CHAPTER – III

STUDIES ON SILICA AND CARBON/SILICA BASED GLASSES USING BIS PHENOL-A AND PHENOLIC RESIN

III.1 Introduction

Silica sols were prepared by the hydrolysis of tetraethoxy silane with acidified water. To the partially hydrolyzed sol, carbon precursor e.g. Bis phenol-A and phenolic resin were added respectively.

III.2 Studies on hydrolysis of TEOS

III.2.1 Estimations of –OH groups using pyridine- acetic anhydride reagent

• Experimental:

The hydrolysis of TEOS was carried out by using acidified water. During the hydrolysis ethoxy groups of TEOS are replaced with hydroxyl groups and estimation of hydroxyl groups shows extent of TEOS hydrolysis. The results of –OH estimation are shown in Table III.1. After 5hr of hydrolysis maximum value of 31% was reached. From the table, it can be said that the hydroxyl group. % value is found to increase in the beginning very fast and then slow down with increasing time of hydrolysis, time passes after 5 hrs, this value becomes almost constant showing completion of hydrolysis at that stage.
Chapter III

III.2.2 Hydrolysis of TEOS

The hydrolysis of TEOS was carried out with acidified water. Since TEOS and water are mutually immiscible, ethanol was used as a common solvent. Further it is a slow reaction therefore H\(^+\) ions were used to catalyze the reaction. The hydrolysis of tetraethyl orthosilicate (TEOS) with water takes place in steps as:

Table III.1 Results for the estimation of hydroxyl value

<table>
<thead>
<tr>
<th>No.</th>
<th>Wt. of sample (gm)</th>
<th>volume (ml)</th>
<th>Density (gm/ml)</th>
<th>Black reading (ml)</th>
<th>Sample reading (ml)</th>
<th>Difference (ml)</th>
<th>% of OH value</th>
<th>Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1)</td>
<td>0.8510</td>
<td>01</td>
<td>0.851</td>
<td>29.2</td>
<td>26.2</td>
<td>2.6</td>
<td>11.63</td>
<td>0</td>
</tr>
<tr>
<td>2)</td>
<td>0.9109</td>
<td>01</td>
<td>0.9109</td>
<td>29.2</td>
<td>24.0</td>
<td>5.2</td>
<td>21.54</td>
<td>1</td>
</tr>
<tr>
<td>3)</td>
<td>0.4379</td>
<td>0.5</td>
<td>0.8758</td>
<td>29.2</td>
<td>26.3</td>
<td>2.9</td>
<td>27.47</td>
<td>2</td>
</tr>
<tr>
<td>4)</td>
<td>0.4376</td>
<td>0.5</td>
<td>0.8752</td>
<td>29.2</td>
<td>26.1</td>
<td>3.1</td>
<td>29.38</td>
<td>3</td>
</tr>
<tr>
<td>5)</td>
<td>0.4278</td>
<td>0.5</td>
<td>0.8556</td>
<td>29.2</td>
<td>26.1</td>
<td>3.1</td>
<td>30.06</td>
<td>4</td>
</tr>
<tr>
<td>6)</td>
<td>0.4274</td>
<td>0.5</td>
<td>0.8548</td>
<td>29.2</td>
<td>26.0</td>
<td>3.2</td>
<td>31.06</td>
<td>5</td>
</tr>
<tr>
<td>7)</td>
<td>0.4302</td>
<td>0.5</td>
<td>0.8604</td>
<td>29.2</td>
<td>26.3</td>
<td>2.9</td>
<td>27.96</td>
<td>6</td>
</tr>
<tr>
<td>8)</td>
<td>0.4376</td>
<td>0.5</td>
<td>0.8752</td>
<td>29.2</td>
<td>26.0</td>
<td>3.2</td>
<td>30.33</td>
<td>7</td>
</tr>
<tr>
<td>9)</td>
<td>0.4300</td>
<td>0.5</td>
<td>0.8600</td>
<td>29.2</td>
<td>26.2</td>
<td>3.0</td>
<td>28.93</td>
<td>8</td>
</tr>
</tbody>
</table>

Fig. III.1. Reaction kinetics of estimation of hydroxyl alcohol
HYDROLYSIS

\[
\text{Si}(\text{OC}_2\text{H}_5)_4 + 4\text{H}_2\text{O} + 2\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{H}^+} \text{Si}(\text{OC}_2\text{H}_5)_3(\text{OH}) + \text{C}_2\text{H}_5\text{OH} \\
\text{Si}(\text{OC}_2\text{H}_5)_2(\text{OH})_2 + 2\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{H}_2\text{O}} \text{Si}(\text{OC}_2\text{H}_5)(\text{OH})_3 + 3\text{C}_2\text{H}_5\text{OH} \\
\text{Si}(\text{OH})_4 + 4\text{C}_2\text{H}_5\text{OH}
\]

Polymerization reaction

\[
\text{Si} - \text{O} \cdot \text{H} + \text{C}_2\text{H}_5 - \text{O} - \text{Si} \longrightarrow \text{Si} - \text{O} - \text{Si} + \text{C}_2\text{H}_5\text{OH}
\]

In most alkoxide systems, hydrolysis and condensation reactions rapidly proceed until one of the reacting groups, \(-\text{OR}\) and \(-\text{OH}\) is finally exhausted. Under the given hydrolysis condition, the relative concentrations of \(-\text{OH}\) and \(-\text{OR}\) depends on the availability of water, aging, dilution and type of alkoxide.

In silicon alkoxide, the hydroxyl and alkyl groups can coexist in significant numbers. The chemical makeup of the hydrolysis product in these cases can be represented as:

\[
\text{SiO}_{2x+y/2}(\text{OH})_x(\text{OR})_y
\]

Given sufficient times and availability of water \(y\) becomes small enough to be negligible for compositional purposes. When this occurs, the hydroxylation product can be considered as an inorganic polymer whose main skeleton is an oxide framed in hydroxyl groups.
The stoichiometric equation for the hydrolysis of TEOS shows that for each mole of TEOS, four moles of water are required [1]. However transparent sols [2-3] have been prepared, when four or more than four moles of water are added. Amount of water added affect the hydrolysis of TEOS. Therefore, in order to have more understanding of the mechanism, systematic studies were performed on hydrolysis of TEOS with varying amount of TEOS to water molar ratio. The data on the effect of water to TEOS molar ratio on time of hydrolysis to get a transparent gel is complied in Table III.2.

Table III.2 Composition of sol vs. hydrolysis time in presence of solvent

<table>
<thead>
<tr>
<th>Hydrolysis of TEOS</th>
<th>Amount of TEOS mole</th>
<th>Amount of ( \text{H}_2\text{O} ) mole</th>
<th>( \text{C}_2\text{H}_5\text{OH} ) mole</th>
<th>pH</th>
<th>Hydrolysis Time (hr)</th>
<th>Physical appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis of TEOS with solvent</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>Slightly hazy</td>
</tr>
<tr>
<td>Hydrolysis of TEOS with solvent</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>Transparent</td>
</tr>
</tbody>
</table>

As seen from the table, lower TEOS to water molar ratio (lower than that based on stoichiometric reaction) results in hazy sols. When TEOS to water molar ratio is increased to four transparent sols are obtained. If the amount of water added is less than that required stoichiometrically, the hydrolysis is incomplete and resulting liquid is a mixture of hydrolyzed TEOS, unhydrolyzed TEOS and hence hazy. When the amount of water is twice than that required stoichiometrically, the apparent increase in hydrolysis time is perhaps due to much evolution of ethanol as a result of hydrolysis and hence more mixing time is required to have workable gel to yield good sintered products. The initial addition of ethanol as solvent also affect the rate of reaction i.e., rate of hydrolysis. Therefore, hydrolysis of TEOS was carried out at room temperature. For each mole of TEOS, two moles of ethanol are required to make
TEOS and water as mutually miscible mixtures. For hydrolysis of TEOS to take place, it is essential that water molecule must come in contact with TEOS molecule. In an absence of ethanol, since TEOS and water are not miscible, the probability gets reduced and hence the hydrolysis reaction is slow. With passage of time, ethanol is generated as a by-product, and afterwards acts as solvent and help in miscibility of water and TEOS, which then accelerates the reaction. However, in an absence of ethanol also if TEOS to water ratio is increased to certain limit, there is much increase in apparent hydrolysis time.

Hydrolysis of TEOS with water is a very slow reaction. The rate of reaction can be increased by using a catalyst. Both acids and bases can be used as catalysts. In the present studies, hydrochloric acid was used as a catalyst. In the studies mentions above, the hydrolysis was carried out by varying TEOS to water molar ratio while keeping the pH of water nearing to two (pH-2). The pH of sol also affects the gelling time after hydrolysis and casting.

After hydrolysis the sols were casted for gelation. During the sol-gel transition period, vapours of volatile liquid are allowed to escape in a controlled way. Monolithic gels were obtained at room temperature when the evaporation of the vapours in sol was slow. It was observed that rapid evaporation of the solvent resulted in formation of pores and cracks through the cracks were directional and projected towards the centre. It may be due to drying of the samples at a faster rate. Drying of gels results in polymeric cross linking with evolution of water vapours and solvent and is accompanied by dimensional change i.e. shrinkage. Above room temperature, the evaporation of solvent and water vapours is fast resulting in cracking of gels in temperature range of 60-80°C followed by large dimensional shrinkage in the
samples. At higher temperature drying resulted in the formation of pieces of various sizes of gels, hence shrinkage could not be measured.

**III.2.3 Thermal analysis of silica gels**

The thermal analysis of gels and glasses were performed on Mettler TGA/DTA thermal analysis system. The thermogram of dried gel were taken in nitrogen atmosphere is shown in fig. III.2. Dried gels exhibited a decrease in weight loss on heating upto 40-100°C. This weight loss is attributed to evaporation of absorbed moisture from atmosphere suggesting hygroscopic nature of gels prepared from the hydrolysis of TEOS. Therefore, thermal analysis was initiated only after stabilizing the weight of sample at 100°C. Even after stabilization at 100°C, the weight loss is found to start at low temperature and continuous up to 400°C but at a rapid rate. This may be due to the polycondensation of adjacent silanol groups present on the surface resulting in evolution of water and alcohols [4]. A large amount of water and organics are removed below 400°C. A gradual and slight decrease in weight of the gel is continued at higher temperatures. The weight loss is prominent at around 800°C. This may be because of the vaporization or decomposition of organic groups with high molecular weight or may be attributed to sintering of material to a compacted silica structure.
III.2.4 FTIR studies of pure silica system

The chemical transformation was studied using FTIR. It gives information’s about the backbone structure of siloxanes network as well as organic groups attached to it. The IR bands were used to study the development of hybrid organic-inorganic gels as well as their pyrolytic product by comparing the spectra of pyrolyzed silica gel and modified silica gel [5-8].

Fig. III.3 shows the IR spectrum of dried gel. The dried gel exhibited prominent peaks at 457 cm\(^{-1}\) corresponding to O-Si-O deformation stretching i.e. formation of ring structure of SiO\(_4\) tetrahedron along with peak at 960 cm\(^{-1}\) due to Si-OH silanol groups [9-10], 570 cm\(^{-1}\) due to unreacted ethoxy –O-Et groups and a broad band at around 1000-1200 cm\(^{-1}\) due to the formation of silica (-O-Si-O-) asymmetric stretching vibrations [9-11] and another broad band at around 3200-3600 cm\(^{-1}\) due to the Si-OH silanol groups. The peak at 1600 cm\(^{-1}\) and 2360 cm\(^{-1}\) might be due to C-O stretching frequency corresponding to the moisture present in the sample.
III.3 Studies on Carbon/Silica based glasses using Bis phenol-A and Phenolic resin

III.3.1 Effect of TEOS/ Bis phenol-A and TEOS/ Phenolic resin molar ratio on physical structure of cured and pyrolyzed samples

The organic-inorganic hybrids were synthesized by sol-gel route. The co-polymerization of hydrolyzed TEOS and bis phenol-A or phenolic resin was carried out in order to incorporate carbon in the silica network. In all experiments, optimized parameters for hydrolysis of TEOS to silica were used. These were

- TEOS/water molar ratio = 4
- TEOS/ ethanol molar ratio = 2
- pH = 2
- Time of hydrolysis = 4 hours
- TEOS: Bis phenol-A was taken 1:1.4.
- TEOS: Phenolic resin i.e. C/Si = 0.55.

Fig. III.3 FTIR spectrum of dried silica
Since TEOS and water are quite immiscible, ethyl alcohol was used as solvent for obtaining better homogeneity between hydrolyzed TEOS and bis phenol-A or phenolic resin. Sols were casted at different temperatures i.e 70°C, 90°C and 110°C for different time intervals. The samples were pyrolyzed to 1000°C in nitrogen atmosphere. Hydrolyzed TEOS will yield in silica formation where as bis phenol-A and phenolic resin were the precursor for carbon. On co-polymerization and pyrolysis generate a carbon-silica network. The various reaction taking place are shown in fig. III.4. All the samples were analyzed for presence of functional groups and thermal behavior.

Fig. III.4 Copolymerization reaction of TEOS to Bis phenol-A
III.3.2 Free carbon, %, free silica, % and black glass, % in the pyrolyzed samples

On heating copolymerized product at 1000°C, decomposition reaction take place, resulting in the formation of black glass along with free carbon and free silica. During decomposition, there is a removal of volatiles i.e. hydrocarbon gas, carbon dioxide and other impurities. The free silica, % and free carbon, % content in the copolymer heated at 1000°C was determined.

\[
\begin{align*}
\text{SiO}_2 + 4\text{HF} & \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O} \\
\text{SiF}_4 + 2\text{HF} & \rightarrow \text{H}_2\text{SiF}_6 \uparrow
\end{align*}
\]

The free silica was dissolved in hydrofluoric acid (40%) and loss in weight was determined as free silica present as

\[
\text{Free silica Content, } \% = \frac{W_1 - W_2}{W_1} \times 100
\]

Where, \( W_1 \) = weight of the sample before adding HF

\( W_2 \) = weight of the sample after treatment of HF leaching

The remaining solid mass was heated to 650°C at a heating rate 1.5°Cmin\(^{-1}\) in air. This resulted in oxidation of carbon to carbon dioxide.

\[
\text{C} + \text{O}_2 \rightarrow \text{CO}_2 \uparrow
\]

The loss in weight of sample was determined from where free carbon % was calculated:

\[
\text{Free Carbon Content } \% = \frac{W_1 - W_2}{W_1} \times 100
\]

Where, \( W_1 \) = weight of the sample before heat treatment

\( W_2 \) = weight of the sample after heat treatment
After the removal of carbon as carbon dioxide the remaining solid product was weighed as black glass. The results are given in Table III.3

Table III.3 free carbon %, free silica % and black glass % of copolymerized product

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample Name</th>
<th>% yield</th>
<th>% of free carbon</th>
<th>% of free silica</th>
<th>% of black glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TEOS/ Bis phenol-A</td>
<td>16.86</td>
<td>27.92</td>
<td>72.32</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>TEOS/ Phenolic resin</td>
<td>77.22</td>
<td>24.79</td>
<td>67.76</td>
<td>7.45</td>
</tr>
</tbody>
</table>

The results show that the yield obtained on co-polymerization of TEOS with bis phenol-A was only 17%. This may be due to decomposition of benzene ring into carbon which eventually reacted with oxygen and got removed as carbon dioxide. Apart from low yield of co-polymerized product, there was large amount of unreacted silica along with unreacted carbon. It appears that due to less reactivity of bis phenol A with partially hydrolyzed TEOS, black glass formation did not take place. In view of above results it was concluded that bis phenol A was not a suitable carbon precursors because of low yield of pyrolyzed product and due to its less reactivity with hydrolyzed silica.

In case of phenolic resin, the reaction between phenolic resin and partially hydrolyzed TEOS was a vigorous reaction and immediately became a gel. The gel was casted into moulds at room temperature. After sometimes formation of solid mass took place along with the separation of liquid layer. The separation of solid gel into two products, either an incomplete reaction or formation of byproducts.

The study was extended by using different organic solvents i.e. acetone, methanol and ethanol. In all cases, a solid product along with solvent formation were observed.
III.3.3 FTIR studies of TEOS/Bis phenol-A and TEOS/Phenolic resin cured and pyrolyzed sample

III.3.3a FTIR studies of TEOS/Bis phenol-A

![FTIR spectrum of pure Bis phenol-A](image)

Fig. III.5 FTIR spectrum of pure Bis phenol-A

FTIR spectrum of pure bis phenol-A compound is shown in fig. III.5. It shows broad band around at 3200-3600 cm\(^{-1}\) due to the -OH stretching frequency present in the sample. The peak at 758 cm\(^{-1}\) is due to the out of a plane C-H aromatic ring. The peaks at 827 cm\(^{-1}\), 1450-1500 cm\(^{-1}\) and 1500-1600 cm\(^{-1}\) show presence of prarasubstituted benzene ring, aromatic C=C weak to strong bond and conjugated C-C with a benzene ring present in the sample respectively. The peak at 933 cm\(^{-1}\) is due to the monosubstituted alkenes. The peak at 1100 cm\(^{-1}\) confirms the presence of secondary alcohol groups present in the sample. The peak present at 1230 cm\(^{-1}\) is due to the C-OH groups of phenols. The peak at 3020 cm\(^{-1}\) confirms presence of C=CH vinyl groups present in the sample. The peak at 1296 cm\(^{-1}\), 1357 cm\(^{-1}\), 2857 cm\(^{-1}\),
2968 cm$^{-1}$ are due to the methyl groups i.e. strong and medium to strong stretching frequency. This conforming to groups present in bisphenol A.

FTIR spectrum of co-polymer of partially hydrolyzed TEOS to bis phenol-A is shown in fig. III.6

![FTIR spectrum of copolymerised product of partially hydrolyzed TEOS to Bis phenol-A](image)

Fig. III.6 FTIR spectrum of copolymerised product of partially hydrolyzed TEOS to Bis phenol-A

The spectrum has some similar band of FTIR to presence of bis phenol A. An additional peak observed at 1000-1200 cm$^{-1}$ confirmed Si-O-Si i.e. silica group present in the sample. The peak at 1100 cm$^{-1}$ confirmed the Si-OH groups of TEOS. The peak at 400-450 cm$^{-1}$ confirmed presence of silica tetrahedron formation i.e. [SiO$_4$]$^4$. The peak at 800 cm$^{-1}$ shows presence of Si-O-C group. This data confirmed that reaction took place between partially hydrolyzed TEOS and bis phenol A.

FTIR spectrum of co-polymer heated at 1000$^\circ$C is shown in fig. III.7. Broad band around at 1000-1200 cm$^{-1}$ shows presence of silica precursors. The peak at 1100
cm\(^{-1}\) is due to the Si-O vibration in Si-O-Si. Presence of peak at 850 cm\(^{-1}\) suggest silicon atoms bonded to carbon atoms. The peak at 500 cm\(^{-1}\) is assigned to Si-OH (or -OEt) stretching.

**III.3.3b FTIR spectrum of TEOS/Phenolic resin**

FTIR spectrum of cured phenolic resin is shown in fig. III.8. The peaks at 700 cm\(^{-1}\) and 750 cm\(^{-1}\) are due to mono substituted and ortho disubstituted benzene ring respectively. The peak at 800-850 cm\(^{-1}\) is due to presence of para disubstituted benzene ring. The peak at 669 cm\(^{-1}\) shows presence of cis disubstituted alkenes. The peak at 950 cm\(^{-1}\) is assigned to presence of 1, 2, 4- substituted benzene ring. The peak at 1100 cm\(^{-1}\) is assigned to secondary and alcohols groups respectively. The peaks at 1328 cm\(^{-1}\), 1477 cm\(^{-1}\) and 2890 cm\(^{-1}\) are due to C-H stretching frequency of

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Fig. III.7 FTIR spectrum of copolymerised product of partially hydrolyzed TEOS to Bis phenol-A heated at 1000°C
methylene groups. The peak present at 1500-1600 cm\(^{-1}\) assigned to C=C aromatic ring.

Fig. III.8 FTIR spectrum of cured phenolic resin

Fig. III.9 shows the IR spectrum of co-polymerised product of partially hydrolyzed TEOS and phenolic resin. Broad band around at 3200-3600 cm\(^{-1}\) may be assigned to the -OH stretching frequency present in the sample. The peaks at 827 cm\(^{-1}\), 1450-1500 cm\(^{-1}\) and 1500-1600 cm\(^{-1}\) confirm that parasubstituted benzene ring, aromatic C=C or C=C benzene ring obscured by methylene bridge and conjugated C-C with a benzene ring present in the sample respectively. The peak at 950 cm\(^{-1}\) is due to the presence of 1, 2, and 4- substituted benzene ring. The peak at 1000-1200 cm\(^{-1}\) show presence of Si-O-Si i.e. silica group present in the sample. The peaks at 2898
cm\(^{-1}\), 2947 cm\(^{-1}\), 2979 cm\(^{-1}\) are due to the presence of methyl groups i.e. strong and medium to strong stretching frequency. The peak at 400-450 cm\(^{-1}\) is confirmed the formation of silicon tetrahedron taking place i.e. [SiO\(_4\)]\(^-\).  

![FTIR spectrum](image.png)

**Fig. III.9** FTIR spectrum of copolymerised product of partially hydrolyzed TEOS to phenolic resin

FTIR spectrum of co-polymerised hydrolyzed TEOS and phenolic resin at 1000\(^0\)C is shown in fig. III.10. Broad band around 1000-1200 cm\(^{-1}\) shows presence of silica precursors. The peak at 1200 cm\(^{-1}\) is due to the Si-O vibration in Si-O-Si. A peak at 829 cm\(^{-1}\) suggesting silicon atoms bonded to carbon atoms. The peak at 500 cm\(^{-1}\) is assigned to Si-OH (or -OEt) stretching.
III.3.4 Thermal analysis of TEOS/Bis phenol-A pyrolyzed sample

The thermo gram of copolymerized product of TEOS/Bis phenol A was subjected to heat treatment to 950°C in nitrogen atmosphere is given in fig.III.11(A) along with differential thermogram. It shows a decrease of 85% weight at 350°C. This decrease in weight correspond to decomposition of bis phenol-A molecule leaving behind 15% carbon in accordance to its chemical structure.

![FTIR spectrum of copolymerised product of partially hydrolyzed TEOS to Phenolic resin heated at 1000°C](image)

- Mol. Formula = C_{15}H_{16}O_{2}
- Mol. Wt. = 228 gm/mole
- Experimentally yield = 16.86 %
- Theoretical yield = 78.94 %
- Carbon yield due to alkyl chain = 15.76 %

The carbon atom present in the alkyl chain gives free carbon. The carbon is imparted to react with hydrolyzed silica to give black glass.
The TGA graph of TEOS/bis phenol-A copolymer was heat treated in air up to 950°C is shown in fig. III.11(B). Around 80% weight losses took place around 350°C due to decomposition of bisphenol A. An additional weight loss observed from 500-550°C temperatures. This loss in weight is due to oxidation of carbon to carbon dioxide.

From the two TGA graphs, it is seen that yield of copolymer after heating to 950°C was very low. Therefore it was concluded that bis phenol-A molecule was not consider as a suitable carbon precursor.
Fig. III.11 (A) TGA of TEOS + Bisphenol A in N$_2$ atm (B) TGA of TEOS + Bisphenol A in static air
III.4 References