structures of silsesquioxanes\textsuperscript{6}
2.5.2 Methods of POSS cage synthesis

Silsesquioxanes molecules were first discovered in 1946.\textsuperscript{7} Since then, many well-defined POSS frameworks have been reported. Several completely condensed (complete Si–O cage) and incompletely condensed POSS molecules (partial Si–O cage with multiple Si atoms capped with –OH, also called silanols) have been investigated.\textsuperscript{142} These unique structures of POSS are generally formed by hydrolysis and condensation reactions of trialkoxy- or trichlorosilanes. The POSS-cage is synthesized by hydrolytic condensation.

2.5.2.1 Completely condensed POSS

Of the two synthesis routes, the most common process to obtain completely condensed POSS is one-step hydrolytic condensation of tri-functional monomers $R\text{Si}Y_3$, where $R$ is H or a chemically stable organic substituent, and $Y$ is a highly reactive substituent, such as Cl or alkoxy, shown in Figure 10. This process requires careful control of several factors, such as the concentration of initial monomer in the solution, nature of the solvent, type of catalyst employed, temperature, character of substituted group X and functional group in the initial monomer, solubility of the polyhedral oligomers, quantity of water added, and the rate of its addition.\textsuperscript{141}
Figure 10. Scheme of completely condensed polyhedral oligosilsesquioxanes synthesis by hydrolytic condensation of trichloro- or trialkoxysilanes

Generally, synthesis method must be carefully evaluated. For example, room temperature or subambient temperature is preferred to avoid the formation of highly condensed polymers. A slow addition of water helps keep a low concentration of silanol groups formed. This can also be achieved by the careful selection of a suitable solvent, such as an alcohol, which stabilizes the silanol groups adequately.

2.5.2.2 Incompletely condensed POSS

Recently, incompletely condensed silsesquioxanes and oligosilsesquioxanes, containing more than one hydroxyl group, have drawn increased attention since they can be used as molecular building blocks in many polymer systems, which bring significant property enhancements by imparting a nanosized inorganic particulate into an organic matrix. Reactions of trisilanols with ligand-deficient trivalent-metal complexes are popular in synthesis of incompletely condensed silsesquioxanes, due to their lack of ability to support trigonal planar coordination which is required for more complex materials. Two examples of synthesis of incompletely condensed POSS are mentioned as follows.
Feher and his research group\textsuperscript{148} have described a procedure for synthesis of three closely related groups of incompletely condensed POSS via slow hydrolytic condensation of cyclohexyltrichlorosilane $c$-$C_6H_{10}$SiCl\textsubscript{3} in aqueous acetone, shown in Figure 11.

![Figure 11. Scheme of incompletely condensed polyhedral oligosilsesquioxanes synthesis by slow hydrolytic condensation\textsuperscript{8}](image)

Recently, reactions of silsesquioxanes with strong bases and acids have caused great interest. For example, Feher et al.\textsuperscript{149, 150} used acid-mediated cleavage and rearrangement of $(c$-$C_6H_{11})_6Si_6O_9$ to $(c$-$C_6H_{11})_6Si_6O_8X_2$ and base-mediated cleavage of POSS, which is shown in Figure 12.
2.5.3 Applications

Incorporation of POSS into a polymer system generally yields better oxygen permeability,\textsuperscript{6} higher glass-transition and degradation temperatures, better thermal stability, better flame and heat resistance, and enhancements in the modulus and melt strength.\textsuperscript{151} Noticeably, low POSS contents (< 10 mol %) are sufficient enough for these property enhancements. Therefore, POSS and POSS-hybrid nanomaterials have wide applications in fields of surface modification, membrane materials, optical materials coatings, catalysts, and catalyst supports.\textsuperscript{152}

One primary application of POSS is found as surface modifier of coupling agents, for example, with the sulfides in the bridging group in silica-filled rubber. The POSS
nanomaterials in addition offer reinforcements.\textsuperscript{153} Recently, another application of POSS molecules drew great interest, in the form of hydrophobic, readily gelled, alkylene-POSS for encapsulation of sol–gel networks.\textsuperscript{6} Also, the high surface area and chemical functionality of POSS materials are suitable for catalyst supports.\textsuperscript{152} Moreover, functional POSS have been applied as high-capacity adsorbents,\textsuperscript{154} because their functionalities can also be used to bind metals.\textsuperscript{8} Furthermore, by incorporating chromophores in the organic component of POSS-based materials, a useful strategy for preparing waveguides, sensors, light emitting diodes, and nonlinear optical materials\textsuperscript{8} has been developed, because of an exceptionally high loading of chromophores and little phase separation of the dye molecules. Even more, POSS materials can be used as the core of dendrimers, which have potential applications ranging from drug-delivery agents, micelle mimics, nanoscale building blocks, high-performance polymers, and nanoscale reactors.\textsuperscript{155} Their rigid spheroidal architecture offers properties like low intrinsic viscosity, high solubility, high miscibility, and high reactivity due to multiple side chains. Recent investigations about POSS-dendrimer systems focus on the following: biomimetic catalysts, building blocks for fabrication of designed biomaterials, molecular carriers for chemical catalysts and drug delivery, and light-emitting diodes, signal amplifiers, frequency converters and other photonic devices.\textsuperscript{8}
3.1 Materials and synthesis methods

Silica aerogels have many potential applications but their usage is limited due to their fragile and moisture absorbing nature.\textsuperscript{33} The primary objective of this research was to reinforce the silica-based aerogels and to modify the surface by incorporating polymers and hybrid particles into the networks, while preserving low density and high porosity. It was discussed in Chapter 2 that in previous efforts on reinforcement of silica aerogel networks by polymers such as isocyanates,\textsuperscript{108, 114} epoxies,\textsuperscript{110} polystyrene\textsuperscript{116} etc., the polymer was introduced into the networks after the gels were formed and before supercritical drying. In this research, several types of polyhedral oligomeric silsesquioxanes (POSS) were used to reinforce the gel structures by introducing POSS molecules before or after the gelation step. In one case, several types of POSS with silanol groups were introduced before gelation, anticipating that these POSS molecules would form a part of the aerogel network by directly reacting with Si-OH groups of the silica network. In another case, a POSS molecule carrying epoxide groups was introduced to react with the –NH\textsubscript{2} groups in the gel structure and to form a POSS coating layer after the gels were formed from hydrolysis and condensation of appropriate silane formulation. The second approach proposed a post-gelation modification method that can produce super hydrophobic aerogels. A trifluoropropyl substituted silane was used instead of a
chloro-substituted silane reported in literature\textsuperscript{156} to eliminate the residual $–\text{OH}$ groups on the surface of secondary particles. It is worthy to note that the residual $–\text{OH}$ groups are responsible for the moisture absorbing nature of the silica aerogels. To achieve this, the alcogels were soaked in the solution of fluorosilane compound and the fluorosilane molecules were allowed to react with the residual $–\text{OH}$ groups. Aerogels with small changes in surface area and porosity but significant improvements of hydrophobicity were expected.

In another approach, modification of aminopropyltriethoxysilane (APTES) with polyurethanes was considered before APTES was allowed to undergo hydrolysis and condensation with other silane precursors. The aerogels were expected to offer better strength and large compressive strains due to the introduction of flexible polyurethanes as part of the hybrid aerogels. This approach presented a scenario that one polyurethane chain was introduced into the gel network for introduction of every two APTES molecules. Consequently, the amount of APTES introduced in the aerogel structures also quantified the amount of polyurethanes in the aerogel.

The final approach was to introduce multi-functionality into polyurethane chains by using a chain extender with trimethoxy silane substitutes. This trimethoxy silane substitutes could undergo hydrolysis and condensation with the silane precursors during the formation of the alcogels. The size and reactivity rate of this self-crosslinkable polyurethane-urea suggested that the polymer chains would remain at the surfaces of the secondary particles. Once the polymer side chains reacted, there was no place for another silane to react at this site. The multifunctionality helps to bond the polyurethane/urea
chains along the surface and at the neck regions between the secondary particles, thus concealing the hydrophilic groups inside the polyurethane/urea chains.

3.1.1 POSS nanoparticles for reinforcement of aerogels

POSS nanoparticles were selected as reinforcement for silica aerogels based on their compatibility with silica network rising from the similarity of chemical nature, for example, both carrying the silanol (Si-OH) functional groups. In view of chemical structure, we anticipated less phase separation compared to silica aerogels reinforced by polymers. Several POSS molecules were selected offering differences in the nature of the side functional groups. The details of the materials and synthesis procedures are described as follows.

3.1.1.1 Materials selection

Tetraethoxysilane (TEOS) and aminopropyltriethoxysilane (APTES) were selected to form the silica backbones of the aerogels. TEOS was chosen based on its previous successful use and the positive aspects of safety. APTES was used for introduction of -NH₂ groups into the silica networks, which in turn were used for carrying out several chemical reactions with epoxy functionalized POSS, silane end-capped polyurethane and multi-functional polyurethane-urea. Multi-functional POSS particles used in the study were trisilanolphenyl POSS® (tri-POSS), glycidyl POSS® Cage Mixture (epoxy-POSS), trisilanolcyclopentyl POSS® (cyclo-POSS), trisilanolisobutyl POSS® (i-butyl-POSS), and tetrasilanol phenyl POSS® (tetra-POSS). The structures of these compounds are presented in Figure 13.

All solvents and reagents were used as received from the manufacturers. Tetraethoxysilane (TEOS), aminopropyltriethoxysilane (APTES), and nitric acid (70%)
were purchased from Sigma Aldrich. Reagent grade tetrahydrofuran (THF), methanol and ethanol, were purchased from Fisher Scientific. Trisilanolphenyl POSS® (SO1458, denoted as *tri*-POSS), glycidyl POSS® Cage Mixture (EP 0409, denoted as *epoxy*-POSS), trisilanolcyclopentyl POSS® (SO1430, denoted as *cyclo*-POSS), trisilanolisobutyl POSS® (SO1450, denoted as *i*-butyl-POSS), and tetrasilanol phenyl POSS® (SO1460, denoted as *tetra*-POSS) were obtained from Hybrid Plastics (Hattiesburg, MS).
Figure 13. Structures of tetraethoxysilane (TEOS), aminopropyltriethoxysilane (APTES), trisilanolphenyl POSS (tri-POSS), glycidyl POSS® Cage Mixture (epoxy-POSS), trisilanol cyclopentyl POSS® (cyclo-POSS), trisilanolisobutyl POSS® (i-butyl-POSS), and tetrasilanol phenyl POSS® (tetra-POSS)
3.1.1.2. Preparation of silica aerogels reinforced with POSS nanoparticles

The preparation of silica aerogels reinforced with different types of POSS nanoparticles are described as follows.

3.1.1.2.1 Synthesis of hybrid aerogels with tri-POSS, cyclo-POSS, i-butyl-POSS and tetra-POSS

The procedure presented below describes how tri-POSS molecules were introduced into aerogel structures for possible reinforcement. The synthesis of aerogel involved two steps as shown in Figure 14: (1) preparation of the alcogel, and (2) removal of solvent from alcogels via supercritical drying. The alcogels were prepared by a two-step acid-base catalyzed sol-gel process. Solution A, containing 1 mol/L TEOS, stoichiometric amount of water, and different content of tri-POSS was dissolved in a co-solvent of ethanol/THF, and was partially hydrolyzed under acidic conditions using nitric acid (pH=2). The mixture was sealed and stirred by a stir bar for 1h and then cooled in a dry ice-acetone bath. Solution B, which contained excess amount of water, ethanol, and a base catalyst (pH=9), NH₄OH, was cooled in dry ice-acetone bath to control premature gelation before it was mixed with solution A. The total molar ratio of TEOS to H₂O was maintained at 1:7. Five Norm-ject® 12 mL polypropylene syringes—usually 16 mm in diameter were used as molds. For this purpose, the needle ends were cut off. Then the plunger was pulled to make 10 mL volume inside. The syringe assembly was erected in a holder with the plunger facing down for support. Solution B was poured into solution A in a capped container and the container was shaken vigorously. The mixture was then poured into the molds and allowed to gel and age for 24 hours. After the gels were formed, water was exchanged with ethanol by rinsing the gels in ethanol 3-4 times. The resultant alcogels
were finally supercritically dried in an autoclave, using liquid CO$_2$ as the supercritical liquid, at $55^\circ C$ under a pressure of 10 MPa, which is above the critical point of CO$_2$ ($31^\circ C$, 7.4 MPa). The chemical structure of the silica networks is shown in Figure 15. Silanol groups from $tri$-POSS were expected to participate in the condensation reaction with hydrolyzed silane specie. The hydrolyzed silanes condense faster than $tri$-POSS and form the basic backbone of the network. The $tri$-POSS molecules then condense with Si-OH groups of silane networks and become a part of the networks.

Figure 14. Schematic illustration of synthesis of $tri$-POSS-reinforced TEOS-based aerogels
Figure 15. Illustration of reaction TEOS and tri-POSS after silane network formation

The procedures for synthesis of aerogels with cyclo-POSS, i-butyl-POSS, and tetra-POSS followed the same route as tri-POSS-reinforced aerogels. Only different weight contents
of cyclo-POSS, \textit{i}-butyl-POSS, \textit{tetra}-POSS instead of \textit{tri}-POSS were added in solution A. The synthesis route and drying conditions were the same as mentioned above. The sample compositions are presented in Table 2.

Table 2. Composition of silica aerogels in conjunction with different types of POSS

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<thead>
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<th>sample compositions</th>
<th>wt% of POSS</th>
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<td></td>
<td>TEOS (mol/L)</td>
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<tr>
<td>T-0</td>
<td>1</td>
</tr>
<tr>
<td>T-\textit{tri}-POSS-1</td>
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</tr>
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<td>T-\textit{tri}-POSS-3</td>
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</tr>
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</tr>
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</tr>
<tr>
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</tr>
<tr>
<td>T-\textit{tetra}-POSS-3</td>
<td>1</td>
</tr>
<tr>
<td>T-\textit{tetra}-POSS-5</td>
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</tr>
<tr>
<td>T-\textit{cyclo}-POSS-1</td>
<td>1</td>
</tr>
<tr>
<td>T-\textit{cyclo}-POSS-3</td>
<td>1</td>
</tr>
<tr>
<td>T-\textit{cyclo}-POSS-5</td>
<td>1</td>
</tr>
<tr>
<td>TA-\textit{epoxy}-POSS-1</td>
<td>0.75</td>
</tr>
<tr>
<td>TA-\textit{epoxy}-POSS-3</td>
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</tr>
<tr>
<td>TA-\textit{epoxy}-POSS-5</td>
<td>0.75</td>
</tr>
</tbody>
</table>
3.1.1.2.2 Synthesis of hybrid aerogels with *epoxy*-POSS

Aerogels strengthened by *epoxy*-POSS were synthesized following a similar two-step acid-base catalyzed sol-gel process described in the previous section with the difference that *epoxy*-POSS was introduced in the system after the formation of alcogels. The synthetic route is shown in Figure 16. Solution A was composed of 0.75 mol/L TEOS, stoichiometric amount of water, and ethanol. It was partially hydrolyzed with water under acidic conditions (pH=2) using nitric acid. The components of solution A were mixed for 1 hour and cooled in a dry ice-acetone bath. Solution B contained with 0.25 mol/L APTES, excess amount of water, and ethanol (pH=9 since APTES is basic). Solution B was cooled in dry ice-acetone bath and poured into solution A. The mixture was shaken vigorously and immediately poured into the syringe molds. The total silicon/water molar ratio was maintained at 1:7. The gelation reaction was carried out for 24 hours, and the alcogels were rinsed with different weight percent of *epoxy*-POSS/THF solutions (2 wt%, 3 wt%, 5 wt%) and kept at 60 °C for 2 days. This time period allowed reactions between the epoxy groups of *epoxy*-POSS and the amino groups of APTES used in the synthesis of gels. The sample compositions are listed in Table 2. The expected structure is shown in Figure 17. Following the solvent-exchange step, the alcogels were supercritically dried using liquid CO₂ at 55°C under a pressure of 10 MPa, a condition above the critical point of CO₂ (31°C, 7.4 MPa). Note that the aerogel produced by the methods described above were not reinforced with polymers. Accordingly, all reinforcement effects should be derived from the *tri*-POSS, *cyclo*-POSS, *i*-butyl-POSS, *tetra*-POSS and *epoxy*-POSS molecules.
Figure 16. Schematic illustration of synthesis of epoxy-POSS reinforced TEOS/APTES-based aerogels
Figure 17. Illustration of reaction between TEOS/APTES and epoxy-POSS
3.1.2 Dimethoxy-methyl(3,3,3-trifluoropropyl) silane modified silica aerogels

A silane with trifluoropropyl substitution, dimethoxy-methyl (3,3,3-trifluoropropyl) silane, noted as SiF3, was used to modify the silica aerogels after their formation and to eliminate the hydrophilic residual, –OH groups, on the surface of secondary particles during aging step. This step was used to render the aerogel hydrophobic.

3.1.2.1. Materials Selection

TEOS was selected based on the reasons mentioned in section 3.1.1. Dimethoxy-methyl (3,3,3-trifluoropropyl) silane (SiF3) was selected based on the high contents of fluorine atoms. Previous research has shown that silica aerogels aging in the solution of silanes with high content of halogen atoms gave hydrophobic properties,\(^\text{111, 137, 157}\) and even super-hydrophobicity\(^\text{156}\) in some cases. Alkyl-alkoxy silanes with chlorine atoms are most commonly used\(^\text{137, 156}\) for the purpose. Here alkyl-alkoxy silanes with fluorine atoms were used instead with the exception that hydrophobicity and oleophobicity would be higher with fluorine atoms due to a higher surface energy compared with chlorine atoms.

All solvents and reagents were used as received from the manufacturers. TEOS, nitric acid (70%), and ammonium hydroxide were purchased from Sigma Aldrich. Reagent grade ethanol was purchased from Fisher Scientific. Dimethoxy-methyl (3,3,3-trifluoropropyl) silane (SiF3) (97.0% GC grade) was purchased from Gelest (Morrisville, PA), with structure shown in Figure 18.

![Figure 18. Structure of dimethoxy-methyl(3,3,3-trifluoropropyl)silane](image-url)
3.1.2.2. Preparation of silica aerogels modified with SiF3 silane

The aerogels were prepared following a similar procedure mentioned in the previous section. The synthesis of aerogels included two steps: (1) preparation of the alcogel, and (2) removal of solvent from alcogels via supercritical drying. The alcogels were prepared by a two-step acid-base catalyzed sol-gel process. Solution A, containing 1 mol/L TEOS, and stoichiometric amount of water, was hydrolyzed under acidic conditions using nitric acid (pH=2). The mixture was sealed and stirred by a stir bar for 1h and then cooled in a dry ice-acetone bath. Solution B, which contained excess amount of water, ethanol, and a base catalyst (pH=9), NH₄OH, was also cooled in dry ice-acetone bath to control the premature gelation when combined with solution A. The total molar ratio of TEOS to H₂O was maintained at 1:7. Five Norm-ject® 12 mL polypropylene syringes—usually 16 mm in diameter are used as molds by cutting off the needle ends, extending the plunger to make 10 mL volume inside and erecting in a holder with plunger down for support. Solution B is poured into solution A, in a capped container and the container is shaken vigorously. The mixture is then poured into the molds and allowed to gel and age for 24 hours. After the gels formed, different weight percents of SiF3/Ethanol solution (5wt%, 10wt%, 15wt%, 20wt%, 25wt%, total solution 100g) were prepared, shown in Table 3. Ten alcohol gels are soaked in each solution for 3 days. Then the wet gels were rinsed with ethanol for 4 times. The resultant alcogels were finally supercritically dried in an autoclave, using CO₂ as the supercritical liquid, at 55 °C under a pressure of 10 MPa, which was above the critical point of CO₂ (31 °C, 7.4 MPa). The expected reactions and final structure are shown in Figure 19. During the aging stage, the SiF3 molecules diffuse to the pores of alcogels. The dimethoxy groups slowly react with the residual –OH
groups on the surface of the gel network, eliminating the cause of hydrophility and replacing with hydrophobic methyl and trifluoropropyl groups.

Table 3. Composition of silica aerogels modified with SiF3 solution

<table>
<thead>
<tr>
<th>sample</th>
<th>wt% of SiF3/EtOH solution</th>
<th>Days soaked in solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-SiF3-0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>T-SiF3-5</td>
<td>5.0</td>
<td>3</td>
</tr>
<tr>
<td>T-SiF3-10</td>
<td>10.0</td>
<td>3</td>
</tr>
<tr>
<td>T-SiF3-15</td>
<td>15.0</td>
<td>3</td>
</tr>
<tr>
<td>T-SiF3-20</td>
<td>20.0</td>
<td>3</td>
</tr>
<tr>
<td>T-SiF3-25</td>
<td>25.0</td>
<td>3</td>
</tr>
</tbody>
</table>
3.1.3 APTES end-capped polyurethanes and hybrid aerogels reinforced with such polyurethanes

Polyurethanes with high content of hard segments are often selected for reinforcement of aerogels due to their strong mechanical properties and high glass transition temperatures. However, the post-gelation reinforcement of the gels by polyurethanes suffers from phase separation issues, which weaken the reinforcement effects. This is especially true if high molecular weight polyurethanes are introduced into a gel network. Another associated issue is that of slow diffusion of polymer chains into pores. That leads to gradient
polymer concentration which is non-ideal for uniform reinforcement. In view of this, in this study, the silane end-capped polyurethane was uniformly dispersed in the sol. The condensation of silanes chemically bonded the polyurethane to the silica network. In addition, minimum of phase separation was anticipated. The properties of APTES-modified polyurethanes can be varied by using poly diol of different molecular weight and molecular types, such as ester or ether. Polyether diols provide excellent resistance to hydrolysis and microbial attack and good flexibility at low temperatures. In view of this, a polyether type polydiol was used in this study.

3.1.3.1 Materials selection

TEOS was selected to form the silica backbones. APTES was selected to co-form the silica backbones and to introduce -NH$_2$ groups into the network. Structures of TEOS and APTES were shown in section 3.1.1. Reagent-grade ethanol, THF, and N,N’-dimethylformamide (DMF) were obtained from Sigma Aldrich. THF was purified and dried with Na$_2$SO$_4$ followed by vacuum distillation. DMF was dehydrated with molecular sieves and used as a solvent.

4, 4’-diphenylmethane diisocyanate (MDI, Mondur M) with molecular weight 250.25 g/mol and a melting point of 39°C was purchased from Bayer Material Science (PA, USA). The polyurethanes based on MDI often form crystalline hard segments which lead to phase separation of the urethane linkages as hard segment. Polytetramethylene glycol (PTMG), with a number average molecular weight of 1000 (Terathane® 1000) was obtained from Aldrich (Milwaukee, WI). A diol, 1, 4-butanediol (BD), with molecular weight of 90.12 g/mol was used as a chain extender, which was purchased from Sigma Aldrich. The chemical structures of the chemical compounds were shown in Figure 20.
Figure 20. Structures of 4, 4’-diphenylmethane diisocyanate, 1, 4-butanediol, and polytetramethylene glycol.

The prepolymerization reaction was carried out without catalysts. The chain extension reaction between the prepolymer and BD carried out in solution polymerization was catalyzed by dibutyltin dilaurate ($C_{32}H_{64}O_4Sn$, DABCO T120), whose structure is shown in Figure 21. Dibutyltin dilaurate (DBTDL) (95%) was purchased from Aldrich and diluted to 1 wt% using anhydrous tetrahydrofuran.

3.1.3.2 Sample preparation

Polyurethane was prepared by a two-step synthesis method. First, prepolymer was synthesized from the reaction between diisocyanate and poly diol. The prepolymer was then chain extended to obtain polyurethanes. After that, the chains with isocyanate end groups were end-capped with APTES.
3.1.3.2.1. Preparation of APTES end-capped prepolymer

PTMG 1000 was dried overnight in a vacuum oven at 80 °C before use. MDI was used as received. BD was vacuum dried at 80 °C for 2 hours before use. DMF was dried over 4 Å molecular sieves for at least 24 h. The prepolymer was synthesized as follows. A 500 mL three-neck round bottom flask was used and kept in an oil bath, equipped with a mechanical stirrer and a thermometer. The system was purged with a continuous flow of dry nitrogen. First, PTMG was loaded into flask and melted under the protection of dry nitrogen. Then a desired amount of MDI was added. The molar ratio of MDI/poly diol was kept at 2.05:1 to ensure that –NCO capped prepolymer was obtained. The mixture was stirred vigorously for 2 hours. A small amount of prepolymer was taken for analysis by FT-IR and 1H NMR to ensure the completion of the reaction. The structure was determined by solution 1H NMR, in which the peaks for –OH (~ 2.78 ppm) in polydiol should disappear. Then the oil bath was removed, and the excess amount of APTES in 50 mL of dried DMF was added dropwise in 30 min. The flask was cooled down to room temperature and kept for 24 hours for complete end-capping reactions. The synthesized end-capped prepolymer was kept in solution in sealed bottle to avoid contact with moisture. The weight percentage of the end-capped prepolymer/DMF solution was evaluated from the weight of specimen obtained by evaporation of the solvent followed by vacuum drying at 60 °C for 2 days. The structure was evaluated by FT-IR to ensure completion of each reaction step. The overall synthesis route is shown in Figure 22.
3.1.3.2.2. Preparation of APTES end-capped polyurethane

A two step polymerization was utilized for the synthesis of chain extended polyurethanes using a setup shown in Figure 23. First, the –NCO end-capped prepolymer was synthesized by following a procedure mentioned above. The reaction was carried out in a 500 mL three-neck round bottom flask at 80 °C under nitrogen environment. After 2 hours, one drop of the catalyst DABCO 120 (0.1-0.2 mL of 1wt% DABCO/THF solution) was added to the flask for the chain extension reaction. Then a desired amount of butanediol in dehydrated DMF was added drop wise over a period of 1 hour under nitrogen protection. After that, the additional funnel was washed with another 20 mL of dried DMF and the reaction mixture diluted. The total concentration of the polymer in DMF was kept at 20 wt%. The total molar ratio of MDI/polydiol/BD was 6/1/5. This chain extension reaction was carried out at 80 °C for 24 hours to ensure complete reaction. Then 0.5 g excess amount of MDI was added, and the solution was kept under stirring for
another 2 hours to obtain PU with –NCO end groups. A small amount of the –NCO end-capped polyurethane was taken out for analysis by FT-IR and 1H NMR to ensure that the materials contained –NCO ends groups. Then the flask was removed from the oil bath, and a desired amount of APTES was added. The flask was cooled down to room temperature and kept for 24 hours for allowing the reaction between –NCO and –NH₂ groups. The reaction was completed when no isocyanate peaks were detected from FT-IR spectra. The synthesized end-capped polyurethane was kept in solution in sealed bottle to avoid moisture. The weight percentage of the end-capped polyurethane/DMF solution was evaluated by evaporation of the solvent followed by overnight vacuum drying. The overall synthesis route is shown in Figure 24.

Figure 23. Experimental set-up for synthesis of chain extended polyurethane via a two-step route.
3.1.3.2.3 Preparation of aerogels

The aerogels were obtained by removing solvents from wet gels via supercritical drying. The wet gels were prepared by a one step sol-gel process. TEOS (0.75 mol/L), APTES (0.25 mol/L), water (4 mol/L) and different weight percentage of APTES-endcapped polyurethane /DMF or APTES-endcapped prepolymer/DMF (see Table 4) over total silane were dissolved in DMF. Ten Normject® 10 mL polypropylene syringes—usually 16 mm in diameter were used as molds by cutting off the needle ends, extending the plunger to make 5 mL volume inside, and erecting in a holder with plunger down for support. The mixture was poured into molds, and allowed to sit for 24 hours for complete
gelation. After the gels formed, DMF was exchanged with pure ethanol for four times. The resultant alcogels were supercritically dried in an autoclave at 55 °C under a pressure of 10 MPa, which is above the critical point of CO₂ (31 °C, 7.4 MPa). The expected reaction and schematic structure are shown in Figure 25.

Figure 25. Synthesis of APTES end-capped polyurethane reinforced aerogels
Table 4. Composition of silica aerogels with end-capped polyurethane/ end-capped prepolymer

<table>
<thead>
<tr>
<th>sample</th>
<th>Composition of polymers (molar ratio)</th>
<th>wt% of APTES-endcapped prepolymer (over total silane)</th>
<th>wt% of APTES-endcapped polyurethane (over total silane)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA-0</td>
<td>1 2.05 0</td>
<td>0</td>
<td>0</td>
</tr>
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<td>0</td>
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3.1.4. Self-crosslinkable polyurethane reinforced hybrid aerogels

The APTES end-capped polyurethane and its prepolymer provided bifunctional groups that could react with the silane network. The comparison of properties between the aerogels thus produced would provide information on the influence of molecular weight. In order to obtain further insight on the effect of reaction with multifunctional polymers
with functionality greater than 2, a polyurethane-urea type polymer was used for reaction with the silane network. This polyurethane-urea material had a structure similar to APTES end-capped polyurethane, but carried more numbers of functional groups along the polymer chains. This multifunctional material could crosslink with itself in the presence of moisture. This self-crosslinkable polyurethane-urea material (sPU) was synthesized by following a two-step synthesis route. First, the –NCO end-capped prepolymer was obtained via bulk polymerization. Second, the prepolymer was chain-extended with a different chain extender, amino ethyl aminopropyl trimethoxysilane (AEAPS), instead of butanediol. Each AEAPS molecule carried three methoxy groups that could undergo hydrolysis and condensation later with the silane precursors.

3.1.4.1 Materials selection

Tetraethoxysilane and aminopropyltriethoxysilane were selected based on the reasons mentioned in the previous section. Anhydrous DMF was purchased from Sigma Aldrich. MDI (Mondur M) with molecular weight 250.25 g/mol and a melting point of 39°C was purchased by Bayer Material Science (PA, USA). PTMG with a number average molecular weight of 1000 (Terathane® 1000) was obtained from Aldrich (Milwaukee, WI) and vacuum dried at 80 °C overnight before use. Amino ethyl aminopropyl trimethoxysilane (AEAPS) with a purity of >97% was purchased from Sigma Aldrich. The structure of AEAPS is shown in Figure 26. AEAPS was purified by vacuum distillation and used immediately after purification. The prepolymerization reaction was carried out without catalysts. The chain extension reaction between the prepolymer and AEAPS is carried out in solution polymerization was catalyzed by DBTDL (C_{32}H_{64}O_{4}Sn, DABCO T120), whose structure was shown in Figure 21.
3.1.4.2 Preparation of hybrid aerogels reinforced with self-crosslinkable polyurethane-urea (sPU)

The sPU was synthesized via a two-step synthetic route described as follows. The different weight percentage of sPU (over total silane weight) was added in the preparation of TEOS/APTES aerogels via a one-step base-catalyzed route.

3.1.4.2.1. Preparation of self-crosslinkable polyurethane-urea

The synthesis route for the sPU is shown in Figure 27. A typical preparation was carried out as follows. PTMG 1000 was dried overnight in a vacuum oven overnight at 80 °C before use. MDI was used as received. AEAPS was purified by vacuum distillation and used immediately after purification. Anhydrous DMF was used to avoid moisture which may cause gelation of sPU due to hydrolysis and condensation of the side tri-methoxy groups in the chain extender. The prepolymerization reaction was carried out in a 500 mL three-neck round bottom flask at 80 °C under nitrogen environment. The three-neck round bottom flask was kept in an oil bath, equipped with a mechanical stirrer and a thermometer. The system was purged with a continuous flow of dry nitrogen. First, PTMG was loaded into flask and melted under the protection of dry nitrogen. Then a desired amount of MDI was added. The molar ratio of MDI/poly diol was kept at 2.1:1 to ensure that –NCO capped prepolymer was obtained. The mixture was stirred vigorously
for 2 hours. A small amount of prepolymer was taken for studying FT-IR spectra to ensure the completion of the reaction.

After 2 hours, one drop of catalyst DABCO 120 (0.1-0.2 mL of 1wt% DABCO/THF solution) was added to the flask for the chain extension reaction. A desired amount of purified AEAPS in anhydrous DMF was added drop wise for chain extension over a period of 1 hour under nitrogen atmosphere. After that, the additional funnel was washed with 20 mL of anhydrous DMF and the solution diluted. The total concentration of polymer in DMF was kept at 10 wt%. The total molar ratio of MDI/polydiol/AEAPS was 3/1/2. This chain extension reaction was carried out at 75 °C for 20 hours to ensure complete reaction. The synthesized polymer was kept in solution in sealed bottle to avoid moisture. The weight percentage of the self-crosslinkable polyurethane-urea/DMF solution as determined after evaporation of the solvent and overnight vacuum drying. The overall synthetic route is shown in Figure 27.
3.1.4.2.2. Preparation of TEOS/APTES aerogels reinforced with sPU

The aerogels were obtained by removing solvents from wet gels via supercritical drying. The wet gels are prepared by a one step sol-gel process. TEOS (0.75 mol/L), APTES (0.25 mol/L), water (4 mol/L) and different weight percentage of self-crosslinkable polyurethane-urea in DMF solution (see Table 5) over total silane were dissolved in DMF and formed a clear solution. Ten Norm-ject® 10 mL polypropylene syringes—usually 16 mm in diameter were used as molds by cutting off the needle ends, extending the plunger to make 5 mL volume inside and erecting in a holder with the plunger down for support. The mixture was poured into molds, and allowed to sit for 24 hours for complete gelation. After the gels formed, DMF was exchanged with pure ethanol for four times. The resultant alcogels were supercritically dried in an autoclave at 55 °C under a pressure of 10 MPa, which is above the critical point of CO2 (31 °C, 7.4 MPa). The
illustration of the reactions and schematic of the structure are shown in Figure 28. Self-crosslinkable polyurethane-urea condenses later than the silane species, and coats the surface of secondary particles along the curvature. In this manner, the residual –OH groups of secondary silane particles were either eliminated by the reaction with AEAPS or were hidden inside the coating formed by the polymer chains.

Self-crosslinkable polyurethane-urea gels were also prepared simply by diluting the sPU/DMF solution to 10wt% concentration and pouring the solution into molds. The solution was left under atmospheric conditions and allowed to absorb up moisture in the air. The solution gelled in 2 days and formed transparent sPU gels with good elasticity.
Figure 28. Synthesis of self-crosslinkable polyurethane-urea reinforced silica aerogels
Table 5. Composition of silica aerogels reinforced with self-crosslinkable polyurethane-urea

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition of polymers</th>
<th>wt% of self-crosslinkable polyurethane-urea (over total silane)</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>PTMG</td>
<td>MDI</td>
</tr>
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<td>TA-sPU-0</td>
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<td>3</td>
</tr>
<tr>
<td>sPU</td>
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<td>3</td>
</tr>
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<td>TA-sPU-1</td>
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<td>3</td>
</tr>
<tr>
<td>TA-sPU-25</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>
3.2 Analysis and characterization techniques

The structure, morphology, and properties of silica aerogels were characterized by the techniques as follows.

3.2.1 Structural analysis

Bulk density was obtained by measuring the mass and volume of each aerogel specimen. The diameter and length of aerogel specimen were measured by a caliper with a precision of measurement of 0.001 mm. Three measurements for each specimen and five specimens for each type of aerogels were used to obtain reproducible data. The density was obtained from the ratio of mass/volume.

Solid state $^{13}$C and $^{29}$Si nuclear magnetic resonance (NMR) spectra were taken to investigate the extent of hydrolysis and condensation reactions of the silanes and the reactions between the silanes and the reinforcing materials added, such as POSS nanoparticles and silane modified polymers.$^{159}$ The data were collected on a Varian INOVA 400 MHz (9.4T) spectrometer using a Varian 4mm DR-T3 probe. A typical acquisition of $^{29}$Si spectra commonly requires multiple days of acquisition time. Cross polarization is one of the most important techniques in solid state NMR to drastically reduce the amount of time required to measure a sample in a few hours. The use of cross polarization$^{159}$ creates enhanced signal contrast between dipolarly coupled spins. However, an intended consequence of this technique is the amplification of peaks associated with silicon atoms containing incomplete substitution during condensation reactions relative to completely condensed silica.$^{51, 159, 160}$ In the $^{29}$Si NMR spectrum from silica materials, it is typical to observe several distinct peaks that arise from the Si sites with structures of $\text{Si}(-\text{OSi})_2(-\text{OH})_2$, $\text{Si}(-\text{OSi})_3(-\text{OH})$ and $\text{Si}(-\text{OSi})_4$. These species are
labeled $Q_2$, $Q_3$ and $Q_4$ respectively, with the peaks occurring more upfield with larger $Q$ value. With the use of the cross polarization, higher $Q_3$ peak than $Q_4$ peak maybe be displayed despite being almost fully condensed. This is attributed to the proximity of hydrogen atoms from hydroxyl groups to the silicon atoms in incompletely condensed silanes. This phenomenon cannot be corrected, but simply should be noted.

Fourier transform infrared spectroscopy (FT-IR) was used to confirm the completion of the chemical reaction during polymer synthesis process. FTIR is most useful for identifying chemicals that are either organic or inorganic. FTIR can help to identify types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined.

Size exclusion chromatography (SEC) was used to collect information about the molecular weight of synthesized end-capped polyurethanes and its prepolymer. The solvent used was spectrophotometric grade tetrahydrofuran (THF) for polyurethane prepolymer, and spectrophotometric grade N, N-dimethylformamide (DMF) for end-capped polyurethane. The condition is set at 1 mL/min at room temperature, with the signal traced from light scattering detector.

Small angle X-ray scattering (SAXS) is a choice method for studying the structure of porous materials in the 1-100 nm range.\textsuperscript{162} SAXS is proposed as a tool for solving fractal features of silica aerogels.\textsuperscript{156, 163-165} SAXS patterns are typically represented as scattered intensity as a function of the magnitude of the scattering vector, which is written as in equation (1):

$$q = \frac{4\pi \sin \theta}{\lambda} \quad (1)$$
Here $\theta$ is the angle between the incident X-ray beam and the detector measuring the scattered intensity, and $\lambda$ is the wavelength of the X-rays.

In order to determine structure-related geometrical parameters, one can start from the hypothesis that aerogels can be approximately described by a "two-electronic density" model in which $\rho_e$ is the electronic density of the matrix and $\rho = 0$ corresponds to the empty (air-filled) pores.$^{162}$

If part of the material is occupied by a low volume fraction, the structure can be described as a dilute system of particles. If the system is composed of identical particles, i.e. if particles are monodispersed, the intensity of X-ray scattered at low angles follows Guinier’s law,$^{166}$ written in equation (2).

$$I(q) = N\rho_e^2 v^2 \exp \left( -\frac{1}{3} R_g^2 q^2 \right)$$

where $I(q)$ is the SAXS intensity at low angles as a function of the modulus of the scattering vector $q = 4\pi \sin \theta / \lambda$, $2\theta$ being the scattering angle, $\lambda$ the X-ray wavelength, $N$ the number of particles (or voids) of volume $v$ and $R_g$ the (electronic) radius of gyration of the particles. The value of $R_g$ can be determined from SAXS measurements on a relative scale.

For a polydispersed system, a weighted average radius of gyration of the particles can be obtained considering the fractions of particles with a gyration radius.

For a non-diluted (dense) particle system, Guinier’s law is still approximately obeyed in a rather wide angular domain but the intensity curve may show a maximum. In such systems, the radius of gyration is an “apparent” radius of gyration, which is usually lower than that of the diluted system. The apparent radius of gyration is a geometrical
parameter that can be used to indicate variations or tendencies associated with the average sizes of the particles.\textsuperscript{162}

Information can also be obtained from SAXS on a two-density system. For a two-density system, the expression $I(q)q^4$ tends, for high q-values, towards a constant $P$ over a wide range of $q$, written as equation (3):

$$\lim_{q \to \infty}[I(q)q^4] = P$$  \hspace{1cm} (3)

This is Porod's law which holds if the interface is smooth. If the surface exhibits "fractal" features, the classical surface area has an ambiguous meaning. The fractal dimension is measured from the power-decay of the static structure in the Porod region.\textsuperscript{164} For this type of surfaces, Porod's law is modified as in equation (4):

$$\lim_{q \to \infty}[I(q)q^{(6-Ds)}] = P$$ \hspace{1cm} (4)

where $Ds$ is the dimensionality of the fractal surface. A value of $Ds = 2$ corresponds to classical (two-dimensional) surfaces. Several humid gels were shown to exhibit interfaces having the fractal properties with $2 < Ds < 3$, which has a slope between -3 and -4,\textsuperscript{167} describing the elementary units as 3D particles with fractally rough surfaces.\textsuperscript{97, 168}

The SAXS intensity was collected using an X-ray generator of Rigaku MicroMax-002+ and Cu as the X-ray source with a wavelength of 1.54 Å. The voltage was set at 45 KV with a current of 0.88 mA. The scattering signal was detected by SAXS legacy 120 mm detector. The range of angle was selected by setting scattering vector $q$ in the range of 0.017~0.32 Å\textsuperscript{-1}.

3.2.2 Mechanical properties

The compressive modulus of aerogels is determined from the stress-strain data obtained using a tensile tester, Instron 5567, Canton, MA following ASTM D695-85 method for
compressive test. The ASTM standard calls for a slenderness ratio of 11:1 to 16:1, however, using this sample size would have caused some of the lower density specimens to buckle. Due to the difficulty of molding a standard “dog bone” tensile bar, cylindrical samples of a diameter approximately 15 mm and height approximately 20 mm were used instead. Each aerogel cylinder was sanded at the top and bottom to ensure that they were smooth and level. The crosshead speed for the test is chosen 1.27 mm/min.

3.2.3 Morphology
The morphology of aerogels was characterized by scanning electron microscopy (SEM). For this purpose, the aerogels were fractured at room temperature and SEM images were taken after sputter coating the fractured surface with silver. SEM images were taken using Scanning Electron Microscope (SEM, JEOL JSM5310).

The Optical Microscope (OM) and Atomic Force Microscope (AFM) were utilized to examine the surface roughness of compressed silica aerogel discs for contact angle measurement. Optical microscope offered a visual look of the surface of the compressed silica aerogel discs. On the other side, AFM provided detail surface characteristics with very accurate resolution ranging from 100 μm to less than 1μm. The AFM was conducted on a Veeco Multi Mode AFM in a tapping mode at ambient condition with a tip spring constant of 42 N/m.

3.2.4. Surface properties
The surface area, average pore size, and pore size distribution were measured via gas adsorption measurement by studying the adsorption and desorption isotherms. All adsorption isotherms were fitted into one of the types shown in Figure 29, according to Brunauer, Deming, Deming and Teller. Type I isotherms are encountered when
adsorption is limited to, at most, only a few molecular layers. Type II isotherms are most frequently encountered when adsorption occurs on nonporous powders or on powders with pore diameter larger than micropores. Type III isotherms are characterized principally by heats of adsorption which are less than the adsorbate heat of liquefaction. Type IV isotherms occur on porous adsorbents possessing pores in the radius range of approximately 1.5-100 nm. Type V isotherms result from small adsorbate-adsorbent interaction potentials, while Type VI isotherm exhibits a series of steps. The wide hysteresis loop shown in Figure 30 in Type IV is typical of mesoporous and macroporous materials, i.e., those that have pores with openings greater than 2 nm and 50 nm, respectively. A typical adsorption-desorption isotherm for a mesopore material is shown in Figure 30. The initial adsorption comes from the monolayer adsorption of the adsorbate, and then followed by the multilayer adsorption, which is also known as the BET region. The amount of adsorbate increases rapidly with relative pressure due to condensation of the adsorbate in pores until all pores are completely filled. The hysteresis loop indicates that evaporation from a pore is a distinctly different process from condensation within it.
Figure 29. IUPAC classification of sorption isotherms\textsuperscript{171} (adapted from Ref. 171)

Figure 30. Typical adsorption and desorption isotherms for mesoporous materials
The surface area can be evaluated by Brunauer, Emmett, and Teller (BET) method. The main assumption of BET theory is multilayer adsorption. It assumes that 1) gas molecules physically adsorb on a solid in layers; 2) there is no interaction between each adsorption layer; 3) the Langmuir theory valid for monolayer can be applied to each layer. This method measures the pressure and the amount of gas adsorbed on the surface of porous materials. Dry nitrogen is used as a gas for aerogels. Based on the Brunauer, Emmett, and Teller (BET) relationship between the pressure and the amount of gas adsorbed, the surface area and the porosity can be obtained as follows:

\[
\frac{1}{w(P/P_o - 1)} = \frac{1}{w_m c} + \frac{c}{w_m c} \left( \frac{P}{P_o} \right),
\]

where \( P \) and \( P_0 \) are the equilibrium pressure and the saturation pressure of gas, respectively, \( w \) is adsorbed gas weight and \( w_m \) is monolayer adsorbed gas weight, and \( c \) is the BET constant.

![BET plot](image)

Figure 31. BET plot to determine slope and intercept
The BET constant and the weight of gas adsorbed can be calculated from the slope and the intercept by plotting left hand side of equation (1) as the y-axis, and \( P/P_0 \) as the x-axis in Figure 31. The porosity is easily obtained from the amount of gas adsorbed. The surface area can be calculated by equation (6):\(^{172}\)

\[
S_t = N_m A_x = \frac{w_m NA_x}{M}
\]

In equation (6), \( A_x \) is the cross-sectional area of the gas molecule, \( M \) is the gas molecular weight, \( N \) is Avogadro’s number, and \( w_m \) is the monolayer adsorbed gas weight.

Silica aerogels contain pores in a wide range, from micropores to mesopores and macropores. Mesopores are generally defined as those having dimension between 2 nm and 50 nm and macropores are those with widths greater than 50 nm. It is well established that the condensed adsorbate fills the pores of a mesoporous solid at pressure somewhat below the prevailing saturated vapor pressure of the adsorbate.\(^{170}\) The knowledge of a correlating function that relates pore size with critical condensation pressure can be used to characterize the mesopore size distribution of the adsorbent. The correlating function most commonly used is the Kelvin equation, which is written as follows:\(^{171,173}\)

\[
\ln \left( \frac{P^*}{P_0} \right) = -\left( \frac{2\gamma v \cos \theta}{R T r_m} \right)
\]

in equation (7), \( P^* \) is the critical condensation pressure, \( \gamma \) the liquid surface tension, \( v \) the molar volume of the condensed adsorptive, \( \theta \) the contact angle between the solid and condensed phase (which is taken to be zero when the adsorptive is nitrogen), \( r_m \) the mean radius of curvature of the liquid meniscus, \( P_0 \) is the saturation pressure of gas, and \( R \) and \( T \) are gas constant and the absolute temperature, respectively. The capillary condensation
will proceed in pores of radius \( r_m \), when the condensate meniscus is concave, as long as the adsorbate pressure is greater than the critical condensation pressure \( P^* \). The Kelvin equation describes the relationship between pore condensation pressure and pore radius, assuming complete wetting of the surface. The procedure for calculating the pore size distribution using the Kelvin equation involves an imaginary emptying of the condensed adsorbate in the pores in a stepwise manner as the relative pressure is likewise decreased. All pores must be considered filled in the mathematics either following the adsorption branch of isotherm downward from high to low pressure or following the desorption branch. Typically this is taken to be at about 99.5% relative pressure. The calculation method follows generally what was described by Barrett, Joyner and Halenda,\(^\text{174}\) hence called the BJH method.

The thickness of the nitrogen layer remaining on the pore walls, \( t \), is calculated from a thickness relationship from the Halsey equation,\(^\text{173, 175, 176}\) which is written as:

\[
t = 3.54 \left[ \frac{5.00}{2.303 \log \left( \frac{P}{P_0} \right)} \right]^{1/3}
\] (8)

A straight cylindrical pore model is chosen regarding to the shape of the pore. The actual pore radius is given by\(^\text{173}\)

\[
r_p = r_k + t
\] (9)

Each \( P/P_0 \) is known based on the volume of the gas used, and thus the changes in volume of gas. An average of \( r_p \) and \( r_k \) at each \( P/P_0 \) can be calculated. Then the change in film thickness \( \Delta t \) can be also calculated by equation (5). Then the pore volume \( V_p \) associated with that pore size range is given as:\(^\text{171, 173}\)

\[
V_p = \left( \frac{r_p}{r_k} \right)^2 [\Delta V_{\text{liquid}} - (\Delta t \Sigma S)]
\] (10)
The term $\Delta V_{\text{liquid}}$ is the volume of liquid corresponding to the change in adsorbed volume of gas. It can be directly calculated by converting the change of amount of adsorbed gas, such as nitrogen at standard pressure and temperature. The $\Delta t \Sigma S$ term is the volume change of the adsorbed film remaining on the walls from which the core has evaporated. As such, this term is taken to be equal to zero at the start of the calculations. There are no previously emptied pores, so the cumulative surface area is zero. After calculating the first two relative pressures, the known cumulative surface area is used.\textsuperscript{171}

The surface area for the pore walls at each average pore size is calculated via:\textsuperscript{171, 173}

$$S = \frac{2V_p}{\bar{r}_p} \quad (11)$$

The cumulative surface area, $\Sigma S$, is just the sum of all surface areas $S$ for each $\bar{r}_p$ previously calculated. For the desorption isotherm, this leads to successively smaller average pore sizes to be considered, until the entire pore volume has been probed down to the limit of around 2 nm. The desorption isotherm is the preferred isotherm as the adsorption isotherm is prone to metastable states of condensation.\textsuperscript{171} In this manner, the pore volume distribution and the surface area distribution with pore diameter can be determined.

The utilization of the technique of comparison of an isotherm of a microporous material with a standard Type II isotherm was proposed by de Boer et al.\textsuperscript{177} for the determination of micropore volume and surface area, based on the $t$-curve, a plot of $t$, the statistical thickness, versus the relative pressure, $P/P_0$. The standard $t$-curve is expressed by the empirical de Boer equation:

$$t (\bar{A}) = \left[ \frac{13.99}{\log(P/P_0)+0.034} \right]^{1/2} \quad (12)$$
The calculation of $t$ from this equation involves the assumption of hexagonal close packing, that is, that the thickness of a single molecular layer of nitrogen is 3.54 Å. The calculated statistical thickness at various relative pressures is then used to replot the analysis isotherm as a $t$-curve, a plot of the volume of gas adsorbed versus $t$. For a nonporous material, the $t$-plot is a straight line passing through the origin, the slope of which is a measure of surface area. For a microporous material, the $t$-plot is linear and when extrapolated to the adsorption axis, shows a positive intercept, equivalent to the micropore volume. For a material with micropores and mesopores, the corresponding $t$-plot is shown in Figure 32. The initial slope of the $V_A$–$t$ curve corresponds to small values of $t$ which represents an adsorbed film within large pores and complete filling of smaller pores. From the initial slope, the total surface area can be obtained, which should agree with that calculated from BET method. The surface area of the wide pores is obtained from the slope of the upper linear portion of the $t$-plot. This area represents the build-up of a statistical thickness in all pores except the micropores which are presumed filled at higher $t$ values. The difference between these two surface areas is the surface area of the micropores only. The region between the two linear portions represents the transition that occurs as the micropores become filled while multilayer adsorption continues to occur in the larger pores.
The surface area, pore size, and pore size distribution are measured using TriStar II from Micromeritics. Each sample is cut and placed in the chamber followed by outgassing either at 40°C or at room temperature until sample’s mass is constant and does not change. Adsorption/desorption isotherms are collected by using nitrogen as adsorbent at -196 °C using liquid nitrogen bath to achieve this temperature.

The surface properties were studied by measuring the contact angle of water and diiodomethane. To eliminate the effect of pore structures, aerogel specimens will be converted into discs by compressing the specimens in a cylindrical mold at a pressure of 345-379 MPa. The resultant aerogel discs were kept in vacuum oven at 55°C for 6 days to eliminate any residual solvent. The contact angle was measured using the static sessile drop method by capturing an image of a drop of liquid sitting on the surface. For each disc, 10-15 measurements were taken to obtain reproducible results. For each image, the contact angle values were calculated on both edges using the software (ImageJ 1.42
version) supplied with the instrument-Rame-Hart contact angle goniometer (model 100-00) under ambient conditions (1 atm, 24±2°C). For each disc, 10-15 measurements were taken to obtain reproducible results. For each image, the contact angle values were calculated on both edges of the drop using the software, ImageJ 1.42, supplied with the instrument Rame-Hart contact angle goniometer (model 100-00).

Following Wu’s theory,178 the values of total surface energy $\gamma$, and the polar $\gamma^p$ and dispersion $\gamma^d$ components of total energy were computed from the value of contact angle using equation (13):

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d\gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p\gamma_2^p}{\gamma_1^p + \gamma_2^p}$$

(13)

In equation (13), $\gamma_{12}$ is the interfacial energy, $\gamma_i$ is the surface free energy of $i$-th component, $\gamma_i^d$ is dispersion (non-polar) component of the surface free energy, and $\gamma_i^p$ is the polar component of the surface free energy. A more detailed procedure for using contact angle data of two liquids and Wu’s harmonic mean equation to compute the surface free energy values is described elsewhere.178 The following numerical values of the surface energy of the components were used for pure liquids: $\gamma^d = 21.8$ dyn/cm and $\gamma^p = 50.7$ dyn/cm for water and $\gamma^d = 44.1$ dyn/cm and $\gamma^p = 6.7$ dyn/cm for diiodomethane.179 The value of surface polarity ($p$) was computed as the ratio of the polar ($\gamma^p$) component of free energy to surface free energy ($\gamma$).179
CHAPTER IV
SILICA AEROGELS REINFORCED WITH POSS NANOPARTICLES

4.1 Research Objectives
This chapter evaluates the effects of different types of POSS nanoparticles introduced into the silica network before or after gelation steps on mechanical properties of resultant aerogels. The POSS nanoparticles chosen either participated directly in the formation of the secondary particles via condensation or coated the surfaces of secondary particles after gelation. In both cases, hydrophobic side groups were introduced in the gel networks. The high surface area and low density were expected to be preserved without disturbing the morphology of the aerogels. The small fractions of organic group introduced into gel networks were not expected to affect the thermal stability. The POSS molecules containing Si-OH groups in their structures were expected to participate in gelation. On the other hand, POSS molecules containing epoxide groups were expected to form conformal coating layers on secondary silica particles.

4.2 Results and Discussion
The structure and properties of POSS nanoparticles-reinforced silica aerogels are discussed as follows.

4.2.1 Density and mechanical properties
The TEOS-based aerogels were found to be semi-transparent. The silica aerogels reinforced with tri-POSS, cyclo-POSS, i-butyl POSS and tetra-POSS maintained the
translucent appearances, as shown in Figure 33. The TEOS/APTES based aerogels looked opaque and TEOS/APTES aerogels reinforced with epoxy-POSS showed little difference in color but exhibited a smooth surface. As expected, the materials became denser and stronger with the addition of tri-POSS with small changes in shrinkage, in the range of 7.3 - 8.5%, shown in Figure 34. The trends for density, shrinkage, and compressive modulus are presented in Figure 34. The data points are joined with straight line segments to guide the eye. The density is in the range of 0.08 g/cm$^3$ - 0.11 g/cm$^3$, while the compressive modulus changed from 0.6 MPa to 3.3 MPa, a five-fold increase.

![Image of POSS nanoparticles reinforced silica aerogels](Figure 33. The appearance of POSS nanoparticles reinforced silica aerogels (noting that the sample ID is listed in Table 2))
Figure 34. Density, shrinkage and compressive modulus of silica aerogels reinforced with tri-POSS nanoparticles.

Similar trends are observed for density, shrinkage, and compressive modulus of cyclo-POSS, i-butyl POSS and tetra-POSS reinforced TEOS aerogels, which are shown in Table 6, noting that the sample names and the correlated compositions are listed in Table 2. In Table 6, TEOS based aerogels without any POSS reinforcement have a density of 0.08 g/cm$^3$ with a standard deviation of 0.0016 g/cm$^3$. Small increases in density with different extent were observed for all types of aerogels reinforced with POSS nanoparticles. It is seen that aerogels reinforced with i-butyl POSS had the lowest level of increase in density. It is known that density is related to both the total amount of
materials added and the amount of shrinkage. Since the total amount of silane and POSS nanoparticles added were the same at a certain loading level, the less shrinkage of \textit{i}-butyl POSS reinforced silica aerogels, the lower the density should be. The less shrinkage explained why \textit{i}-butyl POSS reinforced silica aerogels had a lower density compared to aerogels reinforced with other types of POSS nanoparticles at the same loading level. The density and shrinkage of \textit{tri}-POSS and \textit{cyclo}-POSS reinforced silica aerogels were close to each other. This observation was reasonable in terms of the similar side groups of \textit{tri}-POSS and \textit{cyclo}-POSS. Silica aerogels reinforced with \textit{tetra}-POSS had relatively higher density and shrinkage than aerogels reinforced with other types of silanol-POSS. It is likely that the condensation of the silanol groups from \textit{tetra}-POSS was not completed since probably only one of the two reactive sites had reacted. The compressive moduli of POSS nanoparticles reinforced aerogels were increased up to six times of that of unreinforced silica aerogels. The \textit{tri}-POSS reinforced silica aerogels showed the highest increase (up to 560\%) and the \textit{tetra}-POSS reinforced silica aerogels showed the lowest increase (up to 380\%). The reinforcing effects and comparison of each type of POSS nanoparticles which were related to their structures and reaction mechanisms will be discussed later in this chapter.
Table 6. Density, shrinkage and compressive modulus of *tri*-POSS, *cyclo*-POSS, *tetra*-POSS and *i*-butyl-POSS reinforced TEOS based aerogels and *epoxy*-POSS reinforced TEOS/APTES based aerogels.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g/cm³)</th>
<th>Shrinkage (%)</th>
<th>Compressive modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-0</td>
<td>0.080 ± 0.0016</td>
<td>7.40 ± 0.628</td>
<td>0.61 ± 0.060</td>
</tr>
<tr>
<td>T-<em>tri</em>-POSS-1</td>
<td>0.093 ± 0.0037</td>
<td>7.45 ± 0.426</td>
<td>0.80 ± 0.131</td>
</tr>
<tr>
<td>T-<em>tri</em>-POSS-2</td>
<td>0.094 ± 0.0022</td>
<td>7.59 ± 0.356</td>
<td>1.13 ± 0.121</td>
</tr>
<tr>
<td>T-<em>tri</em>-POSS-3</td>
<td>0.098 ± 0.0018</td>
<td>7.98 ± 0.596</td>
<td>1.95 ± 0.242</td>
</tr>
<tr>
<td>T-<em>tri</em>-POSS-5</td>
<td>0.102 ± 0.0082</td>
<td>8.47 ± 0.432</td>
<td>3.20 ± 0.302</td>
</tr>
<tr>
<td>T-<em>i</em>-butyl-POSS-1</td>
<td>0.083 ± 0.0032</td>
<td>5.43 ± 0.436</td>
<td>1.06 ± 0.365</td>
</tr>
<tr>
<td>T-<em>i</em>-butyl-POSS-3</td>
<td>0.083 ± 0.0027</td>
<td>5.08 ± 0.337</td>
<td>1.76 ± 0.476</td>
</tr>
<tr>
<td>T-<em>i</em>-butyl-POSS-5</td>
<td>0.084 ± 0.0029</td>
<td>4.49 ± 0.782</td>
<td>2.81 ± 0.182</td>
</tr>
<tr>
<td>T-<em>i</em>-butyl-POSS-10</td>
<td>0.086 ± 0.0028</td>
<td>4.40 ± 0.461</td>
<td>3.01 ± 0.332</td>
</tr>
<tr>
<td>T-<em>tetra</em>-POSS-1</td>
<td>0.102 ± 0.0023</td>
<td>9.83 ± 0.657</td>
<td>1.26 ± 0.456</td>
</tr>
<tr>
<td>T-<em>tetra</em>-POSS-2</td>
<td>0.105 ± 0.0015</td>
<td>10.13 ± 0.365</td>
<td>1.49 ± 0.587</td>
</tr>
<tr>
<td>T-<em>tetra</em>-POSS-3</td>
<td>0.104 ± 0.0029</td>
<td>10.21 ± 0.559</td>
<td>2.07 ± 0.465</td>
</tr>
<tr>
<td>T-<em>tetra</em>-POSS-5</td>
<td>0.107 ± 0.0074</td>
<td>9.92 ± 0.797</td>
<td>2.46 ± 0.170</td>
</tr>
<tr>
<td>T-<em>cyclo</em>-POSS-1</td>
<td>0.092 ± 0.0041</td>
<td>6.60 ± 0.218</td>
<td>1.02 ± 0.530</td>
</tr>
<tr>
<td>T-<em>cyclo</em>-POSS-3</td>
<td>0.106 ± 0.0063</td>
<td>7.36 ± 0.587</td>
<td>1.53 ± 0.547</td>
</tr>
<tr>
<td>T-<em>cyclo</em>-POSS-5</td>
<td>0.111 ± 0.0052</td>
<td>8.96 ± 0.327</td>
<td>2.54 ± 0.090</td>
</tr>
<tr>
<td>TA-0</td>
<td>0.112 ± 0.0055</td>
<td>12.27 ± 0.234</td>
<td>1.08 ± 0.060</td>
</tr>
<tr>
<td>TA-<em>epoxy</em>-POSS-1</td>
<td>0.125 ± 0.0046</td>
<td>13.39 ± 0.133</td>
<td>1.53 ± 0.213</td>
</tr>
<tr>
<td>TA-<em>epoxy</em>-POSS-3</td>
<td>0.137 ± 0.0039</td>
<td>14.46 ± 0.539</td>
<td>2.16 ± 0.131</td>
</tr>
<tr>
<td>TA-<em>epoxy</em>-POSS-5</td>
<td>0.144 ± 0.0036</td>
<td>14.87 ± 0.362</td>
<td>3.31 ± 0.262</td>
</tr>
</tbody>
</table>
The silica aerogels based on TEOS/APTES mixture appeared white and the surfaces of aerogels with epoxy-POSS became relatively smoother. The appearance of TEOS/APTES based aerogels reinforced with epoxy-POSS suggested that epoxy-POSS had a certain effect on the surface of these aerogels. Since epoxy-POSS was introduced into the gel network after the gels were formed, epoxy-POSS would react on the surface of the aerogel network. The density, shrinkage, and compressive modulus data were shown in Table 6 and were plotted in Figure 35. In this figure, a tripled modulus with slight increase in density and shrinkage was seen. Silica aerogels based on TEOS/APTES had a higher density than TEOS-based aerogels due to a more condensed structure was formed.

![Figure 35. Density, shrinkage and compressive modulus of epoxy-POSS nanoparticles reinforced TEOS/APTES aerogels](image-url)
4.2.2 Morphology and surface properties

The SEM images in Figure 36 show the morphology of silica aerogels reinforced with different types of POSS nanoparticles. In Figure 36(a), it showed the morphology of TEOS-based silica aerogels without any reinforcement. This type of aerogels was synthesized from sol-gel chemistry and had an open structure with pores between the interconnected secondary particles, with typical size ranging from 20 – 50 nm. The primary particles were not seen in SEM images due to their small sizes. Pores in the range of 20 – 100 nm were observed in this figure. The morphology of TEOS-based silica aerogels reinforced with 5 wt% of tri-POSS, 5 wt% cyclo-POSS, 5 wt% tetra-POSS, 5 wt% i-butyl-POSS and 10 wt% i-butyl-POSS are shown in Figure 36(b), (c), (d), (e), and (f), respectively. In these images, the pearl-necklace structure was preserved with the reinforcement of different types of POSS nanoparticles. The average particle sizes for these aerogels are in the range of 80 – 120 nm, noticing the particles were aggregated secondary particles instead of secondary particles themselves. Wide ranges of pore sizes are also observed in these images, including mesopores and macropores both. The distribution of pore sizes was determined by BET gas adsorption method, which will be discussed in details in this chapter later. In all these images, no distinction could be made between backbone network and POSS nanoparticles considering both of them had similar chemical structure (mainly Si-O-Si bonds). In all these cases, TEOS molecules were relatively smaller and provided relatively faster reaction rate of hydrolysis and condensation because of less steric hindrance. Consequently, the Si atoms inside the secondary particles in the aerogel structure originated mainly from the hydrolyzed TEOS species. On the other hand, the Si atoms derived from tri-POSS, cyclo-POSS, tetra-POSS,
and *i*-butyl-POSS formed thin layers on the surfaces of aerogels due to condensation reaction between the Si-OH groups on silanol-POSS and residual Si-OH groups on secondary particles surface. The coating also led to high population of the hydrophobic organic side groups. As a result, the hydrophilic TEOS-based aerogels were rendered hydrophobic with the addition of POSS nanoparticles in the aerogel formulation. In Figure 36 (g) and (h), it showed the morphology of TEOS/APTES based aerogels with and without reinforcement from *epoxy*-POSS. In this case, the TEOS/APTES based aerogels were formed first, and then *epoxy*-POSS diffused into the pores of the wet gels and grafted on to the surface of the secondary particles. There was no obvious distinction between these two images, which would be reasonable in terms of the similar chemical structure of aerogel backbones and POSS cages.
Continued…

Figure 36. SEM images of aerogels without/with POSS (a) TEOS-based aerogel without POSS reinforcement, (b) TEOS-based aerogel with 5 wt% tri-POSS, (c) TEOS-based aerogel with 5 wt% cyclo-POSS, (d) TEOS-based aerogel with 5 wt% tetra-POSS, (e) TEOS-based aerogel with 5 wt% i-butyl-POSS (f) TEOS-based aerogel with 10 wt% i-butyl-POSS, (g) TEOS/APTES-based aerogel without POSS reinforcement, (h) TEOS/APTES-based aerogel with 5 wt% epoxy-POSS.

The modification of surfaces of TEOS-based aerogels by different types of POSS nanoparticles was investigated by contact angle measurements. Here the static drop method was utilized, which meant a drop of water was placed on the surface of a compressed disc and the image was captured by a high speed camera. The images were analyzed by the software called ImageJ, which are shown Figure 37. The compressed disc was used instead of original aerogels in order to eliminate the effect of pore structure and capillary forces. The surface of compressed discs was observed by optical microscopy and AFM to determine if appreciable roughness was present on the surface. The optical microscopy image of one compressed disc is shown in Figure 38. The relatively uniform transparence
in the optical microscope image suggested an even thickness in a scale of micrometers. The AFM height image of the compress disc of the same sample shows that the surface has a derivation of less than 10 nm in an area of 3×3 µm², shown in Figure 39. If we combine the height image with optical microscope image, the surface can be considered as a smooth one. Thus, the contact angle results truly reflected the real surface chemistry of silica particles and not the influence of surface roughness.

Figure 37. Contact angle by static sessile drop method for T-tri-POSS-2
Figure 38. Optical microscopy image of one of compressed aerogel discs (T-tri-POSS-5)
Figure 39. AFM height image of one of compressed aerogel discs (T-tri-POSS-5)
The results of contact angles of compressed aerogel samples with both water and diiodomethane along with the calculated surface energy components and polarity are summarized in Table 7. The total surface energy and its components, including dispersion part and polar part, and polarity are calculated from Wu’s theory (see section 3.2.4). It was found that water droplet spread easily on the surfaces of TEOS-based aerogel discs. Overall, TEOS-based aerogel discs had the lowest contact angle value with deionized water out of all types of aerogels listed in Table 7. The polar part of the surface energy was larger than the dispersion part of surface energy, suggesting a polar surface for TEOS-based aerogel disc. Since the effect of pore structure was removed, this result reflected the properties of the surface of secondary particles of the aerogels. For aerogels containing different types of POSS, the values of contact angle with deionized water increased significantly but to different extent. For each type of POSS nanoparticles reinforced aerogels, the static contact angle data and the polarity are in accordance with the trend observed for density. The polarity data showed that i-butyl-POSS is more effective in surface modification, and it gave a lowest polarity at the same loading level compared to other types of POSS. In comparison, cyclo-POSS and tri-POSS had analogous effects on the contact angle and polarity. Possible reasons could be that the less steric hindrance of the i-butyl side groups instead of large phenyl and cyclopentyl groups made the chemical reactions easier. Aerogel discs with tetra-POSS showed less improvements, which might arise from probably only one of the two reactive sites participated in condensation and chemical bond formation with the silica network. This implied that the total –OH groups on the surface were not effectively eliminated. Aerogels synthesized from TEOS/APTES mixture and reinforced with epoxy-POSS
showed an analogous trend for contact angle and polarity. The contact angle images for aerogel compressed discs reinforced with different contents of \textit{i-butyl}-POSS are shown in Figure 40. The TEOS-based aerogels without reinforcement of POSS with a density of 0.081 g/cm\(^3\) and shrinkage of 6.3 % had a contact angle value of only 23.2\(^\circ\) with deionized water. With the increasing content of \textit{i-butyl}-POSS, the contact angle showed distinct increase from the images. For example, the aerogel disc reinforced with 10 w\% \textit{i-butyl}-POSS with a density of 0.086 g/cm\(^3\) and shrinkage of 5.7 % had a contact angle value of 118.8\(^\circ\) with deionized water. A visual inspection of the silica aerogels with and without reinforcement of \textit{i-butyl}-POSS is shown in Figure 41. Figure 41(a) showed how a drop of water was absorbed readily in the uncompressed aerogels. The water droplet went into the aerogels immediately and the aerogels structure collapsed due to capillary stress. The Figure 41(b) showed that a water droplet can sit on top of a TEOS-based aerogel reinforced with 10 wt\% \textit{i-butyl}-POSS. The water contact angle of T-\textit{i-butyl}-POSS-10 aerogel itself was 132.2\(^\circ\). In Figure 41(c), the image showed a piece of TEOS-based aerogel reinforced with 10 wt\% \textit{i-butyl}-POSS floating on top of water without absorbing water and sinking. All three images suggested that this aerogel reinforced with 10 wt\% \textit{i-butyl}-POSS was hydrophobic compared to unreinforced aerogels.
Table 7. Values of contact angles and surface energy components of TEOS-based aerogels reinforced with different types of POSS

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Contact angle (°)</th>
<th>Surface energy and its components (dyn/cm)</th>
<th>polarity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H₂O</td>
<td>CH₃I₂</td>
</tr>
<tr>
<td>T-0</td>
<td>23.2 ± 0.3</td>
<td>25.7 ± 0.4</td>
<td>31.7</td>
</tr>
<tr>
<td>T-tri-POSS-1</td>
<td>29.8 ± 0.5</td>
<td>26.4 ± 0.7</td>
<td>31.7</td>
</tr>
<tr>
<td>T-tri-POSS-2</td>
<td>34.9 ± 0.7</td>
<td>28.8 ± 0.7</td>
<td>31.1</td>
</tr>
<tr>
<td>T-tri-POSS-3</td>
<td>37.9 ± 0.6</td>
<td>29.3 ± 0.8</td>
<td>31.1</td>
</tr>
<tr>
<td>T-tri-POSS-5</td>
<td>68.3 ± 0.2</td>
<td>33.0 ± 0.6</td>
<td>31.7</td>
</tr>
<tr>
<td>T-i-butyl-POSS-1</td>
<td>31.1 ± 0.4</td>
<td>23.6 ± 0.3</td>
<td>32.5</td>
</tr>
<tr>
<td>T-i-butyl-POSS-3</td>
<td>51.0 ± 0.3</td>
<td>36.6 ± 0.5</td>
<td>29.1</td>
</tr>
<tr>
<td>T-i-butyl-POSS-5</td>
<td>99.3 ± 0.5</td>
<td>37.0 ± 0.4</td>
<td>30.1</td>
</tr>
<tr>
<td>T-i-butyl-POSS-10</td>
<td>118.8 ± 0.3</td>
<td>37.4 ± 0.3</td>
<td>33.4</td>
</tr>
<tr>
<td>T-tetra-POSS-1</td>
<td>28.2 ± 0.5</td>
<td>25.5 ± 0.5</td>
<td>31.9</td>
</tr>
<tr>
<td>T-tetra-POSS-2</td>
<td>30.1 ± 0.5</td>
<td>25.2 ± 0.6</td>
<td>32.0</td>
</tr>
<tr>
<td>T-tetra-POSS-3</td>
<td>39.3 ± 0.3</td>
<td>25.3 ± 0.5</td>
<td>32.4</td>
</tr>
<tr>
<td>T-tetra-POSS-5</td>
<td>45.3 ± 0.6</td>
<td>24.8 ± 0.3</td>
<td>32.9</td>
</tr>
<tr>
<td>T-cyclo-POSS-1</td>
<td>33.9 ± 0.3</td>
<td>27.8 ± 0.7</td>
<td>31.4</td>
</tr>
<tr>
<td>T-cyclo-POSS-3</td>
<td>51.6 ± 0.4</td>
<td>29.4 ± 0.4</td>
<td>32.4</td>
</tr>
<tr>
<td>T-cyclo-POSS-5</td>
<td>76.8 ± 0.6</td>
<td>31.2 ± 0.4</td>
<td>34.5</td>
</tr>
<tr>
<td>TA-0</td>
<td>37.5 ± 0.6</td>
<td>27.1 ± 0.5</td>
<td>31.8</td>
</tr>
<tr>
<td>TA-epoxy-POSS-1</td>
<td>39.8 ± 0.7</td>
<td>27.0 ± 0.5</td>
<td>31.9</td>
</tr>
<tr>
<td>TA-epoxy-POSS-3</td>
<td>46.3 ± 0.3</td>
<td>27.3 ± 0.3</td>
<td>32.3</td>
</tr>
<tr>
<td>TA-epoxy-POSS-5</td>
<td>58.8 ± 0.6</td>
<td>27.9 ± 0.3</td>
<td>33.0</td>
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</tbody>
</table>
Figure 40. Contact angle trend of TEOS-based aerogels with *i*-butyl POSS

Figure 41. Images of TEOS-based aerogels with and without *i*-butyl POSS when exposed to deionized water: (a). deionized water absorbed in TEOS-based aerogels without POSS nanoparticles, (b). a deionized water droplet on top of the TEOS-based aerogels reinforced with 10 wt% *i*-butyl POSS, (c). a piece of TEOS-based aerogels reinforced with 10 wt% *i*-butyl POSS floats on top of deionized water
The adsorption/desorption isotherms of TEOS-based aerogels reinforced without and with 10 wt% \textit{i}-butyl POSS are shown in Figure 42. The initial rise in adsorption resulted from the micropores inside the network. The adsorption and desorption isotherms overlapped with each very well in the BET region, indicating an equilibrated isotherm. The adsorption and desorption isotherms are typical for a combination of Type II and Type IV isotherms. The hysteresis loop at P/P\textsubscript{0}>0.5 is typical for slit-shaped pores than the more common spherical pores, also suggesting the existence of mesopores in both samples. The isotherms for other samples are not plotted since they all showed similar isotherms and hysteresis loops as those presented in Figure 42.

![Figure 42. Adsorption and desorption isotherms of TEOS-based aerogels without POSS and \textit{T}-\textit{i}-butyl-POSS-10](image-url)
The surface area and average pore size can be calculated from the adsorption/desorption isotherms for each sample. The surface area can be obtained from BET method and the average pore size can be calculated from BJH method both mentioned in section 3.2.4. The summary of the surface area and the average pore size is listed in the first two columns in Table 8. The average pore diameter was in the range of 10 – 19 nm for TEOS-based aerogels without and with reinforcement of POSS nanoparticles. The aerogels reinforced with POSS had average pore diameters slightly higher than that of TEOS-based aerogels without POSS. But the BET surface areas of aerogels with POSS nanoparticles were lower than that of aerogels without POSS. This can be attributed to the introduction of POSS nanoparticles. The two series of data suggested that POSS nanoparticles coated the surface of the secondary nanoparticles, which might be the reason for the reduction of surface area. Details of the reaction mechanism and structure-property relationship will be discussed later in section 4.2.5.

The pore size distribution of aerogels reinforced with tri-POSS, tetra-POSS, i-butyl-POSS, cyclo-POSS, and epoxy-POSS as determined by BJH method are shown in Figure 43, Figure 44, Figure 45, Figure 46, and Figure 47, respectively. In Figure 43, TEOS-based aerogels without POSS nanoparticles showed one broad peak indicating a predominant pore diameter of 22 nm. Interestingly, TEOS-based aerogels reinforced with 1 wt % tri-POSS showed two very broad peaks, one at 3 nm, and one at 21 nm. However, only one peak was observed for TEOS-based aerogels reinforced with 3 wt % and 5 wt% tri-POSS, at 23 nm and 32 nm, respectively. Similar phenomena were observed for aerogels reinforced with tetra-POSS, i-butyl-POSS, and cyclo-POSS. In Figure 44, aerogels reinforced with 1 wt % and 3 wt% tetra-POSS both showed two peaks, at 6 nm
and 31 nm, 3 nm and 31 nm, respectively. The peak at lower values was broad and the peak at higher values was relatively clear. In Figure 45, aerogels reinforced with 1 wt% \textit{i}-butyl-POSS and 3 wt% \textit{i}-butyl-POSS both had two peaks in the mesopore range, at 4 nm and 33 nm, 3 nm and 33 nm, respectively. Aerogels reinforced with 5 wt% \textit{i}-butyl-POSS and 10 wt % \textit{i}-butyl-POSS showed a peak at 22 nm and 33 nm, respectively. Similarly, in Figure 46, aerogels reinforced with 3 wt% \textit{cyclo}-POSS showed two peaks at 3 nm and 33 nm, and aerogels reinforced with 5 wt% \textit{cyclo}-POSS had one peak at 31 nm. One possible reason for the appearance of the peak at lower value with lower POSS contents (mostly at 1 wt% and 3 wt%) might be that the POSS nanoparticles grafted to the surface of secondary particles when the network was still growing, and the attachment of POSS nanoparticles made the secondary particles pack less densely compared to unreinforced silica aerogels. Another possible reason might be that two POSS molecules may not prefer to react at adjacent sites on the surface of the secondary particles due to steric hindrance. However, grafting of POSS molecules also eliminates further growth of network near the reacted sites. Thus, the intervals between POSS molecules could form mesopores with small diameters during gelation. These could be the reasons for the appearance of a smaller predominant pore size. However, only one peak was observed for aerogels reinforced with higher POSS contents (mostly at 5 wt% and 10 wt%). It is likely that POSS nanoparticles coated the surface of secondary particles more evenly and smoothly than they did at lower contents such that the hindrance for packing of the secondary particles was no longer present. A summary of these predominant pore diameters is shown in the last column in Table 8.
For TEOS/APTES based aerogels reinforced with epoxy-POSS, the gel structure was formed first, and then epoxy-POSS diffused into the pores and grafted on the surface of secondary particles via the reaction of epoxy groups from POSS and amine groups from APTES. The coated epoxy-POSS layers could hide the micropores inside the secondary particles, narrow the pores, and thus the micropore surface area from the total BET surface area. This would be the reason for the reduction of BET surface area and average pore diameter for this type of aerogels in Table 8. Moreover, the pore size distribution of TEOS/APTES based aerogels reinforced with epoxy-POSS is shown in Figure 47. This figure showed a different phenomenon than TEOS-based aerogels mentioned above. The TEOS/APTES based aerogels did not have a predominant pore size in the mesopore range. With the addition of more epoxy-POSS, one peak at the value of around 32 nm started to appear and became more distinct. If the effect of epoxy-POSS coating layers is taken into account, it can be explained that the pore diameter at 33 nm became distinct due to the coverage of micropores.
<table>
<thead>
<tr>
<th>sample</th>
<th>BET surface area (m²/g)</th>
<th>Average pore diameter (nm)</th>
<th>Dominant pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEOS/EtOH</td>
<td>804.7</td>
<td>11</td>
<td>22</td>
</tr>
<tr>
<td>T-i-butyl-POSS-1</td>
<td>681.0</td>
<td>13</td>
<td>32, 4</td>
</tr>
<tr>
<td>T-i-butyl-POSS-3</td>
<td>688.9</td>
<td>16</td>
<td>33, 3</td>
</tr>
<tr>
<td>T-i-butyl-POSS-5</td>
<td>612.4</td>
<td>18</td>
<td>22</td>
</tr>
<tr>
<td>T-i-butyl-POSS-10</td>
<td>597.7</td>
<td>15</td>
<td>33</td>
</tr>
<tr>
<td>T-tetra-POSS-1</td>
<td>665.9</td>
<td>18</td>
<td>31, 6</td>
</tr>
<tr>
<td>T-tetra-POSS-3</td>
<td>640.9</td>
<td>18</td>
<td>31, 3</td>
</tr>
<tr>
<td>T-tetra-POSS-5</td>
<td>597.3</td>
<td>18</td>
<td>32</td>
</tr>
<tr>
<td>T-tri-POSS-1</td>
<td>694.8</td>
<td>14</td>
<td>21, 3</td>
</tr>
<tr>
<td>T-tri-POSS-3</td>
<td>651.3</td>
<td>13</td>
<td>23</td>
</tr>
<tr>
<td>T-tri-POSS-5</td>
<td>624.4</td>
<td>14</td>
<td>32</td>
</tr>
<tr>
<td>T-cyclo-POSS-3</td>
<td>658.9</td>
<td>16</td>
<td>33, 3</td>
</tr>
<tr>
<td>T-cyclo-POSS-5</td>
<td>623.7</td>
<td>14</td>
<td>31</td>
</tr>
<tr>
<td>TEOS/APTES</td>
<td>685.3</td>
<td>23</td>
<td>32</td>
</tr>
<tr>
<td>TA-epoxy-POSS-2</td>
<td>668.9</td>
<td>12</td>
<td>n/a</td>
</tr>
<tr>
<td>TA-epoxy-POSS-3</td>
<td>602.0</td>
<td>10</td>
<td>31</td>
</tr>
<tr>
<td>TA-epoxy-POSS-5</td>
<td>593.0</td>
<td>16</td>
<td>32</td>
</tr>
</tbody>
</table>
Figure 43. Pore size distribution of TEOS-based aerogels with tri-POSS

Figure 44. Pore size distribution of TEOS-based aerogels with tetra-POSS
Figure 45. Pore size distribution of TEOS-based aerogels with \textit{i-butyl}-POSS

Figure 46. Pore size distribution of TEOS-based aerogels with \textit{cyclo}-POSS
Figure 47. Pore size distribution of TEOS-based aerogels with *epoxy*-POSS

4.2.3 Structure of aerogels via solid state NMR

The following information was sought from the use of solid state NMR in collaboration with Dr. Anna Reinsel, Bimala Lama and Dr. Matthew Espe from Department of Chemistry. First, if the POSS molecules at all reacted with the silica network? Second, if POSS-silica network reaction did occur, what was the extent of such reaction? In view of this, the material compositions were studied by solid-state NMR.

4.2.3.1 Solid state NMR study of aerogels reinforced with *tri*-POSS and *epoxy*-POSS

The $^{13}$C solid state NMR spectrum of TEOS-based aerogels reinforced with *tri*-POSS is shown in Figure 48. The $^{13}$C solid state NMR spectrum from the TEOS only aerogel contained two peaks at 58.2 and 15.9 ppm attributed respectively to -OCH$_2$- and -CH$_3$ groups, as shown in Figure 48a. The presence of these peaks indicate that a small fraction of the ethoxy groups did not participate in hydrolysis of TEOS and therefore in the
formation of silica networks. In Figure 48b, in addition to the peaks from ethoxy groups, the $^{13}$C solid state NMR spectrum of TEOS/5% tri-POSS aerogel also showed peaks between 125 and 140 ppm due to the phenyl groups of tri-POSS. Considering the molar ratios used in aerogel synthesis, the relative peak amplitudes from ethoxy groups and tri-POSS indicate that the fraction of unreacted ethoxy groups from TEOS in TEOS-based aerogel and TEOS/ tri-POSS samples was \( \leq 5\% \) of the starting amount. The $^{13}$C solid state NMR spectrum for TEOS/APTES aerogel in Figure 48c shows the peaks from CH2 groups in APTES are observed at 43.3, 25.1 and 9.7 ppm, indicating that APTES was incorporated into the aerogel structure. Considering the peak intensities and mole ratios and assuming that all of the APTES molecules were incorporated into the aerogel network, the fraction of unreacted ethoxy groups from TEOS and APTES was \( \leq 2\% \) in TEOS/APTES based aerogels. The $^{13}$C solid state NMR spectrum for the TEOS/APTES/5% epoxy-POSS sample, in Figure 48d, shows the peak at 72.9 ppm due to -CH2O- groups of epoxy-POSS, indicating that epoxy-POSS was a part of the aerogel network. The carbons of the epoxide ring of epoxy-POSS have been shown to have peaks at 44 and 50 ppm in the $^{13}$C NMR spectrum.\(^\text{180}\) The absence of a discernable peak at 50 ppm in the $^{13}$C NMR spectrum from the aerogel, shows that most of the epoxide rings of the glycidyl ether groups underwent ring opening upon exposure to the TEOS/APTES gel, and consequently this POSS derivative formed an integral part of the aerogel network. However, the remaining peaks arising from epoxy-POSS overlapped with the peaks from APTES. Thus complete characterization of composition could not be determined for this sample.
Figure 48. Solid-state $^{13}$C NMR spectra of (A) TEOS, (B) TEOS/5% $tri$-POSS, (C) TEOS/APTES and (D) TEOS/APTES/5% epoxy-POSS.

The $^{29}$Si solid state NMR spectra of the aerogels are shown in Figure 49. In the NMR spectrum from silica materials it is typical to observe two distinct peaks that arise from the two structures $Si(-OSi)_3(-OH)$ and $Si(-OSi)_4$. These species are labeled $Q_3$ and $Q_4$ respectively, and the peaks from the $Q_4$ species appear more upfield. The peaks at -77 and -86 ppm arise from pure $tri$-POSS, Figure 49a, along with the more downfield peak arising from Si sites that are bonded to an $–OH$ group. The $^{29}$Si solid state NMR spectrum for TEOS aerogel sample shows peaks at -108 ppm ($Q_3$) and -117 ppm ($Q_4$), Figure 49b, which are expected resonances in the silica region of the spectrum. The larger population of $Q_3$ sites relative to $Q_4$ sites results from the very large surface area of the material. In Figure 49c, the new peaks at -77 and -86 ppm are assigned to $tri$-POSS compared to Figure 49a. The chemical shifts of the peaks from $tri$-POSS occur downfield relative to those from silica as a result of the Si in $tri$-POSS being directly bonded to carbon.
TEOS/APTES aerogels, the peaks are again observed at -108 and -117 ppm as well as in the region near -70 ppm (Figure 49d). The peak near -70 ppm arises from the presence of the silicon-carbon bond in APTES. The presence of Si-OH species gives the peak at -65 ppm, and the absence of Si-OH species gives the peak at -75 ppm. The population of the upfield peak (-75 ppm) for Q3 and Q4 sites is more intense than that of the downfield peak (-65 ppm) for APTES. Si sites from APTES are less likely to contain –OH groups bonded to the Si atom, because one of the substituent groups is already an aminopropyl group. So the relative population of Si sites with -OH groups is less from APTES than from TEOS. Since APTES takes up part of the surface Si sites, the population of Q3 sites relative to the Q4 sites is reduced, Figure 49d. The reduction in the peak at -100 ppm (Q3) relative to the peak at -110 ppm (Q4), when APTES is present, shows that APTES is occupying a portion of the surface sites in the aerogel. There also is no indication of any reaction of the amine group of APTES with the silanol groups of TEOS and APTES or the surface hydroxyl groups of the silica, as this would produce a peak around -25 ppm, which is absent in the $^{29}\text{Si}$ NMR data. Also, the lack of a peak at -45 ppm, the $^{29}\text{Si}$ chemical shift of neat, liquid APTES, indicates the absence of trapped, unhydrolyzed APTES molecules within the aerogel network. The peaks from epoxy-POSS occur in the same region as the peaks from APTES since both species contain a Si-C bond. The peaks from epoxy-POSS occur in the same region as the peaks from APTES since both species contain a Si-C bond. The increase in the intensity of the peaks at -58 and -66 ppm when epoxy-POSS is present, results from the silicon in the cage portion of the molecule, as shown in Figure 49e.
4.2.3.2 Solid state NMR study of TEOS-based aerogels reinforced with tetra-POSS

The material composition of the tetrasilanol phenyl POSS (TetPh-POSS) with or without TEOS molecules were studied using $^{13}$CNMR as well as $^{29}$Si NMR techniques. Figure 50(a-c) shows the $^{13}$C SSNMR spectra of tetra-POSS with or without TEOS. The aromatic carbon peaks from phenyl group present in tetra-POSS are observed at 127ppm, 130ppm and 134ppm (Figure 50a). The $^{13}$CNMR spectrum of T-tetra-POSS-2 aerogel (Figure 50b) shows the carbon peaks at 15ppm and 59ppm from the ethoxy group from incompletely hydrolyzed TEOS molecules and carbon peaks at 127ppm and 134ppm from phenyl group present in the aerogel. The peak at 127 ppm seems broader due to structural heterogeneity or restricted motion in the aerogel. Presence of more phenyl group is observed in the aerogel containing more tetra-POSS as a reactant which
indicates that the reactivity of tetra-POSS with TEOS increases with increase in concentration of tetra-POSS in the reaction mixture.

Figure 50. Solid-state $^{13}$C NMR spectra of (a) tetra-POSS (scans=2400), (b) T-tetra-POSS-2 (scans=28160) and (c) T-tetra-POSS-5 (scans=14376)

The reactivity and product compositions of tetra-POSS and its aerogel with TEOS were also studied by $^{29}$SiNMR study. $^{29}$SiNMR spectrum of tetra-POSS contains three peaks at -80ppm, -76 ppm and -67 ppm. R-Si(-OSi)$_3$ species of tetra-POSS silica network gives two peaks at -80 ppm and -76 ppm due to the different chemical environment for Si sites. The peak at -67 ppm is due to the presence of R-Si(-OSi)$_2$(·OH) species in tetra-POSS (Figure 51a). $^{29}$Si NMR spectrum of TEOS/ tetra-POSS 5% aerogel shows the presence of silica with peaks at -104ppm from Q$_4$, Si(-OSi)$_4$ species. -95 ppm from Q$_3$, Si(-OSi)$_3$(·OR/H) species and -85 ppm from Q$_2$, Si(-OSi)$_2$(·OR/H)$_2$ species(Figure 51b). A portion of the Q$_3$ and/or Q$_2$ sites arise from the incomplete hydrolysis of TEOS, as shown in the $^{13}$CNMR study. Q$_3$ species has higher concentration in comparison to Q$_4$ which is
consistent with the high surface area of aerogels. There is one distinct peak at -77ppm due to the presence of R-Si(-OSi)$_3$ species but there is no observable peak at -67ppm from R-Si(-OSi)$_2$(-OH) species. This observation indicates that R-Si(-OSi)$_2$(-OH) sites in the POSS species form Si-O-Si bond with TEOS and are an intimate portion of the silica network. The intensity of the peak at -77ppm is increased with higher concentration of tetra-POSS in the reaction mixture (Figure 51b-c). This observation suggests that all the tetra-POSS present in the aerogel has reacted with and integrated into the silica network. Quantitative analysis shows that approximately 90% of added tetra-POSS is in the aerogel.

Figure 51. Solid-state $^{29}$Si NMR spectra of (a) tetra-POSS (scans=3032), (b) T-tetra-POSS-2 (scans=12128) and (c) T-tetra-POSS-5 (scans=26364)

4.2.3.3 Solid state NMR study of TEOS-based aerogels reinforced with cyclo-POSS

$^{13}$C NMR spectra of cyclo-POSS and its aerogel with TEOS were used to study the composition and reactivity of the cyclo-POSS with TEOS. In $^{13}$C NMR spectrum of
cyclo-POSS (Figure 52a), the peak at 24ppm is from the Si-CH- carbon and the peak at 28 ppm is from the remaining carbons of cyclopentyl ring. T-cyclo-POSS-1 aerogel shows the presence of cyclo-POSS with peaks at 28 ppm and 24 ppm due to cyclopentyl group. There are peaks at 59ppm and 15 ppm from ethoxy group due to incompletely hydrolysed TEOS molecules (Figure 52b). This observation suggests that cyclo-POSS is incorporated into the aerogel with silica network.

![Figure 52. Solid-state $^{13}$C NMR spectra of (a) cyclo-POSS (scans=2000), (b) T-cyclo-POSS-1 (scans=42804)](image)

The reactivity and product compositions of cyclo-POSS and its aerogels with TEOS were studied by $^{29}$Si NMR study. $^{29}$Si NMR spectrum of cyclo-POSS contains two peaks at -68 ppm and -66 ppm from R-Si(-OSi)$_3$ sites and two peaks at -59 ppm and -61 ppm from R-Si(-OSi)$_2$(OH) species (Figure 53a). $^{29}$Si NMR spectrum of T-cyclo-POSS-1 aerogel shows the presence of silica species with peaks at -110 ppm from Q$_4$, Si(-OSi)$_4$ species, -101 ppm from Q$_3$, Si(-OSi)$_3$(-OR/H) species and -90 ppm from Q$_2$, Si(-OSi)$_2$(-OR/H)$_2$ species.
species (Figure 53b). Presence of Q₃ and Q₂ species with ethyl group were also confirmed by the $^{13}$C NMR study. Higher concentration of Q₃ species in comparison to Q₄ species means the larger surface area for the aerogel. There is only one peak at -67ppm due the presence of R-Si(-OSi)$_3$ species but there is no observable peak at -60ppm from R-Si(-OSi)$_2$(-OH) species. This is the evidence of reaction of R-Si(-OSi)$_2$(-OH/R) species of cyclo-POSS with TEOS in forming silica network. This observation suggests that all cyclo-POSS present in the aerogel has reacted with TEOS to form the silica network with TEOS. Quantitative analysis indicates that nearly >90% cyclo-POSS added to the mixture have reacted to form silica network.

Figure 53. Solid-state $^{29}$Si NMR spectra of (a) cyclo-POSS (scans=2716) and (b) T-cyclo-POSS-1 (scans=26908)

4.2.3.4 Solid state NMR study of TEOS-based aerogels reinforced with i-butyl-POSS

The $^{13}$C NMR spectra of trisilanolisobutyl POSS (i-butyl-POSS) with or without TEOS were shown in Figure 54a-d. There are two peaks at 24 ppm and 27 ppm from isobutyl
group in the $^{13}$C NMR spectrum of $i$-butyl-POSS (Figure 54a). In the aerogels with TEOS, two peaks are seen at 59 ppm and 15 ppm from incompletely hydrolysed ethoxy group of TEOS and another broad peak 23 ppm from $i$-butyl-POSS (Figure 54b-d). Two isobutyl peaks collapse due to the structural heterogeneity or restricted motion to give a broader peak at 23 ppm. These spectra show that with increase in concentration of $i$-butyl-POSS in the mixture from 5%-10%, the amount of $i$-butyl-POSS present in the aerogels is increased. This observation suggests that the reactivity of $i$-butyl-POSS with TEOS increases with increase in reactant concentration of $i$-butyl-POSS.

Figure 54. Solid-state $^{13}$C NMR spectra of (a) $i$-butyl-POSS (scans=1000) (b) T-$i$-butyl-POSS-1 (scans=42228), (c) T-$i$-butyl-POSS-5 (scans=28160) and (d) T-$i$-butyl-POSS-10 (scans=13040)

$^{29}$Si SSNMR study was also used to understand the reactivity and product compositions of $i$-butyl-POSS and its aerogel with TEOS. There are two peaks at -67 ppm and -69 ppm from R-Si(-OSi)$_3$ species due to different environment of Si species and other peak at R-
Si(-OSi)₂(-OH) species from *i*-butyl-POSS (Figure 55a). $^{29}$Si NMR spectrum of *T-i*-butyl-POSS-1 aerogel shows the presence of silica species with peaks at -110ppm from Q₄, Si(-OSi)₄ species, -100 ppm from Q₃, Si(-OSi)₃(-OR/H) species and -90ppm from Q₂, Si(-OSi)₂(-OR/H)₂ species. Higher intensity of Q₃ species indicates the larger surface area in the aerogel. Presence of Q₃ and Q₂ species with ethyl group is consistent with observation in the $^{13}$CNMR study. There is only one peak at -67 ppm due the presence of R-Si(-OSi)₃ species but there is no peak at -60 ppm from R-Si(-OSi)₂(-OH) species. That means there is no R-Si(-OSi)₂(-OH) species present in the aerogel due to the conversion of all R-Si(-OSi)₂(-OH) species to R-Si(-OSi)₃. The intensity of -67 ppm peak increases with increase in concentration of *i*-butyl-POSS in the reaction mixture (Figure 55c-d). This observation suggests that all *i*-butyl-POSS present in the aerogels have reacted and integrated into the silica network. A quantitative analysis show that approximately 95% *i*-butyl-POSS added to the mixture is present in the TEOS/ *i*-butyl-POSS aerogels.
Figure 55. Solid-state $^{29}$Si NMR spectra of (a) $i$-butyl-POSS (scans=840) (b) $T$-$i$-butyl-POSS-1 (scans=13184), (c) $T$-$i$-butyl-POSS-5 (scans=8536) and (d) $T$-$i$-butyl-POSS-10 (scans=27892)
4.2.4 Composition of POSS reinforced silica aerogels

Solid state NMR results showed the chemical bonding formed between POSS and silica network. However, since the signal intensities are not quantitative when using cross-polarization (CP), the integrated signal intensities could not represent the relative amounts of tri-POSS and TEOS. An easy method to estimate the amount of POSS nanoparticles remaining in the aerogels is to calculate the amount of POSS nanoparticles that have been washed out during solvent exchange step. The POSS nanoparticles remaining in the wash were collected by completely removing the solvent. The residual solid was washed with THF, which could completely dissolve POSS nanoparticles. Then the solution was filtrated, and the solvent was completely removed. The amount of solid extracted from the THF solution would provide an estimated amount of POSS that was washed out. The amount of POSS nanoparticles that remained in the aerogels is listed in Table 9. The compositions of aerogels at the synthesis steps are shown in Table 2. The second column in Table 9 indicated the weight percentage of POSS over the initial POSS weight added. The last column indicated the weight percent of POSS (over the initial POSS weight added) remained in the aerogels.
Table 9. Compositions of TEOS-based aerogels reinforced with POSS nanoparticles

<table>
<thead>
<tr>
<th>sample</th>
<th>amount of POSS in the wash</th>
<th>percentage of added POSS remaining in aerogels</th>
<th>amount of POSS (over total silane) remaining in aerogels</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-i-butyl-POSS-1</td>
<td>0.0 %</td>
<td>100.0 %</td>
<td>1.0 %</td>
</tr>
<tr>
<td>T-i-butyl-POSS-3</td>
<td>6.4 %</td>
<td>93.6 %</td>
<td>2.8 %</td>
</tr>
<tr>
<td>T-i-butyl-POSS-5</td>
<td>5.4 %</td>
<td>94.6 %</td>
<td>4.7 %</td>
</tr>
<tr>
<td>T-i-butyl-POSS-10</td>
<td>7.6 %</td>
<td>92.4 %</td>
<td>9.2 %</td>
</tr>
<tr>
<td>T-tetra-POSS-1</td>
<td>6.3 %</td>
<td>93.7 %</td>
<td>0.9 %</td>
</tr>
<tr>
<td>T-tetra-POSS-3</td>
<td>9.7 %</td>
<td>90.3 %</td>
<td>2.7 %</td>
</tr>
<tr>
<td>T-tetra-POSS-5</td>
<td>8.2 %</td>
<td>91.8 %</td>
<td>4.6 %</td>
</tr>
<tr>
<td>T-tri-POSS-1</td>
<td>2.4 %</td>
<td>97.6 %</td>
<td>1.0 %</td>
</tr>
<tr>
<td>T-tri-POSS-3</td>
<td>4.7 %</td>
<td>95.3 %</td>
<td>2.9 %</td>
</tr>
<tr>
<td>T-tri-POSS-5</td>
<td>5.2 %</td>
<td>94.8 %</td>
<td>4.7 %</td>
</tr>
<tr>
<td>T-cyclo-POSS-3</td>
<td>5.7 %</td>
<td>94.3 %</td>
<td>2.8 %</td>
</tr>
<tr>
<td>T-cyclo-POSS-5</td>
<td>2.1 %</td>
<td>97.9 %</td>
<td>4.9 %</td>
</tr>
</tbody>
</table>

Table 9 provided the estimated amounts of POSS nanoparticles that remained in the aerogels, indicating over 90 % of POSS nanoparticles that were added in the original formulation remained in the aerogels. To study the exact amount, the collected wash was analyzed by solution $^1$H and $^{13}$C NMR spectra by taking the absolute integral of the POSS peaks in the $^{13}$C spectra of pure POSS, the aerogels, and the wash to investigate the amount of weight loss through solvent exchange step. The masses in the NMR sample rotors and the total sample masses were used as comparison to the pure tri-POSS to calculate the tri-POSS % in the aerogels and the wash. The result showed that 6.89 % of tri-POSS was found in the wash. This in turn meant that 93.11% of tri-POSS
effectively participated in the skeletal structure of silica network. The minimum amount of POSS participated in the aerogels was found in the case of tetra-POSS reinforced aerogels.

4.2.5 Fractal dimension from SAXS

The fractal dimension of silica aerogels reinforced with POSS nanoparticles was studied by SAXS to determine if the presence of POSS nanoparticles interfered with the fractal dimensions of the original silica particle networks. The SAXS intensity $I(q)$ as a function of the scattering vector $q$ for tri-POSS and epoxy-POSS reinforced aerogels is shown in Figure 56 and Figure 57, respectively, where the scattering intensity decreased rapidly with increasing $q$. No distinct peaks are observed in Figure 56 and Figure 57, indicating the disordered structure of the aerogel network. In order to detect the fractal dimensions, the results shown in Figure 56 and Figure 57 are plotted as $\log I(q)$ versus $\log q$ in Figure 58 and Figure 59, respectively. Similar scattering behavior was observed for other types of silanol POSS. The intensity follows a power law behavior in the interval $0.06 \leq q \leq 0.18 \text{Å}^{-1}$, and the related fractal dimensions $D_s$ are listed in Table 10. The power law is not satisfied for $q \geq 0.18 \text{Å}^{-1}$ because $q$ has become so large that the scattering process can resolve structures of the size of individual atoms and the two-phase approximation is no longer satisfied. The fact that the slopes of the plot in the Porod’s range fell between -4 and -3, implies rough surfaces. Interestingly, the fractal dimension rises with addition of POSS nanoparticles, implying a more curved surface after reinforcement and surface modification. One easy way to explain this trend is to visualize a secondary particle with surfaces of larger curvature resulting from the aggregation of primary particles by POSS. When a cage-structured POSS is chemically attached to the surface, a molecule with
comparable dimension with the primary particles is bonded to the surface. Notice that POSS molecules cannot bond two adjacent sites due to their steric hindrance to each other. Therefore, these bumped structure caused by POSS molecules make the surface more curved than those before POSS reinforcement. POSS molecules that bond to the neck regions of the silica network are responsible for the mechanical reinforcement, which should lower the fractal dimension since they fit in the curved region. However, the neck regions are much smaller compared to the free surfaces of secondary particles. Therefore, an increase in fractal dimension is a final outcome.

Figure 56. SAXS intensity as a function of the modulus of the scattering vector

![Graph showing SAXS intensity as a function of the modulus of the scattering vector.](image-url)
Figure 57. SAXS intensity as a function of the modulus of the scattering vector

Figure 58. Porod’s plot of SAXS intensity as a function of $q$ on a log-log scale
Figure 59. Porod’s plot of SAXS intensity as a function of $q$ on a log-log scale.
Table 10. Slopes from Porod’s plots and fractal dimension for different types of POSS-reinforced silica aerogels

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porod Slope</th>
<th>Ds</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEOS/EtOH</td>
<td>-3.41</td>
<td>2.59</td>
</tr>
<tr>
<td>T-i-butyl-POSS-3</td>
<td>-3.34</td>
<td>2.66</td>
</tr>
<tr>
<td>T-i-butyl-POSS-5</td>
<td>-3.16</td>
<td>2.74</td>
</tr>
<tr>
<td>T-i-butyl-POSS-10</td>
<td>-3.16</td>
<td>2.84</td>
</tr>
<tr>
<td>T-tetra-POSS-3</td>
<td>-3.42</td>
<td>2.58</td>
</tr>
<tr>
<td>T-tetra-POSS-5</td>
<td>-3.28</td>
<td>2.72</td>
</tr>
<tr>
<td>T-tri-POSS-3</td>
<td>-3.44</td>
<td>2.56</td>
</tr>
<tr>
<td>T-tri-POSS-5</td>
<td>-3.18</td>
<td>2.82</td>
</tr>
<tr>
<td>T-cyclo-POSS-3</td>
<td>-3.33</td>
<td>2.67</td>
</tr>
<tr>
<td>T-cyclo-POSS-5</td>
<td>-3.26</td>
<td>2.74</td>
</tr>
<tr>
<td>TEOS/APTES</td>
<td>-3.76</td>
<td>2.24</td>
</tr>
<tr>
<td>TA-epoxy-POSS-3</td>
<td>-3.43</td>
<td>2.57</td>
</tr>
<tr>
<td>TA-epoxy-POSS-5</td>
<td>-3.29</td>
<td>2.71</td>
</tr>
</tbody>
</table>

4.2.6 Reinforcement mechanism and comparison of POSS types

The aerogels synthesized from sol-gel chemistry have an open structure with large pores between the interconnected secondary particles. Thus, the primary particles were first formed and then aggregated into secondary particles. The large side groups on Si atoms in tri-POSS molecules slowed down the condensation reaction. Thus TEOS molecules reacted at relatively faster reaction rate both in hydrolysis and in condensation reactions because of less steric hindrance. Accordingly, the Si atoms from tri-POSS possibly remained at the surfaces of primary particles resulting in a continuous or discontinuous
coating layer of secondary particles. This in turn rendered TEOS-based aerogels more hydrophobic as was seen from the contact angle data presented in Table 7. Also, the additional silicon derived from tri-POSS possibly caused higher density of the aerogels, as evidence from the density data in Table 6. The same reaction mechanism occurred for cyclo-POSS, i-butyl-POSS, and tetra-POSS, as shown in Figure 60.

Difference in pore size distribution and visible changes in fractal dimensions were observed for TEOS-based silica aerogels reinforced with different contents of POSS. For each type of POSS with silanol groups, two peaks were observed in the mesopore range at low content of POSS (mainly 1 wt% and 3 wt%). Interestingly, the peak at lower value disappeared, and only one peak was observed from the pore size distribution at the range of 20 – 35 nm for TEOS-based aerogels at high content of POSS (mainly 5 wt% and 10 wt%). One possible reason for the appearance of the peak at lower value with lower POSS contents (mostly at 1 wt% and 3 wt%) might be that the POSS nanoparticles grafted to the surface of secondary particles when the network was still growing, and the attachment of POSS nanoparticles made the secondary particles pack less densely compared to unreinforced silica aerogels, as shown in Figure 61(a) and Figure 61(b). Another possibility might be that two POSS molecules may not prefer to react at adjacent sites on the surface of the secondary particles due to steric hindrance. Thus, intervals between POSS molecules could form mesopores with small diameters during gelation, as shown in Figure 61(a) and Figure 61(b). The POSS molecules grafted to the surface were also responsible for the increase of fractal dimension, shown in Table 10, since more curvature was introduced to the surface. However, only one peak was observed for aerogels reinforced with higher POSS contents (mostly at 5 wt% and 10 wt%). It is likely
that POSS nanoparticles coated the surface of secondary particles more evenly than they did at lower contents. These POSS nanoparticles behaved like an extra layer of primary particles since they have comparable dimension with primary silica particles. In this case, the hindrance for less close packing of the secondary particles was no longer present, as shown in Figure 61(c). Since the POSS nanoparticles could not react at adjacent sites, the bumped intervals added roughness to the surface, related to a higher fractal dimension.
Figure 60. Illustration of the reaction mechanism of TEOS-based aerogels reinforced with *tri*-POSS, *i*-butyl POSS, and *cyclo*-POSS.
Figure 61. Illustration of the reaction of TEOS-based aerogels reinforced with different content of POSS (a) TEOS-based native silica aerogels without reinforcement of POSS, (b) TEOS-based silica aerogels reinforced with low content of POSS (1 wt% and 3 wt%), (c) TEOS-based silica aerogels reinforced with low content of POSS (5 wt% and 10 wt%)

In case of TEOS/APTES-based aerogels, epoxy-POSS solution was added after the formation of the primary pearl-necklace structure of the aerogel. It is believed that the epoxy groups of epoxy-POSS reacted with the APTES-originated NH$_2$ groups on the surface of the secondary particles, shown in Figure 62. These secondary particles, as a result, were coated with a layer of epoxy-POSS molecules. Since there were eight epoxy groups in each POSS molecule, the NH$_2$ groups could be eliminated more effectively and the junctions between the secondary particles could be strengthened. The aerogels treated with higher wt% epoxy-POSS solution showed higher density, modulus, and contact angle. This may have resulted from greater amounts of epoxy-POSS particles reacted on the surface of secondary particles.
Figure 62. Illustration of the reaction between TEOS/APTES and epoxy-POSS
The comparison of different types of POSS as reinforcement and surface modification agents for silica aerogels is shown in Figure 63. The data in Figure 63 were obtained from individual measurements of 10 sample specimens of the same compound. Note that solution of a given formulation was prepared all at once and 10 cylindrical molds were filled with the same solution. Therefore, the data presented in Figure 63 took into account sample to sample variation with the same solution. In order to check if batch to batch variation was significant, three separate solutions were prepared which had the same composition. Five sample specimens were then prepared using each solution and this compressive modulus was evaluated. Such data are presented in Table 11. It is seen that the effect of batch to batch variation of formulation was negligible, as the compressive modulus data in Table 11 are statistically the same.

Table 11. Batch to batch variation of compressive modulus of T-tri-POSS-5 aerogels

<table>
<thead>
<tr>
<th>Batch No.</th>
<th>Compressive modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.33 ± 0.543</td>
</tr>
<tr>
<td>2</td>
<td>3.09 ± 0.601</td>
</tr>
<tr>
<td>3</td>
<td>2.97 ± 0.486</td>
</tr>
</tbody>
</table>

In view of the above discussion, the data presented in Figure 63 will be discussed below and conclusions will be made and attributed only to reinforcement effects by POSS molecules. The density of all aerogels showed similar dependence on the types of POSS for both TEOS-based and TEOS/APTES-based aerogels, with density varying in the range of 0.08 g/cm³ to 0.15 g/cm³. It is seen for TEOS-based aerogels reinforced with silanol POSS nanoparticles, that i-butyl POSS can modify the surface more effectively
than other types of silanol POSS, probably due to less steric hindrance.\textsuperscript{187, 188} Tri-POSS and cyclo-POSS show similar effect in terms of mechanical reinforcement and surface modification. However, slightly higher contact angle is observed for cyclo-POSS which might be due to its less rigid side groups compared to phenyl side groups. Tetra-POSS gave less improvement in compressive modulus. It is quite possible that both reactive sites of tetra-POSS might not have chemically attached to the silica network. This is also supported by the limited improvement of the contact angle values. The mechanical modulus shows almost a sixfold improvement compared to unreinforced silica aerogels. But tri-POSS, with the most rigid side groups of the four types of silanol POSS, appears to offer a higher value. Overall, it appears that the reinforcement of TEOS-based aerogels from POSS with silanol groups gave better improvements in hydrophobicity because the surface modification could happen at every point. In contrast, TEOS/APTES-based aerogels are modified with epoxy-POSS only at the sites of amine groups. The amount of amine groups was limited by the concentration of APTES. But it gave better improvement in mechanical properties as multi-functional epoxy-POSS worked as a cross-linker and thus possibly reinforced the neck regions between the secondary particles. Previous efforts in reinforcements via post-gelation crosslinking using very high concentration of polymer crosslinkers (50\% or even higher) showed a two orders of magnitude increase\textsuperscript{101} in modulus but with the great sacrifice of surface area and noticeable increase of density. Reinforcements at lower loading level (5 wt\%) by carbon nanofibers\textsuperscript{118} with no penalty of density and porosity showed tripling of compressive modulus compared to unreinforced silica aerogels. In our case, the pre-gelation
modification process using POSS nanoparticle reinforced silica aerogels by effectively eliminating the diffusion step and produced silica aerogels with no density penalty and small sacrifice of surface area, and a six-fold increase in compressive modulus. Furthermore, the hydrophilic surface of native silica aerogels was modified and became hydrophobic at the same time. The thermal stability of silica aerogels was also not affected since POSS cages are composed of mainly Si-O bonds with limited amount of organic groups. More importantly, the method of making the aerogels was greatly simplified by eliminating two wash steps before cross-linking and the diffusion step. This reduced the amount of solvent needed to make the aerogels by at least half with no compromise in properties.

![Figure 63. Comparison of different types of POSS as reinforcement and surface modification agents for silica aerogels](image-url)
4.3 Conclusions

The TEOS-based aerogels were modified with silanol POSS molecules carrying different side groups for reinforcement effects. The TEOS/APTES-based aerogels were treated with different weight ratios of epoxy-POSS solutions for the purpose of bonding epoxy-POSS with amine groups in secondary particles and to obtain reinforcement effects. Slight increases in density (less by 10 %) and noticeable increases in modulus (up to sixfold of unreinforced aerogels) were observed, especially significant improvements in hydrophobicity were observed. The structure and the possible mechanisms of such mechanical reinforcement were discussed.
CHAPTER V
SURFACE MODIFICATION OF TEOS-BASED SILICA AEROGELS BY USING
FLUOROSILANE AS A SILYLATING AGENT

5.1 Research Objectives

Aerogels are highly porous sol–gel-derived materials. Their properties, which are extremely fascinating as well as very promising for a large number of applications, are due to their nanostructured morphology and porosity.189 In this chapter, the hydrophobic silica aerogels were prepared by two-step sol–gel method–acid catalyzed hydrolysis and base catalyzed condensation–with TEOS as the silica precursor. The prepared alcogels were surface modified with dimethoxy-methyl (3,3,3-trifluoropropyl) silane (SiF3) as the silylating agent, and supercritically dried after replacing alcohol with liquid carbon dioxide. The residual –OH groups on the surfaces of the secondary particles of native silica aerogels, responsible for their hydrophilicity, were replaced by non-polar organic groups during silylation reactions. Silylation is the introduction of a substituted silyl group (R₃Si–) by replacing active hydrogens in a molecule.190 Silylation is useful to modify the solubility and stability of organic materials, and also a means of temporarily blocking organic functional groups containing active hydrogen. The most commonly used silicon chemicals for silylation are chlorosilanes or silazanes.190,191 One example of the silylation reaction is shown in Figure 64:
However, in our case, the reaction mechanism is based on hydrolysis and condensation of methoxy groups, which is shown as follows in Figure 65.

Figure 65. Silylation reaction of TEOS-based aerogels with SiF3

5.2 Results and discussion

The structures of SiF3-modified silica aerogels were studied by solid state $^{13}$C and $^{29}$Si NMR. Their density, shrinkage, and compressive modulus were examined. The surface properties, including morphology, contact angles, surface areas, and pore size distributions, were investigated by SEM, contact angle goniometry, and nitrogen adsorption methods.

5.2.1 Density, shrinkage, and mechanical properties

The TEOS-based silica aerogels had a translucent appearance, and the TEOS-based silica aerogels reinforced with different amount of SiF3 showed little change in appearance, as shown in Figure 66. The average diameters are labeled in Figure 66. The density and shrinkage data of these unmodified and modified aerogels are listed in
Table 12. A slight increase (less than 10 %) in density is shown due to silylation of –OH on the surface by SiF3. The shrinkage of the sample specimen after supercritical drying gradually decreased with the amount of SiF3 in solution in ethanol used for silylation. It is noted that the percentage of shrinkage reduced from 7.2 % for unmodified aerogels to 2.8 % when a 25 wt% solution of SiF3 was used. The compressive modulus, shrinkage, and density data are shown in Figure 67. It is noted that the compressive modulus doubled when the gels were treated with higher concentration of SiF3 solution and with less than 10 % change in density. The doubled improvement in compressive modulus could be attributed to the addition of SiF3 molecules at the adjunctions between the secondary particles. This will be examined further while discussing morphology, surface area, and fractal dimensions.

Figure 66. Appearance of SiF3 modified TEOS-based aerogels with average diameters (a) TEOS-based aerogels without SiF3 modification, (b) TEOS-based aerogels modified with 5 wt% SiF3, (c) TEOS-based aerogels modified with 15 wt% SiF3, (d) TEOS-based aerogels modified with 25 wt% SiF3
Table 12. Density and shrinkage data of SiF3 modified TEOS aerogels

<table>
<thead>
<tr>
<th>Post-treatment</th>
<th>Density (g/cm³)</th>
<th>Shrinkage (%)</th>
<th>Compressive modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>without SiF3</td>
<td>0.119 ± 0.0032</td>
<td>7.2 ± 2.20</td>
<td>0.616 ± 0.0424</td>
</tr>
<tr>
<td>SiF3/EtOH 5wt%</td>
<td>0.123 ± 0.0073</td>
<td>6.6 ± 2.19</td>
<td>0.674 ± 0.0593</td>
</tr>
<tr>
<td>SiF3/EtOH 10wt%</td>
<td>0.121 ± 0.0044</td>
<td>4.7 ± 2.01</td>
<td>0.794 ± 0.0624</td>
</tr>
<tr>
<td>SiF3/EtOH 15wt%</td>
<td>0.125 ± 0.0024</td>
<td>4.2 ± 1.72</td>
<td>1.272 ± 0.0324</td>
</tr>
<tr>
<td>SiF3/EtOH 20wt%</td>
<td>0.128 ± 0.0019</td>
<td>4.1 ± 1.48</td>
<td>1.318 ± 0.0689</td>
</tr>
<tr>
<td>SiF3/EtOH 25wt%</td>
<td>0.135 ± 0.0018</td>
<td>2.8 ± 1.27</td>
<td>1.312 ± 0.0428</td>
</tr>
</tbody>
</table>
Figure 67. Density, shrinkage, and compressive modulus data of SiF3 modified TEOS-based silica aerogels

5.2.2 Morphology

The SEM images of silica aerogels with or without modification by SiF3 are shown in Figure 68. It is seen that the morphology of particle aggregates was preserved before and after the modification by SiF3 molecules. The apparent average particle sizes are in the same range as revealed by SEM images. This is no surprise since the silica backbone structure was formed first, and the modification of the surface by SiF3 molecules followed. A thin layer of SiF3 molecules was anticipated to form since once the residual of –OH groups were eliminated at a site, no further reaction could happen at these sites. Based on this possibility, no changes in morphology were expected.
Figure 68. SEM images of TEOS aerogels without/with modification of SiF3 (a) TEOS-based aerogels without SiF3 modification, (b) TEOS-based aerogels modified with 5 wt% SiF3, (c) TEOS-based aerogels modified with 10 wt% SiF3, (d) TEOS-based aerogels modified with 15 wt% SiF3, (e) TEOS-based aerogels modified with 20 wt% SiF3, (f) TEOS-based aerogels modified with 25 wt% SiF3
5.2.3 Surface properties

The surface properties of POSS nanoparticles reinforced silica aerogels were studied by BET gas adsorption method and contact angle measurements.

5.2.3.1 Surface area and pore size distribution from gas adsorption method

The surface properties were studied by gas adsorption method and from the measurement of contact angle. The adsorption and desorption isotherms of TEOS aerogels without or with the modification of SiF3 are shown in Figure 69. The adsorption isotherms showed the existence of micropores and mesopores, respectively from the initial adsorption curve and hysteresis loop. The clearly visible hysteresis loop in Figure 69 indicates the existence of a large amount of mesopores. It is noted that the presence of hysteresis loop is an indication of the existence of mesopores in the range of 2 - 50 nm. The smaller hysteresis loop in the adsorption and desorption isotherm of TEOS aerogels without modification by SiF3 indicated the existence of less mesopores, probably due to the size of some of the pores are out of this range (> 50 nm), as noted from SEM images and the lowest density. The pore size distributions of these unmodified/modified TEOS aerogels from the desorption isotherm by BJH method are shown in Figure 70. The dominant pore size shifted left to a lower range for aerogels with modification by SiF3 molecules. The peak for dominant pore size became more distinct due to probably a reduction of the portion of micropores. This was also revealed by the decrease of micropore surface area as in Table 13. The small decrease of the BET surface area after modification by SiF3 molecules indicated that the treatment by SiF3 maintained the high surface area of the materials. This small reduction in surface area can possibly be attributed to SiF3 blocking some of the micropores in the aerogels. The average pore size for aerogels with and
without modification by SiF3 fell in the range of 10 – 13 nm. The pore size showed small reduction indicating that only a monolayer coating of SiF3 molecules could form on the surface of the secondary particles. The results from gas adsorption method suggested that SiF3 molecules eliminated the residual –OH groups on the surface of secondary particles, forming a thin coating layer.

Figure 69. Adsorption and desorption isotherms of TEOS aerogels without/with modification of SiF3
Figure 70. Pore size distribution of TEOS aerogels without/with modification of SiF3 from desorption isotherm determined by BJH method.

Table 13. BET surface area, average pore size, and dominant pore size from gas adsorption method of TEOS aerogels without and with modification by SiF3.

<table>
<thead>
<tr>
<th>sample</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore diameter from BJH method (nm)</th>
<th>Dominant pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEOS w/o SiF3</td>
<td>804.7</td>
<td>2.54</td>
<td>12</td>
<td>22</td>
</tr>
<tr>
<td>SiF3- 5wt%</td>
<td>790.3</td>
<td>2.55</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>SiF3- 10wt%</td>
<td>752.6</td>
<td>2.85</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>SiF3- 15wt%</td>
<td>756.8</td>
<td>2.76</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>SiF3- 20wt%</td>
<td>733.0</td>
<td>2.26</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>SiF3- 25wt%</td>
<td>726.2</td>
<td>2.63</td>
<td>11</td>
<td>10</td>
</tr>
</tbody>
</table>
5.2.3.2 Contact angle

The measurement of contact angle is used to characterize the surface hydrophobicity of silica aerogels.

5.2.3.2.1 Rationale for choosing post-gelation modification process

The surface modification of TEOS aerogels by SiF3 molecules altered the hydrophilic nature. The reason to use post-gelation process for the modification of silica aerogels is that SiF3 molecules are much smaller than POSS nanoparticles and other polymers. The two methoxy groups in SiF3 molecules are able to undergo hydrolysis and condensation like ethoxy groups from TEOS during the preparation of alcogels. It is likely that SiF3 molecules would be hidden inside the secondary particles, instead of coating the surfaces like POSS nanoparticles, if they were added at the initial step. Therefore, a screening study was conducted to study the effect of different modification processes by SiF3 modification through adding the fluorosilane before the hydrolysis step, condensation step, and after the gelation stage, respectively. The preparation process and composition of each type of aerogels is shown in Table 14. All these aerogels were prepared by a two-step acid-base catalyzed sol-gel process (see section 3.1.1.2), and the concentration of TEOS was kept the same as 1 mol/L for these five compositions. The amounts of SiF3 used to modify the TEOS-based aerogels are also listed in Table 14. Sample No. 1 was prepared as control without any SiF3 modification. Then 4.0 g and 5.0 g of SiF3 were mixed with TEOS and pre-hydrolyzed under pH=2 for sample No. 2 and 3, respectively. In preparation of sample No. 3, TEOS was pre-hydrolyzed under pH=2 and then 4.0 g of SiF3 were added with base catalysis. Thus the hydrolyzed species started to condense and form alcogels. In the last modification process (sample No. 5), the alcogels were
prepared by following the same procedure as those in sample No. 1. Then these gels were soaked in the ethanol solution of 5.0 g SiF3. The gels were allowed to age in the solution for 5 days. The contact angle data of the compressed disc of these different types of aerogels with various modifications are shown in Table 14. The compressed disc of TEOS-based aerogels without modification by SiF3 gave a contact angle of 27° with deionized water and 26° with diiodomethane. All the aerogels modified with SiF3 showed significant increase in contact angle both with deionized water and diiodomethane, suggesting effective modification of the surface occurred. However, difference still existed as function of different modification processes. A glance at Table 14 could give us a hint that post-modification offers a more effective surface modification. The comparison of sample No. 2 and 4 would suggest that pre-hydrolysis process is better than pre-condensation process. In the pre-hydrolysis process, SiF3 underwent hydrolysis along with TEOS, and the hydrolyzed specie condensed as the condition was changed to basic. In the pre-condensation process, TEOS was pre-hydrolyzed, and condensed very fast under basic condition. This did not give enough time for SiF3 molecules to hydrolyze and co-condense with hydrolyzed TEOS. Thus, the reactions between hydrolyzed TEOS and SiF3 might not be as effective as those in pre-hydrolysis process. This would be the possible reason to explain the lower contact angle of only 71° with deionized water. The comparison of sample No. 3 and 5 would suggest that the post-gelation process is more effective than pre-hydrolysis process. Considering the high possibility that SiF3 molecules would be hidden inside the secondary particles instead of coating the surfaces for pre-hydrolysis process, the SiF3 would only age on the surfaces of the secondary particles via silylation reaction for post-gelation process. Based
on these preliminary results, the post-gelation approach is selected to achieve more effective surface modification. It is believed that, in this manner, the SiF3 molecules are allowed to eliminate the residual \(-\text{OH}\) groups on the surface at a reasonable reaction period, instead of co-condensing with hydrolyzed TEOS species.

Table 14. Composition and contact angles data of TEOS-based aerogels as function of different modification steps

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Modification process</th>
<th>weight of SiF3 added (g)</th>
<th>Contact angle with H(_2)O</th>
<th>Contact angle with CH(_3)I(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TEOS w/o SiF3</td>
<td>n/a</td>
<td>27.5 ± 0.32 °</td>
<td>25.7 ± 0.36 °</td>
</tr>
<tr>
<td>2</td>
<td>pre-hydrolysis</td>
<td>4.0</td>
<td>106.0 ± 0.58 °</td>
<td>51.5 ± 0.97 °</td>
</tr>
<tr>
<td>3</td>
<td>pre-hydrolysis</td>
<td>5.0</td>
<td>134.0 ± 0.98 °</td>
<td>85.9 ± 0.61 °</td>
</tr>
<tr>
<td>4</td>
<td>pre-condensation</td>
<td>4.0</td>
<td>70.6 ± 0.86 °</td>
<td>38.6 ± 0.58 °</td>
</tr>
<tr>
<td>5</td>
<td>post-gelation</td>
<td>5.0</td>
<td>142.2 ± 0.79 °</td>
<td>106.1 ± 0.81 °</td>
</tr>
</tbody>
</table>

5.2.3.2.1 Contact angle results for post-gelation process

The post-modification strategy shows a remarkable improvement in the surface property in terms of hydrophobicity. Significant improvements in their hydrophobicity are achieved even with low concentration of SiF3/EtOH solution. Modification using SiF3/EtOH solution produced hydrophobic aerogels. In one case super hydrophobic aerogels with water contact angle greater than 150° was produced, as shown in Figure 71. The significant improvement for SiF3 modified aerogels are easily observed in Figure 71. The first image in Figure 71 showed that the compressed disc of unmodified aerogel had a very low contact angle with deionized water. However, the compressed disc of TEOS-based aerogels modified with 15wt% SiF3 had a contact angle of 135°. Furthermore, the compressed disc of TEOS-based aerogels modified with 25wt% SiF3 showed a

147
superhydrophobic surface, with a contact angle of 154°. The contact angle data of compressed TEOS based aerogel discs with SiF3/EtOH solution for post-modification is shown in Table 15. The dramatic improvements for SiF3 modified aerogels were observed. Based on these contact angle data, the surface energy, including polar and dispersion components, and the value of polarity, were calculated as listed in Table 16. Note that surface energy at SiF3 concentration higher than 10wt% was not calculated as a dramatic decrease in polar component occurred. Nevertheless, the surface energy and polarity showed radical changes up to 10 wt% SiF3 in ethanol solution. It is seen that the surface energy dropped to almost half the value of unmodified aerogels. On the other hand, the polarity reduced from 0.53 for unmodified TEOS-based aerogels to 0.12 for TEOS-based aerogels treated with 10wt% SiF3 solution. Figure 72(a) shows that a drop of water could sit on a monolithic aerogel without being absorbed. Figure 72(a) shows that a monolithic aerogel could float in water. The curvature of the water surface is clearly apparent in Figure 72(b), indicating hydrophobic nature of the aerogels.

Table 15. Contact angle data of compressed TEOS based aerogel discs with SiF3/EtOH solution for post-modification

<table>
<thead>
<tr>
<th>Post-treatment</th>
<th>H₂O</th>
<th>CH₂I₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEOS w/o SiF3</td>
<td>27.3 ± 0.43 °</td>
<td>25.4 ± 0.33 °</td>
</tr>
<tr>
<td>SiF3/EtOH 5wt%</td>
<td>70.5 ± 0.86 °</td>
<td>38.6 ± 0.58 °</td>
</tr>
<tr>
<td>SiF3/EtOH 10wt%</td>
<td>106.1 ± 0.58 °</td>
<td>51.5 ± 0.97 °</td>
</tr>
<tr>
<td>SiF3/EtOH 15wt%</td>
<td>134.7 ± 0.98 °</td>
<td>98.5 ± 0.43 °</td>
</tr>
<tr>
<td>SiF3/EtOH 20wt%</td>
<td>145.2 ± 0.79 °</td>
<td>108.1 ± 0.54 °</td>
</tr>
<tr>
<td>SiF3/EtOH 25wt%</td>
<td>154.1 ± 0.45 °</td>
<td>124.6 ± 0.54 °</td>
</tr>
</tbody>
</table>
Table 16. Surface energy data of compressed TEOS based aerogel discs with SiF3/EtOH solution for post-modification

<table>
<thead>
<tr>
<th>Post-treatment</th>
<th>Surface energy (dyn/cm)</th>
<th>polarity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dispersion</td>
<td>polar</td>
</tr>
<tr>
<td>TEOS w/o SiF3</td>
<td>31.80</td>
<td>36.64</td>
</tr>
<tr>
<td>SiF3/EtOH 5wt%</td>
<td>30.44</td>
<td>14.82</td>
</tr>
<tr>
<td>SiF3/EtOH 10wt%</td>
<td>30.37</td>
<td>4.30</td>
</tr>
</tbody>
</table>

Figure 71. Contact angle images of SiF3 modified TEOS based aerogels with water

Figure 72. Pictures of hydrophobic TEOS-based aerogels modified with 15wt% SiF3/EtOH solution (a) one water droplet on top of the aerogels (b) a monolithic aerogel floating on the top of water
5.2.4 Comparison with POSS reinforced silica aerogels

The properties of TEOS-based aerogels modified with POSS nanoparticles and those with fluorosilane can now be compared. It is seen that SiF3 was more effective in rendering the aerogel hydrophobic than most types of POSS nanoparticles discussed in Chapter IV. One exception is the aerogels reinforced with \textit{i-butyl} POSS. The aerogel reinforced with 5 wt\% \textit{i-butyl} POSS gave even higher water contact angle than those modified with 5 wt\% SiF3 solution. Furthermore, mechanical reinforcement was more prevalent in the case of aerolgels modified by POSS. Even low concentration of POSS can offer effective surface modification as well as mechanical reinforcement. Such difference might have originated from the fact that POSS can support the neck region by chemically bonding to the silica network during pre-gelation method, while SiF3 molecules form a thin layer of coating evenly distributed along the surface of secondary particles instead of preferably located at the neck region.

5.3 Summary

Overall, several modification methods were compared using the fluorosilane as silylating agent. A post-gelation scheme with SiF3 molecules was found effective in terms of changing the hydrophobic nature of the unmodified silica aerogels. Some superhydrophobic aerogels were prepared, which is not commonly seen in literature.\(^{133,192-194}\) It is believed that the SiF3 molecules formed a monolayer coating on the surface of the secondary particles. Consequencely, the surface area reduced slightly, but the surface energy reduced significantly. Mechanical reinforcement was not significant at low concentration of SiF3 in solution.
6.1 Research objectives

In previous efforts on reinforcement of silica aerogel networks by polymers such as isocyanates, epoxies, and polystyrene, the polymer was introduced into the network after the gel was formed. This manner of introduction of reinforcing agents was time consuming as the process was dictated by the speed of diffusion. Our work included introduction of pre-modified polyurethane with aminopropyltriethoxysilane (APTES) before the silanes were allowed to undergo hydrolysis and condensation. As a result, diffusion limited post-gelation crosslinking was avoided and the amount of chains introduced in the aerogel structures was uniquely set by the APTES moieties participating in the reaction. The intimate mixing before gelation also benefited the dispersion of polymers in the system. This avoided the problems associated with diffusion of polymers into small pores encountered in post-gelation modification. These gels were anticipated to produce aerogels with better strength and large compressive strains while preserving low density. The approach presented a favorable scenario that one polyurethane chain was introduced into gel network for introduction of every two APTES molecules.
Consequently, the amount of APTES introduced in the aerogel structures also quantified the amount of polyurethanes introduced in the aerogel.

6.2 Results and Discussion

The experimental results are discussed as follows.

6.2.1 Synthesis and structure of polymers

The FT-IR spectra of PTMG 1000, MDI endcapped prepolymer and APTES endcapped prepolymer are shown in Figure 73. A wide peak at 3400 cm$^{-1}$ indicates hydrogen bonding, either from $-\text{OH}$ group or $-\text{NH}$ group, and are observed for both PTMG 1000 and MDI-end capped prepolymer. The appearance of a strong peak at 1740 cm$^{-1}$ indicates the formation of carbonyl group from urethane reactions between PTMG 1000 and MDI. A medium strong peak at 2250 cm$^{-1}$ indicates the prepolymer were end-capped with isocyanate groups. After the reaction of MDI end-capped prepolymer with APTES, the peak from isocyanate group disappeared, which indicates the completion of modification of MDI-end capped prepolymer with APTES. The SEC result gives a Mn of 4200 for MDI-end capped prepolymer and a polydispersity index (PDI) of Mw/Mn =1.68. For APTES end-capped prepolymer, the molecular weight was also detected by SEC, giving a Mn=5200 and PDI = 1.73.

The SEC curves give a high molecular weight for both MDI-end capped polyurethane and APTES end-capped polyurethane. For MDI end-capped polyurethane, Mn was 28.7K, Mw was 63.5K, and PDI (Mw/Mn) was 2.2. For APTES end-capped polyurethane, the molecular weight was similar to MDI end-capped polyurethane, e.g. Mn= 28.5K, Mw= 63.4K, and Mw/Mn=2.2. The close molecular weight and polydispersity indicates the absence of crosslinking after APTES end functionlization. The FR-IR spectra of MDI
end-capped chain extended polyurethane and APTES end-capped chain extended polyurethane are shown in Figure 74. The appearance of the peak at 1740 cm$^{-1}$ indicated the existence of carbonyl groups formed between –OH groups of polydiol and isocyanate groups of MDI. The absence of the peak at 2250 cm$^{-1}$ was due to low concentration of isocyanate end groups. The spectra for different materials did not show significant difference due to their high molecular weights. The $^1$H NMR spectra of MDI end-capped polyurethane and APTES end-capped polyurethane are shown in Figure 75. The assignments of resonance peaks are illustrated in the figure according to the standard spectra. The peaks in both spectra match the structure of polyurethane units. The two spectra look identical due to the small portion of different end groups compared to the urethane units of polymers. The peaks appearing at 1.45 ppm and 1.66 ppm were from the methylene groups in the PTMG linkage. The peak at 2.48 ppm arose from the DMSO solvent. The group of peaks at 3.27 ppm was from the methylene group connected to oxygen in the PTMG linkage. The peak at 3.74 ppm was from the methylene group between two aromatic rings in the MDI linkage. The peaks at 4.05 ppm and 4.00 ppm were from the methylene group connected to oxygen in the butane-diol linkage. The peaks at 7.05 ppm and 7.32 ppm were from the aromatic rings of MDI, in which the peak at 7.05 ppm arose from the –CH closer (ortho-position) to methylene group substitution, and the peak at 7.32 ppm arose from the –CH at the meta-position of the methylene substitution. The peak at 9.49 ppm was from the hydrogen atom of the urea linkage. The combination of FT-IR and $^1$H NMR confirmed that expected structure was obtained.
Figure 73. FT-IR spectra of PTMG1000, MDI end-capped prepolymer and APTES end-capped prepolymer

Transmission %
wave number (cm\(^{-1}\))

a: PTMG1000
b: MDI end-capped prepolymer
c: APTES end-capped prepolymer

Figure 74. FT-IR of MDI end-capped polyurethane and APTES end-capped polyurethane

Transmission %
wave number (cm\(^{-1}\))

a: MDI end-capped PU
b: APTES end-capped PU

No significant NCO peaks observed due to high MW
Figure 75. $^1$H NMR of PTMG based polyurethane

6.2.2 Structure of aerogels

The supercritically dried aerogels were characterized by $^{13}$C solid-state NMR to determine the material composition. This work was finished with the help of Bimala Lama and Dr. Matthew Espe from Department of Chemistry. The $^{13}$C NMR spectrum of APTES end-capped polyurethane is shown in Figure 76a. The peaks at 27.2, 65.9, and 71.2 ppm are from butyl group of the butanediol monomer. The peak at 27.2 ppm is from the middle carbons of $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ group, peak at 65.9 is from carbon attached to ether oxygen and the peak at 71.2 ppm arises from the carbons attached to oxygen of the amide group of the polymer. The small peak around 41.0 ppm is from the $-\text{CH}_2$ group connecting the two phenyl groups. The peaks at 121.2 and 130.2 ppm are from the protonated carbons of the phenyl groups and the peak at 136.9 ppm is due to the
nonprotonated aromatic carbons. The ester group attached to amine group gives a peak at 154.6 ppm.

The APTES molecule contains five types of carbons. The two carbons attached to silicon through C-O-Si bonds should give peaks at 58.2 ppm and 15.9 ppm. The three CH₂ carbons from the propyl group should show peaks at 43.5, 23 and 10 ppm. In the ¹³C spectrum from the polymer alone, in Figure 76a, peaks were observed from the polyurethane but not from the APTES group. This suggested that the concentration of APTES end groups was small compared to the urethane units of the polymer. During gelation, if the reaction is incomplete, the ¹³C NMR spectrum should contain peaks at 58.2 and 15.9 ppm from the -OCH₂- and -CH₃ groups of TEOS or APTES. The ¹³C NMR spectrum of the TEOS/APTES aerogel, Figure 76b, contains only three peaks from the propyl group of APTES. These results indicate that the condensation of ethoxy groups went to completion and that all the ethoxy groups were removed in hydrolysis step. The small peak at 165 ppm observed in APTES containing aerogels was attributed to the residue of DMF solvent.

The ¹³C NMR spectrum from TEOS/APTES/0.5 wt% APTES end-capped polyurethane aerogel, shown in Figure 76c, contains the peaks from propyl group of APTES. Due to the very low concentration of polymer in this sample, in comparison to the APTES concentration, no peaks were detected from the polyurethane group. In ¹³C NMR spectrum from TEOS/APTES/15 wt% APTES end-capped polyurethane aerogel, shown in Figure 76d, we clearly observe the peaks from APTES as well as the polyurethane. Since the peaks from the APTES end groups of the polymer have a very low
concentration in these materials, we are not able to determine the extent of reactivity of the APTES units in the PU polymer.

Figure 76. $^{13}$C CP/MAS SSNMR spectra of (a) APTES end-capped polyurethane, (b) TEOS/APTES based aerogel, (c) TEOS/APTES/0.5 wt % APTES end-capped polyurethane, and (d) TEOS/APTES/15 wt % APTES end-capped polyurethane

The reactivity and product composition of the aerogels were also studied using $^{29}$Si solid-state NMR. In the $^{29}$Si NMR spectrum from silica materials, it is typical to observe several distinct peaks that arise from the Si sites with structures of Si(-OSi)$_2$(OH)$_2$, Si(-OSi)$_3$(OH) and Si(-OSi)$_4$\textsuperscript{161}. These species are labeled Q$_2$, Q$_3$, and Q$_4$ respectively, with the peaks occurring more upfield with larger Q value. The $^{29}$Si NMR spectrum from the TEOS/APTES aerogel, shown in Figure 77b, has the expected resonances in the silica region of the spectrum, with peaks at -92 ppm (Q$_2$), -101 ppm (Q$_3$) and -110 ppm (Q$_4$). The larger population of Q$_3$ sites relative to Q$_4$ sites results from the very high surface
area of the material and the large number of surface hydroxyl groups present. The additional peak around 66 ppm is due to the R-Si(-OSi)$_3$ group from APTES. In the $^{29}$Si NMR spectrum from the polymer, the peaks near 66ppm, from the APTES end groups are observed, shown in Figure 77a. The signal intensity was low indicating that the APTES end group concentration was very low in comparison to the polymer. Since the APTES in the silica network was present at a much higher concentration than the APTES end groups in the polymer, it was not possible to distinguish between them and to study the interaction between the polymer and the silica network using $^{29}$Si NMR data, Figure 77c-e.

Figure 77. $^{29}$Si CP/MAS SSNMR spectra of (a) APTES end-capped polyurethane, (b) TEOS/APTES based aerogel, (c) TEOS/APTES/0.5 wt % APTES end-capped polyurethane, (d) TEOS/APTES/10 wt % APTES end-capped polyurethane, and (e) TEOS/APTES/15 wt % APTES end-capped polyurethane
The compositions of TEOS/APTES reinforced with APTES end-capped polyurethane and its prepolymer were studied by obtaining weight loss of different samples in air using TGA instrument. The weight loss of TEOS/APTES aerogels with APTES end-capped polyurethane is shown in Figure 78. TEOS/APTES aerogel had a 78.6% residue at 600°C, at which temperature the APTES end-capped polyurethane almost decomposed completely and left a 10.0% residue. The residue came from the APTES end groups and excess of APTES added during the synthesis of end-capping reaction. The difference of weight loss between TEOS/APTES aerogels with and without APTES end-capped polyurethane indicates the contents of polymer in each sample. The percentage of weight loss agrees well with the amount of polymer added in the initial mixture, as presented in Table 17. The combination of TGA results and solid state NMR implies that almost all the added polymers remained in the aerogel and must have reacted with the silane network. Similar results are also observed for aerogels with APTES end-capped polyurethane prepolymer, as shown in Table 18 and Figure 79.

The DSC curves of TEOS/APTES aerogels with and without APTES end-capped polyurethane is shown in Figure 80. APTES end-capped polyurethane shows a melting temperature at ~ 185 °C and a T_g around 86 °C. Most aerogels with low weight percentage of polymer do not show any thermal transitions due to an amorphous network. Only at very high weight percentage of polymer, e.g. at 15% and 50% levels, thermal transitions could be observed. This became clear for a polymer content of 50 wt%. Sample TA-PU-50 showed a broad melting peak around 166 °C and a T_g around 53 °C, suggesting that some domains were formed with high concentration of polyurethane.
Figure 78. Weight loss of TEOS/APTES aerogels with APTES end-capped polyurethane

Figure 79. Weight loss of TEOS/APTES aerogels with APTES end-capped prepolymer
Figure 80. DSC scans of TEOS/APTES aerogels with APTES end-capped prepolymer

Table 17. Weight loss of TEOS/APTES-based silica aerogels reinforced with APTES end-capped polyurethane at 600 °C

<table>
<thead>
<tr>
<th>sample</th>
<th>PU wt% added initially</th>
<th>Residual weight%</th>
<th>Weight loss% from PU</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA-PU-0</td>
<td>0</td>
<td>76.1</td>
<td>n/a</td>
</tr>
<tr>
<td>TA-PU-3</td>
<td>3.0</td>
<td>73.0</td>
<td>3.1</td>
</tr>
<tr>
<td>TA-PU-5</td>
<td>5.0</td>
<td>71.1</td>
<td>5.0</td>
</tr>
<tr>
<td>TA-PU-7</td>
<td>7.0</td>
<td>69.2</td>
<td>6.9</td>
</tr>
<tr>
<td>TA-PU-10</td>
<td>10.0</td>
<td>66.3</td>
<td>9.8</td>
</tr>
</tbody>
</table>
Table 18. Weight loss of TEOS/APTES based silica aerogels with APTES end-capped prepolymer at 600°C

<table>
<thead>
<tr>
<th>sample</th>
<th>prePU wt% added initially</th>
<th>Residual weight%</th>
<th>Weight loss% from prePU</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA-prePU-0</td>
<td>0</td>
<td>79.4</td>
<td>n/a</td>
</tr>
<tr>
<td>TA-prePU-3</td>
<td>3.0</td>
<td>76.3</td>
<td>3.1</td>
</tr>
<tr>
<td>TA-prePU-5</td>
<td>5.0</td>
<td>74.3</td>
<td>5.1</td>
</tr>
<tr>
<td>TA-prePU-7</td>
<td>7.0</td>
<td>72.1</td>
<td>7.3</td>
</tr>
<tr>
<td>TA-prePU-10</td>
<td>10.0</td>
<td>69.5</td>
<td>9.9</td>
</tr>
</tbody>
</table>

6.2.3 Properties of aerogels

The properties of aerogels, including density, shrinkage, compressive modulus, morphology and surface properties are discussed as follows.

6.2.3.1 Density and shrinkage

The optical clarity of aerogels is a strong function of the reinforcement means. The baseline aerogel was semi-transparent, as shown in Figure 81(a), aerogels containing APTES end-capped prepolymer appeared translucent (Figure 81(b)), and aerogels with APTES end-capped chain extended polyurethane was opaque (Figure 81(c)). The trends of density and shrinkage of TEOS/APTES-based aerogels reinforced with APTES end-capped polyurethane (APTES-PU) and APTES end-capped prepolymer (APTES-prePU) are shown in Figure 82. The density increased with the addition of polymers, for both APTES-prePU and APTES-PU modified aerogels. The shrinkage depended on the pore structure and the supercritical drying conditions. In view of the magnitude of error bars,
we can infer that the shrinkage beyond 3 wt% polymer content remained almost insensitive to the addition of polymers.

Figure 81. Appearance of TEOS/APTES aerogels (a) without reinforcement, (b) with APTES end-capped prepolymer, and (c) with APTES end-capped polyurethane
Figure 82. Density and shrinkage of TEOS/APTES based aerogels reinforced with APTES end-capped polyurethane (APTES-PU) and APTES end-capped polyurethane prepolymer (APTES-prePU)
6.2.3.2 Morphology and surface properties

The morphology of TEOS/APTES aerogels modified with APTES end-capped PU or APTES end-capped prepolymer was characterized by SEM and SAXS. The surface properties were evaluated from contact angle measurements and BET gas adsorption.

6.2.3.2.1 Morphology from SEM

The morphology of aerogels examined by SEM is shown in Figure 83 and Figure 84. In Figure 83, it is apparent that TEOS/APTES-based aerogels (TA-prePU-0) had relatively uniform size secondary particles, as shown in Figure 83(a). With the addition of APTES end-capped prepolymer, the size of the secondary particles did not change much, as shown in Figure 83(b), (c), and (d). In the case of addition of APTES end-capped polyurethane, the pearl-necklace structure was preserved, and the aggregated particle sizes appeared uniform in the range of 90 – 110 nm, as shown in Figure 84(a), (b), (c) and (d). It was expected that a coating layer began to appear and widened the weak neck regions between adjacent secondary particles. However, conclusive comments would be made with further information from SAXS. The change of the contact angle would also be a further evidence for the existence of the coating layer. In the presence of very high concentration polyurethane, e.g. 50 wt%, most particles were seen with sizes in the range of 90 – 110 nm. However, some noticeably larger particles were also observed with sizes in the range of 300 – 400 nm, as seen clearly in Figure 84(e). Most of these big particles had regular round shape and looked different than just aggregates of small particles. A close observation of one of these larger particles (marked with white circle in Figure 84(e)) was shown in Figure 84(f) with high magnification. Small particles in the range of silica particles were observed on the surfaces of some of these big particles. If we recall
the DSC results that were discussed in section 6.2.2, the DSC curve of the aerogel with 50 wt% APTES end-capped polyurethane had a broad melting peak around 166 °C and a $T_g$ around 53 °C, which suggested that some domains with high content of polyurethane were formed. Therefore, some reasonable inferences could be made. First, it was likely that the dissolved polymer chains in the pore structure became phase separated when exposed to a bad solvent during solvent exchange step. Thus, they formed some domains containing high content of polyurethane. Second, it was possible that the polymer chains encapsulated some silica particles during phase separation as is evident from some of the silica particles on the surface of these domains in Figure 84(f).
Figure 83. SEM image of TEOS/APTES-based silica aerogels reinforced without and with APTES end-capped prepolymer (a) TA-0, (b) TA-prePU-3, (c) TA-prePU-7, (d) TA-prePU-10. Compositions are presented in Table 4, page 69.
Figure 84. SEM image of TEOS/APTES based aerogels reinforced with APTES end-capped polyurethane (a) TA-0, (b) TA-PU-3, (c) TA-PU-5, (d) TA-PU-15, (e) and (f) TA-PU-50 at different magnifications. Compositions are presented in Table 4, page 69.

6.2.3.2.2 Morphology from SAXS

The SAXS intensity $I(q)$ as a function of the scattering vector $q$ of TA-PU and TA-prePU samples is shown in Figure 85 and Figure 86, respectively, where the scattering intensity decreased rapidly with increasing $q$. No distinct peaks are observed in Figure 85 and Figure 86, indicating the disordered structure of the aerogels. In order to detect fractal behavior of the particle aggregates, the result shown in Figure 85 and Figure 86 were plotted as log $I(q)$ versus log $q$ in Figure 87 and Figure 88, respectively. The intensity
follows a power-law in the interval $0.06 \leq q \leq 0.18 \, \text{Å}^{-1}$ with exponents of $-3.78 \sim -3.31$. These correspond to fractal dimensions $D_s$ in the range of $2.22 \sim 2.69$, which is listed in Table 19. The power law is not satisfied for $q \geq 0.18 \, \text{Å}^{-1}$ because $q$ has become so large that the scattering process can resolve structures of the size of individual atoms and the two-phase approximation is no longer satisfied. The values of the slope of the Porod’s plot in the range of $-4 \sim -3$, imply fractal surfaces. A reduction of fractal dimension (Table 19) implies that the curved surface of the pore in baseline aerogel turned into smooth cylindrical pore with the introduction of APTES end-capped prepolymer and chain extended polyurethane. This also supports that the smoothness of the pores was due to the polymer coatings on the secondary silica particles. Aerogels reinforced with APTES end-capped prepolymer had a larger fractal dimension than those reinforced with same amount of APTES end-capped chain extended polyurethane, suggesting chain extended polyurethane could coat the surfaces of the secondary particles and the neck regions more effectively that prepolymer did.
Figure 85. SAXS intensity of TA-PU samples as a function of the scattering vector

Figure 86. SAXS intensity of TA-prePU samples as a function of the scattering vector
Figure 87. Porod’s plot of SAXS intensity as a function of $q$ on a log-log scale (TA-PU)

Figure 88. Porod’s plot of SAXS intensity as a function of $q$ on a log-log scale (TA-prePU)
The SAXS curves are also plotted on a log $I(q)$ versus $q^2$ scale, in order to verify the extent of Guinier’s law. These plots for aerogels reinforced with APTES end-capped polyurethane are presented in Figure 89. Linear regions within a more or less extended $q$ domain depend on the samples. The linear portions of these plots are used to calculate the apparent average radius of gyration $R_g$ of the “particles” in every sample. The values of $R_g$ for aerogels reinforced with APTES end-capped prepolymer were calculated in the same method. The values of $R_g$ are assembled in Table 19. The trend of the apparent average radius of gyration $R_g$ of the “particles” agrees with the data of fractal dimension, suggesting that a polymer coating was formed at the surface of secondary particles as well as around the neck regions between the secondary particles.

![Figure 89. Guinier's plots of TEOS/APTES-based aerogels reinforced with APTES end-capped polyurethane](image-url)
Table 19. Slopes and fractal dimension of TEOS/APTES aerogels reinforced with APTES end-capped polyurethane via Porod’s plot and $R_g$ from Guinier's law.

<table>
<thead>
<tr>
<th></th>
<th>slope</th>
<th>Ds</th>
<th>$R_g$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA-0</td>
<td>-3.31</td>
<td>2.69</td>
<td>27.4</td>
</tr>
<tr>
<td>TA-PU-3</td>
<td>-3.46</td>
<td>2.54</td>
<td>27.6</td>
</tr>
<tr>
<td>TA-PU-7</td>
<td>-3.62</td>
<td>2.38</td>
<td>27.9</td>
</tr>
<tr>
<td>TA-PU-10</td>
<td>-3.64</td>
<td>2.36</td>
<td>30.9</td>
</tr>
<tr>
<td>TA-PU-15</td>
<td>-3.75</td>
<td>2.25</td>
<td>32.3</td>
</tr>
<tr>
<td>TA-PU-50</td>
<td>-3.78</td>
<td>2.22</td>
<td>38.6</td>
</tr>
<tr>
<td>TA-prePU-3</td>
<td>-3.40</td>
<td>2.60</td>
<td>28.8</td>
</tr>
<tr>
<td>TA-prePU-5</td>
<td>-3.51</td>
<td>2.49</td>
<td>28.7</td>
</tr>
<tr>
<td>TA-prePU-7</td>
<td>-3.58</td>
<td>2.42</td>
<td>29.0</td>
</tr>
</tbody>
</table>
6.2.3.2.3 Surface properties from contact angle measurements

For contact angle measurements, the different aerogel specimens were compressed into discs to eliminate the influence of pore structure, so that surface energy and hydrophobicity of the modified silica could be studied. The APTES end-capped polyurethane and MDI end-capped polyurethane were cast into films from their solutions, and vacuum dried to form a flat film. The contact angles of these two polyurethanes are shown in Figure 90. The MDI end-capped polyurethane showed a contact angle of 100.4° with deionized water, while the APTES end-capped polyurethane showed a contact angle of 69.9° with deionized water. The hydrophilicity of the APTES end groups gave a lower value of contact angle compared to the MDI end-capped polyurethane which was mostly composed of hydrophobic groups. The contact angles of TEOS/APTES aerogels with APTES end-capped PU or APTES end-capped prepolymer are shown in Figure 91. Aerogels without polymer modification has a contact angle of only 36.7° with deionized water. The addition of APTES end-capped prepolymer and APTES end-capped polyurethane both lowered the moisture sensitivity and enhanced the hydrophobicity. The hydrophobicity increased with an increase of polymer content. At the same loading level, polyurethane seems to have made the surface more hydrophobic than its prepolymer, possibly due to a lower concentration of the moisture-absorbing end groups in the former. The contact angles of aerogels with APTES end-capped PU are higher than that of APTES end-capped polyurethane polymer but lower than that of MDI end-capped polyurethane polymer, indicating the reaction between the APTES-end groups and the silica network. Contact angles of only MDI end-capped prepolymer and APTES end-
capped prepolymer were not measured since they were viscous liquid at room temperature.

The values of contact angles of TEOS/APTES based aerogels reinforced with APTES-PU and APTES-prePU are listed in Table 20. It is observed that the introduction of both APTES-PU and APTES-prePU improved the water contact angles of TEOS/APTES based aerogels, and APTES-PU was found to be more effective than APTES-prePU in terms of improvement of hydrophobicity. Furthermore, APTES-PU could help increase the contact angles of TEOS/APTES based aerogels with both water and diiodomethane, while in contrast, APTES-prePU could only improve the water contact angles of TEOS/APTES based aerogels. In terms of surface energy, both types of polymer could effectively reduce the polar components of surface energy. But only APTES-PU could lower both the dispersion and polar components, which means a reduction of total surface energy. In other words, APTES-PU could improve the hydrophobicity and reduce the total surface energy, while APTES-prePU could only improve the hydrophobicity.
Figure 90. Water contact angle images of APTES-end PU and MDI-end PU

Figure 91. Water contact angle images of TEOS/APTES/PU aerogels and TEOS/APTES/prePU aerogels
Table 20. Values of contact angles and surface energy components of TEOS/APTES-based aerogels reinforced with APTES-PU and APTES-prePU

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Contact angle (°)</th>
<th>Surface energy and its components (dyn/cm)</th>
<th>polarity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H$_2$O</td>
<td>CH$_3$I</td>
</tr>
<tr>
<td>MDI-PU</td>
<td>100.4 ± 0.4</td>
<td>55.3 ± 0.5</td>
<td>31.4</td>
</tr>
<tr>
<td>APTES-PU</td>
<td>69.9 ± 0.2</td>
<td>38.1 ± 0.6</td>
<td>30.5</td>
</tr>
<tr>
<td>TA-0</td>
<td>36.7 ± 0.6</td>
<td>37.2 ± 0.5</td>
<td>30.5</td>
</tr>
<tr>
<td>TA-PU-3</td>
<td>71.2 ± 0.4</td>
<td>60.5 ± 0.3</td>
<td>20.6</td>
</tr>
<tr>
<td>TA-PU-5</td>
<td>75.7 ± 0.3</td>
<td>61.7 ± 0.7</td>
<td>20.5</td>
</tr>
<tr>
<td>TA-PU-7</td>
<td>85.5 ± 0.7</td>
<td>62.6 ± 0.5</td>
<td>21.5</td>
</tr>
<tr>
<td>TA-PU-10</td>
<td>90.8 ± 0.6</td>
<td>68.4 ± 0.7</td>
<td>19.6</td>
</tr>
<tr>
<td>TA-prePU-3</td>
<td>37.3 ± 0.3</td>
<td>27.2 ± 0.3</td>
<td>31.7</td>
</tr>
<tr>
<td>TA-prePU-5</td>
<td>53.9 ± 0.5</td>
<td>29.0 ± 0.6</td>
<td>32.2</td>
</tr>
<tr>
<td>TA-prePU-7</td>
<td>72.5 ± 0.5</td>
<td>31.6 ± 0.6</td>
<td>33.7</td>
</tr>
<tr>
<td>TA-prePU-10</td>
<td>79.2 ± 0.5</td>
<td>32.1 ± 0.4</td>
<td>35.0</td>
</tr>
</tbody>
</table>
6.2.3.2.4 Surface area, and pore size distribution from gas adsorption measurements

The surface area and pore size distribution were both obtained by gas adsorption methods. The adsorption/desorption isotherms of TEOS/APTES based aerogels reinforced with APTES end-capped polyurethane and APTES end-capped prepolymer are shown in Figure 92 and Figure 93, respectively. The adsorption/desorption isotherms for each type of aerogels resembled each other. The initial increase of the quantity of gas absorbed indicated the presence of micropores. In the BET region, $0.05 \leq P/P_0 \leq 0.3$, the adsorption curve and desorption isotherms overlayed on top of each other. This region was due to the formation of monolayers and multilayers adsorption. The existence of hysteresis loops suggested the presence of mesopores in all the samples. These isotherms are typical for a combination of Type II and Type IV isotherms. The hysteresis loop at $P/P_0 > 0.5$ is typical for slit-shaped pores rather than the more common spherical pores.\textsuperscript{173} All remaining samples that are not plotted in the figures showed similar isotherms and hysteresis loops.

The pore size distribution was obtained from BJH desorption method. The pore size distributions of TEOS/APTES based aerogels reinforced with APTES end-capped polyurethane and APTES end-capped prepolymer are shown in Figure 94 and Figure 95, respectively. For a majority of samples, no dominant pore radius was seen in these figures. This might be due to lack of mesopores since the BJH method is used to determine the mesopore size distribution. The estimated pore sizes from visual inspection of the SEM images are in the range of 80 nm to 100 nm, and the existence of mesopores is not apparent. In Figure 94, the pore size distribution for TEOS/APTES based aerogels with high weight percent of APTES end-capped polyurethane (e.g. 10 wt%, 50 wt%)
showed a broad peak at a pore diameter of around 22 nm, which might have resulted from the elimination of mesopores in the lower range by the polymer coatings.

The values of surface areas, micropore surface areas from \( t \)-plot, average pore size from BJH method, and domain pore size from pore size distribution from BJH method of several aerogel samples are listed in Table 21. It is presumed that the polymer coatings covered the micropores inside the secondary particles and smoothed the surfaces of the secondary particles by reducing the fractal dimension. This may lead to a reduction of the surface area. It is seen from Table 21 that the BET surface area and micropore surface area from \( t \)-plot reduced in the presence of silane end-capped polyurethanes and its prepolymer, indicating the coverage of micropores inside the secondary particles by the polymer coating layers formed on the surfaces of secondary particles. In Table 21, the TEOS/APTES based aerogel without reinforcement from APTES end-capped polymer had a BET surface area of 485.5 \( \text{m}^2/\text{g} \), in comparison, the BET surface area of TA-PU-10 dropped to 226.8 \( \text{m}^2/\text{g} \) and that of TA-prePU-10 dropped to 242.9 \( \text{m}^2/\text{g} \). A similar trend was observed for micropore surface area. Such reduction of micropore surface area and total surface area would indicate the formation of the polymer coating layers on the particle surfaces. No significant difference was observed for the average pore diameter, which makes sense considering the little change in morphology from SEM images. The average pore sizes of all the samples were in the range of 9 nm ~ 13 nm. The dominant pore diameters were obtained by taking the peak diameters from the pore size distribution from BJH desorption method in Figure 94 and Figure 95.
Figure 92. Adsorption and desorption isotherms for TEOS/APTES aerogels with/without silane end-capped polyurethane reinforcement.
Figure 93. Adsorption and desorption isotherms for TEOS/APTES aerogels with/without silane end-capped polyurethane prepolymer reinforcement.
Figure 94. The pore size distributions of TEOS/APTES aerogels reinforced with APTES end-capped polyurethane determined by BJH method.

Figure 95. The pore size distributions of TEOS/APTES aerogels reinforced with APTES end-capped polyurethane prepolymer determined by BJH method.
Table 21. BET surface area, micropore surface area, average pore diameter, and the dominant pore size of APTES-PU and APTES-prePU reinforced silica aerogel samples

<table>
<thead>
<tr>
<th>sample</th>
<th>BET surface area (m²/g)</th>
<th>Micropore surface area (m²/g)</th>
<th>BJH Desorption average pore diameter (nm)</th>
<th>Dominant pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA-PU-0</td>
<td>485.5</td>
<td>22.9</td>
<td>10.2</td>
<td>n/a</td>
</tr>
<tr>
<td>TA-PU-3</td>
<td>322.1</td>
<td>18.7</td>
<td>12.1</td>
<td>n/a</td>
</tr>
<tr>
<td>TA-PU-5</td>
<td>287.9</td>
<td>16.5</td>
<td>11.4</td>
<td>n/a</td>
</tr>
<tr>
<td>TA-PU-7</td>
<td>241.1</td>
<td>12.9</td>
<td>11.9</td>
<td>n/a</td>
</tr>
<tr>
<td>TA-PU-10</td>
<td>226.8</td>
<td>10.5</td>
<td>11.4</td>
<td>21.4</td>
</tr>
<tr>
<td>TA-PU-50</td>
<td>192.6</td>
<td>9.9</td>
<td>13.1</td>
<td>21.6</td>
</tr>
<tr>
<td>TA-prePU-1</td>
<td>303.2</td>
<td>19.7</td>
<td>9.2</td>
<td>n/a</td>
</tr>
<tr>
<td>TA-prePU-3</td>
<td>268.7</td>
<td>15.5</td>
<td>9.2</td>
<td>n/a</td>
</tr>
<tr>
<td>TA-prePU-5</td>
<td>250.6</td>
<td>15.3</td>
<td>9.5</td>
<td>n/a</td>
</tr>
<tr>
<td>TA-prePU-7</td>
<td>239.4</td>
<td>11.9</td>
<td>9.90</td>
<td>n/a</td>
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<tr>
<td>TA-prePU-10</td>
<td>242.9</td>
<td>8.9</td>
<td>10.8</td>
<td>n/a</td>
</tr>
</tbody>
</table>

6.2.4 Mechanical properties

Native silica aerogels are very brittle materials. They cannot withstand high load or strain, and they usually crack at 5 ~ 10 % strain. With the addition of APTES end-capped polyurethane and its prepolymer, these aerogels can bear higher load and much higher deformation without breaking. The stress-strain curves of TA-PU aerogels and TA-prePU aerogels are shown in Figure 96 and Figure 97, respectively. In the presence of APTES end-capped polyurethane, the native silica aerogels broke at 5 – 10 % strain with strength of 0.04 MPa at the breaking point, as shown in Figure 96. Aerogels reinforced with...
higher than 3 wt% APTES end-capped polyurethane showed the ability to take higher load and withstand higher deformation. However, TEOS/APTES-based aerogels reinforced with higher than 7 wt% APTES end-capped polyurethane showed some buckling behavior at different strain depending on the concentration of APTES end-capped polyurethane. Similar stress-strain diagrams were seen for aerogels reinforced with APTES end-capped prepolymer, as shown in Figure 97. Aerogels reinforced with 3 wt% APTES end-capped prepolymer broke at 15 – 20 % strain, showing the ability to take higher load and withstand higher deformation than unreinforced aerogels. Buckling behavior was also observed for aerogels reinforced with 10 wt% APTES end-capped prepolymer. A striking difference is that the modulus of TA-PU is higher considering the same concentration of polymers added into the system. This indicates that polyurethane is more effective in modification of structure and strength of aerogels as seen in Figure 98. Overall, the compressive moduli increased and became fivefold than that of native aerogels in the presence of more end-capped polyurethane. This can be explained in terms of the polymer coatings on the surfaces of the secondary particles as well as the widening of the neck regions. Figure 99 shows that TA-PU-15 and TA-PU-50 could stand a strain of higher than 80 % in comparison with TA-0 and TA-PU-7, and behaves like a compressed solid material at high strain as all the pores were removed.
Figure 96. Stress-strain curve of TEOS/APTES aerogels with APTES-end polyurethane

Figure 97. Stress-strain curve of TEOS/APTES aerogels with APTES-end prepolymer
Figure 98. Compressive modulus vs. polymer wt% of TA-PU and TA-prePU aerogels

Figure 99. Stress-strain curve of TA-PU-15 and TA-PU-50
6.3 Discussion

The pre-gelation modification method using silane end-capped polyurethane and its prepolymer effectively shortened the production time for aerogels\textsuperscript{110}, and chemically reinforced and modified the structures at the same time. In this method, the gels were prepared with incorporation of reinforcing polymers, and then solvent exchanged to alcohol and supercritically dried. The typical time for production of one batch of aerogels in this method required 4-5 days. In comparison, post-gelation modification by polymer required ~ 10 days, as the gels were prepared, solvent exchanged with a good solvent for the crosslinkers, reacted at a certain temperature for a few days, then solvent exchanged with a good solvent that is miscible with liquid carbon dioxide, and finally supercritically dried. A fivefold improvement in mechanical modulus was observed for aerogels with 10 wt% of APTES end-capped polyurethane. Similar extent of reinforcement was seen in other pre-gelation modification\textsuperscript{110}. It is believed that a polymer coating layer was formed on the surfaces of secondary particles, which also strengthened the neck regions between the secondary particles. The reduction of BET surface area and micropore surface area seen in Table 21 and the SAXS data supported the above argument. The coating layer was also responsible for the larger values of contact angle with deionized water and improved compressive modulus. The presence of these polymer coatings in the aerogel structure was assumed as the origin of the high contact angle and their stress-strain curve similar to “soft” materials. The polymer helped to maintain the structure and dissipated energy at relatively high load and high strain during compressive tests.
6.4 Conclusions

A new reinforcement method was developed to strengthen the native silica aerogels and to chemically modify their hydrophilic surfaces. In addition, the pre-gelation modification provided a shorter production time. The modified aerogels had either translucent or opaque appearance, with slight increase in density due to the addition of polymers. With different load levels, these aerogels show different structural changes along with the surface properties and mechanical properties. At low weight percent of polymers, non-uniform secondary particles were observed with slight increase in compressive moduli. With increasing weight percent of polymers, the coating layers were formed which widened the neck regions effectively modifying the surfaces of secondary particles to make it much less hydrophilic and strengthened their ability to withstand higher load and exhibit higher strain. At very high content of polymers, the reinforced aerogels were able to stand above 70% strain without breaking, having the similar mechanical behavior as soft polymeric aerogels, such as syndiotactic polystyrene aerogels. In summary, the brittleness of silica network and hydrophilicity were altered in the presence of APTES end-capped polymers.
CHAPTER VII
SELF-CROSSLINKABLE POLYURETHANE-UREA REINFORCED SILICA
AEROGELS VIA PRE-GELATION MODIFICATIONS

7.1 Research Objectives
The reinforcement of silica aerogels by silane end-capped polyurethane and its prepolymer were presented in Chapter 6. In this chapter, the results on the use of multi-functional polyurethane-urea as multi-functional polymer crosslinker are presented. The multi-functional polymer chains were expected to attach along the surfaces of secondary particles as well as at the neck regions, giving rise to more effective coverage and reinforcement of the aerogels. The methods of preparation of sample specimen were presented in Chapter III, section 3.1.4.

7.2 Results and Discussion
The experimental results are discussed as below.

7.2.1 Structure of self-crosslinkable polyurethane-urea from FT-IR
The self-crosslinkable polyurethane-urea (denoted as sPU) was sealed in an amber colored bottle after the synthesis. Since sPU self-crosslinks when exposed to moisture, it is very hard to characterize the exact structure from $^1$H NMR and molecular weight from GPC. Therefore, FT-IR is utilized to confirm the complete of the reaction between the prepolymer with MDI end groups and the chain extender AEAPS. The reaction scheme is shown in Figure 27 in section 3.1.4.2. FT-IR is also a useful tool to identify some main
functionally groups of sPU. The FT-IR spectra of PTMG 1000, MDI end-capped prepolymer, and self-crosslinkable polyurethane-urea are shown in Figure 100. A wide peak at 3400 cm$^{-1}$ indicates hydrogen bonding, either from $-\text{OH}$ group or $-\text{NH}$ group, are observed for both PTMG 1000 (in Figure 100(a)) and MDI end-capped prepolymer (in Figure 100(b)). Two strong peaks in the range of 2890 cm$^{-1}$ – 2950 cm$^{-1}$ from the C-H stretching were observed for both spectra. The appearance of a strong peak at 1740 cm$^{-1}$ indicates the formation of carbonyl group from urethane reactions between PTMG 1000 and MDI. A medium strong peak at 2250 cm$^{-1}$ indicates the prepolymer were end-capped with isocyanate groups. The disappearance of the wide peak at 3400 cm$^{-1}$ and the medium strong peak at 2250 cm$^{-1}$ indicates that the isocyanate groups and free $-\text{OH}$ and $-\text{NH}$ groups were complete gone in the sPU spectrum (in Figure 100(c)), suggesting that the complete reaction between the prepolymer and AEAPS. The peak at 1050 cm$^{-1}$ in the sPU spectrum is assigned to the Si-O bonds, implying that the crosslinkable functional groups were present in the sPU structure. No strong hydrogen bonding peak is observed for sPU spectrum, suggesting the absence of moisture or $-\text{OH}$ residual groups from hydrolysis, and thus the lack of crosslinking.
Figure 100. FT-IR spectrum of self-crosslinkable polyurethane-urea, (a) PTMG1000, (b) prepolymer with isocyanate end-groups, (c) sPU

7.2.2 Density, shrinkage, and compressive modulus

These sPU gels shrunked up to 60 % in diameter after supercritical drying and became stiff opaque specimens. The appearance of sPU gel and sPU-reinforced silica aerogels are presented in Figure 101.

The sPU-reinforced silica aerogels appeared translucent at low concentration of sPU (Figure 101(a), (b), and (c)) and changed to totally opaque appearance with smooth surfaces at higher concentration of sPU (Figure 101(d), (e), and (f)). It was observed that sPU could form a gel by itself in air after absorbing moisture from the environment. This sPU gel was totally transparent and hold its original shape in a good solvent, e.g. in DMF, and it shrunk up to 60 % in diameter in a bad solvent, e.g. in acetone. The sPU gel was elastic and recovered to original shape after compress, as shown in Figure 101(g) and (h).
Figure 101. Appearance of sPU gel and sPU-reinforced silica aerogels (a) TA-0, (b) TA-sPU-5, (c) TA-sPU-10, (d) TA-sPU-15, (e) TA-sPU-20, (f) TA-sPU-25. Compositions are listed in Table 5, page 70. (g) transparent sPU gel, (h) transparent sPU gel compressed with fingers.

The density-shrinkage-compressive modulus data of sPU-reinforced aerogels is presented in Figure 102. A notable increase of shrinkage in diameter is observed for sPU-reinforced aerogels. The shrinkage of 25 wt% sPU-reinforced aerogels is four times of that of unreinforced TEOS/APTES aerogels. It is observed that density tripled due to significant shrinkage at high concentration of sPU. At the same time, dramatic improvements in
compressive modulus are observed. For example, almost sixty-fold increase of compressive modulus is observed for aerogels reinforced with 25 wt% sPU.

![Graph showing density-shrinkage-modulus of sPU reinforced silica aerogels](image)

**Figure 102. Density-shrinkage-modulus of sPU reinforced silica aerogels**

7.2.3 Morphology and surface properties

The morphology of unreinforced and reinforced silica aerogels is shown in Figure 103. The aggregated particles of typical diameters in a range of 85 – 100 nm are easily identified for unreinforced aerogels. The aggregated particle morphology is slight different when reinforced with sPU. The adsorption and desorption isotherms of several unreinforced and reinforced silica aerogels are plotted in Figure 104. The adsorption and desorption isotherms overlapped with each other at the range of $\frac{P}{P_0} \leq 0.5$, suggesting an
equilibrated isotherm. The hysteresis loop became more distinct with sPU reinforcement implying the existence of abundant mesopores.

The pore size distribution of unreinforced TEOS/APTES aerogels and those reinforced with sPU are shown in Figure 105. It is clear that there is no dominant pore diameter in the range of micropores and mesopores for unreinforced silica aerogel. However, in the presence of the reinforcing sPU chains, several changes took place. First, the fraction of mesopores with small diameters dropped. Second, the fraction of mesopores with larger diameters increased. Third, dominant pore diameters in mesopore range appeared and became more prominent with the increase of sPU concentration. This change of the predominant pore diameter is summarized in Table 22. This suggests that a majority of smaller size (<10 nm) mesopores were covered by the polymer coating layers.

The surface area and average pore size are also listed in Table 22. A conspicuous drop in BET surface area is observed suggesting the effective formation of polymer coatings and the coverage of micropores inside the secondary particles by sPU chains. The micropore surface area measured from t-plot method, as shown in the second column of Table 22, also showed a reduction trend, indicating the coating of polymer chains on the surface of secondary particles. The average pore diameter showed a small change, falling in the range of 11 – 14 nm.
Figure 103. SEM images of sPU reinforced silica aerogels (a) TA-0, (b) TA-sPU-1, (c) TA-sPU-5, (d) TA-sPU-10, (e) TA-sPU-15, (f) TA-sPU-20. Compositions are listed in Table 5, page 70
Figure 104. Adsorption and desorption isotherms of TEOS/APTES based silica aerogels without/with sPU reinforcement

Figure 105. Pore size distribution of sPU reinforced TEOS/APTES based silica aerogels

198
Table 22. Surface area, average pore size and pore size distribution of sPU reinforced silica aerogels from gas adsorption method

<table>
<thead>
<tr>
<th>sample</th>
<th>BET surface area (m²/g)</th>
<th>Micropore surface area (m²/g)</th>
<th>Average pore diameter (nm)</th>
<th>Dominant pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEOS/APTES</td>
<td>485.5</td>
<td>22.9</td>
<td>10</td>
<td>n/a</td>
</tr>
<tr>
<td>TA-sPU-1</td>
<td>381.3</td>
<td>17.5</td>
<td>10</td>
<td>n/a</td>
</tr>
<tr>
<td>TA-sPU-5</td>
<td>322.2</td>
<td>14.3</td>
<td>14</td>
<td>21</td>
</tr>
<tr>
<td>TA-sPU-10</td>
<td>280.2</td>
<td>9.8</td>
<td>11</td>
<td>17</td>
</tr>
<tr>
<td>TA-sPU-15</td>
<td>249.9</td>
<td>5.9</td>
<td>13</td>
<td>22</td>
</tr>
<tr>
<td>TA-sPU-20</td>
<td>215.6</td>
<td>4.2</td>
<td>14</td>
<td>17</td>
</tr>
<tr>
<td>TA-sPU-25</td>
<td>161.6</td>
<td>4.0</td>
<td>13</td>
<td>14</td>
</tr>
</tbody>
</table>

7.2.3 Compositions and Thermal properties

There is no obvious thermal transitions for TEOS/APTES based aerogels, their composites with sPU reinforcement, and pure sPU polymer, which are shown in Figure 106. There are no peaks or glass transition stages observed in the range of -25 °C up to 200 °C. The lack of melting behavior indicates that the absence of crystallization. The lack of glass transition is typical for a crosslinked structure since the movement of segments of chains is restricted. The thermal degradation of sPU polymer in air gave an 8.7 wt% residual weight at 650 °C, which is shown in Figure 107. The difference of the residual weight between the unreinforced aerogels and reinforced aerogels gives a rough idea about the content of polymer in each aerogel specimen. For example, sample TA-sPU-0 has a residual weight of 76.6 wt% and TA-sPU-15 has a residual weight of 61.5 wt%, shown in Table 23. The difference is 15.1 wt%, which matches the amount of
polymer added into system. The amount of reinforcement from self-crosslinkable polyurethane-urea in each sample is determined by the same method, as shown in Table 23 and Figure 107. The amounts of sPU remaining in the aerogels matches with the initial amounts of sPU added in with a variation of less than 1 wt%.

Table 23. Weight loss of TEOS/APTES aerogels with sPU at 650 °C

<table>
<thead>
<tr>
<th>sample</th>
<th>Residual weight%</th>
<th>Weight loss% from PU</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA-sPU-0</td>
<td>76.6</td>
<td>n/a</td>
</tr>
<tr>
<td>TA-sPU-5</td>
<td>71.3</td>
<td>5.3</td>
</tr>
<tr>
<td>TA-sPU-10</td>
<td>65.8</td>
<td>10.8</td>
</tr>
<tr>
<td>TA-sPU-15</td>
<td>61.5</td>
<td>15.1</td>
</tr>
<tr>
<td>TA-sPU-20</td>
<td>56.1</td>
<td>20.4</td>
</tr>
<tr>
<td>TA-sPU-25</td>
<td>51.0</td>
<td>25.6</td>
</tr>
</tbody>
</table>
Figure 106. DSC curves of TEOS/APTES aerogels with/without sPU reinforcement

Figure 107. TGA curves of TEOS/APTES-based aerogels reinforced with/without sPU
7.2.4 Fractal dimension from SAXS

The SAXS intensity $I(q)$ as a function of the scattering vector $q$ is shown in Figure 108, where the scattering intensity decreased rapidly with increasing $q$ in the range of $0.02 \leq q \leq 0.22$. No distinct peaks are observed in Figure 108, indicating no dominant sizes in this range. It is suggesting an even distribution of particle sizes. In order to detect fractal behavior, the result shown in Figure 108 are plotted as $\log I(q)$ versus $\log q$ in Figure 109. The intensity follows a power law in the Porod region with the exponent of $-3.85 \sim -3.31$, corresponding to fractal dimensions $D_s$ in the range of $2.15 - 2.69$, which is listed in Table 24. The slopes in the Porod’s region is in the range of $(-4) - (-3)$, implying rought surfaces$^{162}$. The decrease in fractal dimension implies that the curved surfaces of the original aerogel turned smooth, providing supporting evidence of the existence of polymer coating layers.

![Figure 108. SAXS intensity as a function of the scattering vector](image-url)
The SAXS curves were also plotted on a log $I(q)$ versus $q^2$ scale, in order to verify, the extent of Guinier’s law. These plots are presented in Figure 110. The extent of linear regions within a more or less extended $q$ domain depended on the samples. The linear portions of these plots were used to calculate the apparent average radius of gyration $R_g$ of the “particles” in each sample. The values of $R_g$ are listed in Table 24. The trend of the apparent average radius of gyration $R_g$ of the “particles” suggested a polymer coating on the surfaces of secondary particles as well as around the neck regions between them, agreeing with the data of fractal dimension.
Table 24. Slopes and fractal dimension of TEOS/APTES aerogels reinforced with sPU via Porod’s Plot and $R_g$ from Guinier’s law

<table>
<thead>
<tr>
<th></th>
<th>slope</th>
<th>Ds</th>
<th>$R_g$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TA-sPU-0</td>
<td>-3.31</td>
<td>2.69</td>
<td>45</td>
</tr>
<tr>
<td>TA-sPU-5</td>
<td>-3.65</td>
<td>2.35</td>
<td>57</td>
</tr>
<tr>
<td>TA-sPU-10</td>
<td>-3.71</td>
<td>2.29</td>
<td>68</td>
</tr>
<tr>
<td>TA-sPU-20</td>
<td>-3.85</td>
<td>2.15</td>
<td>69</td>
</tr>
</tbody>
</table>
7.3 Summary

The previous chapter discussed the structure and properties of silane end-capped polyurethane and its prepolymer reinforced silica aerogels. In this chapter, a similar approach was utilized by introducing multifunctional self-crosslinkable polyurethane-urea as reinforcement. The multifunctionality of sPU helped attach and align the polymer chains along the surface of secondary particles as well as the neck regions. The coating of sPU along the surface of silica aerogels produced smooth skeletal structure and hid the micropores inside the secondary particles. The reinforced aerogels have a smooth surface like plastics without any dusty external appearance. An increase of sixty times in compressive modulus was achieved but it came with a sacrifice of surface area and large increases of density. Similar extents in improvements in modulus and loss of surface area were found in literature with post-gelation process and the pre-gelation process with monomer cross linker, e.g. expoy. The drawback appeared as the self-crosslinkable polyurethane-urea gels shrank in a bad solvent, thus it drove the aerogels to shrink more than unreinforced aerogels. In comparison to silane-end capped polyurethane reinforced silica aerogels, sPU made the aerogels more rigid, instead of “soft” and flexible aerogels obtained with silane-end-capped polyurethanes.
CHAPTER VIII
CONCLUSIONS

Hybrid silica aerogels were reinforced by incorporating different types of POSS nanoparticles before gelation step. It was found that all types of POSS nanoparticles provided improvements in compressive stress, compressive modulus, and compressive strain, and modification of hydrophilic nature of the surfaces. The pearl-necklace structure was preserved and no significant change in morphology was seen. The aerogels exhibited small increases in density but notable increase in compressive modulus. The treatment with POSS significantly improved the hydrophobicity as the water contact angle of compressed aerogel disc changed from $27^\circ$ up to $119^\circ$. The uncompressed aerogels reinforced with 10wt% $i$-butyl POSS had an even higher water contact angle of $132.2^\circ$. The data from Chapter IV showed that POSS nanoparticles reacted at the surface of secondary particles by eliminating the residual –OH groups on the surface and also at the neck regions between two adjacent secondary particles. The mechanical properties of aerogels are a strong function of the density. The improvement of mechanical properties, e.g. compressive modulus, may be attributed to the increase of density. In case of tri-POSS, cyclo-POSS, and tetra-POSS reinforced aerogels, higher density was observed compared to $i$-butyl POSS reinforced silica aerogels at the amount of POSS added. Density is dependent on the amount of materials used and also the shrinkage. Aerogels reinforced with $i$-butyl POSS have less shrinkage, and therefore lower density. Let us
now discuss how compressive modulus of various POSS-reinforced silica aerogels depended on density. The data is Table 6 showed that compressive modulus of tri-POSS reinforced aerogels varied with density as \( \rho^{6.4} \), i-butyl-POSS reinforced aerogels as \( \rho^{13.4} \), tetra-POSS reinforced aerogels as \( \rho^{4.2} \), and cyclo-POSS reinforced aerogels as \( \rho^{4.1} \). Another reason responsible for the improvement of compressive modulus is that the POSS molecules reacted at the neck regions by linking two adjacent secondary particles and widened these weak regions. The improvements are observed for all types of POSS reinforced silica aerogels. It was observed from solid state NMR results that i-butyl POSS reacted with the aerogel network more effectively than other type of POSS. It was reported\(^{187}\) that i-butyl POSS which had flexible side groups had better performance. Here, i-butyl POSS also performed better in surface modification. Tri-POSS, cyclo-POSS and tetra-POSS which resulted in a higher density of reinforced aerogels and reacted with the network less effectively gave an overall comparable compressive modulus with i-butyl POSS reinforced aerogels. Therefore, for an overall consideration of the change of the density and compressive modulus, i-butyl POSS offered better improvements in both mechanical and surface properties compared to other type of POSS used in this work.

A method of surface modification based on fluorosilane as the silylating agent was studied by subjecting the silylating agent to participate in surface modification before hydrolysis, before condensation, and after gelation. It was found that post-gelation scheme was more effective in terms of changing the hydrophobic nature of unmodified silica aerogels. It is believed that the SiF3 molecules formed a monolayer coating on the surfaces of the secondary particles. In this case, the surface area reduced slightly as the
micropores inside the secondary particles were not accessible. Since the monolayer coating formed on all secondary particles only limited reinforcement effect was observed. A new reinforcement method based on APTES end-capped polyurethane prepolymer and chain extended polymer was developed. This method was intended to avoid the diffusional limitations encountered in post-gelation polymer reinforcement methods. The modified aerogels had either translucent or opaque appearance, with small increases in density. With the addition of polymers, an increase up to sixfold in compressive moduli was observed. It is believed that the coating layers were formed which widened the neck regions effectively, thus modifying the surfaces of secondary particles to make them much less hydrophilic and strengthened their ability to withstand higher load and higher strain. At very high content of polymers (e.g. above 15 wt%), the reinforced aerogels were able to withstand greater than 70% strain without breaking. This behavior is similar to some soft polymeric aerogels, such as syndiotactic polystyrene aerogels. In summary, the brittleness of silica network and hydrophilicity were altered with introduction of APTES end-capped polymers.

The study was extended to the use of multifunctional self-crosslinkable polyurethane-urea as a means of reinforcement before gelation. The multifunctionality of sPU helped attach and align the polymer chains along the surface of the secondary particles as well as the neck regions. The coatings of sPU along the surface of silica aerogels produced smooth skeletal structures and covered the micropores inside the secondary particles. The reinforced aerogels had a smooth surface like plastics without any dusty external appearance. A sixty fold increase in compressive modulus was achieved but it came with the sacrifice of surface area and a fivefold increase of density. The self-crosslinkable
polyurethane-urea gels were prone to shrinking in a bad solvent, which also caused higher shrinkage of aerogels.

Among all the reinforcing mechanisms that have been discussed above, pre-gelation method could effectively shorten the production time. Aerogels reinforced with silane end-capped polymers exhibited the ability to take high strain (higher than 70% strain for 15 wt% polymer) and high load (more than 50 times of unreinforced aerogels). However, sacrifice in density and surface area was found for this reinforcing method. Aerogels reinforced with polymers with multi-functionality showed sixty times improvements in compressive moduli but apparent increase in density and shrinkage. In contrast, POSS nanoparticles reinforced silica aerogel showed no penalty of density and little reduction in surface area along with noticeable improvement in compressive modulus and obtain of hydrophobic aerogels. In the field of bioscience, these types of aerogels could be used as matrix for bioactive materials or as the carrier of bacteria.\textsuperscript{192}
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APPENDICES
APPENDIX A

SOLID STATE NMR RESULTS AND COMPOSITIONS OF SiF₃ MODIFIED TEOS-BASED SILICA AEROGELS

Figure 111. Solid-state $^{13}$C NMR spectra of (a) TEOS (CP time= 3ms, scans=13800) (b) TEOS/ SiF₃ 5% (scans=32768), (c) TEOS/ SiF₃ 10% (scans=26760) and (d) TEOS/ SiF₃ 20% (scans=28756)

The $^{13}$C NMR spectra of TEOS aerogels with or without dimethoxy (methyl) (3, 3, 3-trifluoropropyl) silane (SiF₃) are shown in Figure 111(a-d). There are two peaks seen at 59 ppm and 15 ppm from incompletely hydrolyzed ethoxy groups of TEOS in $^{13}$CNMR
spectra of TEOS aerogels (Figure 111.a-d). The peaks at -3.5 ppm (Si-CH₃), 8.0 ppm (Si-CH₂-), 27 ppm (-CH₂-) and 49 ppm from incomplete hydrolyzed (Si-OCH₃) are observed from SiF₃ groups along with peaks from TEOS (Figure 111.b-d). The peaks at 126 ppm and 129 ppm are observed from –CF₃ carbon of the SiF₃ group. The presence of –OCH₃ group suggests that some of the Si species are not completely hydrolyzed (Figure 111.b-d). These spectra show that with increase in concentration of SiF₃ in the reaction mixture from 5%-20%, the amount of SiF₃ present in the aerogels is increased. This observation suggests that the reactivity of SiF₃ with TEOS increases with increase in reactant concentration of SiF₃.

Figure 112. Solid-state ²⁹Si NMR spectra of (a) TEOS (scans=4908) (b) TEOS/ SiF₃ 5% (scans=27268), (c) TEOS/ SiF₃ 10% (scans=12964) and (d) TEOS/ SiF₃ 20% (scans=9596)
The reactivity and product compositions of SiF$_3$ and its aerogels with TEOS were also studied by $^{29}$Si NMR study. $^{29}$Si NMR spectrum of TEOS aerogel shows the presence of silica with peaks at -109 ppm from Q$_4$, Si(-OSi)$_4$ species, -102 ppm from Q$_3$, Si(-OSi)$_3$(OR/H) species and -89 ppm from Q$_2$, Si(-OSi)$_2$(OR/H)$_2$ species (Figure 112.a). A portion of the Q$_3$ and/or Q$_2$ sites arise from the incomplete hydrolysis of TEOS, as shown in the $^{13}$C NMR study. Q$_3$ species has higher concentration in comparison to Q$_4$ which is consistent with the high surface area of TEOS aerogels. But both the Q$_3$ and Q$_4$ species have relatively similar concentration in the presence of SiF$_3$ species in aerogels (Figure 112 b-d). $^{29}$Si NMR spectrum of TEOS/SiF$_3$ 5% contains extra two peaks at -11 ppm and, -17 ppm due to Si(-OSi)(-OR/H)(-R)$_2$ species and Si(-OSi)$_2$(R)$_2$ species originality from SiF$_3$ species in the aerogel (Figure 112.b). The concentration of Si(-OSi)$_2$(R)$_2$ in comparison with Si(-OSi)(-OR/H)(-R)$_2$ species increased with increase in concentration of SiF$_3$ in the reaction mixture. The peak at -5 ppm due to the unreacted SiF$_3$ i.e Si(-OR/H)$_2$(R)$_2$ species are not observed. This observation indicates that all the SiF$_3$ present in the aerogel has reacted with and integrated into the silica network. The reactivity of SiF$_3$ with TEOS increased with increase in concentration of SiF$_3$ in the reaction mixture. There is no neat SiF$_3$ spectrum. Thus the above explanation is based on considering that SiF$_3$ has only Si(-OR/H)$_2$(R)$_2$ species.

The integration of peaks from SiF$_3$ and peaks from TEOS could give an estimation of the amount of SiF$_3$ molecules remained in the aerogels. The ratio of intergration of peaks from SiF$_3$ and peaks from TEOS in 5 wt% SiF$_3$ modified aerogels is 1:2, which means that 33% of the total Si atoms are from SiF$_3$ molecules, and 67% of the total Si atoms are from TEOS molecules. In the same way, the ratio of integration of peaks from SiF$_3$ and
peaks from TEOS is 1:1.7 for 10 wt% SiF3 modified aerogels, and is 1:1.5 for 20 wt% SiF3 modified aerogels.
The aerogel materials were characterized by $^{13}$C solid-state NMR to determine the material composition. The $^{13}$C NMR spectrum of aerogel containing TEOS and APTES is shown in Figure 113.a. The APTES molecule contains five types of carbons, two carbons attached to silicon through oxygen bonds which should give peaks around 58 ppm and 15...
ppm and three CH₂ carbons from propyl group attached to the silicon which give peaks at 43.5, 23 and 10 ppm respectively. Figure 113.a shows the ¹³C NMR spectrum from TEOS/APTES aerogel which contains three peaks only from the propyl group. It indicates that all the ethoxy group from TEOS and APTES were removed and silica group were incorporated in the silica network. The middle peak at 23 ppm shows splitting due to the different conformations in the structures. The small peak at 165 ppm has been observed previously in APTES containing aerogels and is attributed to the residue of DMF solvent.

The ¹³C NMR spectra of aerogels containing TEOS, APTES and different concentrations of self crosslinked polyurethane (sPU) are shown in Figure 113.b-d. The peaks at 27 and 71 ppm are from butyl group coming from butanediol monomer. The peak at 27 ppm is from middle carbons of –OCH₂CH₂CH₂CH₂O- and the peak around 71 ppm is due to the carbons attached to oxygen in polymer. The peaks at 119 ppm and 129 ppm are from protonated carbons from phenyl groups and the peak around 138 ppm is due to the nonprotonated aromatic carbons. The ester group attached to amine group gives peak at 155 ppm. The small peak around 41.0 ppm is from –CH₂ group connecting two phenyl groups is overlapped with the carbon peak of the APTES molecule in the aerogel. The peak from middle CH₂ of propyl group and the middle carbon of butanediol unit in polyurethane are overlapped and big peak is seen at 27 ppm. The polymer contains the APTMS end but there is no peak around 50 ppm from Si-OCH₃ group indicating that CH₃ group is hydrolyzed and removed forming silica network. These spectra show that the amount of sPU present in the aerogels is increased with increase in concentration of
sPU in the mixture from 5%-20%. These studies suggest that the reactivity of sPU with TEOS increased with increase in reactant concentration of sPU in the aerogel mixture.

The reactivity and product composition of the aerogels were also studied using $^{29}$Si solid-state NMR. In the $^{29}$Si NMR spectrum from silica materials, it is typical to observe several distinct peaks that arise from the Si sites with structures of Si(-OSi)$_2$(OH)$_2$, Si(-OSi)$_3$(OH) and Si(-OSi)$_4$. These species are labeled $Q_2$, $Q_3$ and $Q_4$ respectively, with the peaks appearing more upfield with larger $Q$ value. The $^{29}$Si NMR spectrum from the TEOS/APTES aerogel, Figure 114 a, has the expected resonances in the silica region of the spectrum, with peaks at -92 ppm ($Q_2$), -101 ppm ($Q_3$) and -110 ppm ($Q_4$). The larger population of $Q_3$ sites relative to $Q_4$ sites results from the very high surface area of the material and the large number of surface hydroxyl groups present. The additional peak
around 66 ppm is due to the R-Si(-OSi)$_3$ group from APTES with shoulder at -57 ppm from incompletely hydrolyzed R-Si(-OSi)$_2$(-OR/H) species.

Since the APTES group from silica network is in very high concentration in comparison to the APTMS end in the polymer added and they have very similar chemical shift, it is very difficult to distinguish between them. Thus study of interactions between polymer and silica network is difficult to understand from Figure 114 b-d. Since there is no peaks at -50 ppm from R-Si(-OSi)(-OR/H)$_2$ and -46 ppm from R-Si(-OR/H)$_3$, there is no evidences of the presence of unreacted species of APTES and APTMS from sPU polymer in the aerogel.