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## Effect of Processing Conditions on Chemical Makeup of Di-isocyanate Crosslinked Silica Aerogels

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# EFFECT OF PROCESSING CONDITIONS ON CHEMICAL MAKE-UP OF DI-ISOCYANATE CROSSLINKED SILICA AEROGELS

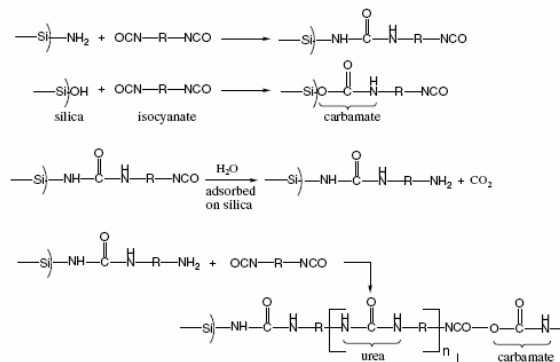
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## Introduction

Sol-gel derived silica aerogels are attractive candidates for many unique thermal, optical, catalytic, and chemical applications<sup>1</sup> because of their low density and high mesoporosity. However, their inherent fragility has restricted their use to, for example, insulation in extreme temperature environments such as Mars. We have previously reported crosslinking the mesoporous silica structure of an aerogel with di-isocyanates reacted with silanols on the surface,<sup>2,3</sup> or epoxies reacting with an amine decorated silica surface.<sup>4</sup> Either approach has been shown to significantly increase the strength of the aerogel with only a small effect on density or porosity. Thus, these hybrid materials may be enabling for future space exploration missions as well as advanced aeropropulsion systems which demand lighter weight, robust, dual purpose materials for insulation, radiation protection and/or structural elements of habitats, rovers, astronaut suits and cryotanks.

Utilizing amine-decorated silica particles to react with di-isocyanate oligomers analogous to the epoxies will produce polyurea crosslinks, in addition to carbamates produced from reaction with silanols on the surface as shown in Scheme 1. Since it is suggested in the literature that polyureas are mechanically more robust in general than are polyurethanes<sup>5</sup>, this approach might result in yet stronger materials.



Scheme 1.

Herein, we have examined the effects of four processing parameters for producing this type of polymer crosslinked aerogel on properties of the resulting monoliths. Concentration of total silane (total APTES plus TMOS in a 1 to 3 v/v ratio) from 7 to 30% by volume in acetonitrile (CH<sub>3</sub>CN) and the amount of water (7 to 25% by volume) used to catalyze gelation should determine the density of the underlying silica. The number of washes (from 0 to 4) to remove water and by-products of gelation, and concentration of di-isocyanate crosslinker (7 to 34% by weight in CH<sub>3</sub>CN) used for soaking the silica gels should determine the amount/length of polymer forming the crosslinks. A statistical experimental design methodology was employed to reduce the number of experiments and to allow computation of empirical models describing the relationship between the variables and the measured responses. In all, 30 different runs using different combinations of the four variables plus 5 repeats were utilized to produce a total of 35 separate crosslinked aerogels. These were evaluated by NMR, microscopy, surface analysis, mechanical testing and skeletal and bulk density. Herein, we will focus on the results of CP-MAS NMR, giving insight to the amount of polymer crosslink present in the monoliths and relate this to microstructure.

## Experimental

**Materials.** Tetramethylorthosilicate (TMOS), aminopropyltriethoxy-silane (APTES) and anhydrous acetonitrile were purchased from the Aldrich

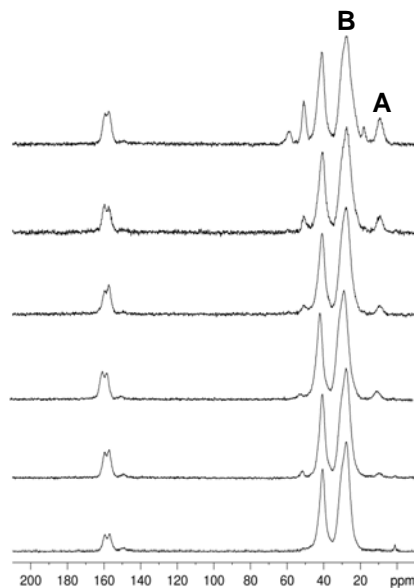
Chemical Co. Di-isocyanate oligomer (Desmodur N3200 a 1,6 hexamethylene di-isocyanate-based oligomer) was donated by Bayer Corporation. All reagents were used without further purification.

**Instrumentation.** Solid CP-MAS <sup>13</sup>C NMR spectra of the polymer crosslinked aerogels were obtained on a Bruker Avance-300 spectrometer with a 4 mm solids probe. Spectra were externally referenced to the carbonyl of glycine which appears at 176.1 relative to TMS.

**Preparation of di-isocyanate crosslinked aerogels.** Amine modified silica gels were produced as previously reported from TMOS and APTES in a 3:1 ratio in concentrations of 7, 18.6 or 30 v/v % total silane in CH<sub>3</sub>CN, noting that the use of amine-rich APTES eliminates the need for additional base catalysis.<sup>5</sup> The wet gels were washed 0, 2 or 4 times to wash away water and alcohol. To crosslink with isocyanate, the wet gels were placed in a di-isocyanate bath of concentrations of 7, 20 or 34% w/w for approximately 24 hours. Afterwards, the monomer solution was decanted, replaced with fresh acetonitrile, and allowed to react for 72 hours in a 71°C oven. At the end of the period, oven-cured gels were cooled to room temperature, and the solvent was replaced four times in 24 hour intervals to remove any un-reacted monomer from the mesopores of the wet gels. These gels were then dried using supercritical CO<sub>2</sub> extraction to give the resulting polymer crosslinked aerogel monoliths.

## Results and Discussion

A representative selection of CP-MAS C-13 NMR spectra of the aerogel monoliths are shown in Figure 1. All spectra show carbonyl peaks at 157 and 159 ppm for the carbamate and polyurea structures. In addition, one of the methylenes of APTES which is bonded to Si appears at 9 ppm (peak A). (The other two are hidden under other peaks.) The two methylenes that are bonded directly to nitrogen in each of the hexamethylene repeat units of N3200

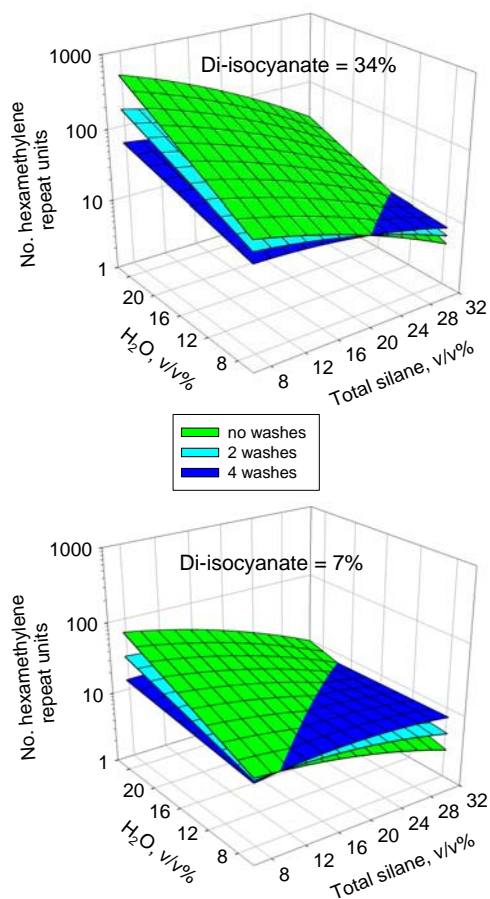


**Figure 1.** CP-MAS NMR of aerogels crosslinked with increasing chain the length of di-isocyanate crosslink from 3 (top) to 600 (bottom) hexamethylene repeat units.

appear at 41 ppm while the four other methylenes appear at 27 ppm (peak B). Other minor peaks (present in samples where water is at the lowest concentration and silane is high, especially with 0 washes) can be attributed to ethoxy and methoxy groups either attached to Si or at the end of dangling isocyanates. Peaks A and B if integrated one against the other in all spectra can be used to calculate the number of repeat units of di-isocyanate between APTES terminal groups, assuming one APTES at each end.

Empirical models were derived relating the number of repeat units from end group analysis to the four variables studied, starting with a full quadratic model and eliminating terms not deemed statistically significant (<90%

confidence) using a step-wise modeling technique. Graphs of the resulting models are shown in Figure 2 with di-isocyanate concentration held constant at 34% (top graph) and at 7% (bottom graph).



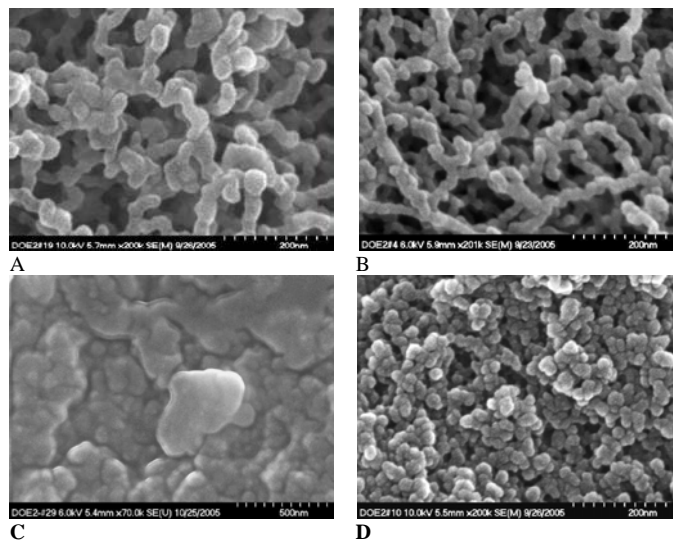
**Figure 2.** Empirically derived graphs showing number of repeat units as measured by end group analysis vs. total silane and water concentration where top, di-isocyanate is at a high concentration, and bottom at a low concentration.

From these graphs, it can be clearly seen that all four variables have a significant effect on the chain length of polymer crosslink present in the final aerogel monoliths. As seen by comparing Figure 2 top and bottom, not unexpectedly, using less concentrated di-isocyanate solutions produces shorter polymer crosslinks in all cases. At high silane concentration, this is even more pronounced, since the ratio of silane to polymer is even lower. More washing also reduces the size of the crosslinks.

The largest number of repeat units per APTES is obtained where total silane is at a low, water and di-isocyanate are high and the samples are not washed before soaking in polymer. The presence of excess water (obtained by either not washing or from high initial concentration) during polymerization of di-isocyanate facilitates the formation of amine, and hence more polyurea is formed. There is less of an effect on the number of washes when silane concentration is high and water concentration is at a low, presumably because there is not a lot of excess water present. Hence, it may be possible to eliminate washing steps by striking a balance between silane concentration and water in the initial sol. This will considerably shorten processing time to produce the polymer crosslinked aerogels as in the present process, each washing adds 24 hours.

A comparison of scanning electron micrographs (SEM) of selected samples shown in Figure 3 also gives insight into the crosslinking. Figures 3A and 3B show micrographs of monoliths produced at low concentrations of silane, water and di-isocyanate. The sample in Figure 3A was produced with no washes while 3B was washed four times before polymerization. There is

very little difference between the two micrographs, both clearly illustrating the pearl necklace structure of an aerogel coated with polymer and the presence of much mesoporosity (dark areas). In contrast, Figures 3C and 3D were both produced with high concentrations of silane, water and di-isocyanate, but C was produced with no washes and D with the maximum number of washes. The monolith in D, while a higher density aerogel than that shown in A or B, still shows a large amount of mesoporous structure whereas the part shown in C has very little porosity, having most of the void space filled with polymer.



**Figure 3.** SEM of crosslinked aerogels produced from low concentrations of water, di-isocyanate and silane with A) 0 washes, and B) 4 washes; and high concentrations of water, di-isocyanate and silane with C) 0 washes and D) 4 washes.

Clearly, initial silane, water and di-isocyanate concentration, and the amount of washing have a profound effect on the chemistry and nanostructure of the polymer crosslinked aerogel monoliths produced. Using a balanced amount of silane and water in the initial sol helps to shorten processing by reducing the number of washings necessary to produce a porous structure. Even more important is the effect of these processing parameters on properties such as thermal conductivity and strength. These measurements are in progress with the ultimate goal of producing polymer crosslinked aerogels with the desired combination of properties.

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