Chapter 3
Crosslinked Organic Inorganic Hybrid Networks Dried at Ambient Pressure

Ambient pressure drying techniques for the preparation of aerogel like highly porous networks has evolved into a process, competent enough to replace supercritical drying in recent years. Aging of the wet gel in a precursor solution leads to stiffening of the gel network, reducing shrinkage during drying. 

Modifying the gel surface with alkyl groups prevents condensation of silanol groups during drying and results in a spring back effect of the network, reversing the shrinkage during drying. Gels prepared from methyltrimethoxysilane can be dried at ambient pressure owing to this spring back effect. Coexisting organic inorganic hybrid networks have received considerable attention in recent years due to the increased mechanical strength observed in such systems.

Leventis prepared a polyurethane reinforced silica network by reacting the surface silanol groups of the wet gel with a diisocyanate. The properties of the final gel depend on their density, which in turn depended on the concentration of diisocyanate in the bath. Relative to native silica, composite aerogels shrink by up to 10-12% and they become up to ~3 times more dense and the shrinking was associated with cross-linking. A new material was seen introduced conformally to the secondary particles, but individual particles and the necklace-like structure remained. The mesoporosity reduced, as secondary particles appeared fused. It took more than 100 times higher load to break a monolith with density 0.447 gcm⁻³ than to break a native silica aerogel monolith. Wider interparticle necks formed from the accumulation of isocyanate increased the stiffness of the gels as well. By replacing the silanol species with an amine bearing alkyl group the isocyanate could be used to create a polyurea network. Since amines react with isocyanate faster than hydroxyls, crosslinking could be achieved at room temperature. The polymer conformally coats the surface of the skeletal nanoparticles, leaving the mesoporous voids open. The skeletal framework of APTES-modified aerogels also
allowed incorporation of larger number of particles than observed with typical native silica aerogels. The cross-linked samples had porosity in the order of 65%. The thermal diffusivity of a polyurea cross-linked APTES-modified aerogel was in the range of that of glass wool. The specific compressive stress at ultimate failure of these aerogels were in the same order of magnitude as poly(methyl methacrylate) (PMMA)20 and Kevlar-49 epoxy.12 The amine can also react with diepoxo bearing organic compound to give a crosslinked organic inorganic network.14 The diisocyanate crosslinking reinforces the underlying silica network by almost 300 times and enables drying at ambient pressure to obtain aerogel properties.15 These crosslinked aerogels were sensitive to the surface tension of the solvent and when submerged in low molecular weight, low surface tension hydrocarbons (e.g., pentane, hexane) suffer the least shrinkage, and a crosslinked aerogel soaked in pentane and subsequently re-dried at ambient pressure, retained the microstructure practically identical to that of another crosslinked monolith dried supercritically. Density, surface area, average pore diameter and rupture strength (by a three-point flexural bending test) of the of crosslinked aerogels dried at ambient pressure were identical to that dried supercritically. The dimensional stabilization gained by crosslinking was seen to depend on the amount of the crosslinker. Aerogels with density below 0.3 g cm\(^{-3}\) could not be dried at ambient pressure suggesting a threshold above which the total bond energy added per unit volume by crosslinking is greater than the energy that would be released by the collapse of the underlying plain silica framework. They were able to dry cross-linked hydrogels under ambient pressure with dimensions larger than what could be achieved by supercritical drying owing to the limitation in autoclave space.15 Nguyen recently experimented with the idea of unifying the concepts of flexible aerogels obtained by alkyl modification and conformal polymer coating obtained by crosslinking.6,10,16 Bis(trimethoxysilyl)hexane was used to induce flexibility and vinyl silane was used to create polymerisable group on the inorganic network. Styrene was polymerised with the vinyl group using AIBN initiator. It was found that incorporation of the hexyl links from BTMSH improved elastic recovery after
compression to 25% strain in the resulting monoliths. The inclusion of BTMSH also lead to more hydrophobic aerogels.\textsuperscript{16}

3-Glycidoxypropyltrimethoxysilane (GPTMS) is an important organically modified precursor that can crosslink through the polymerization of the epoxy group. Even though initial use for GPTMS was for enhancing moisture stability of glass-fiber-reinforced plastics, it also provides similar benefits in numerous applications where a metal oxide–adhesive interface needs improvement.\textsuperscript{17} Organic-inorganic polymer membranes were prepared by reacting 3-glycidoxypropyltrimethoxysilane with diamines containing polyether segments, followed by hydrolysis and condensation with acid catalysis for gas separation.\textsuperscript{18} Organic-inorganic hybrids derived from GPTMS have been as host materials for lithium salts for application as solid electrolytes.\textsuperscript{19} It has also been used to prepare optical waveguides by including zirconia and titania.\textsuperscript{20-22} Incorporation of fullerenes, infrared dyes and push pull chromophores has extended their use to optical limiting, and optical amplification applications.\textsuperscript{23-25} To improve energy conversion efficiency and to avoid CO poisoning of catalysts, polymer electrolyte-type fuel cells which can operate in the medium temperature range (100–200 °C) are strongly desired. Proton conductive inorganic–organic hybrid films with high proton conductivity, even at temperatures higher than 100 °C and at low humidity have been prepared from GPTMS for this purpose.\textsuperscript{26,27}

Epoxy groups of GPTMS react to form polyethylene oxide (PEO) chains via photo or thermal induced polymerization or via basic or acid catalysis.\textsuperscript{28-30} Many of the compounds used as initiators of organic polymerization often act, at the same time, as catalysts of the siloxane polymerization. 1-methylimidazole and (\textgreek{gamma}-aminopropyl)triethoxysilane are examples of basic catalysts.\textsuperscript{19,31} These compounds act at the same time as catalysts of the siloxane polymerization. Lewis acids, such as titanium, zirconium, or aluminum alkoxides, are also efficient initiators of organic polymerization.\textsuperscript{21,32,33} These alkoxides, cohydrolyzed, with GPTMS will be incorporated into the silicon-based inorganic network. BF\textsubscript{3} etherate has also been used in the synthesis of GPTMS-derived hybrid materials that can act as a host for fullerene derivatives to
fabricate an optical limiting device. BF$_3$ can also promote the inorganic polymerization to a larger extent compared to other metal alkoxides. An important point in the synthesis of this class of hybrids is related to the effect on the PEO chain lengths of the simultaneous organic and inorganic polymerization. For example, larger amounts of BF$_3$ enhance the inorganic network crosslinking and give oligo(ethylene oxide) derivatives. Boron has been found to remain in the matrix as a network former of the inorganic side. If the silica network is formed much faster than the organic polymer, the organic chains cannot find enough space to grow and their length is greatly reduced. Diethylenetriamine is a very fast and reactive epoxy-ring opening reagent and most of the organic network is completed at room temperature. Since the amines are basic, they also catalyse the condensation of silanol groups to form the silica network. Davis et al developed epoxy-based inorganic–organic hybrid polymers, for use as a matrix in coatings, starting from 3-glycidoxypropyltrimethoxysilane by a sol–gel process. Diethylenetriamine was used to open the epoxy rings and form the organic network and the results indicated that the formation of the two networks did not occur independently and the rate or extent of organic cross-linking had a direct effect on the extent of the inorganic network formation, and vice-versa.

These studies had shown that sol-gel hydrolysis, condensation reactions of glycidoxypropyltrimethoxysilane can proceed without causing the epoxy ring opening. This gives considerable leverage in the preparation of porous hybrids. Surprisingly there is little information available on the use of this precursor in the preparation of cross linked porous systems. Husing had earlier used it as a co-precursor to obtain organically modified aerogels through supercritical drying.

Extending the findings from the first chapter here we have investigated the preparation of porous hybrid networks from 3-glycidoxypropyltrimethoxysilane and tetraethoxysilane precursors and their drying at ambient pressure. The ambient pressure drying technique presented in the first chapter is utilized for the drying of the hybrid networks. Considering the facts that glycidoxypropyltrimethoxysilane is frequently reported for the preparation of dense organic inorganic hybrids and as binders in coatings
and also considering the fact that hydrolysis-condensation reactions of alkyl substituted alkoxides preferentially give cyclic structures, increasing gelation times and inducing phase separation in mixed alkoxide systems, the right balance of precursor ratio and control of hydrolysis-condensation reactions are required to obtain highly porous organic inorganic hybrid systems. Hence the effect of water molar ratio used for hydrolysis of the alkoxide groups and the effect of varying the molar ratio between the organically modified precursor and the inorganic precursor is investigated. Further the the nature of the organic network is also varied by adding a crosslinker diepoxyoctane. The crosslinker provides a way to develop an organic network which has less anchorage to the inorganic network. Here the network should be flexible and the influence of increasing the extent of this network is also investigated. The nature of the organic networks formed at various organic content is also investigated using Fourier Transform Infrared Spectroscopy.

Experimental

3-glycidoxypropyltrimethoxysilane (GPTMS), tetraethyloxysilicate (TEOS) 1,2,7,8 diepoxyoctane (DEO) and diethylenetriamine (DETA) were procured from Aldrich (Steinheim, Germany) and used as obtained. Isopropyl alcohol and hydrochloric acid were obtained from S.D. Fine chemicals (Mumbai, India). Water used for the preparation was doubly distilled. In a typical preparation, weighed amounts of GPTMS and TEOS were mixed with weighed quantity of isopropanol by stirring on a magnetic stirrer. To this solution weighed amount of 10⁻³ N HCl was added. The initial water content is the amount of the acid taken for the preparation of the gel. The solution was stirred for 3 hours. Weighed amount of DETA was then added to this solution under stirring. In samples prepared with a crosslinking agent DEO was added prior to DETA. After stirring for 5 minutes the solutions were transferred to polypropylene vials. The vials were kept at 50 °C for gelation. Gelation occurred within 30 minutes for all samples. DETA catalyzes the organic networking through a nucleophilic attack on the epoxy ring. The GPTMS/DETA molar ratio was fixed at 3 for all preparations. In crosslinked samples DEO/GPTMS molar ratio was varied. Gels were prepared with
varying precursor (TEOS/GPTMS) molar ratio and initial water content. Samples with precursor molar ratio of 3, 2, 1 and 0.5 were prepared. Initial water content was varied according to H$_2$O/OR molar ratio of 0.5, 1 and 2. Samples with crosslinker were prepared with crosslinker ratio (DEO/GPTMS) 0.25, 0.5, 1 and 1.5. Samples with crosslinker were prepared only for the precursor ratio 2 and water ratio 0.5. So a sample with crosslinker of 1 contained an organic network equivalent to the sample with precursor ratio 1 without any crosslinker, but an inorganic network equivalent to the precursor ratio 2, i.e. the organic network is increased independent of the inorganic network.

A mole of alkoxy group requires 0.5 mole water for complete hydrolysis and condensation according to the stoichiometry of the equation.

\[
\text{Si(RO)}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{ROH}
\]

In practice complete hydrolysis may require more water and an H$_2$O/OR molar ratio of 1 represent the availability of a water molecule for each Si-OR bond. Use of excess water for hydrolysis is represented by the molar ratio of 2. Gels are designated as xPyWzCwd, where ‘x’ is the precursor molar ratio and ‘y’ is the H$_2$O/OR molar ratio, ‘z’ is the DEO/GPTMS molar ratio and ‘d’ is the fixed density for the rest of the text. Only for samples prepared with a fixed density is the notation d included in the designation. The isopropanol/Si molar ratio was either kept constant at 4 or evaluated to fix the final density of the gel.

The theoretical densities of the gels are calculated by assuming that the gel network is formed from SiO$_2$, RSiO$_{1.5}$, DEO (if crosslinker present) chains and DETA becomes part of the network. So the dried gel consists of only SiO$_2$, RSiO$_{1.5}$, DEO and DETA. So the weight of the dried gel network will be

\[
W_{\text{gel}} = n_{\text{TEOS}} \times M_{\text{SiO}_2} + n_{\text{GPTMS}} \times M_{\text{RSiO}_{1.5}} + n_{\text{DEO}} \times M_{\text{DEO}} + n_{\text{DETA}} \times M_{\text{DETA}}
\]

The volume of the gel will be the total volume of all the components used, assuming that there will be no change in volume after drying.

\[
V_{\text{gel}} = V_{\text{TEOS}} + V_{\text{GPTMS}} + V_{\text{DEO}} + V_{\text{DETA}} + V_{\text{Alcohol}} + V_{\text{Water}}
\]

and the calculated density of the gel will be

\[
\rho_{\text{gel}} = \frac{W_{\text{gel}}}{V_{\text{gel}}}
\]
So if the density of the final gel needs to be fixed keeping all other variables like precursor ratio, water ratio, crosslinker ratio etc constant, the alcohol volume needs to be changed. Volume of alcohol is calculated as

\[ V_{\text{alcohol}} = \frac{W_{\text{Gel}}}{\rho_{\text{Gel}}} - (V_{\text{TEOS}} + V_{\text{GPTMS}} + V_{\text{DEO}} + V_{\text{DETA}} + V_{\text{Water}}) \]

The density were fixed for a set of samples with precursor ratio 2 and water ratio 0.5 prepared without the crosslinker. The densities were fixed as 0.16, 0.2 and 0.25. All samples with crosslinker were prepared by fixing the density at 0.187. This is the density calculated for the gel prepared with (TEOS/GPTMS) ratio of 2 and a water ratio of 0.5. The density of crosslinked samples was fixed at this value so that the effect of increasing the organic network independent of inorganic network can be followed.

Scheme 3.1. Synthesis scheme for the crosslinked hybrids

The alcogels were aged in water for a period of 24 hours followed by solvent exchange with isopropanol. In order to exchange the solvent, the gels were immersed in isopropanol and the solution replaced with fresh alcohol, 5 times in 24 hours. The solvent exchanged gels were then aged in a solution of 50% TEOS in isopropanol for a period of 48 hours. The silane aged gels were washed with n-hexane following the same procedure.
used for solvent exchange. In all the steps the soaking solutions had volume twice as that of the gels immersed in them. The gels were then kept for drying in sealed containers at 70 °C. The container seals were perforated with pins after a day for the solvent to escape slowly. The dried gels were used for further characterization. The procedure is presented as scheme 3.1.

The bulk density of the dried gels was calculated from the measured dimensions and weight. Thermal analysis of the gels were performed on a Thermogravimetric analyzer (Shimadzu TG 50, Kyoto, Japan) and a Differential thermal analyzer (Shimadzu DTA 50, Kyoto, Japan) in air at a heating rate of 5 °C/min. A Fourier Transform Infrared Spectroscope (Magna 560, Nicolet, Madison, Wisconsin) was used for recording the FTIR spectra of the sample. The spectra were acquired using the KBr pellet method in the range 4000-400 cm⁻¹. The samples were stored in an oven maintained at 70 °C and care was taken to avoid excessive exposure to atmosphere prior to measurement. The precautions prevent interference of humidity in the measurements. The Fourier Self Deconvolution Trace analysis was carried out using the Omnic software provided by the manufacturer on the spectra obtained for the crosslinked samples. For Fourier trace analysis the samples were degassed in flowing Nitrogen at 150 °C for 4 hours prior to taking FTIR. Nitrogen adsorption data were obtained using a BET surface area analyzer (Gemini 2375, Micromeritics, Norcross, U.S.A) at 77 K. All analysis were conducted after degassing the sample at 150 °C for 6 hours. The pore size distributions were calculated using the Barrett Joiner-Halenda (BJH) method from the desorption curve of the isotherm. The calculations were performed by the software StarDriver V2.03 supplied by the manufacturer. The BJH average pore radius was calculated using the equation (2V/A), where V is the BJH desorption total pore volume and A is the specific surface area. Skeletal density measurements were performed on a He pycnometer (Accupyc, Micromeritics, Norcross, U.S.A). The samples were heated at 100 °C for 24 hours prior to measurements. TEM observations were made on a FEI high-resolution transmission electron microscope (Technai 30 G2 S-TWIN, Eindhoven, Netherlands). Dielectric measurements were done on pellets prepared by polishing dried gel rods. Silver paste was
used for preparing the electrodes and copper leads for contact. The measurements were made on a HP impedance analyzer HP 4192 A. Temperature dependence of dielectric property was studied by heating the samples to the respected temperature and measuring the dielectric constant.

Results and Discussion

The success of the drying technique is evident from figure 3.1. The figure shows a sample with low shrinkage along with the wet gel. Figure 3.2. includes most of the samples prepared along with the pellets used for dielectric measurements.

![Images of dried and wet gel](image)

*Figure 3.1.:Photograph of (a) dry (b) wet gel prepared at a precursor ratio 2 and water ratio 0.5*

The characterization of the samples prepared without the crosslinker will be discussed first. The structural characteristics of the hybrids were investigated using FTIR spectroscopy. The FTIR peaks were assigned based on available literature. The FTIR spectra of the samples with varying precursor ratio, without any crosslinker, in the region 4000 cm\(^{-1}\) to 3500 cm\(^{-1}\) are provided as figure 3.3.
Figure 3.2.: Photographs of dried gels with precursor ratio (a) 1 (b) 2 (c) 3 (d) 2 (e) 2. Numbers represents the water ratios used (1) 2 (2) 1 (3) 0.5. In (e) crosslinker ratio increases as 0.25, 0.5, 1 and 1.5 from right to left. (d) is prepared by fixing the target density and it increases as 0.16, 0.2 and 0.25 from left to right.

Figure 3.3.: FTIR spectra of samples prepared with a precursor ratio of (a) 2 (b) 1 and (c) 0.5 and water ratio of 0.5 in the region 4000 cm\(^{-1}\) to 3500 cm\(^{-1}\).

The broad absorption centred on 3400 cm\(^{-1}\) is due to the OH groups in the sample.\(^{39}\) The strong absorption around 2900 cm\(^{-1}\) is due to the alkyl hydrogen, which are
part of the organic network, stretching vibrations.\textsuperscript{40,41} The increase in intensity of the C-H stretch is proportional to the GPTMS content in the sample. But the intensity of the hydroxyl absorption for the samples with TEOS/GPTMS molar ratio 2 and 1 are comparable, while there is a much higher absorption when the ratio decreases to 0.5.

The absorption of the samples in the IR region 1800 cm\(^{-1}\) to 400 cm\(^{-1}\) is given in figure 3.4. The absorption at 1650 cm\(^{-1}\) is due to the bending vibrations of adsorbed water.\textsuperscript{41} The peak around 1460 cm\(^{-1}\) is the bending vibrations of the CH bonds of the alkyl groups in the organic network. The Si-O-Si asymmetric stretching vibration absorbs intensely around 1100 cm\(^{-1}\) and can be seen as a strong and broad band in this region.\textsuperscript{39,41-44} The small shoulder to this peak at 950 cm\(^{-1}\) is due to the asymmetric stretching vibrations of Si-OH groups.\textsuperscript{39,41,42,44,45} It can be seen that when the molar ratio of GPTMS in the sample increases, the Si-O-Si stretching vibrations split indicating the presence of hybrid structures.\textsuperscript{45}

\begin{center}
\textbf{Figure 3.4.: FTIR spectra of samples prepared with a precursor ratio of (a) 2 (b) 1 and (c) 0.5 and water ratio of 0.5 in the region 1800 cm\(^{-1}\) to 400 cm\(^{-1}\)}
\end{center}

The asymmetric C-O-C stretching vibration of the ether linkage in the organic network also absorbs in this region, 1150-1085 cm\(^{-1}\).\textsuperscript{40} The absorption due to the Si-OH bond
stretches weakens as the molar ratio of GPTMS increases in the sample. The symmetric Si-O-Si stretching vibrations are visible at 785 cm\(^{-1}\).\(^{41,42,44,45}\) The O-Si-O stretching vibrations can be observed at 575 cm\(^{-1}\) and 455 cm\(^{-1}\).\(^{41,42,44,45}\) The out of plane bending of the C-O-H group is observed at 687 cm\(^{-1}\).\(^{46}\) It can be seen that this peak shows a significant increase in intensity when the precursor molar ratio is 0.5. The epoxy ring breathing vibrations appear as sharp absorptions at 1250 cm\(^{-1}\) and asymmetric ring stretch around 850 cm\(^{-1}\) region.\(^{40}\) The absence of these bands in the hybrid confirms the complete opening of the epoxy rings. Figure 3.5. presents the FTIR spectra of samples prepared at a precursor ratio of 0.5 and water ratios of 0.5 and 2. There is no significant change in the spectra when the water ratio used for hydrolysis is varied.

![FTIR spectra](image)

**Figure 3.5.: FTIR spectra of samples prepared with a precursor ratio 0.5 and water ratio (a) 2 (b) 0.5**

Adsorbed water is a major source of OH vibrations in porous materials. In the investigated systems, the DTA curves (discussed later) do not show the pronounced endotherm near 100 °C usually observed for adsorbed water. Moreover, it can be seen that the hybrid with precursor ratio 0.5 has the lowest surface area for all initial water content and have intensity of hydroxyl stretching frequency considerably higher compared to the 1 and 2 precursor ratio hybrids. This is evidence to the fact that adsorbed
water is not the major contributor to the observed hydroxyl stretching frequency. The epoxy polymerization is initiated by the nucleophilic attack of the catalyst on the epoxy carbon and the nucleophilic oxygen of the epoxide ring attack another epoxy carbon propagating the chain. A hydroxyl group will result when the epoxide ring cleaves and the oxygen takes up a proton instead of attacking another epoxy group leading to the termination of the chain. In presence of proton donors this is a highly probable mechanism of chain termination. This is presented in scheme 3.2. But the increase in hydroxyl absorption is not proportional to the GPTMS concentration. This would mean that the 0.5 molar ratio hybrids are characterized by organic network with shorter chains, more terminated ends. The COH bending vibration at 687 cm$^{-1}$ also show considerable increase in intensity when the precursor ratio changes from 1 to 0.5. The hybrids with precursor ratio 2 and 1 have almost the same intensity for these vibrations supplementing the above discussion.

\begin{center}
\textbf{Scheme 3.2.: Termination of epoxy polymerization}
\end{center}

Increasing the GPTMS molar ratio to 1, results in the incorporation of the glycidoxypropyl groups into the organic network without much termination or rather linear chains of higher molecular weight are formed. The epoxy ring opening is expected to continue beyond 24 h and this would mean that the epoxy polymerization will continue even after gelation in this case.\textsuperscript{47} Hence a TEOS/GPTMS molar ratio of 1 seems to form a gel structure where the glycidoxypropyl groups are ideally placed for the epoxy polymerization to proceed unhindered. Further increase in the concentration of GPTMS
results in a crowding of glycidoxy groups in the pores and together with the constraints imposed by the rigid gel network results in shorter chains.

Figure 3.6: FTIR of sample with precursor ratio 2, water ratio 0.5 and crosslinker ratio 1.5

In order to perform the Fourier Self Deconvolution, the FTIR spectra of the crosslinked samples were taken in the absorbance mode and all FTIR spectra of crosslinked samples are presented in the absorbance scale. The Si-O-Si asymmetric stretch is the most intense of the bands and always has the highest intensity. So all bands were normalized against this band for better comparison. The FTIR spectrum of sample with crosslinker ratio 1.5 is shown in the figure 3.6. The spectrum contains peak due to both silica network and alkyl group from cross linker and glycidoxypropyl group. The broad peak observed around 3500 cm\(^{-1}\) is due to the stretching vibration of hydroxyl group. The peak around 2850 cm\(^{-1}\) corresponds to alkyl (C-H) stretching vibration of GPTMS and DEO. A sharp peak observed at about 1660 cm\(^{-1}\) is accounted for the bending vibration of adsorbed water. The alkyl hydrogen bending bands can be observed around 1460 cm\(^{-1}\). The broad and intense band observed around 1090 cm\(^{-1}\) contains the fundamental Si-O-Si stretching vibration of the silica network. The C-O-C vibration due
to the ether linkage in the glycidoxypropyl group is also expected in this region. Due to its very low intensity compared to the absorption due to the silica network this peak cannot be identified. The shoulder peak at 962 cm\(^{-1}\) is due to the Si-OH stretching vibrations. Another fundamental vibration of the Si-O-Si network is found at 796 cm\(^{-1}\). Absorption at 457 cm\(^{-1}\) and 569 cm\(^{-1}\) is due to the O-Si-O bonds. The peak at 687 cm\(^{-1}\) out of plane bending of the C-O-H group is rather weak to observe in the absorbance scale. From the 4000-3000 cm\(^{-1}\) region of the spectra, figure 3.7, we can observe that when the crosslinker ratio increases there is a corresponding increase in the alkyl stretching frequency. Again, this type of behaviour is not observed in the case of hydroxyl stretching frequency. Like in the case of non cross linked samples, the analysis of the OH stretching frequency can provide valuable insights to the nature of the organic network formed at various crosslinker concentrations. In order to give more evidence to the arguments in the case of non crosslinked samples we performed Fourier Self Deconvolution (FSD) on the FTIR spectra of crosslinked samples. The samples were degassed for 4 hours at 150 °C in flowing N\(_2\) atmosphere prior to performing the FTIR measurements. The results are shown in figure 3.8.

![Figure 3.7: Alkyl hydrogen stretching absorptions of samples with precursor ratio 2, water ratio 0.5 and crosslinker ratio (a) 1.5 (b) 0.5 (c) 0.25](image)

*Figure 3.7: Alkyl hydrogen stretching absorptions of samples with precursor ratio 2, water ratio 0.5 and crosslinker ratio (a) 1.5 (b) 0.5 (c) 0.25*
Figure 3.8.: **Fourier Self Deconvolution Trace analysis on the 4000-3000 cm\(^{-1}\) region of the FTIR spectra of crosslinked samples and silica gel**

The most significant contributions to the broad peak corresponding to the OH stretching in the silica sample come from six different peaks. This is in accordance with reported literature and a comprehensive discussion of various silanol groups responsible for these peaks can be seen in the review by Nawrocki.\(^{48}\) The peak around 3790 cm\(^{-1}\) is due to the isolated silanol groups. Three hydrogen bonded silanol species are identified and they appear at 3630, 3450 and 3250 cm\(^{-1}\). The adsorbed water gives rise to the peak at 3080 cm\(^{-1}\). The peak at 3900 cm\(^{-1}\) is also due to surface silanols but the exact nature of the silanol groups is still under debate. In the hybrid samples it is evident that the silanol groups have disappeared and new peaks have formed. The silanol peak at 3900 and 3790 cm\(^{-1}\) are fingerprints for silanols and appear in the same region for all silica. The absence of these peaks is used as confirmation for the absence of silanol group. Hydrogen bonded COH groups are reported to appear in the 3600-3220 cm\(^{-1}\) region as observed in our spectra. So we can conclusively say that the hydroxyl absorption arise from the COH groups formed during the polymerization of the epoxy group in these hybrids. The adsorbed water must have arisen from the KBr used for the preparation of the pellets.
since the samples were heat treatment prior to measurements. Even then its contribution is very low to the total hydroxyl peak.

Figure 3.9. shows the spectra of hybrids with different crosslinker ratios in the 4000-3000 cm\(^{-1}\) region. From the figure we can see that the intensity of hydroxyl stretching frequency is maximum for the crosslinker ratio 0.25. When the ratio increases to 0.5 the intensity of the hydroxyl stretching decreases, which indicates that the added DEO is incorporated into the organic network and the organic chains become more networked by the addition of DEO. This continues with the addition of DEO up to the molar ratio of 1. But, when the crosslinker ratio increases to 1.5, the intensity of hydroxyl stretching increases. So further increase in DEO no longer results in linear networking and rather a fragmentation of the network occurs. Localized network of polymer chains with lower molecular weight is formed.

Figure 3.9.: The FTIR spectra of crosslinked samples in the region 4000-3000 cm\(^{-1}\)

The differential thermal analysis curves for various samples are provided in figure 3.10. The DTA patterns for the samples are similar and the decomposition of the organic network, observed as an exothermic peak occurs in a broad range from 210 °C to 480 °C. Markedly the endothermic peak usually observed for porous silica close to 100 °C is very
weak for all samples indicating that the amount of adsorbed water in the samples are very small.

Figure 3.10.: DTA curves of samples prepared with precursor ratio (a) 0.5 (b) 1 and (c) 2 and water ratio of 1

The thermogravimetric analysis of the samples is provided in figure 3.11. The weight loss pattern is similar for all the gels. Initial water content has no influence on the weight loss. TG curve of the hybrids contains a two step weight loss. The smaller first step extending up to 150 °C indicate the removal of volatilities like drying solvent and corresponds to a weight loss of about 6% in all the samples. The extensive organic networking in the samples imparts hydrophobic nature to the gel surface which must have resulted in the gel surface retaining some amount of the drying solvent. The total weight loss depends on the amount of organically modified precursor in the gel. There is no weight loss above 600 °C for all samples.

Based on the following assumptions the weight loss due to the decomposition of the organic network in different hybrids can be calculated.

1) Only SiO$_2$ is present above 700 °C.
2) The organic network dissociates from the inorganic network by the cleavage of the Si-C bond.
3) The weight loss due to the removal of the organic network occurs only in the second step i.e. above 150 °C.

4) DETA is removed during the thermal decomposition.

![TG curves of samples with precursor ratio (a) 0.5 (b) 1 and (c) 2, water ratio (▲) 0.5, (●) 1 and (⊗) 2](image)

Figure 3.11.: TG curves of samples with precursor ratio (a) 0.5 (b) 1 and (c) 2, water ratio (▲) 0.5, (●) 1 and (⊗) 2

The results obtained are compiled in table 3.1. The calculated weight loss values are higher than the observed weight loss indicating that a part of the organic precursor is excluded from the gel. The difference between the calculated weight loss and the observed weight loss increases as the concentration of GPTMS increases in the hybrid. During aging of the gels in water, the formation of a jelly mass around the gels was observed, which was washed clean before the solvent exchange step. This was observed for all gels prepared. Assuming that the difference in weight loss corresponds to washing off of GPTMS and the corresponding amount of DETA, this would mean that for an initial precursor molar ratio (TEOS/GPTMS) of 2 approximately 75 % and for the ratio of 1, 70 % and for the ratio of 0.5, 65 % of GPTMS gets incorporated into the gel network.

The DTA patterns of the gels containing the crosslinker are provided as figure 3.12. and contain strong exothermic peak spanning a wide region of 220 – 420 °C, similar to that observed for the gels without the crosslinker. The exotherm becomes more
resolved in higher molar ratio hybrids. Maxima at 260 °C and 400 °C can be distinguished. The endotherm observed for the weight loss around 150 °C is very weak. This clearly indicates that the volatiles contain only low vapour pressure solvents, since they have small heat of vaporisation.

![Figure 3.12. DTA of sample with precursor ratio 2, water ratio 0.5 and crosslinker ratio (a) 1.5 (b) 1 (c) 0.25](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calculated Weight loss (%)</th>
<th>Observed Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Corresponding to removal of Organic network</td>
<td></td>
</tr>
<tr>
<td>2P1W</td>
<td>46.5</td>
<td>34.1</td>
</tr>
<tr>
<td>1P1W</td>
<td>59.7</td>
<td>42.9</td>
</tr>
<tr>
<td>0.5P1W</td>
<td>72.3</td>
<td>46.4</td>
</tr>
<tr>
<td>0.5P2W</td>
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<td>46.9</td>
</tr>
<tr>
<td>0.5P0.5W</td>
<td>71.8</td>
<td>46.1</td>
</tr>
</tbody>
</table>

*Table 3.1.: Weight loss corresponding to the removal of organic network, observed and calculated from thermo gravimetric curves*
Thermal analysis curves obtained for the crosslinked hybrids are given in figure 3.13. The TG patterns are similar to that observed for the samples without crosslinker and has a continuous weight loss up to around 620 °C. There are two distinct regions for the weight loss pattern. A small weight loss up to around 10% can be observed in the temperature regime 50-150°C due to the removal of volatiles like drying solvent. The weight loss from 150 °C to 620 °C is due to the removal of the organic network in the gel. A change in slope can be observed along this weight loss region. This happens above 400 °C and can be an indication of the organic networking being removed in two separate stages.

The standard bond energy for Si-C bond is 76 kcalmol⁻¹, C-C is 83 kcalmol⁻¹ and C-O-C is 85.5 kcalmol⁻¹.⁴⁹ The evidence point to the fact that during thermal decomposition, the organic network breaks off from the inorganic network followed by the decomposition of the organic chains. The smaller fragments of the organic chain containing the ether linkages will decompose at higher temperatures. So during thermal decomposition, initially the organic network separates from the inorganic network and organic network decomposes through the temperature interval.
The adsorption isotherms of the gels prepared with varying precursor ratio at the same water ratio is provided as figure 3.14. The gels are all mesoporous as evident from the hysteresis loop. There is a gradual change in shape of the loop as the precursor ratio decreases. So there is a gradual change in shape of the pores from smooth pores, to necked pores as precursor ratio decreases. The change in water ratio does not change the pore structure of a particular precursor ratio hybrid as can be seen from figure 3.15. So the pore structure, particularly towards the larger radius end of the pore size distribution is strongly influenced by the precursor ratio.

The BET surface area analysis of the samples is provided in table 3.2. The lower surface area values indicate the presence of the organic network on the pore walls of the hybrids. The presence of organic groups on the surface prevents N\textsubscript{2} adsorption, lowering the surface area. The influence of initial water content on surface area is more pronounced for the precursor ratio 2. Similar influence is observed for the pore volume and pore radius. Total pore volume does not differ significantly when the precursor ratios are less than 2. The average pore radii are also close for these hybrids. The hybrids with precursor ratio 2 have C parameter in the range of 60 while other hybrids have the value
close to 50, suggesting that the former has a higher hydrophilic nature due to the lower organic content. The hybrids prepared with the precursor ratio 2 have the larger pore volumes. Higher surface area is obtained when the contribution to pore volume is higher from pores with smaller pore radius. The BJH pore size distribution obtained for the hybrids are given as figure 3.16. The BJH pore size distribution curves show that the distribution stretches to a larger interval when the precursor ratio is 2. The distribution shifts to lower pore sizes when the water content increases. The pore size distribution curves are narrow for the precursor ratio 0.5 and 1 compared to that of 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific Surface Area (m²g⁻¹)</th>
<th>C parameter</th>
<th>Total Pore Volume (cm³g⁻¹)</th>
<th>Average pore radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2P0.5W</td>
<td>179</td>
<td>63.59</td>
<td>0.7876</td>
<td>8.8</td>
</tr>
<tr>
<td>2P1W</td>
<td>251</td>
<td>61.72</td>
<td>0.7154</td>
<td>5.7</td>
</tr>
<tr>
<td>2P2W</td>
<td>331</td>
<td>59.78</td>
<td>0.4965</td>
<td>3.0</td>
</tr>
<tr>
<td>1P0.5W</td>
<td>268</td>
<td>46.07</td>
<td>0.4288</td>
<td>3.2</td>
</tr>
<tr>
<td>1P1W</td>
<td>273</td>
<td>51.74</td>
<td>0.4368</td>
<td>3.2</td>
</tr>
<tr>
<td>1P2W</td>
<td>303</td>
<td>47.80</td>
<td>0.4998</td>
<td>3.3</td>
</tr>
<tr>
<td>0.5P0.5W</td>
<td>151</td>
<td>50.9</td>
<td>0.2492</td>
<td>3.3</td>
</tr>
<tr>
<td>0.5P1W</td>
<td>153</td>
<td>51.91</td>
<td>0.2907</td>
<td>3.8</td>
</tr>
<tr>
<td>0.5P2W</td>
<td>169</td>
<td>50.77</td>
<td>0.2788</td>
<td>3.3</td>
</tr>
</tbody>
</table>

*Table 3.2.: BET analysis of the hybrid samples*
Figure 3.15.: Adsorption isotherms of gels with precursor ratio (a) 0.5 (b) 1 (c) 2 and water ratio 2

Figure 3.16.: BJH pore size distribution curves (dV/dlogR) of samples with precursor ratio (a) 2 (b) 1 and (c) 0.5 and initial water ratio (■) 0.5 (○) 1 and (▲) 2
The adsorption isotherms of samples prepared with highest and lowest crosslinker ratio is provided as figure 3.17. The adsorption isotherms are similar to that obtained for the samples prepared at the same precursor ratio (2) and water ratio (0.5), but without crosslinker. So the pores are smooth for the samples with the crosslinker. The pore structure is governed by the organic part which is directly linked to the inorganic network. Further crosslinking of the network does not influence the pore structure. The BET analysis and the total pore volume data obtained for the hybrids are provided as table 3.3. Adding to the above discussion it can be seen that the average pore radius is almost same as the one obtained for the sample with the same precursor ratio and water ratio, but without the crosslinker. The average surface area decreases as the organic content increases in the sample. Total pore volume can also be seen to decrease with the increase in organic content. This is similar to the trend observed for the samples without the crosslinker. But smaller pore volumes are obtained for the hybrid samples without the crosslinker, but with similar organic content, for example (sample with crosslinker ratio 1 and hybrid sample with precursor ratio 1). This would also mean that the organic network in the hybrid without crosslinker is formed close to the inorganic surface, while using a
crosslinker provides a network that is flexible or is rather a loose cover for the inorganic network.

Meador et al, working with supercritically dried epoxy crosslinked aerogels, found that the epoxy crosslinker with a tri-epoxy functionality gives the aerogels with better mechanical strength compared to di-epoxy functionality. From the present results it can be seen that as the organic network becomes closely linked to the inorganic network, then the best results in terms of mechanical strength is achieved. Meador used an amine modified silica surface to crosslink using the epoxy crosslinker. So a trifunctional crosslinker allows three linkages to the inorganic network compared to two in the case of the diepoxy. In the present case, the organic network is intimately bound to the inorganic network, in the absence of crosslinker since every organic chain is anchored to the inorganic network.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific Surface Area (m²g⁻¹)</th>
<th>C parameter</th>
<th>Total Pore Volume (cm³g⁻¹)</th>
<th>Average pore radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25C</td>
<td>171</td>
<td>57</td>
<td>0.7267</td>
<td>8.5</td>
</tr>
<tr>
<td>0.5C</td>
<td>161</td>
<td>51</td>
<td>0.6698</td>
<td>8.3</td>
</tr>
<tr>
<td>1.0C</td>
<td>147</td>
<td>46</td>
<td>0.6057</td>
<td>8.2</td>
</tr>
<tr>
<td>1.5C</td>
<td>135</td>
<td>43</td>
<td>0.5570</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Table 3.2: BET analysis of crosslinked samples

Desorption pore size distribution curves obtained for the crosslinked samples are provided as figure 3.18. The identical nature of the distribution to that obtained for the samples with the same precursor ratio and water ratio is evident. The distributions span similar regions. There is a slight decrease in distribution towards larger pore radii compared to their non crosslinked counterparts. The distribution is similar for all crosslinker ratios and the difference is in the volume. The volume decreases with the increasing crosslinker.
Figure 3.16.: BJH pore size distribution curves ($dV/d\log R$) of samples with precursor ratio 2, water ratio 0.5 and crosslinker ratio (a) 0.5 (b) 1 and (c) 1.5

Bulk density of the samples without crosslinker is plotted against the initial water content in figure 3.17. The bulk density of the samples relies heavily on the proportion of the organic content. When the molar ratio of GPTMS increases in the sample there is a corresponding increase in the bulk density. While the samples prepared with a TEOS:GPTMS molar ratio of 2:1 have density in the range 0.3 to 0.4, it is between 0.5 to 0.6 when the ratio is 1:1 and the density is between 0.7 and 0.8 when the ratio becomes 1:2. On the other hand when the initial water content increases, density of the dry gel also increases. But the effect of water content on the density is very less compared to the precursor ratio. The density calculated for the gels prepared without crosslinker and that actually measured from the dimensions of the dry gel is provided as table 3.3. Two immediate observations can be made. When the precursor content increases the calculated density increases. But when water content increases the calculated density decreases. The increase in density with water content can then be due to an increased shrinkage arising from the low density of the network.
Figure 3.17.: Bulk density of samples with precursor ratio (a) 0.5 (b) 1 (c) 2 and (d) 3 plotted against initial water ratio

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho$ (Calc.)</th>
<th>$\rho$ (Obs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p3r.5c0</td>
<td>0.168</td>
<td>0.22</td>
</tr>
<tr>
<td>p2r.5c0</td>
<td>0.188</td>
<td>0.3</td>
</tr>
<tr>
<td>p1r.5c0</td>
<td>0.227</td>
<td>0.52</td>
</tr>
<tr>
<td>p3r1c0</td>
<td>0.158</td>
<td>0.22</td>
</tr>
<tr>
<td>p2r1c0</td>
<td>0.177</td>
<td>0.34</td>
</tr>
<tr>
<td>p1r1c0</td>
<td>0.215</td>
<td>0.56</td>
</tr>
<tr>
<td>p3r2c0</td>
<td>0.142</td>
<td>0.33</td>
</tr>
<tr>
<td>p2r2c0</td>
<td>0.16</td>
<td>0.49</td>
</tr>
<tr>
<td>p1r2c0</td>
<td>0.195</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 3.3.: Density of samples without crosslinking agent

In order to verify this, a series of gels were prepared with varying calculated density keeping the water ratio and precursor ratio constant. The values are provided in table 3.4.
The observed density of the gels increases with the target density. So, increasing the target density cannot make a difference in ambient pressure drying. The effect of increasing wet gel density on shrinkage during drying is too small compared to the increased weight acquired due to the added solid content. So the dry gel density is rather determined by the chemical nature of the gel structure. So the increase in density in the case of increasing water content must then be due to some other factor that has been overlooked.

Similar tabulation has been done for samples with the crosslinker and is provided as table 3.5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \rho ) (calc.)</th>
<th>( \rho ) (Obs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p2r.5c0d.16</td>
<td>0.16</td>
<td>0.29</td>
</tr>
<tr>
<td>p2r.5c0d.18</td>
<td>0.188</td>
<td>0.3</td>
</tr>
<tr>
<td>p2r.5c0d.2</td>
<td>0.2</td>
<td>0.31</td>
</tr>
<tr>
<td>p2r.5c0d.25</td>
<td>0.25</td>
<td>0.39</td>
</tr>
</tbody>
</table>

*Table 3.4.: Density of samples by varying the target density without crosslinking agent*

The target density of all gels prepared with varying crosslinker ratio was fixed to the same value. The effect is obvious; increasing organic networking increases the density. Increasing the organic network need not improve the response of the gels to drying shrinkage. Meador et al has observed a similar surface saturation effect, where
they found that the maximum strength of the network was not obtained at the maximum density or at the maximum concentration of amine groups, used to anchor the organic network to the inorganic network.\(^{14}\)

The acid catalyzed hydrolysis of silicon alkoxides has a first order dependence on the concentration of water. So increase in concentration of water increases the rate of hydrolysis. Under acidic conditions the hydrolysis of silicon alkoxides proceeds through the protonation of the alkoxide group in a fast step followed by an S\(_{\text{N}2}\) attack of water opposite to the leaving group. This leaves the Si atom in a pentacoordinated configuration in the transition state. The bulky glycidoxypropyld group will destabilize the penta coordinated transition state due to steric repulsion, reducing the hydrolysis rate of GPTMS compared to that of TEOS. The condensation mechanism operative at pH above the isoelectric point involves the attack of an anionic silanolate species on a neutral silanol species. The acidity of the silanol species depends on the groups attached to the Si atom. Electron donating groups like GPTMS, decrease the acidity of the silanol while electron withdrawing groups like O-Si increase the acidity. So the more condensed species will be more acidic and condensation will proceed through the addition of less condensed or monomeric species to the more condensed clusters. More over the intermediate formed during the condensation reaction is a penta or hexa coordinated species and steric factors can limit the condensation rates of silane molecules.\(^{50}\) Hence GPTMS should undergo condensation at a slower rate than TEOS. This would mean that the siloxane network will be mostly contributed by the TEOS derived particles and GPTMS will condense on to the network at a much slower rate. Husing arrived at similar conclusions for base catalysed hydrolysis-condensation of mixed precursor systems containing TEOS and various monoalkyl substituted silanes including GPTMS, for a water ratio of 1.\(^{38}\)

The addition of DETA for the polymerization of epoxy group also catalyzes the inorganic condensation by increasing the pH of the solution. The faster gelation observed, even for hybrids with high GPTMS content is due to the dual role played by DETA. The relative concentrations of Q3/Q4 Si species would have given conclusive evidence to the
variation in networking with the varying precursor ratio, but we were not able to perform Si CP-MAS NMR spectroscopy for this work.

The influence of the organic networking on the gel structure is reflected on the variation of density with the organic precursor content; whereas the influence of the inorganic networking on the structure is reflected on the variation of density with initial water content. Increasing the amount of initial water increases the hydrolysis rates facilitating the concentration of silanol groups as soon as the reaction commences. This in turn will increase the condensation rate and considerable condensation would have occurred by the time DETA is added. This will result in a precursor gel with a highly condensed inorganic network. When the precursor ratio is 2 the organic networking strengthens the gel network to withstand the drying stress, decreasing shrinkage and density of the dried gel.

The organic precursor has three alkoxy groups compared to four in the inorganic precursor. Hence the inorganic networking ability has to be sacrificed for the organic networking when the proportion of the organic precursor increases. The inorganic network ends in the direction in which the organic group is oriented when the organic precursor becomes part of the inorganic network. As the ratio of the organic precursor increases, this results in the weakening of the inorganic network, due to the frequent terminations of the network at the organic precursor. When the GPTMS content increases, the inorganic networking decreases due to its lower networking ability compared to TEOS, increasing shrinkage and the density of the dried gel.

The BET analysis provides information on the influence of the processing parameters on the pore structure of the gels. The average pore diameter obtained for the various hybrids shifts to lower values when the GPTMS content increases. Porosity in aerogel like porous materials resides in two places. The smaller pores are formed between primary particles and larger ones between secondary particles. Primary particles are the result of the initial condensation reactions where by clusters are formed. Due to the lower hydrolysis condensation rates of the GPTMS precursor there is only a very small probability for the presence of the glycidoxypropyl group within the initially formed
clusters. The contribution to the smaller pore sizes come from within these clusters. This is represented in scheme 3.3.

![Scheme 3.3.: Porosity in aerogels](image)

Scheme 3.3.: Porosity in aerogels

The glycidoxypropyl groups condense on to these initially formed clusters and strongly influence the secondary structure. As the proportion of GPTMS increases, the inorganic network between secondary particles reduces and the structure easily shrinks, reducing porosity between them. This in turn decreases the volume of the larger pores and primarily results in the shifting of the average pore radius to the lower region. The initial water content has a much larger influence on the pore structure for the precursor ratio 2 due to the larger proportion of the TEOS precursor. The higher water content results in a more condensed gel network resulting in lower pore volume. Since the hydrolysis rates of GPTMS are low compared to that of TEOS, the TEOS molecules will have a much higher ratio of water available for their hydrolysis than what the H$_2$O/OR ratio indicates. So, for a lower precursor ratio, a water content of 0.5 represents an excess of water for the hydrolysis of TEOS and this is also the reason for the insensitivity of the average pore radii towards the variation in water ratio for these hybrids. The narrow pore size distribution curves obtained for the precursor ratio 0.5 and 1 are indicative of the effects of the reducing contribution from larger pores mainly formed between secondary particles. On the other hand the added crosslinker seem to have an effect comparable to increasing precursor ratio but at a much lower magnitude.

The skeletal densities of the samples prepared, measured using He pycnometry is provided in table 3.6. The skeletal density data of samples varies in the range of 1.6 to 2.2 g cm$^{-3}$ and is in the range observed for aerogels. The data shows that as organic precursor
content increases skeletal density decreases. As water ratio for hydrolysis increases the skeletal density also increases.

\[
\begin{array}{ccc}
\text{samples} & \rho_{\text{skel.}} & \text{sample} & \rho_{\text{skel.}} \\
p3r.5c0 & 1.8 & p2r.5c.25 & 2.2 \\
p2r.5c0 & 1.8 & p2r.5c.5 & 1.9 \\
p1r.5c0 & 1.6 & p2r.5c1 & 2.1 \\
p3r1c0 & 1.8 & p2r.5c1.5 & 1.9 \\
p2r1c0 & 1.7 & p2r1c.25 & 1.8 \\
p1r1c0 & 1.6 & p2r1c.5 & 1.7 \\
p3r2c0 & 2.2 & & \\
p2r2c0 & 2.1 & & \\
p1r2c0 & 1.9 & & \\
\end{array}
\]

*Table 3.6.: Skeletal density of samples*

It has been observed that the presence of lower density chemical species like methoxy groups lower the skeletal density of aerogel than that of dense silica.\textsuperscript{51,52} So the increasing precursor ratio increases the organic groups which in turn decrease the skeletal density. Increase in water content increases the degree of condensation of the inorganic network. Consequently the skeletal density also increases.

The TEM images of hybrids prepared with the precursor ratio 2 and water ratios 0.5 and 2 are provided as figure 3.18. The largely condensed nature of the hybrid with higher water content is visible. TEM micrograph of the hybrid with lower water content, at a higher magnification is provided as figure 3.19. The aerogel like networked structure can be seen in this image.\textsuperscript{53} Hybrids with higher organic content were unstable under the operating voltage.

The TEM images of samples with crosslinker ratio 0.5 and 1.5 are presented as figure 3.20. On the right is the corresponding high resolution image. The SAED pattern shows that the material is highly amorphous. The high resolution image shows the
networked structure of the material. The denser nature of the sample with increase in concentration of the organic crosslinker can be seen in the image.

![TEM images](image1.png)

**Figure 3.18.: TEM of samples with precursor ratio 2 and water ratio (a) 0.5 and (b) 1**

![TEM image](image2.png)

**Figure 3.19.: TEM of sample with precursor ratio 2 and water ratio 0.5 at a higher magnification**

The dielectric properties of the hybrid networks were investigated for two main reasons. Even though dielectric response of aerogels has been reported, there are only a few reports on the dielectric response of subcritically dried aerogels. The dielectric property, unlike thermal conductivity is dependent on the nature of the solid network forming the porous network. So the dielectric response of subcritically dried aerogels
needs to be recorded to establish the nature of the gels formed at ambient pressure. On the other hand this will also be a test to the hybrids prepared, to stand up to the performance of supercritically dried aerogels.

![Figure 3.20: TEM image of samples with crosslinker ratio a) 0.5 b) 1.5](image)

**Figure 3.20: TEM image of samples with crosslinker ratio a) 0.5 b) 1.5**

The dielectric properties of aerogels are mostly determined by the gases present inside the pores. The dielectric constants observed for aerogels are lower than that of amorphous fused silica (~3.8) and higher than that of air (1).\(^\text{54}\) Initial attempts to measure the dielectric constant of silica aerogels were made by da Silva et al and they treated the aerogel as a bicomponent system with air as one component and silica as the other.\(^\text{55}\) They calculated the dielectric constant of the bicomponent system from the Looyenga’s equation given as \[ \varepsilon'_{伽} = [\varepsilon_2^{1/3} + (1 - P)(\varepsilon_1^{1/3} - \varepsilon_2^{1/3})]^3 \]. \(\varepsilon_1\) and \(\varepsilon_2\) are the dielectric constants of silica and air respectively and \(P\) the porosity. The dielectric response was measured in the lower frequency region from 50-10\(^5\) Hz and they obtained dielectric constants less than 2. They could correlate the observed response to the bicomponent
system where the dielectric constant of silica had a higher value of 7. This value was reported by Chandrashekar et al and was attributed to the presence of carbon.\textsuperscript{56}

A more comprehensive approach was made by Hrubesh and he measured the dielectric response of aerogels in the GHz region which was more required for the microelectronics industry.\textsuperscript{54} In this approach the dielectric property of aerogels is considered from the perspective that since the gas inside the pores is largely responsible for the low dielectric property of aerogels, their dielectric properties should also be gas like rather than solid like. The dielectric constant of a gas is linearly dependent on the density and is given by the Clausius- Mosotti equation.  

$$
\varepsilon = 1 + \left( \frac{N_0 \alpha}{M \varepsilon_0} \right) \rho
$$

Where $\varepsilon$ is the dielectric constant, $N_0$ is the Avogadro number, $\alpha$ is the polarizability of the gas, $M$ is the molecular mass, $\varepsilon_0$ is the permittivity of free space and $\rho$ is the density.

In the case of aerogels the density refers to the bulk density of the aerogel. On a physical sense, the slope ($N_0 \alpha / M \varepsilon_0$) can be considered as the dielectric constant per bulk density. When the bulk density is zero i.e. in the absence of the solid network we will get the dielectric constant of air. Hrubesh could obtained slopes for various aerogels and found that it varied with the composition of the aerogel. For silica aerogel the value obtained was $1.6 \times 10^{-3}$ and for organic aerogel, $1.75 \times 10^{-3}$ (for resorcinol-formaldehyde) and $1.83 \times 10^{-3}$ (for melamine formaldehyde) when dielectric constant was plotted against density in kgm$^{-3}$. He found that the contribution to the dielectric constant from adsorbed water correspond to about 7%.

The dielectric constants obtained for hybrid gels at 2MHz is plotted against density of the gels, in Kgm$^{-3}$ in figure 3.21. The dielectric loss factors obtained for the gels were in the range 0.02-0.08. Three distinct dielectric responses can be seen. In the initial region at low densities the dielectric response increases with temperature. In the second region the dielectric constant is rather less dependent on density. Final region is distinguished by high sensitivity of dielectric constant on density.
In the first region it can be seen that the density is linearly dependent on the density and a straight line fit is given by the equation, $\varepsilon = 1.6 + 0.0009\rho$. The values are close to the values obtained by Hrubesh for silica aerogels. But we have a value of 1.6 for the dielectric constant of air which is rather high. But if we look at the processing sequence of our gels we can very well see that the dielectric constant of the drying solvent, hexane has a dielectric constant of 1.8. Hence this unexpected value of dielectric constant of air must be due to the contribution of hexane. As we had seen in the thermogravimetric curve there is some presence of hexane in the gels due to its retention by the organic network. Then the lower value of 1.6 must be due to the fact that the adsorbed hexane can no longer be considered as a liquid and is in dynamic equilibrium with its vapour phase in the pores. In order to test this hypothesis, the gels were calcined at a temperature of 200 °C. In presence of air the calcinations led to shrinkage and charring of the gels. So a gel was calcined in flowing Ar atmosphere at 200 °C for 2 hours. The dielectric constant was then measured and we obtained a value of 1.43 for the gel with density 0.22 gcm$^{-3}$. It can be seen that this value is related to the density as $\varepsilon = 1 + 0.00195\rho$. We did not have the set up to calcine all the gels in Ar atmosphere and in

Figure 3.21: Dielectric response of hybrids

![Diagram](image)
the absence of the inert atmosphere the gels showed large shrinkage. So we could not perform the measurements on all gels.

We tried to calculate the value of the dielectric constant of our gels from the Looyenga’s equation. Dielectric constant of silica was chosen as 3.8 and that of air was taken as 1.6. Porosity of the hybrids was calculated as \( P = \frac{\rho_{\text{Skel}} - \rho_{\text{Bulk}}}{\rho_{\text{Skel}}} \), skeletal densities were obtained from pycnometry and bulk densities were measured. The obtained results are provided in figure 3.22. It can be seen that the obtained dielectric constants are close to the values obtained from the Looyenga’s equation. The dielectric constants obtained, if the dielectric constant of air was taken as 1, is also provided in the figure. Hence the modification of the dielectric constant of the hybrid aerogels is due to the hexane adsorbed on to the pore walls.

![Figure 3.22: Plot of dielectric constant against density where the dashed line indicates fit to theoretical (Looyenga’s equation) data (open circle) using the dielectric constant 1.6 for air, continuous line indicate fit to observed data(solid circles) and triangle indicates fit to theoretical data with dielectric constant of air =1.](image)

Figure 3.22: Plot of dielectric constant against density where the dashed line indicates fit to theoretical (Looyenga’s equation) data (open circle) using the dielectric constant 1.6 for air, continuous line indicate fit to observed data(solid circles) and triangle indicates fit to theoretical data with dielectric constant of air =1.
It can be seen that many samples falling in the second region have densities same as that observed for samples in region 1. The porosity and density are plotted for different samples in figure 3.22. Here it can be seen that the porosity of most of the samples, which show dielectric response in the region 2 have porosities close to 80% which is expected for aerogels. So the observed values were tried to fit using the Looyenga’s equation. The closest values were obtained when the value of $\varepsilon_1$ was 1.8 and $\varepsilon_2$ was 3.8. The value of 1.8 is the dielectric constant of liquid hexane. So the values may be shifted due to the higher hexane content in the samples. But the probability of such a situation is perplexing since all pellets were heated at 100 °C for 24 hours prior to electroding the samples. So the probability of excess concentration of hexane is doubtful. Also it can be seen that the sample with precursor ratio 2 prepared with the water ratio 2 lies in the second region that prepared with a water ratio 1 falls in the region 1. One would have expected that the excess water used in the preparation must have reduced the adsorption of hexane even
when aging treatments are performed. Also, in the case of samples prepared with same precursor ratio but different target densities, as the target density increases the dielectric response move into the region 2. More studies are required to clearly identify the reason for this difference in behaviour. In the region 3 the dielectric constant increases steeply with increase in bulk density. Here the dielectric response has more xerogel character and can be assumed from the lower porosity obtained for these samples. Samples prepared from precursor ratio 1 fall in this region.

The variation of dielectric constant of different gels prepared with temperature is given in figure 3.23. There is little effect on increasing temperature on the dielectric constant till 90 °C. Aerogels have also been seen to show such invariant behaviour to temperature.54

![Figure 3.23: The variation of dielectric constant with temperature for various samples (given in the legend). P is the precursor ratio, C the crosslinker ratio, R the water ratio and d the target density)](image)

**Conclusion**

This study has shown that organic inorganic hybrid networks can be successfully dried by the ambient pressure drying technique involving aging and solvent exchange to
produce aerogels. The technique provides highly porous gels >70% porosity in almost all compositions studied. But aerogels are obtained when gels are prepared with a precursor (TEOS/GPTMS) ratio >1. Higher precursor ratios give xerogels. Ratio of organic network to the inorganic network is the predominant factor that affects the density of the final gel and hence the aerogel properties. Water ratio used for condensation has only a secondary effect.

The porosity features are also largely dependent on the extent and nature of the organic network. As the ratio of organic networking decreases there is a larger influence of water ratio on the nature of porosity formed. The organic networking influences the secondary structure of the aerogel network, and increasing the precursor ratio decreases the volume of the pores between secondary particles.

The nature of the organic network formed from the crosslinking is also strongly dependent on the concentration of the organic precursor, be it modified silane or the crosslinker. As the concentration of the organic precursor increases the length of the organic network increases initially, i.e. longer polymer chains are formed and beyond a certain point 1 for the precursor and crosslinker ratio the polymer network is composed of shorter chains or has more terminated ends.

The organic network anchored to the inorganic network is more efficient in reinforcing the inorganic network compared to the loosely bound organic network formed from the use of crosslinker.

The dielectric response of the ambient pressure dried aerogels are similar to supercritically dried ones. But there are gels with high porosity ~80% which shows dielectric response higher than that expected for aerogels even when the porosity features are similar to that of aerogels.

Finally, a subtle balance between the organic part and inorganic part of the network is required to obtain aerogels through ambient pressure drying. The organic network cannot be a substitute for inorganic network and only at symbiotic proportions will the networks resist drying shrinkage.
References


