Chapter 3
Results and Discussion
Part A
Borosiloxane
Oligomers
Chapter 3.1

Synthesis and characterization of borosiloxane oligomers from alkoxysilanes

This chapter reports the synthesis and characterization of borosiloxane oligomers from boric acid and alkoxysilanes such as phenyltrimethoxysilane, phenyltriethoxysilane, vinyltriethoxysilane and tetraethoxysilane. The effect of monomer feed ratio, reaction time and catalyst on the processability, thermal stability and ceramic residue of the oligomers was studied. The oligomers were characterized by GPC, IR, $^1$H-, $^{13}$C- and $^{29}$Si-NMR spectra, TGA and pyrolysis GC.

The results presented in this chapter form the basis for the following publications in International journals and papers presented in National and International Symposia:


3.1.1 Background

From the survey of pertinent literature, it is evident that borosiloxane oligomers have achieved significance as precursors for mixed non-oxide ceramics. There are several methods for the synthesis of polymers containing Si-O-B linkages using di, tri and tetra functional silicon monomers and they were discussed in the introduction. As boric acid is the cheapest source of boron it would be desirable to use it for synthesizing boron and silicon containing polymers/oligomers. Yajima and coworkers\(^1\) synthesized poly(borodiphenylsiloxane) by reacting boric acid with diphenylidichlorosilane (DPDCS) in n-butylether under nitrogen atmosphere at 300°C. Hoshii et al.\(^2\)-\(^4\) prepared borodiphenylsiloxane oligomer by reacting boric acid and diphenylsilanol at 300°C. However, these oligomers give relatively low ceramic residue on pyrolysis (< 50%) and also require high temperature (~300°C) for their synthesis. Ambadas et al.\(^5\) in a preliminary investigation reported the synthesis of borosiloxane oligomers through the condensation of boric acid with phenyltrimethoxysilane (PTMOS) and vinyltriethoxysilane (VTEOS) in diglyme at 150-160°C using boric acid:alkoxysilane mole ratio of 1:2. The oligomers from PTMOS and VTEOS gave ceramic residue of 65 and 85% respectively at 900°C in inert atmosphere. However, a detailed study on the effect of monomer feed ratio, reaction time and catalyst on the synthesis of borosiloxane oligomers has not been reported. Hence, in the present study, the influence of the above parameters on the synthesis of borosiloxane oligomers has been studied. As phenyltriethoxysilane (PTEOS) is much cheaper than PTMOS, attempts have been made to use PTEOS in place of PTMOS.

It is reported\(^5\) that VTEOS-based borosiloxane oligomers are insoluble in organic solvents. Hence, to improve the processability of VTEOS-based oligomers, in the present investigation efforts have been made to synthesize borosiloxane oligomers by reacting boric acid with mixtures of VTEOS and PTMOS/PTEOS.
The present chapter also deals with the synthesis and characterization of borosiloxane oligomers, with less carbon or totally devoid of carbon, for application as precursors for glass coating.

### 3.1.2 Borosiloxane oligomers from PTMOS and PTEOS

#### 3.1.2.1 Comparison of borosiloxane oligomers from PTMOS and PTEOS

As PTEOS is much cheaper than PTMOS it would be cost effective to synthesize borosiloxane oligomers from the former. However, before proceeding with a detailed investigation on the synthesis of borosiloxane oligomers from PTEOS, it is desirable to compare the oligomers synthesized from PTMOS and PTEOS with respect to their molecular weight, thermal stability and ceramic residue. For this purpose, borosiloxane oligomers, BSiPh-1 and BSiPh-2 were synthesized by reacting boric acid with PTMOS and PTEOS respectively in 1:2 mole ratio in diglyme at 150-160°C for 3 h using HCl as catalyst. A typical reaction scheme for the synthesis of borosiloxane oligomer is shown in Scheme 3.1.1.

![Scheme 3.1.1. Synthesis of borosiloxane oligomers from phenyltrialkoxy silane](image)

The oligomers, BSiPh-1 and BSiPh-2 were obtained in 77.2 and 69.4% yield respectively. They are soluble in organic solvents such as THF, 1,4-dioxane, toluene, chloroform and diglyme. They were characterized by GPC, IR, $^1$H-, $^{13}$C- and $^{29}$Si-NMR spectra, TGA and pyrolysis GC. The GPC curves of these two oligomers are compared in Fig. 3.1.1. The oligomers show bimodal molecular weight distribution. BSiPh-1 has $M_w$ of 1370 and $M_n$ of 1040 whereas BSiPh-2 has $M_w$ of 750 and $M_n$ of 480. The yield and molecular weight are higher for BSiPh-1 than for BSiPh-2 and this observation is attributed to the higher reactivity of PTMOS compared to that of PTEOS.
The IR spectra of the oligomers are shown in Fig. 3.1.2 and the assignments of the peaks are given in Table 3.1.1.
Table 3.1.1. IR assignments for borosiloxane oligomers, BSiPh-1 and BSiPh-2

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Assignment</th>
<th>Wave number (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSiPh-1</td>
<td>BSiPh-2</td>
<td>BSiPh-1</td>
<td>BSiPh-2</td>
</tr>
<tr>
<td>3400</td>
<td>3400</td>
<td>Si-OH stretching</td>
<td>1194</td>
</tr>
<tr>
<td>3219</td>
<td>3219</td>
<td>B-OH stretching</td>
<td>997</td>
</tr>
<tr>
<td>2261</td>
<td>2261</td>
<td>Due to B-OH group(Combination band)</td>
<td>882</td>
</tr>
<tr>
<td>1595</td>
<td>1595</td>
<td>C=C Stretching of Si-Ph group</td>
<td>740</td>
</tr>
<tr>
<td>1431</td>
<td>1432</td>
<td>Si-Ph stretching</td>
<td>696</td>
</tr>
<tr>
<td>1361</td>
<td>1379</td>
<td>B-O stretching</td>
<td>488</td>
</tr>
</tbody>
</table>

The \(^1\)H-NMR spectra of the oligomers are shown in Fig. 3.1.3. The \(^1\)H-NMR spectrum of BSiPh-1 shows a broad prominent peak in the region 6.3 to 8.0 ppm corresponding to protons of phenyl group attached to silicon. If PTMOS has not reacted with boric acid, the ratio of peak intensities due to aromatic protons and aliphatic protons (Si-OCH\(_3\)) should have been 1:1.8. The observed ratio of intensities of aromatic protons (6.2 to 8 ppm) to aliphatic protons (3.2 to 3.7 ppm) is 1:0.1. This clearly evidences that the reaction between boric acid and PTMOS as shown in Scheme 3.1.1 has taken place. The peaks observed at 3.3, 3.5 and 3.6 ppm are due to the residual solvent, diglyme present in the system. \(^1\)H-NMR spectrum of BSiPh-2 is similar to that of BSiPh-1 except for the broad peak observed at 1.2 to 1.8 ppm. This peak is probably due to Si-OH group present in the oligomer.
The $^{13}$C-NMR spectra of BSiPh-1 and BSiPh-2 are shown in Fig. 3.1.4. Both the oligomers show peaks at 128, 130 and 134 ppm due to phenyl carbons. Feeble peaks observed at 58.8, 70.6 and 72.1 are due to diglyme. The absence of prominent peaks at 51 (Si-OCH$_3$), 18.7 (CH$_3$ of Si-OEt) and 59.1 ppm (CH$_2$ of Si-OEt) in the $^{13}$C-NMR spectra of the oligomers suggests that Si-OMe and Si-OEt groups have undergone reaction completely.
The $^{29}$Si-NMR spectrum of BSiPh-1 shows three peaks at -68, -72 and -78 ppm and that of BSiPh-2 shows mainly two peaks at -70 and -78 ppm and a shoulder peak at -68 ppm (Fig. 3.1.5). Babonneau et al.\textsuperscript{8,9} studied in detail the $^{29}$Si-NMR spectra of borosiloxane oligomers prepared by sol-gel process of boric acid and organic substituted alkoxy silanes and assigned the chemical shifts to the structural units, $T_1$, $T_2$ and $T_3$, where $T_i$ indicates the unit with \textit{i}' siloxane (O-Si) bonds attached to the central silicon atom. It is reported\textsuperscript{8-11} that the Si-O-Si and the Si-O-B bonds do not differ in their $^{29}$Si-NMR chemical shifts. This implies that the chemical shift values of $T_1$, $T_2$ and $T_3$ structures are not influenced much whether they contain Si-O-Si or Si-O-B bonds. Based on the chemical shift values reported
for the sol-gels synthesized from phenyltrialkoxysilanes and those from boric acid and phenyltrialkoxysilanes, the chemical shift values at -68, -70 to -72 and -78 ppm, can be assigned to T₁, T₂ and T₃ structures respectively and these structures are shown in Fig. 3.1.6.

Fig. 3.1.5. $^{29}$Si-NMR spectra of BSiPh-1 and BSiPh-2
Fig. 3.1.6. Possible structural units present in BSiPh-1 and BSiPh-2

It is interesting to note that the ratio of peak intensities of $T_3$ to $T_1 + T_2$ is 1:0.34 for BSiPh-1 and 1:0.68 for BSiPh-2. This shows that $T_3$ structures are formed more when PTMOS is used and this is due to the higher reactivity of PTMOS compared to that of PTEOS. The chemical reactions, which are responsible for the formation of $T_1$, $T_2$ and $T_3$ structures containing Si-O-Si and the Si-O-B linkages, are shown in Scheme 3.1.2.
The $^{11}$B-NMR spectra of BSiPh-1 and BSiPh-2 are compared in Fig. 3.1.7. Boric acid gives a signal at 20.18 ppm$^{8,9}$ whereas BSiPh-1 and BSiPh-2 give signals at 20.91 ppm and 20.89 respectively. This observation suggests that chemical shifts of boron atom in the structural units B(OSi)(OH)$_2$, B(OSi)$_2$OH and B(OSi)$_3$ would be close to each other. As $^{11}$B-NMR is very broad, no meaningful information could be obtained. Hence, $^{11}$B-NMR spectral studies were not carried out for other systems.

The TG curves of BSiPh-1 and BSiPh-2 are shown in Fig. 3.1.8 and the TG data of the oligomers are summarized in Table 3.1.2. A sudden weight loss of 5-6% is observed in the temperature range 100-150°C and this is attributed to the loss of low molecular weight products present along with the oligomers. The oligomers are stable up to 500°C and above this temperature they undergo degradation. BSiPh-1 and BSiPh-2 give ceramic residue of 72 and 65% respectively at 900°C in argon atmosphere. The higher thermal stability of
BSiPh-1 compared to that of BSiPh-2 is probably due to the higher concentration of branched structures \( T_3 \) in the former resulting from the higher reactivity of PTMOS.

Fig. 3.1.7. \(^{11}\text{B}\)-NMR spectra of BSiPh-1 and BSiPh-2

Fig. 3.1.8. TG curves of BSiPh-1 and BSiPh-2
Table 3.1.2. Comparison of thermal properties of borosiloxane oligomers from boric acid and PTMOS/PTEOS

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>( T_i ) (°C)</th>
<th>( T_{\text{max}} ) (°C)</th>
<th>( T_f ) (°C)</th>
<th>Ceramic residue at 900°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSiPh-1</td>
<td>550</td>
<td>610</td>
<td>660</td>
<td>72.4</td>
</tr>
<tr>
<td>BSiPh-2</td>
<td>505</td>
<td>550</td>
<td>650</td>
<td>64.7</td>
</tr>
</tbody>
</table>

\( T_i \)-initial decomposition temperature; \( T_{\text{max}} \)-maximum decomposition temperature; \( T_f \)-final decomposition temperature

Pyrolysis gas chromatographic studies of BSiPh-1 and BSiPh-2 were carried out at 700°C to understand the nature of pyrolysis products formed. The pyrograms of BSiPh-1 and BSiPh-2 are shown in Fig. 3.1.9.
Pyrolysis GC studies of BSiPh-1 at 700°C reveal the presence of benzene as the main product at retention time of 2.87 min which is formed from phenylsiloxy unit. Similar observation is made with BSiPh-2. In addition to the peak corresponding to benzene, additional peaks are observed at higher retention time and these peaks probably result from the fragmentation of Si- and/or B-containing structural units. It is observed that the peaks at retention time of 5.23 and 5.59 min are more intense in the case of BSiPh-1 than in the case of BSiPh-2. $^{29}$Si-NMR spectral studies reveal that BSiPh-1 contains more of T$_3$ structures than BSiPh-2 and this difference is probably responsible for the above observation.

3.1.2.2. Effect of monomer feed ratio on the properties of borosiloxane oligomers from PTEOS

Borosiloxane oligomers were synthesized by reacting boric acid and PTEOS in the monomer feed ratios 1:2, 1:1.5 and 1:1 using diglyme as solvent and hydrochloric acid as catalyst at 150-160°C for 3 h and the oligomers obtained are designated as BSiPh-2, BSiPh-3 and BSiPh-4 respectively. BSiPh-2, BSiPh-3 and BSiPh-4 were obtained in 69.4, 84.3 and 86.4% yield respectively. GPC curves of the oligomers are compared in Fig. 3.1.10 and the GPC data are summarized in Table 3.1.3.

![GPC curves of BSiPh-2, BSiPh-3 and BSiPh-4](image.png)

Fig. 3.1.10. GPC curves of BSiPh-2, BSiPh-3 and BSiPh-4
The GPC curves indicate that with the increase in boric acid concentration in the monomer feed, $\bar{M}_w$ and $\bar{M}_n$ values as well as the tendency for bimodal molecular weight distribution increase. It is noticed that considerable increase in $\bar{M}_w$, $M_p$ and $\bar{M}_n$ values is observed when boric acid to PTEOS ratio is increased from 1:2 to 1:1.5. With further increase in the ratio to 1:1, only a marginal improvement in $\bar{M}_w$, $M_p$ and $\bar{M}_n$ values is observed.

**Table 3.1.3. Effect of variation of mole ratio of boric acid to PTEOS on molecular weight of borosiloxane oligomers**

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>Mole ratio of boric to PTEOS</th>
<th>$\bar{M}_w$</th>
<th>$M_p$</th>
<th>$\bar{M}_n$</th>
<th>$\bar{M}_w/\bar{M}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSiPh-2</td>
<td>1:2</td>
<td>750</td>
<td>360</td>
<td>480</td>
<td>1.56</td>
</tr>
<tr>
<td>BSiPh-3</td>
<td>1:1.5</td>
<td>1260</td>
<td>800</td>
<td>1010</td>
<td>1.25</td>
</tr>
<tr>
<td>BSiPh-4</td>
<td>1:1</td>
<td>1330</td>
<td>840</td>
<td>1070</td>
<td>1.25</td>
</tr>
</tbody>
</table>

The IR spectra of the oligomers indicate the presence of B-O-Si, Si-O-Si, Si-OH, B-OH and Si-OCH$_2$CH$_3$ groups. It is observed that with the increase in boric acid concentration, the intensity of the peak at 3200 cm$^{-1}$ due to B-OH increases and that at 3400 cm$^{-1}$ due to SiOH decreases considerably.

The $^1$H-NMR spectrum of BSiPh-4 is shown Fig. 3.1.11. Unlike in the $^1$H-NMR spectrum of BSiPh-2, a broad peak is observed in the region 3.2 to 4.0 ppm and this peak is attributed to the presence of Si-OH and B-OH groups present in the oligomer.

The $^{13}$C-NMR spectrum of BSiPh-4 indicates the absence of any unreacted ethoxy group. $^{29}$Si-NMR spectrum of BSiPh-4 is shown in Fig. 3.1.12. The peaks at -67, -69 and -77 ppm are attributed to $T_1$, $T_2$ and $T_3$ structures.\(^8\)\(^{11}\) Similar peaks are observed in the $^{29}$Si-NMR spectrum of BSiPh-3. For BSiPh-4, the ratio of $T_3:T_1+T_2$ is 1:0.51 as against 1:0.68 for BSiPh-2. This observation suggests that with the increase in boric acid concentration in the monomer feed, the population of $T_3$ structure increases.
The TG curves of BSiPh-2, BSiPh-3 and BSiPh-4 are compared in Fig. 3.1.13 and the TG data of these oligomers are summarized in Table 3.1.4. It is noticed that all the oligomers give almost the same amount of ceramic residue (64-65%) at 900°C. The initial weight loss taking place up to 150°C for BSiPh-2, BSiPh-3 and BSiPh-4 is 5.4, 5 and 8% respectively. This weight loss is attributed
to the loss of borate esters formed as a by-product and unreacted boric acid, if any. Increase in initial weight loss with the increase in boric acid concentration in the monomer feed suggests that the byproduct, borate ester, is formed more when boric acid concentration in the monomer feed is increased.

Fig. 3.1.13. TG curves of BSiPh-2, BSiPh-3 and BSiPh-4

Table 3.1.4. Comparison of thermal properties of borosiloxane oligomers

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>Boric acid: PTEOS (Mole ratio)</th>
<th>( T_i ) (°C)</th>
<th>( T_{\text{max}} ) (°C)</th>
<th>( T_f ) (°C)</th>
<th>Ceramic residue at 900°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSiPh-2</td>
<td>1:2</td>
<td>505</td>
<td>550</td>
<td>650</td>
<td>64.7</td>
</tr>
<tr>
<td>BSiPh-3</td>
<td>1:1.5</td>
<td>475</td>
<td>553</td>
<td>670</td>
<td>63.8</td>
</tr>
<tr>
<td>BSiPh-4</td>
<td>1:1</td>
<td>450</td>
<td>582</td>
<td>670</td>
<td>63.8</td>
</tr>
</tbody>
</table>

\( T_i \)-initial decomposition temperature; \( T_{\text{max}} \)-maximum decomposition temperature; \( T_f \)-final decomposition temperature

3.1.2.3 Effect of reaction time on the properties of borosiloxane oligomer from PTEOS

With a view to understanding the effect of reaction time on the properties of borosiloxane oligomer, the reaction between boric acid: PTEOS (mole ratio 1:2)
was carried out in diglyme at 150-160°C for 6 h using HCl as catalyst and the oligomer obtained in 71.1% is referred to as BSiPh-5.

The GPC curves of BSiPh-2 and BSiPh-5 are compared in Fig. 3.1.14. It is worth mentioning that with the increase in reaction time from 3 h to 6 h, $\bar{M}_w$ increases from 750 to 1480 and $\bar{M}_n$ increases from 480 to 1080. Unlike BSiPh-2, BSiPh-5 clearly shows a bimodal molecular weight distribution. This observation suggests that with increase in reaction time, some of the oligomeric chains undergo further condensation reaction involving B-OH and Si-OEt/SiOH groups resulting in a bimodal molecular weight distribution.

![GPC curves of BSiPh-2 and BSiPh-5](image)

**Fig. 3.1.14. GPC curves of BSiPh-2 and BSiPh-5**

The IR spectrum and $^1$H- and $^{13}$C-NMR spectra of BSiPh-5 are similar to that of BSiPh-2. The $^{29}$Si-NMR spectrum of BSiPh-5 is shown in Fig. 3.1.15. It shows peaks at -68 and -76 ppm corresponding to $T_1$ and $T_3$ structures. For BSiPh-5 the ratio of $T_3$ to $T_1+T_2$ is 1:0.32 whereas for BSiPh-2 the ratio is 1:0.68. This clearly evidences the fact that with the increase in reaction time, the population of $T_3$ structures increases.
The TG curves of BSiPh-2 and BSiPh-5 are compared in Fig. 3.1.16. It is noticed that BSiPh-5 has higher thermal stability compared to that of BSiPh-2. BSiPh-2 and BSiPh-5 give ceramic residue of 65 and 72% at 900°C respectively. The higher ceramic residue of BSiPh-5 is attributed to the presence of higher amount of T₃ structures.

Comparison of thermal properties of BSiPh-1 and BSiPh-5 suggests that both the oligomers give ceramic residue of 72% at 900°C. BSiPh-1 was
synthesized by reacting boric acid with PTMOS (1:2 mole ratio, for 3 h) whereas BSiPh-5 was synthesized by reacting boric acid with PTEOS (1:2 mole ratio, for 6 h). Thus, it can be concluded that a borosiloxane oligomer capable of giving the same ceramic residue can be synthesized by using PTEOS in place of PTMOS (which is costlier than PTEOS) just by increasing the reaction time from 3 h to 6 h. It is observed that further increase in reaction time has not resulted in any improvement in ceramic residue.

3.1.3 Synthesis of borosiloxane oligomers from VTEOS

From the foregoing discussion it can be inferred that by reacting boric acid with phenylalkoxysilanes, soluble borosiloxane oligomers capable of giving 65-72% ceramic residue at 900°C can be obtained. Ambadas et al.\textsuperscript{5} reported that borosiloxane oligomer that gives a ceramic residue of 86% can be synthesized by reacting boric acid and VTEOS in 1:2 mole ratio. However, the effect of monomer feed ratio on the processability and thermal stability of the oligomers has not been studied and the present study focuses on this aspect.

Boric acid and VTEOS were reacted in 1:2, 1:1.5 and 1:1 mole ratios in diglyme at 150-160°C for 3 h using HCl as a catalyst and the oligomers obtained are designated as BSiVi-1, BSiVi-2 and BSiVi-3 respectively. The B-OH group of boric acid would undergo reaction with Si-OEt group of VTEOS resulting in the formation of Si-O-B linkages and ethanol as a by-product as shown in Scheme 3.1.3. It is noticed that for all the monomer feed ratios, the oligomers formed are soluble in the reaction medium. After the reaction, the solvent and the by-product were removed by flash evaporation. While carrying out the flash evaporation, the viscosity of the resin gradually increased and finally a gel was obtained. This gel on further drying resulted in the formation of a flaky material. All the three oligomers, after flash evaporation and drying are insoluble in solvents like acetone, chloroform, THF, diglyme, toluene, DMAc and dioxane and hence \textsuperscript{1}H-, \textsuperscript{13}C- and \textsuperscript{29}Si-NMR spectra of the oligomers could not be recorded. They were characterized by IR, TGA and pyrolysis GC.
The insolubility of the oligomers may be due to the following reasons:

(i) During the removal of the solvent and by-product, unreacted B-OH may react with Si-OEt groups resulting in the formation of crosslinked product.

(ii) Part of Si-vinyl group may undergo thermal polymerization resulting in the formation of crosslinked product.

(iii) Si-OH functional group (formed by transesterification and by the hydrolysis of Si-OEt facilitated by HCl) may react with B-OH or Si-OEt or self-condense resulting in the formation of Si-O-B or Si-O-Si linkage.

(iv) One or more of the reactions described above may take place causing insolubility.

As the functionality of boric acid as well as VTEOS is three (without taking into consideration the participation of vinyl group), gel formation may take place when the reaction of B-OH and Si-OEt proceeds above a certain extent.

A typical IR spectrum of the borosiloxane oligomer (BSiVi-1) is shown in Fig. 3.1.17 and the peak assignments are given in Table 3.1.5. The presence of a sharp peak at 1604 cm\(^{-1}\) corresponding to the stretching vibration of vinyl group
suggests that the vinyl group is present in appreciable concentration in BSiVi-1. From the IR spectra of BSiVi-1, BSiVi-2 and BSiVi-3, it is noticed that the intensity of peaks corresponding to vinyl group becomes feeble when boric acid concentration is increased.

![Fig. 3.1.17. IR spectrum of BSiVi-1](image)

**Table 3.1.5. IR spectral data of borosiloxane oligomer from boron acid and VTEOS (BSiVi-1)**

<table>
<thead>
<tr>
<th>Wave number (cm⁻¹)</th>
<th>Assignment</th>
<th>Wave number (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3214</td>
<td>B-OH stretching</td>
<td>1005</td>
<td>Si-O-Si stretching</td>
</tr>
<tr>
<td>2262</td>
<td>Due to B-OH (Combination band)</td>
<td>964</td>
<td>Out of plane C-H deformation</td>
</tr>
<tr>
<td>1604</td>
<td>C=C stretching of vinyl group</td>
<td>883</td>
<td>Si-O-B/B-O-B stretching</td>
</tr>
<tr>
<td>1417</td>
<td>In plane CH₂ (alkene) deformation</td>
<td>765</td>
<td>Out of plane C-H deformation</td>
</tr>
<tr>
<td>1278</td>
<td>C=C bending of vinyl group</td>
<td>546</td>
<td>B-O-B bending</td>
</tr>
<tr>
<td>1128</td>
<td>Si-O-C stretching</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1128</td>
<td>Si-O-C stretching</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The TG curves of BSiVi-1, BSiVi-2 and BSiVi-3 are compared in Fig. 3.1.18. The weight loss up to 170°C is 4.7, 9.9 and 17.2% for BSiVi-1, BSiVi-2 and BSiVi-3 respectively suggesting that the weight loss up to 170°C increases with the increase in boric acid concentration in the monomer feed. The weight loss in this region is probably due to the loss of borate esters formed as a by-product and water formed due to further condensation of unreacted B-OH group with Si-OH or self-condensation of Si-OH groups or due to unreacted boric acid. Above 170°C a gradual weight loss is observed which continues up to 500°C. In the temperature region 500-680°C, BSiVi-1, BSiVi-2 and BSiVi-3 show weight loss of 4, 5 and 6% respectively and the weight loss in this region is attributed to the loss of organic moieties from the oligomer backbone. Above 680°C the weight loss is very less. BSiVi-1, BSiVi-2 and BSiVi-3 give ceramic residue of 89.4, 83.4 and 73.1% at 900°C.

Fig. 3.1.18. TG curves of BSiVi-1, BSiVi-2 and BSiVi-3

The pyrogram of BSiVi-1 (Fig. 3.1.19) shows two peaks, one at retention time of 0.64 min and the other at retention time of 2.47 min. The first peak, which is a major peak, is attributed to C₂ C₃ hydrocarbons resulting from the cleavage of crosslinked vinyl group. The broad peak observed above 2.47 min is probably due to higher hydrocarbons formed by the combination reactions.
3.1.4 Synthesis of borosiloxane oligomers from mixtures of alkoxy silanes

From the thermal analysis data of borosiloxane oligomers presented in the preceding sections, it is observed that for the monomer feed ratio 1:2 (boric acid:alkoxysilane), the oligomer synthesized from VTEOS gives the maximum ceramic residue when compared to the corresponding ones synthesized from PTMOS and PTEOS. The higher ceramic residue of VTEOS-based oligomer is attributed to the crosslinks that may be formed due to the polymerization of vinyl groups. Though the oligomer synthesized from VTEOS gives higher ceramic residue, it undergoes gelation when attempts were made to remove solvent/unreacted monomers by flash evaporation of the reaction mixture. On the other hand, the oligomers synthesized from PTMOS and PTEOS are soluble in organic solvents and do not gel during processing. In an attempt to combine the higher thermal stability of VTEOS-based system and the processability of PTMOS/PTEOS-based systems, in the present study borosiloxane oligomers were synthesized by reacting boric acid with a mixture of VTEOS and PTMOS/PTEOS.
3.1.4.1 Borosiloxane oligomers from PTEOS and VTEOS mixture

To study the effect of mole ratio of boric acid to alkoxy silanes on the processability, yield and thermal stability of the product obtained, the reaction was carried out for the monomer feed ratios (boric acid: PTEOS:VTEOS) 1:1:1, 1.5:1:1 and 2:1:1 using diglyme as solvent at 150-160°C in presence of HCl catalyst for 3 h and the oligomers obtained are referred to as BSiPhVi-1, BSiPhVi-2 and BSiPhVi-3 respectively. The reaction scheme for the synthesis of borosiloxane oligomers from mixtures of PTEOS, VTEOS and boric acid is shown in Scheme 3.1.4.

All the three oligomers are insoluble in solvents like THF, diglyme, dioxane, chloroform, toluene and xylene. A typical IR spectrum of the oligomer (BSiPhVi-1) is shown in Fig. 3.1.20 and the peak assignments are given in Table 3.1.6.

The pyrograms of the three oligomers at 700°C are shown in Fig. 3.1.21. All of them reveal that the copolymers produce C₂, C₃ hydrocarbons (retention time: ~ 0.72 min) and benzene (retention time: ~ 2.46 min) as the main pyrolysis
products along with small amounts of other high molecular weight silicon-substituted products as indicated by the peaks after 3 min.

![IR Spectrum of BSiPhVi-1](image)

**Fig. 3.1.20.** IR spectrum of BSiPhVi-1

<table>
<thead>
<tr>
<th>Wave number (cm⁻¹)</th>
<th>Assignment</th>
<th>Wave number (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3217</td>
<td>B-OH stretching</td>
<td>883</td>
<td>Out of plane C-H deformation of vinyl group/Si-O-B stretching</td>
</tr>
<tr>
<td>1431</td>
<td>C=C stretching of phenyl group</td>
<td>739</td>
<td>Out of plane C-H deformation of phenyl group</td>
</tr>
<tr>
<td>1194</td>
<td>B-OH deformation</td>
<td>697</td>
<td>Si-O-B bending</td>
</tr>
<tr>
<td>1136</td>
<td>Si-O-R stretching</td>
<td>489</td>
<td>O-Si-O bending</td>
</tr>
<tr>
<td>965</td>
<td>C-H deformation</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The peak at retention time of 1.88 min is attributed to ethyl alcohol formed due to the cleavage of residual Si-OEt linkages present in the oligomers. It is noticed that the intensity of this peak reduces when boric acid to alkoxy silane ratio is increased from 1:2 to 1.5:2 and with further increase in the ratio practically no peak is observed corresponding to ethanol. The above observation suggests that with increase in boric acid concentration, the concentration of residual Si-OEt groups reduces as extent of formation of Si-O-B linkages increases. As the lower hydrocarbons are produced from ViSiO moiety and benzene from PhSiO moiety, the relative concentration of C$_2$, C$_3$ hydrocarbon and benzene will depend on the concentration of ViSiO and PhSiO units in the copolymer. The ratio of the area (after subtracting the area due to shoulder peaks) due to C$_2$, C$_3$ carbons and benzene for BSiPhVi-1, BSiPhVi-2 and BSiPhVi-3 is almost the same (~0.83:1). This observation suggests that the concentration of PhSiO and ViSiO units does not change considerably with the change in boric acid concentration in the
monomer feed. In the pyrogram of BSiPhVi-1, a small peak is observed at retention time of 4.73 min and a prominent peak is observed at 5.09 min whereas in the pyrogram of BSiPhVi-2, the peak at 4.73 min is prominent and the peak at 5.09 min has merged with the peak at 4.73 min. It is worth noting that both these peaks are absent in the pyrogram of BSiPhVi-3. The peaks at 4.73 min and 5.09 min are probably due to some high molecular weight fractions containing silicon. Probably, with the increase in boric acid concentration, the formation of siloxane structural units due to self-condensation would be minimal as the possibility of formation of Si-O-B linkage increases. Further study using pyrolysis GC-MS is required to identify the products formed during pyrolysis.

The TG curves of BSiPhVi-1, BSiPhVi-2 and BSiPhVi-3 are compared in Fig. 3.1.22. As observed for PTEOS- and VTEOS-based systems, the ceramic residue decreases with the increase in boric acid concentration in the monomer feed. BSiPhVi-1, BSiPhVi-2 and BSiPhVi-3 give ceramic residue of 83, 80 and 75% respectively at 900°C.

Fig. 3.1.22. TG curves of BSiPhVi-1, BSiPhVi-2 and BSiPhVi-3

3.1.4.2 Borosiloxane oligomers from PTMOS and VTEOS mixture

Borosiloxane oligomers synthesized from mixtures of PTEOS and VTEOS were found to be insoluble in organic solvents. In an attempt to synthesize soluble vinyl-functionalized borosiloxane oligomers, boric acid was reacted with PTMOS
and VTEOS mixture. The oligomers were synthesized using boric acid:PTMOS:VTEOS monomer feed ratios, 1:1:1, 1.5:1:1 and 2:1:1 in diglyme at 150-160°C for 3 h using HCl as catalyst and they are designated as BSiPhVi-4, BSiPhVi-5 and BSiPhVi-6 respectively. BSiPhVi-4, BSiPhVi-5 and BSiPhVi-6 were obtained in 71.5, 86.7 and 95.9% yield respectively. As observed for other systems, for this system also increase in yield is obtained with the increase in boric acid concentration.

BSiPhVi-4 is soluble in THF, diglyme and dioxane and insoluble in chloroform, toluene and xylene whereas BSiPhVi-5 and BSiPhVi-6 are insoluble in these organic solvents. The GPC curve of BSiPhVi-4 is shown in Fig. 3.1.23. The oligomer shows a bimodal molecular weight distribution with $\bar{M}_w$ of 3650 and $\bar{M}_n$ of 1860.

![Fig. 3.1.23. GPC curve of BSiPhVi-4](image)

The IR spectra of the oligomers indicate the presence of B-O-Si at 698 cm$^{-1}$, Si-vinyl at 1603, 1410, 970 and 738 cm$^{-1}$, Si-OR at 1135 cm$^{-1}$, Si-Ph at 1520 cm$^{-1}$ and Si-OH at 3424 cm$^{-1}$. Comparison of the IR spectra of the oligomers suggests that as the concentration of boric acid is increased in the monomer feed the peaks corresponding to Si-vinyl groups become feeble. A broad peak exists around 1028 cm$^{-1}$ indicating the presence of Si-O-Si linkages.

The $^1$H-NMR spectrum of BSiPhVi-4 is shown in Fig. 3.1.24. The broad peak observed in the region 6.8 to 8 ppm is assigned to Si-Ph group and the peak observed in the region 5.5 to 6.3 ppm is due to Si-vinyl. The broad peak observed
in the region 3.5 to 3.8 ppm is attributed to Si-OH and B-OH groups. The two peaks observed at 3.3 and 3.4 ppm are probably due to residual Si-OCH₂CH₃ and Si-OCH₃ groups. The peak at 1.3 ppm is assigned to residual Si-OCH₂CH₃ present in the oligomer. Based on the intensities of phenyl and vinyl protons, the ratio of phenylsiloxy to vinylsiloxy units is estimated to be 1:1.

The ¹³C-NMR spectrum of BSiPhVi-4 (Fig. 3.1.25) shows peaks at 128, 130 and 134 ppm due to phenyl carbons. The signal at 136 ppm corresponds to CH₂ of vinyl group. The signal due to CH of vinyl group has merged with the signal at 130 ppm due to phenyl carbon resulting in line broadening.
The $^{29}$Si-NMR spectrum of BSiPhVi-4 is shown in Fig. 3.1.26. It shows peaks at -69 and -78 ppm and they are attributed to $T_2$ and $T_3$ structures respectively. The ratio of $T_3$ to $T_2$ structure is 1:0.62. The splitting of the peak due to $T_3$ is probably because of the fine structures arising from the presence of phenylsiloxy and vinylsiloxy units.

![Fig. 3.1.26. $^{29}$Si-NMR spectrum of BSiPhVi-4](image)

The pyrogram of one typical oligomer, BSiPhVi-4 at 700°C is shown in Fig. 3.1.27. The pyrogram reveals that the oligomer produces $C_2$, $C_3$ hydrocarbons and benzene as the main pyrolysis products along with small amounts of other high molecular weight silicon-substituted products as indicated by peaks above 3 min. As the lower hydrocarbons are produced from vinylsiloxy moieties and benzene from phenylsiloxy moieties their relative concentration in the products will reflect the concentration of each monomer in the copolymer. The pyrolysis GC data of the oligomers are summarized in Table 3.1.7. It is observed that the ratio of area of benzene peak to area of $C_2$, $C_3$ carbon peak is 0.5:0.5 for BSiPhVi-4. As the ratio of PTMOS:VTEOS in the monomer feed is same for BSiPhVi-4, BSiPhVi-5 and BSiPhVi-6, it is expected that for all the three oligomers, the ratio of area of benzene peak to area of $C_2$, $C_3$ carbon peak should be the same. From Table 3.1.7, it is seen that for BSiPhVi-5 the ratio is almost the same as that of BSiPhVi-4. However, for BSiPhVi-6 the ratio is 0.77:0.23 suggesting that...
phenylsiloxy units are incorporated more than vinylsiloxy units when boric acid:alkoxysilane ratio is increased from 1.5:2 to 1:1 and the reason for this observation is not clearly understood.

The TG curves of BSiPhVi-4, BSiPhVi-5 and BSiPhVi-6 are compared in Fig.3.1.28. It is observed that BSiPhVi-4 synthesized using boric acid:alkoxysilane molar ratio 1:2 gives the maximum ceramic residue (~86%). It is also noticed that

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>Monomer feed ratio Boric acid:PTMOS:VTEOS</th>
<th>Ratio of area of benzene to area of $C_2, C_3$ hydrocarbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSiPhVi-4</td>
<td>1:1:1</td>
<td>0.5:0.5</td>
</tr>
<tr>
<td>BSiPhVi-5</td>
<td>1.5:1:1</td>
<td>0.52:0.48</td>
</tr>
<tr>
<td>BSiPhVi-6</td>
<td>2:1:1</td>
<td>0.77:0.23</td>
</tr>
</tbody>
</table>
the ceramic residue decreases with the increase in boric acid concentration in the reaction mixture. A weight loss of ~3% is observed around 170°C for BSiPhVi-4. The initial weight loss is found to increase with increase in boric acid concentration in the feed. This weight loss is probably due to the loss of borate esters formed during the reaction.

**Fig. 3.1.28.** TG curves of BSiPhVi-4, BSiPhVi-5 and BSiPhVi-6

**Effect of variation of mole ratio of PTMOS to VTEOS:** In the preceding section, the effect of variation of boric acid concentration was studied keeping the ratio of PTMOS to VTEOS as 1:1. In order to understand the effect of variation of PTMOS:VTEOS ratio on the processability, thermal stability and ceramic residue, borosiloxane oligomers, BSiPhVi-7 and BSiPhVi-8 were synthesized using the monomer feed ratios (boric acid:PTMOS:VTEOS) 1:1.67:0.33 and 1:0.33:1.67 respectively in diglyme at 150-160°C for 3 h. BSiPhVi-7 and BSiPhVi-8 were obtained in 95.5 and 91.9% yield. BSiPhVi-7 is soluble in THF, diglyme and dioxane and insoluble in chloroform, toluene and xylene whereas BSiPhVi-8 is insoluble in all these solvents. The GPC curve of BSiPhVi-7 shows a bimodal molecular weight distribution with $\bar{M}_w$ of 2540 and $\bar{M}_n$ of 1700. BSiPhVi-7 was also characterized by $^1$H-, $^{13}$C- and $^{29}$Si-NMR and thermal analysis. The observations made with $^1$H- and $^{13}$C-NMR spectra of BSiPhVi-7 are similar to
those of BSiPhVi-4. Based on the intensity of phenyl and vinyl protons, the ratio of phenylsiloxy to vinylsiloxy units is estimated to be 0.83:0.17 as against the calculated ratio of 0.835:0.165. The $^{29}$Si-NMR spectrum of BSiPhVi-7 is shown in Fig. 3.1.29.

The $^{29}$Si-NMR spectrum shows two broad peaks at -68 and -77 ppm and they are assigned to T$_2$ and T$_3$ structures respectively. The ratio of T$_3$ to T$_2$ structure is 1:0.48. It is worth noting that the ratio of T$_3$ to T$_2$ structures for BSiPhVi-4 is 1:0.62 where PTMOS:VTEOS ratio in the monomer feed is 1:1. This observation suggests that with the increase in PTMOS:VTEOS ratio from 1:1 to 1.67:0.33 in the monomer feed, the population of T$_3$ structures increases and this is attributed to the higher reactivity of PTMOS compared to that of VTEOS.

The oligomers, BSiPhVi-7 and BSiPhVi-8 were characterized by pyrolysis GC. The pyrolysis GC data of BSiPhVi-4, BSiPhVi-7 and BSiPhVi-8 along with the ratio of phenylsiloxy to vinylsiloxy units, as obtained from $^1$H-NMR spectra, are summarized in Table 3.1.8. The $^1$H-NMR spectra give the mole ratio of PhSiO to ViSiO units whereas pyrolysis GC data give weight ratio of PhSiO to ViSiO units and hence these two ratios could not be directly equated. However, in the present study, it is noticed that for BSiPhVi-7 and BSiPh-4, the monomer feed ratio, the ratio of PhSiO to ViSiO units as calculated from $^1$H-NMR, and the ratio of the area of benzene to that of C$_2$, C$_3$ hydrocarbons are close to each other. Thus, the ratio of the area of benzene to that of C$_2$, C$_3$ hydrocarbon could be equated to the mole
ratio of PhSiO to ViSiO units present in borosiloxane oligomer, particularly for the ones insoluble in organic solvents for which $^1$H-NMR could not be recorded. For BSiPhVi-8 which is insoluble, the ratio of the area of benzene to that of C$_2$, C$_3$ hydrocarbons is 0.34:0.66. From this data, it could be inferred that more of PhSiO units are incorporated in the oligomer than expected.

Table 3.1.8. Comparison of pyrolysis GC and $^1$H-NMR data for borosiloxane oligomers from PTMOS and VTEOS

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>Monomer feed ratio (Boric acid: PTMOS:VTEOS)</th>
<th>Ratio of PhSiO to ViSiO units in the monomer feed</th>
<th>Ratio of PhSiO to ViSiO units as calculated from $^1$H-NMR</th>
<th>Ratio of area of benzene to area of C$_2$,C$_3$, hydrocarbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSiPhVi-7</td>
<td>1:1.67:0.33</td>
<td>0.835 : 0.165</td>
<td>0.83:0.17</td>
<td>0.80:0.20</td>
</tr>
<tr>
<td>BSiPhVi-4</td>
<td>1:1:1</td>
<td>0.5:0.5</td>
<td>0.54:0.46</td>
<td>0.5:0.5</td>
</tr>
<tr>
<td>BSiPhVi-8</td>
<td>1:0.33:1.67</td>
<td>0.165:0.835</td>
<td>Insoluble</td>
<td>0.34:0.66</td>
</tr>
</tbody>
</table>

The TG curves of BSiPhVi-4, BSiPhVi-7 and BSiPhVi-8 are compared in Fig. 3.1.30. It is noticed that the ceramic residue increases with the increase in VTEOS concentration in the monomer feed. BSiPhVi-8 synthesized using boric acid:PTMOS:VTEOS in 1:0.33:1.66 ratio gives the maximum ceramic residue (~89%).

![TG curves of BSiPhVi-4, BSiPhVi-7 and BSiPhVi-8](image)

Fig. 3.1.30. TG curves of BSiPhVi-4, BSiPhVi-7 and BSiPhVi-8
3.1.5 Synthesis of borosiloxane oligomers from TEOS

Carbon-carbon (C-C) composites undergo oxidation during reentry and hence, SiC coating is applied onto C-C composites to give protection against oxidation. However, the SiC coating develops cracks due to thermal expansion mismatch between the coating and the substrate. In order to prevent the entry of oxygen through the cracks to the substrate during re-entry of space vehicles, borosilicate glass coating is applied over SiC coating. The glass coating is usually obtained by melting SiO$_2$-B$_2$O$_3$ mixture.\textsuperscript{12-17} When glass coating is applied by this method, there is a possibility that some part of the coating would be rich in SiO$_2$ and some other part of the coating would be rich in B$_2$O$_3$. It would be desirable that the composition is uniform throughout the coating. This could be achieved by using suitable preceramic polymers. The advantage of this approach is that in the preceramic polymer, SiO$_2$ and B$_2$O$_3$ units are mixed in the molecular level thereby offering a very uniform coating. Thus, it would be of interest to investigate the possibility of synthesizing a suitable precursor for this purpose. Preferably, such a precursor should contain only B, Si and O. There should be no carbon present or if carbon is present it should be knocked off during pyrolysis at 900°C. This could be achieved by reacting boric acid with TEOS in suitable proportion.

3.1.5.1 Effect of mole ratio of boric acid to TEOS

To study the effect of mole ratio of boric acid to TEOS on the processability and thermal stability of the borosiloxane oligomer obtained, the reaction was carried out for the monomer feed ratios (boric acid:TEOS) 1:2, 1:1.5 and 1:1 using diglyme as solvent and HCl as the catalyst at 150-160°C for 3 h and the oligomers obtained are referred to as BSiT-1, BSiT-2 and BSiT-3 respectively. BSiT-1, BSiT-2 and BSiT-3 were obtained in 78.0, 66.0 and 35.7% yield respectively. These oligomers are insoluble in organic solvents. They were characterized by IR, TGA and elemental analysis. The IR spectra (Fig. 3.1.31) of these oligomers show peaks due to Si-O-Si, Si-O-B, B-OH and B-O-B groups and the assignments of the peaks were discussed earlier (Table 3.1.1). When the IR spectra of BSiT systems are compared with those of BSiPh or BSiVi systems, it is
noticed that the broad peak at 884 cm\(^{-1}\) due to B-O-Si observed in the IR spectra of organosubstituted borosiloxanes is absent in the IR spectra of BSiT systems and instead a broad peak is observed at 940 cm\(^{-1}\). It is reported that Si-O-B stretching appears at 880 cm\(^{-1}\) when organic substituent is present on silicon.\(^{14}\) In the absence of organic substituents, the stretching vibration of B-O-Si appears at 970 cm\(^{-1}\). The sharp peak observed at 884 cm\(^{-1}\) in BSiT system is due to B-O-B stretching.

Fig. 3.1.31. IR spectra of BSiT-1, BSiT-2 and BSiT-3

The TG curves of the three oligomers are compared in Fig. 3.1.32. BSiT-1, BSiT-2 and BSiT-3 give ceramic residue of 73, 78 and 80% respectively at 900°C in argon. It is observed that the overall thermal stability increases with the decrease in TEOS concentration in the monomer feed. The trend observed for the overall thermal stability and ceramic residue is just the reverse of the trend noticed for borosiloxane oligomers from organoalkoxysilanes such as PTMOS, PTEOS, VTEOS and mixtures of VTEOS and PTMOS/PTEOS. For BSiPh, BSiVi and BSiPhVi systems, with increase in boric acid concentration, the weight loss up to 170°C increases whereas for TEOS-based system, with increase in boric acid concentration in the monomer feed, the weight loss up to 170°C decreases.
This observation suggests that for TEOS-based system, the extent of formation of borate ester increases as TEOS concentration in the monomer feed increases. As borate ester is formed due to the transesterification of B-OH with Si-OEt, such a reaction results in the formation of silanol (Si-OH) groups. When the extent of formation of borate ester increases the formation of Si-OH groups would also increase. The Si-OH group is highly reactive and would undergo self-condensation resulting in the formation of Si-O-Si linkage and water. Thus, silicate-type structures would be predominantly formed when the extent of silanol formation is more. This explains the maximum overall thermal stability and ceramic residue obtained for BSiT-3.

![Fig. 3.1.32. TG curves of BSiT-1, BSiT-2 and BSiT-3](image)

If the reason given above to explain the trend observed for thermal stability is correct, then the boron content in the system should increase with the decrease in boric acid concentration in the monomer feed. The boron content in BSiT-1, BSiT-2 and BSiT-3 is found to be 6.5, 4.1 and 2.5% respectively. It is noticed that the carbon content of the oligomers decreases with increase in boric acid concentration in the monomer feed. BSiT-1, BSiT-2 and BSiT-3 have carbon content of 6.2, 5.7 and 2.4% respectively. The decrease in carbon content with the increase in boric acid concentration is attributed to the increase in the extent of reaction of B-OH group with Si-OEt.
The reverse trend in thermal stability observed for boric acid-TEOS system when compared to boric acid-organoalkoxysilane system suggests that TEOS behaves differently from other organotrialkoxysilanes with respect to its reaction with boric acid. For organotrialkoxysilanes Si-O-B linkage is formed more whereas for TEOS, Si-O-B linkage is formed to a lesser extent and silicate-type structures is probably formed to a higher extent when boric acid concentration in the monomer feed is increased.

3.1.6 Synthesis of borosiloxane oligomers without using catalyst

In the studies presented above, borosiloxane oligomers were synthesized using HCl as catalyst. It would be desirable to carry out the reaction of boric acid and alkoxysilanes without using any catalyst particularly when alkoxysilane contains reactive groups that would undergo polymerization in presence of catalyst.

3.1.6.1 Borosiloxane oligomers from PTMOS and PTEOS

The oligomers, BSiPh-6 and BSiPh-7 were synthesized by reacting boric acid with PTMOS and PTEOS respectively in 1:2 mole ratio in diglyme at 150-160°C without using any catalyst for 3 h and the oligomers were obtained in 76.6 and 64.5% yield respectively. These oligomers are soluble in organic solvents such as THF, 1,4-dioxane, toluene, chloroform and diglyme. The GPC curves of the oligomers are shown in Fig. 3.1.33. The oligomers show bimodal molecular weight distribution. BSiPh-6 has $\overline{M}_w$ of 4160 and $\overline{M}_n$ of 2200 whereas BSiPh-7 has $\overline{M}_w$ of 1520 and $\overline{M}_n$ of 810. Comparison of $\overline{M}_w$ and $\overline{M}_n$ of BSiPh-6 and BSiPh-7 with the corresponding ones synthesized in the presence of catalyst suggests that $\overline{M}_w$ and $\overline{M}_n$ of the former are higher than the latter. When the synthesis of borosiloxane oligomers is carried out in the absence of catalyst, hydrolysis of Si-OR to Si-OH is eliminated and the reaction of B-OH with Si-OR forming Si-O-B and transesterification resulting in the formation of Si-OH and borate ester are only feasible. In the presence of catalyst, in addition to the condensation of Si-OR and B-OH groups forming Si-O-B bond, the formation of Si-OH due to the hydrolysis of Si-OR would also take place. The Si-OH thus
formed would self condense forming Si-O-Si linkage or condense with boric acid resulting in Si-O-B linkage. The GPC results suggest that relatively high molecular weight oligomers are formed when the reaction proceeds through the condensation of Si-OR and B-OH. It is interesting to note that both $M_w$ and $M_n$ of BSiPh-7 are lower than those of BSiPh-6. This is attributed to the higher reactivity of PTMOS compared to PTEOS.

![Fig. 3.1.33. GPC curves of BSiPh-6 and BSiPh-7](image)

The IR spectra of both the oligomers indicate the presence of B-O-Si, Si-O-Si, Si-OH and B-OH. $^1$H- and $^{13}$C-NMR spectral studies of BSiPh-6 and BSiPh-7 indicate the absence of alkoxy groups suggesting that complete reaction of Si-OR with B-OH has taken place.

The $^{29}$Si-NMR spectra of BSiPh-6 and BSiPh-7 are shown in Fig. 3.1.34. For BSiPh-6, $T_1$ and $T_2$ structures are observed at -68 and -71 respectively and $T_3$ structures are observed at -77 and -79 ppm. For BSiPh-7, $T_o$, $T_1$ and $T_2$ structures are observed at -61, -68 and -70 ppm respectively and $T_3$ structures are observed at -77 and -79 ppm. The ratio of $T_3:T_1+T_2$ structures is 1:0.46 for BSiPh-6 and 1:0.54 for BSiPh-7. The lower concentration of $T_1$ and $T_2$ structures in BSiPh-6 compared to that of BSiPh-7 is attributed to the higher reactivity of PTMOS than that of PTEOS.
Fig. 3.1.34. $^{29}$Si-NMR spectra of BSiPh-6 and BSiPh-7

The TG curves of BSiPh-6 and BSiPh-7 show a sudden weight loss of 5-6% in the temperature range of 100-150°C which is attributed to the loss of low molecular weight products and borate esters. It is found that both the oligomers are stable up to 500°C. BSiPh-6 and BSiPh-7 give ceramic residue of 75 and 65% respectively at 900°C in argon atmosphere.

**Effect of reaction time:** As PTEOS is cheaper than PTMOS, in the study presented in the earlier part of this chapter, attention was focused on borosiloxane from PTEOS. It is observed that when the reaction of boric acid and PTEOS in diglyme in presence of HCl is carried out for 6 h instead of 3 h for the monomer
feed ratio 1:2 (boric acid:PTEOS) there is an increase in molecular weight and ceramic residue. Thus, it would be of interest to study the effect of reaction time on the synthesis of borosiloxane oligomer from PTEOS without using any catalyst. The reaction of boric acid with PTEOS for the monomer feed ratio 1:2 was carried out in diglyme at 150-160°C for 6 h in the absence of catalyst and the oligomer obtained in 88% yield is referred to as BSiPh-8. When the reaction time is increased from 3 h to 6 h, \( \bar{M}_w \) increases from 1520 to 3190 and \( \bar{M}_n \) increases from 810 to 2200.

The \(^{29}\text{Si-NMR} \) spectrum of BSiPh-8 is shown in Fig. 3.1.35. It shows peaks at -70 and -78 ppm corresponding to \( T_2 \) and \( T_3 \) structures. It is interesting to note that the peaks at -61 and -68 ppm corresponding to \( T_0 \) and \( T_1 \) structures respectively present in the \(^{29}\text{Si-NMR} \) spectrum of BSiPh-7, is absent in the \(^{29}\text{Si-NMR} \) spectrum of BSiPh-8 suggesting that with the increase in reaction time, \( T_0 \) and \( T_1 \) structures undergo further reaction leading to the formation of \( T_2 \) or \( T_3 \) structures. The ratio of \( T_3:T_2 \) structure for BSiPh-8 is 1:0.51.

![Fig. 3.1.35. \(^{29}\text{Si-NMR} \) spectrum of BSiPh-8](image)

The TG curves of BSiPh-7 and BSiPh-8 are compared in Fig. 3.1.36. It is observed that both the oligomers have almost the same thermal stability though they differ in their molecular weight. The oligomers give a ceramic residue of 65%. It is worth mentioning that BSiPh-5, synthesized by reacting boric acid and PTEOS (1:2 mole ratio) for 6 h in presence of catalyst gives 72% ceramic residue.
at 900°C. \(^{29}\text{Si}\)-NMR spectral studies indicate that for this oligomer the ratio of \(T_3\) to \(T_1+T_2\) structures is 1:0.32, for BSiPh-5 whereas the ratio is 1:0.52 for BSiPh-8. The above observation suggests that higher ceramic residue of BSiPh-5 compared to that of BSiPh-8 is attributed to presence of higher population of \(T_3\) structures in BSiPh-5 than in BSiPh-7 or BSiPh-8.

![Fig. 3.1.36. TG curves of BSiPh-7 and BSiPh-8](image)

3.1.6.2 Borosiloxane oligomers from boric acid and TEOS

The condensation of boric acid and TEOS (mole ratio:1:1.5) was carried out in diglyme at 150-160°C for 3 h in the absence of catalyst and the oligomer obtained is designated as BSiT-4. It is insoluble in organic solvents. The IR spectrum of BSiT-4 is compared with that of the corresponding oligomer synthesized in the presence of catalyst in Fig.3.1.37. It is noticed that the intensity of the peaks due to B-OH group at 2262, 1194 and 884 cm\(^{-1}\) and the intensity of the peak due to O-Si-O at 547 cm\(^{-1}\) decrease considerably, and the intensity of the peak at 940 cm\(^{-1}\) corresponding to Si-O-B increases when the reaction is carried out without using any catalyst. The above observations suggest that when the reaction of boric acid and TEOS is carried out in the absence of catalyst the formation of Si-O-B bond is more favored. BSiT-4 contains 10.9% of carbon. The higher percentage of carbon in BSiT-4 when compared to that of BSiT-2 (2.4%) suggests that unreacted SiOEt group is present more when the reaction of boric acid and TEOS is carried out in the absence of catalyst.
The TG curves of BSiT-2 and BSiT-4 are compared in Fig. 3.1.38. BSiT-2 and BSiT-4 give ceramic residue of 78 and 75% respectively at 900°C. The weight loss up to 170°C is more for BSiT-4 than for BSiT-2 indicating that low molecular weight volatile products are present more in BSiT-4 than in BSiT-2.
3.1.7 Conclusions

Borosiloxane oligomers were synthesized by reacting boric acid with PTMOS, PTEOS, VTEOS, mixtures of phenyl and vinyl alkoxysilanes and TEOS in diglyme at 150-160°C using HCl as catalyst. The reactions were carried out in the absence of catalyst also. Based on the observations presented in the chapter, the following conclusions are drawn for the synthesis of borosiloxane oligomers carried out in the presence of HCl:

i) When the reaction is carried out for 3 h, borosiloxane oligomer synthesized from PTMOS gives higher ceramic residue than PTEOS-based one and this is attributed to the presence of more branched structures (T_2 and T_3) in the former arising due to the higher reactivity of PTMOS. $^{29}$Si-NMR data support this conclusion.

ii) For borosiloxane oligomer from PTEOS, the ceramic residue at 900°C increases from 65 to 72% with the increase in reaction time from 3 h to 6 h.

iii) For PTEOS-based borosiloxane oligomer, with increase in boric acid concentration in the monomer feed both $\bar{M}_w$ and $\bar{M}_n$ increase. TG studies indicated that with increase in boric acid concentration the initial weight loss increases and this is attributed to the formation of borate esters resulting from the trans-esterification reaction. However, the oligomers synthesized using the three different mole ratios (boric acid:PTEOS-1:1, 1:1.5, 1:2) give the same ceramic residue at 900°C.

iv) Borosiloxane oligomers synthesized from VTEOS and boric acid using different mole ratios were found to be insoluble in all organic solvents. Compared to PTMOS- and PTEOS-based systems, VTEOS-based system gives higher ceramic residue and this is attributed to the crosslinking arising from the polymerization of vinyl group. For VTEOS-based system, the ceramic residue decreases with increase in boric acid concentration.

v) In an attempt to obtain processable borosiloxane oligomers capable of giving higher ceramic residue, oligomers were synthesized by reacting...
boric acid with mixtures of PTEOS/VTEOS and PTMOS/VTEOS. Oligomers obtained from PTEOS/VTEOS mixture were insoluble in organic solvents. Soluble oligomers were obtained when the oligomers were synthesized from mixtures of PTMOS/VTEOS for the monomer feed ratios (boric acid:PTMOS:VTEOS) 1:1:1 and 1:1.67:0.33. A maximum ceramic residue of 86% is obtained for this system at 900°C.

vi) For borosiloxanes based on TEOS, the carbon content decreases with increase in boric acid concentration. Unlike for the other systems, where the overall thermal stability decreases with increase in boric acid concentration in the feed, for TEOS-based system the thermal stability increases with increase in boric acid concentration. This is attributed to the trans-esterification of the silanol groups and subsequent condensation of silanol groups forming silicate-type network structure.

The following conclusions are drawn for the synthesis of borosiloxane oligomers in the absence of catalyst:

i) For PTMOS- and PTEOS-based systems, the molecular weight is higher when the reaction is carried out in the absence of catalyst than in the presence of catalyst. This is because in the absence of catalyst, hydrolysis of Si-OR to SiOH is eliminated and the reaction of boric acid and alkoxysilane can take place only through the condensation of B-OH and Si-OEt leading to more number of Si-O-B linkages contributing towards the increase in molecular weight.

ii) For TEOS-based system, the carbon content is found to be more when the reaction is carried out in the absence of catalyst than in the presence of catalyst and this is due to the presence of residual -OEt groups. Comparison of thermal stability of TEOS-based system for the monomer feed ratio 1:1.5 (boric acid:TEOS) suggests that the oligomer (BSiT-4) synthesized in the absence of catalyst is higher than that of the oligomer (BSiT-2) synthesized in the presence of catalyst and this is attributed to the presence of more amount of low molecular weight products in the former.
References

Chapter 3.2

Synthesis of epoxy functionalized borosiloxane oligomers

This chapter reports the synthesis and characterization of epoxy- and epoxy and vinyl-functionalized borosiloxane oligomers. The effect of solvent and monomer feed ratio on the processability, molecular weight and thermal stability was studied.

*The results presented in this chapter form the basis for the following patent applications and publications in International journals:


3.2.1 Background

The previous chapter discussed the synthesis and characterization of borosiloxane oligomers from different alkoxysilanes such as PTMOS, PTEOS, VTEOS, TEOS and mixtures of alkoxysilanes. It is observed that the presence of vinyl-functional group improves the ceramic residue considerably and this is attributed to crosslinking resulting from the thermal polymerization of vinyl group. Unlike vinyl functional group, epoxy functional group can undergo curing at ambient temperature in presence of suitable curative and/or catalyst. Thus, it would be of interest to explore the possibility of synthesizing epoxy functionalized borosiloxane oligomers. There appears to be no report on the synthesis of such oligomers though there are reports on the synthesis of epoxy functionalized sol-gels containing siloxane linkages.\textsuperscript{1-10} Epoxy-functionalized borosiloxane oligomers can also serve as building blocks for inorganic-organic hybrid polymers. Hence, the present study explores the possibility of synthesizing borosiloxane oligomers by reacting boric acid with glycidyloxypropyltrimethoxysilane (GPTMOS) in a suitable solvent. Incorporation of aliphatic linkages (\(\text{CH}_2-\text{CH}_2-\text{CH}_2\)) in the borosiloxane oligomers becomes inevitable when GPTMOS is used.

It would be all the more interesting if one can synthesize borosiloxane oligomers containing both epoxy and vinyl group. The advantage of such an approach is that the epoxy group can undergo curing at ambient temperature and vinyl group can undergo curing at elevated temperature thereby combining the advantages of both epoxy and vinyl functional groups in the same oligomer. Such oligomers can be effectively used as infiltrating resin for CMCs. After the infiltration of the porous composite with epoxy and vinyl functionalized resin, the epoxy group can be first cured thereby preventing the ooze out of the resin from the composite. Subsequently, the vinyl group can be thermally polymerized to improve the ceramic residue. Keeping in view of the above advantages, in addition to the synthesis of epoxy-functionalized borosiloxanes, the present study also
3.2.2 Epoxy-functionalized borosiloxane oligomers

3.2.2.1 Effect of solvents

For the synthesis of epoxy-functionalized oligomers, dioxane and diglyme were used as solvents. The boiling point of dioxane is lower than that of diglyme and hence, it is easier to remove this solvent from the reaction medium. However, the low boiling point of dioxane may limit the temperature for carrying out the condensation reaction. The advantage in using dioxane is that it can be removed by freeze-drying method, thereby providing the scope for processing the borosiloxane oligomer at low temperatures which would prevent the reaction of epoxy functional group with unreacted B-OH groups.

For studying the effect of solvents, boric acid:GPTMOS mole ratio of 0.5:1 was used. For the reaction in dioxane, the oil bath temperature was maintained at around 120°C and for the reaction in diglyme, the bath temperature was maintained at 150-160°C. No catalyst was used for the synthesis. The oligomers synthesized in dioxane and diglyme are designated as BSiEp-1 and BSiEp-2 respectively. Low boiling by-products formed during the reaction were distilled out and analyzed by GC. During the flash evaporation, the oligomers got gelled. The gas chromatogram of the distillate, obtained in the synthesis of BSiEp-1 is given in Fig. 3.2.1. Two major peaks are observed at retention time 0.73 and 1.56 min corresponding to methanol and dioxane respectively. Methanol as a by-product can be formed only when B-OH reacts with Si-OMe groups forming B-O-Si bonds. Based on the GC evidence, the reaction scheme as shown in Scheme 3.2.1 is proposed for the formation of epoxy-functionalized borosiloxane oligomer.

As boric acid and GPTMOS are taken in 0.5:1 mole ratio, B-OH and Si-OMe would be present in 0.5:1 equivalent ratio in the reaction mixture implying that the oligomer would contain unreacted Si-OMe groups. For finding out the yield, the solvents were removed by flash evaporation and during this process the
oligomers got gelled. During flash evaporation, the heat applied may promote the reaction of unreacted B-OH groups with the epoxy groups resulting in the formation of crosslinked network (Scheme 3.2.2). In addition to this reaction, other reactions as shown in Scheme 3.1.2 (Chapter 3.1) may also take place.

Fig. 3.2.1. GC of the distillate obtained during the synthesis of BSiEp-1

Scheme 3.2.1. Synthesis of epoxy-functionalized borosiloxane oligomer
Synthesis of epoxy functionalized...

Scheme 3.2.2. Possible reaction of epoxy group with B-OH group

The IR spectra of crosslinked oligomers, BSiEp-1 and BSiEp-2 synthesized in dioxane and diglyme respectively are shown in Fig. 3.2.2.

![IR spectra of crosslinked BSiEp-1 and BSiEp-2](image)

Fig. 3.2.2. IR spectra of crosslinked BSiEp-1 and BSiEp-2

The peaks corresponding to Si-OH, B-O, Si-O and epoxy groups are observed at 3420, 1415, 1104 and 906 cm\(^{-1}\) respectively. By comparing IR spectrum of the product synthesized in dioxane with that in diglyme, the following
observations were made: (i) the peak at 880 cm\(^{-1}\) due to B-O-Si linkage is present in the IR spectra of both the samples, (ii) the relative intensity of the peaks at 3420 and 1415 cm\(^{-1}\) decreases and the intensity of the peak at 1104 cm\(^{-1}\) increases when diglyme is used in place of dioxane and (iii) the peaks corresponding to B-O-Si linkage at 880 cm\(^{-1}\) is more prominent when the reaction is carried out in diglyme. These observations clearly suggest that the condensation of B-OH groups with Si-OMe takes place and the extent of this reaction is more when diglyme is used as the solvent. Diglyme has higher boiling point (165°C) than dioxane (102°C) and hence, it was possible to increase the reaction temperature when diglyme was used. Higher reaction temperature would enhance the extent of reaction of B-OH and Si-OMe.

3.2.2.2 Effect of mole ratio of boric acid to GPTMOS

For studying the effect of mole ratio of boric acid to GPTMOS on the processability, yield and thermal stability of the product obtained, the reaction was carried out for the monomer feed ratios (boric acid:GPTMOS) 0.5:1.5, 0.5:1, 1:1 and 1.5:1 using dioxane as solvent keeping the oil bath temperature at 120°C. Yield and the nature of the product obtained are given in Table 3.2.1.

Table 3.2.1. Effect of monomer feed ratio on yield and nature of oligomer

<table>
<thead>
<tr>
<th>Mole Ratio (Boric acid : GPTMOS)</th>
<th>Flash-dried</th>
<th></th>
<th>Freeze-dried</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample Code</td>
<td>Yield (%)</td>
<td>Nature of product</td>
<td>Sample Code</td>
</tr>
<tr>
<td>0.5 : 1</td>
<td>BSiEp-1</td>
<td>81.6</td>
<td>Gel</td>
<td>BSiEp-3B</td>
</tr>
<tr>
<td>0.5 : 1.5</td>
<td>BSiEp-3A</td>
<td>92.1</td>
<td>Resinous</td>
<td>BSiEp-4B</td>
</tr>
<tr>
<td>1:1</td>
<td>BSiEp-4A</td>
<td>88.6</td>
<td>Gel</td>
<td></td>
</tr>
<tr>
<td>1.5 : 1</td>
<td>BSiEp-5</td>
<td>90.1</td>
<td>Gel</td>
<td></td>
</tr>
</tbody>
</table>

It is worth mentioning that flash drying of the samples synthesized from the monomer feed ratios (boric acid:GPTMOS) 0.5:1, 1:1 and 1.5:1 results invariably in the formation of a gelled material. It is interesting to note that when the monomer feed ratio is 0.5:1.5, resinous material is obtained both in freeze-drying and flash-drying. When the monomer feed ratio is 0.5:1.5, for each B atom
three Si atoms are available and hence, the availability of B-OH for reaction with epoxy group during flash evaporation is expected to be bare minimum when compared to the resins synthesized using the other monomer feed ratios. For the monomer feed ratio 1:1, the freeze-dried sample is found to be insoluble in common organic solvents. This suggests that irrespective of the processing condition, when boric acid concentration is increased from 0.5:1.5 to 1:1 the oligomer obtained undergoes crosslinking/gelation.

The solid content of BSiEp oligomers obtained by reacting boric acid and GPTMOS in 0.5:1.5 mole ratio was determined and it is found that the resin processed by freeze drying has solid content of 80.6% while the resin processed by flash evaporation has solid content of 74.2%. This suggests that the resins contain residual dioxane. Apparently higher yield obtained for the monomer feed ratio 0.5:1.5 when compared to the other systems is due to the presence of solvent, dioxane. The freeze-dried and flash-dried samples have epoxy values of 3.8 and 4.2 eqv/kg respectively.

When the mole ratio of boric acid:GPTMOS is 0.5:1.5, the product is obtained as a resin which is soluble in organic solvents such as toluene, xylene, THF, chloroform, dioxane and diglyme. The GPC curves of freeze- and flash-dried samples are given in Fig. 3.2.3. The flash-dried sample has $\bar{M}_w$ of 4340 and $\bar{M}_n$ of 330 and the freeze-dried sample has $\bar{M}_w$ of 3300 and $\bar{M}_n$ of 250.

![Fig. 3.2.3. GPC curves of BSiEp-3A and BSiEp-3B](image-url)
The GPC curve of the flash-dried sample shows four peaks and for the freeze-dried one, three peaks are observed. It is interesting to note that the small peak at retention time 11.7 min, which is present in BSiEp-3A is almost absent in BSiEp-3B. In BSiEp-3A, probably chain extension takes place during flash evaporation involving low molecular weight oligomers present in the system and the ones having higher molecular weight.

The TG curves of BSiEp-1, BSiEp-4A and BSiEp-4B are compared are compared in Fig. 3.2.4. It is noticed that the gelled material obtained for the monomer feed ratio 0.5:1 has higher thermal stability when compared to the other two samples synthesized using the monomer feed ratio 1:1. For the latter ones, sudden weight loss of about 12-15% is observed in the temperature range 100-130°C. Interestingly, such instantaneous weight loss is not noticed for the gelled material prepared from the monomer feed ratio 0.5:1. Thus, the above weight loss observed for the ones prepared from the monomer feed ratio 1:1 is probably due to the presence of low molecular weight borate esters which volatilize off. For the monomer feed ratio 1:1, the flash-dried sample gives higher ceramic residue when compared to that of the freeze dried one. This observation supports the view that during flash drying, crosslinking reactions take place involving unreacted B-OH group with Si-OMe groups/epoxy groups.

Fig. 3.2.4. TG curves of a) BSiEp-1, b) BSiEp-4A and c) BSiEp-4B
The IR spectra of the flash-dried and freeze-dried samples look alike and indicate the presence of B-O-Si, Si-O and epoxy groups. $^1$H- and $^{13}$C-NMR spectra of the oligomers are shown in Figs. 3.2.5 and 3.2.6 respectively and the assignments of the chemical shifts are given in Table 3.2.2. The salient feature of the $^{13}$C-NMR spectra is that multiple peaks are observed for Si-CH$_2$ carbon. This is attributed to various possible structures.

Fig. 3.2.5. $^1$H-NMR spectra BSiEp-3A and BSiEp-3B
Fig. 3.2.6. $^{13}$C-NMR spectra of BSIep-3A and BSIep-3B
Table 3.2.2. $^1$H- and $^{13}$C-NMR spectral assignments of BSiEp oligomer

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Chemical shift (ppm)</th>
<th>Carbon</th>
<th>Chemical shift (ppm)</th>
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<tr>
<td></td>
<td>$^1$H</td>
<td>$^{13}$C</td>
<td>$^1$H</td>
</tr>
<tr>
<td>$C_1$</td>
<td>2.59, 2.79</td>
<td>44.27</td>
<td>$C_5$</td>
</tr>
<tr>
<td>$C_2$</td>
<td>3.13</td>
<td>50.30</td>
<td>$C_6$</td>
</tr>
<tr>
<td>$C_3$</td>
<td>3.42</td>
<td>71.41</td>
<td>$C_7$</td>
</tr>
<tr>
<td>$C_4$</td>
<td>3.2-3.4</td>
<td>71.48</td>
<td>$C_8$</td>
</tr>
</tbody>
</table>

The $^{29}$Si-NMR spectra of the flash-dried and freeze-dried samples are given in Fig. 3.2.7. The flash dried sample shows four sets of peaks: i) -40.48 and -41.71 ppm, ii) -47.66, -48.95, and -50.14 ppm, iii) -54.95, -56.30 and -59.17 ppm and iv) -65.23 and -68.80 ppm. Interestingly, the $^{29}$Si-NMR spectrum of the freeze-dried sample exhibits only three sets of peaks: i) -48.16 ppm, ii) -54.91 and -58.23 ppm and iii) -67.80 ppm. Matejka et al.\textsuperscript{11}, for sol-gel polymerisation of GPTMOS, assigned the $^{29}$Si-NMR spectral signals in the region -41 to -43 ppm to $T_o$, -50 to -52 ppm to $T_1$, -55 to -56 ppm to $T_{2C}$ (where $T_{2C}$ is the $T_2$ unit involved in a small cycle), -59 to -61 ppm to $T_2$ and -66 to -69 ppm to $T_3$ where $T_i$ indicates the unit with $i$ siloxane ($O-Si$ bonds) attached to the central silicon. It is reported that Si-O-Si and Si-O-B units do not differ in the $^{29}$Si-NMR chemical shifts.\textsuperscript{12-17} This implies that the partial or complete replacement of O-Si linkage attached to central Si by O-B linkages would not alter the chemical shift. In the flash-dried sample, the peak at -40.48 ppm is due to unreacted GPTMOS and the peak at -41.71 is due to
partially hydrolyzed GPTMOS, i.e., T₀ units with -OH group. As mentioned earlier, these two peaks are not observed in the freeze-dried sample. As freeze drying is more effective than flash drying, the low molecular weight products are probably removed from the reaction product.
As GPTMOS is used in excess of boric acid, the formation of GPTMOS-based cage molecules cannot be completely ruled out. During sol-gel process GPTMOS is reported\textsuperscript{11} to form silsesquioxane (T\textsubscript{8}) cage structure (Fig. 3.2.8) and this structure is observed at -67.2 ppm.\textsuperscript{11} Thus, the peak centered around -67.8 ppm is probably due to the presence of both T\textsubscript{3} and T\textsubscript{8} structures.

![Fig. 3.2.8. Cubic cage structure (T\textsubscript{8}) formed from GPTMOS\textsuperscript{11}](image)

### 3.2.3 Epoxy and vinyl-functionalized borosiloxane oligomers

The foregoing section dealt with the synthesis and characterization of epoxy-functionalized borosiloxane oligomers. As discussed in the background, it is advantageous to combine both epoxy and vinyl functional groups in the same oligomer as they can undergo curing at two different temperature regions.

#### 3.2.3.1 Effect of solvent on the reaction of boric acid, GPTMOS and VTEOS

To study the effect of solvent on the reaction of boric acid, GPTMOS and VTEOS in 1:1:1 mole ratio, the synthesis was carried out by using diglyme and dioxane as solvents following the procedure described in the experimental section. The oligomers synthesized in diglyme and dioxane are referred to as BSiEpVi-1 and BSiEpVi-2 respectively. The reaction scheme for the synthesis of vinyl and epoxy functionalized borosiloxane oligomer is shown in Scheme 3.2.3.

BSiEpVi-1 is insoluble in organic solvents such as THF, 1,4-dioxane, toluene, chloroform and diglyme whereas BSiEpVi-2 is soluble in all the above solvents. When diglyme is used as solvent, higher processing temperature (~150°C) is required for its removal which probably promotes crosslinking. The
GPC of BSiEpVi-2 (Fig. 3.2.9) shows bimodal molecular weight distribution with \( \overline{M}_w \) of 4370 and \( \overline{M}_n \) of 2020. The epoxy value of BSiEpVi-2 is 1.7 eqv/kg and viscosity of the resin is 1830 cps at 30°C.

Scheme 3.2.3. Synthesis of vinyl and epoxy functionalized borosiloxane oligomer

Fig. 3.2.9. GPC curve of BSiEpVi-2
Synthesis of epoxy functionalized....

The IR spectrum of BSiEpVi-1 is shown in Fig. 3.2.10. It shows characteristic absorption peaks due to the presence of B-O-Si at 696 cm\(^{-1}\), Si-Vi at 1633, 1412 and 759 cm\(^{-1}\), Si-OH at 3432 cm\(^{-1}\), Si-O-Si at 1101 cm\(^{-1}\), epoxy group at 903 cm\(^{-1}\) and methylene groups from the glycidyloxypropyl part at 2937 cm\(^{-1}\).

![IR spectrum of BSiEpVi-1](image)

Fig. 3.2.10. IR spectrum of BSiEpVi-1

The \(^1\)H- and \(^{13}\)C-NMR spectra of BSiEpVi-2 are shown in Figs. 3.2.11 and 3.2.12 respectively and the assignments of the chemical shifts are given in Table 3.2.3.

The \(^{29}\)Si-NMR spectrum of BSiEpVi-2 (Fig. 3.2.13) indicates the presence of different kinds of silicon atoms as evidenced by the peaks at -50, -55, -57, -64, -72 and -80 ppm. The peaks at -50, -55, -57 and -64 ppm are due to different kinds of Si atoms arising from the condensation of GPTMOS with boric acid. The peak at -50 ppm is due to T\(_1\) unit and the peak at -55 ppm is probably due to T\(_{2C}\). The broad peak centered around -57 ppm is due to T\(_2\) units and the peak at -64 ppm is attributed to T\(_3\) units. The peaks at -72 and -80 ppm are assigned to T\(_2\) and T\(_3\) units formed due to the reaction of VTEOS with boric acid. The epoxy to vinyl ratio calculated from the \(^1\)H-NMR is 1:1.04 as against 1:1, calculated from the monomer feed ratio.
Fig. 3.2.11. $^1$H-NMR spectrum of BSiEpVi -2

Fig. 3.2.12. $^{13}$C-NMR spectrum of BSiEpVi -2
Table 3.2.3. $^1$H- and $^{13}$C-NMR spectral assignments of BSiEpVi -2 oligomer

<table>
<thead>
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<th>Carbon</th>
<th>Chemical shift (ppm)</th>
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<th>Chemical shift (ppm)</th>
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<td>$^1$H</td>
<td>$^{13}$C</td>
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<tr>
<td>$C_6$</td>
<td>0.68</td>
<td>9.2</td>
<td>$C_{12}$</td>
</tr>
</tbody>
</table>

Fig. 3.2.13. $^{29}$Si-NMR spectrum of BSiEpVi -2
3.2.3.2 Effect of mole ratio on the reaction of boric acid, GPTMOS and VTEOS

To study the effect of mole ratio of boric acid to alkoxysilane on the processability and thermal stability of the product obtained, the reaction was carried out for the monomer feed ratios (boric acid:GPTMOS:VTEOS) 1:0.67:1.33 and 1:1.33:0.67 using dioxane as solvent under the same experimental conditions used for BSiEpVi-1 and the oligomers obtained are referred to as BSiEpVi-3 and BSiEpVi-4 respectively.

It is worth mentioning that the sample synthesized from the monomer feed ratio (boric acid:GPTMOS:VTEOS) 1:0.66:1.33 results in the formation of a gelled product whereas BSiEpVi-4 is resinous and soluble in common organic solvents such as THF, 1,4-dioxane, toluene, chloroform and diglyme.

The oligomer, BSiEpVi-4 was characterized by GPC, IR and $^1$H-, $^{13}$C- and $^{29}$Si-NMR spectral analysis. GPC curve of BSiEpVi-4 is shown in Fig. 3.2.14. BSiEpVi-4 has $M_w$ of 4710 and $M_n$ of 2560. It is interesting to note that BSiEpVi-4 synthesized using the monomer feed ratio (boric acid:GPTMOS:VTEOS) of 1:1.33:0.67 has higher molecular weight compared to BSiEpVi-2 synthesized using the monomer feed ratio 1:1:1. The viscosity at 30°C of BSiEpVi-4 (8130 cps) is also higher than that of BSiEpVi-2 (1830 cps). BSiEpVi-4 has epoxy value of 2.0 eqv/kg.

![Fig. 3.2.14. GPC curve of BSiEpVi-4](image-url)
The IR, $^1$H- and $^{13}$C-NMR spectra of BSiEpVi-4 are similar to those of BSiEpVi-2. $^{29}$Si-NMR spectrum of BSiEpVi-4 is shown in Fig. 3.2.15. The peaks observed for BSiEpVi-2 are present in the $^{29}$Si-NMR spectrum of BSiEpVi-4. As the concentration of GPTMOS in the monomer feed ratio is higher in the case of BSiEpVi-4 than in the case of BSiEpVi-2, the peaks corresponding to glycidyloxypropylsiloxyl units are more prominent. The epoxy to vinyl ratio calculated from the $^1$H-NMR is 1:0.57 as against 1:0.5, calculated from the monomer feed ratio.

Fig. 3.2.15. $^{29}$Si-NMR spectrum of BSiEpVi-4

In order to understand the effect of incorporation of vinyl group on the thermal stability of the epoxy functionalized oligomers, the TG curves of BSiEp-1 (containing only epoxy functional group) and BSiEpVi-3 (containing both epoxy and vinyl functional groups) are compared in Fig. 3.2.16. It is observed that the incorporation of the vinyl group improves the overall thermal stability and the char residue. BSiEp-1 and BSiEpVi-3 give ceramic residue of 42% and 59% respectively. Though the ceramic residue of BSiEpVi-3 is higher than that of BSiEp-1, it is lower than that of BSiVi-1 (containing only vinyl functional group). This is attributed to the presence of aliphatic linkages (glycidyloxypropyl) in BSiEpVi-3.
3.2.4 Conclusions

Epoxy-functionalized borosiloxane oligomers were synthesized by reacting boric acid and GPTMOS in diglyme/dioxane without using any catalyst. Oligomers containing both vinyl- and epoxy-functional groups were also synthesized by reacting boric acid with a mixture of GPTMOS and VTEOS in dioxane/diglyme in the absence of catalyst. Based on the study presented in this chapter, the following conclusions have been drawn:

i) When the oligomer was synthesized using the monomer feed ratio 0.5:1 (boric acid:GPTMOS), a gelled product was obtained irrespective of solvent (dioxane/diglyme) used. This is attributed to the reaction of epoxy groups with unreacted B-OH groups resulting in the formation of a gel.

ii) For the epoxy functionalized borosiloxane oligomers, the effect of monomer feed ratio and processing condition (viz., flash drying or freeze drying) was studied for the reactions carried out in dioxane. Soluble oligomer was obtained only for the monomer feed ratio 0.5:1.5 (boric acid:GPTMOS) and this is probably due to the non-availability of B-OH group for crosslinking reaction.
iii) The $^{29}\text{Si}$ NMR spectral studies indicate the presence of $T_0$, $T_1$, $T_2$, $T_{2c}$ and $T_3$ structures in epoxy functionalized borosiloxane oligomers. In addition to these structural units, $T_8$ (cubic cage) structures formed from GPTMOS were also observed.

iv) The TG studies suggest that the epoxy-functionalized borosiloxane oligomers give ceramic residue in the range of 39-44% at 900°C which is less than that of the borosiloxane oligomers synthesized from PTMOS, PTEOS and VTEOS. The lower ceramic residue of epoxy-functionalized borosiloxanes is attributed to the presence of aliphatic linkages.

v) Borosiloxane oligomers containing both epoxy and vinyl functional groups were synthesized by reacting boric acid, VTEOS and GPTMOS in 1:1:1 mole ratio using dioxane/diglyme as solvent. When diglyme was used as the solvent, insoluble oligomer was obtained, whereas a soluble oligomer was obtained when the reaction was carried out in dioxane. The soluble oligomer has an epoxy value of 1.7 eqv/kg. $^1\text{H}$-NMR spectral studies of this oligomer indicate that epoxy:vinyl ratio is 1:1.04 as against 1:1 calculated on the basis of monomer feed ratio.

vi) When the epoxy and vinyl containing oligomers were synthesized by using monomer feed ratio of 1:0.67:1.33 and 1:1.33:0.67 (boric acid:GPTMOS: VTEOS) using dioxane as solvent, soluble oligomer was obtained for the latter monomer feed ratio. The formation of gelled product for the monomer feed ratio, 1:0.67:1.33 is due to the higher vinyl content.

vii) The soluble oligomer obtained for the monomer feed ratio 1:1.33:0.67 has $M_w$ of 4710 and $M_n$ of 2560 and an epoxy value of 2 eqv/kg. The epoxy to vinyl ratio as obtained from $^1\text{H}$-NMR is 1:0.57 as against 1:0.5, calculated from the monomer feed ratio. TG studies indicate that the incorporation of vinyl group along with epoxy functional group results in improvement in ceramic residue, when compared to that of only epoxy containing oligomer.
References

This chapter reports the synthesis of borosiloxane oligomers from boric acid and alkoxysilanes and mixtures of alkoxysilanes in the absence of solvent. The synthesis was carried out both in the presence and absence of catalyst, HCl. The oligomers were characterized by IR, GPC, $^1$H-, $^{13}$C-, $^{29}$Si-NMR and TGA. The advantages of solventless process is clearly brought out in this chapter.

*The results presented in this chapter form the basis for the patent application:*

3.3.1 Background

The chapters 3.1 and 3.2 dealt with the synthesis and characterization of borosiloxane oligomers from different alkoxysilanes. Effect of monomer feed ratio, reaction conditions and other factors which influence the processability and thermal stability of the oligomers has been dealt in detail. The oligomers reported in these two chapters were synthesized in presence of a high boiling solvent viz., diglyme or dioxane. While attempting to remove the solvent, the oligomers synthesized from functionalized alkoxysilane monomers became insoluble and this is attributed to crosslinking involving the functional groups or due to higher degree of polymerization during the removal of solvent.  

Babonneau et al.\textsuperscript{2,3} in their study reported the synthesis of borosiloxane sol-gels by reacting boric acid and arylalkoxysilane at 60°C in the absence of solvent and leaving the sol in air for more than ten days to gel. In this approach, there exists the possibility of moisture to react with alkoxysilane resulting in the formation of Si-OH groups which would react with B-OH or self condense resulting in the formation of B-O-Si and Si-O-Si linkages respectively.

In the present study, alkoxysilanes were reacted with boric acid at temperatures ranging from 100-150°C and then the alkyl alcohol formed due to the condensation of B-OH and Si-OR group was distilled out. In this approach, the formation of Si-O-B bond is ensured and the formation of Si-O-Si bond is minimized, if not completely ruled out, as the sol is not left out in air. The extent of reaction which in turn controls the molecular weight and processability is regulated by the amount of alkyl alcohol removed from the reaction mixture.

The solventless synthesis of borosiloxanes provides the following advantages:

i) Borosiloxane oligomers in the resinous form or as a solid can be obtained depending on the extent of removal of alkyl alcohol.

ii) The solvent removal step is eliminated and hence, this method provides the scope for the synthesis of functionalized borosiloxane oligomers in the processable form.
iii) Resins with high solid content can be prepared and use of such resins will bring down the number of infiltration cycles required for densifying ceramic components.

iv) By this process, resins, which can be directly used as matrix resin for CMCs and for coating formulation, can be obtained.

Thus, the present chapter deals with the synthesis of borosiloxane oligomers from alkoxy silanes such as PTMOS, PTEOS, VTEOS and GPTMOS without using any solvent or in other words by a solventless process.

3.3.2 Solventless synthesis of borosiloxane oligomers from phenyltrialkoxysilanes in the presence of catalyst

The synthesis of borosiloxane oligomers was carried out by reacting boric acid with phenyltrialkoxysilane in 1:2 mole ratio without using any solvent in the presence of HCl as catalyst for 3 h at 150 -160°C. The oligomer obtained from PTMOS is referred to as BSiPh-9 and the one from PTEOS is referred to as BSiPh-10. They are soluble in common organic solvents such as THF, 1,4-dioxane, toluene, chloroform and diglyme. The GPC curves of the two oligomers are shown in Fig. 3.3.1.

![Fig. 3.3.1. GPC curves of BSiPh-9 and BSiPh-10](image)

The oligomers exhibit bimodal molecular weight distribution. BSiPh-9 has $M_w$ of 1460 and $M_n$ of 1100 whereas BSiPh-10 has $M_w$ of 1030 and $M_n$ of 760. Comparison of GPC data of BSiPh-9 and BSiPh-10 with the corresponding ones
synthesized using diglyme as solvent suggests that the molecular weight of the oligomers synthesized by solventless process is somewhat higher than those synthesized in diglyme and the increase is more pronounced for PTEOS-based oligomer. It is noticed that the molecular weight of BSiPh-9, synthesized from PTMOS, is higher than that of BSiPh-10, synthesized from PTEOS and this is attributed to the higher reactivity of PTMOS.

The IR spectra of BSiPh-9 and BSiPh-10 show absorbance at 1135 cm\(^{-1}\) indicating the presence of unreacted alkoxy groups. It is noticed that the intensity of the peak due to B-OH at 3220 cm\(^{-1}\) is less for BSiPh-9 than for BSiPh-10. This is understood in view of the higher reactivity of PTMOS towards boric acid. \(^1\)H-NMR spectra of BSiPh-9 and BSiPh-10 are shown in Fig. 3.3.2.

![Fig. 3.3.2. \(^1\)H-NMR spectra of BSiPh-9 and BSiPh-10](image)

The absence of strong signals at 3.3 ppm due to Si-OMe and at 1.4 and 3.95 ppm due to Si-OEt suggests that PTMOS and PTEOS have reacted with boric acid resulting in the formation of borosiloxane oligomers. However, less
intense broad peaks are observed in the above regions which are attributed to unreacted alkoxy groups present in the oligomer. Signals due to aromatic protons are observed in the region 6.5-8.0 ppm. $^{13}$C-NMR spectrum of BSiPh-10 shows very feeble peaks at 18 and 58 ppm indicating the presence of trace amounts of unreacted ethoxy group present in the oligomer. $^{13}$C-NMR spectrum of BSiPh-9 does not show the presence of unreacted methoxy groups, though IR spectrum indicates the presence of unreacted methoxy groups. Peaks due to phenyl carbons of Si-Ph group are observed at 128, 131 and 134 ppm. $^{29}$Si-NMR spectra of BSiPh-9 and BSiPh-10 are shown in Fig. 3.3.3. For both the oligomers, peaks due to T$_2$ and T$_3$ structures are observed at -68 and -77 ppm respectively. The ratio of T$_3$ to T$_1$+T$_2$ is 1:0.54 for BSiPh-9 and 1:1.24 for BSiPh-10.

Fig. 3.3.3. $^{29}$Si-NMR spectra of BSiPh-9 and BSiPh-10
For carrying out TG studies, BSiPh-9 and BSiPh-10 were dried at 100°C under vacuum to remove unreacted monomers and alkyl alcohol byproduct. The oligomers obtained in powdery form were subjected to TGA. Other systems were obtained in the resinous form after flash drying. BSiPh-9 and BSiPh-10 give ceramic residue of 73-74% at 900°C in argon atmosphere. Though both the oligomers give almost the same ceramic residue, $T_i$, $T_{max}$ and $T_f$ are higher for BSiPh-9 than that of BSiPh-10 (Fig. 3.3.4). It is worth noting that the oligomers, BSiPh-1 and BSiPh-2, synthesized in diglyme differ in their ceramic residue by about 7%. Such a difference is not observed when the oligomers were synthesized in the solventless process in presence of catalyst.

![Fig. 3.3.4. TG curves of BSiPh-9 and BSiPh-10](image)

**Effect of reaction time on borosiloxane oligomers from PTEOS:** It is observed that with increase in reaction time from 3 h to 6 h, there is increase in molecular weight, thermal stability and ceramic residue for the oligomers prepared by reacting boric acid with PTEOS in diglyme in presence of HCl catalyst. Thus, it would be of interest to study the effect of reaction time in the absence of solvent for the monomer feed ratio (boric acid:PTEOS) 1:2 using HCl as catalyst at 150-160°C. The oligomer obtained after 6 h of reaction is referred to as BSiPh-11.

BSiPh-11 shows bimodal molecular weight distribution similar to that observed for BSiPh-10. BSiPh-11 has $M_w$ of 1220 and $M_i$ of 855. Comparison of
GPC data of BSiPh-10 and BSiPh-11 suggests that with the increase in reaction time, only a marginal increase in the molecular weight is observed. Interestingly, for a similar increase in reaction time, $\bar{M}_w$ increases from 750 to 1480 and $\bar{M}_i$ from 480 to 1080 and peak molecular weight shifts from 360 to 1250 for the reaction carried out in the presence of solvent and catalyst.

The IR and $^1$H-, $^{13}$C- and $^{29}$Si-NMR spectra of BSiPh-11 are similar to that of BSiPh-10. From $^{29}$Si-NMR spectra $T_3:T_2$ ratio for BSiPh-11 is calculated to be 1:1.02 as against 1:1.24 for BSiPh-10. This suggests that doubling the reaction time brings about only a slight change in the relative population of structural units. It is interesting to note that for a similar increase in reaction time, for the oligomers synthesized from PTEOS and boric acid in diglyme in presence of HCl, the ratio of $T_3:T_2$ increases from 1:0.68 (for BSiPh-2) to 1:0.32 (for BSiPh-5). This suggests that in the presence of solvent and catalyst, $T_3$ structures are formed more when the reaction time is increased from 3 h to 6 h. The above observation can be understood by considering the difference in the experimental conditions. For BSiPh-5, the reaction was carried out in the presence of diglyme which is a high boiling solvent (b.p.:165°C) whereas BSiPh-11 was synthesized in the absence of solvent. Though the bath temperature was maintained at 150-160°C in both the cases, the reaction mixture of BSiPh-5 experienced a temperature of 95°C whereas the reaction mixture of BSiPh-11 experienced a temperature of 81°C. Ethanol, formed as a by-product, brings down the temperature in both the cases. When diglyme is used as a solvent, it contributes towards increasing the temperature of the reaction mixture by about 14°C. Higher reaction temperature experienced by BSiPh-5 is probably the reason for the higher population of $T_3$ structures.

The TGA data of BSiPh-10 and BSiPh-11 suggest that both of them have almost the same thermal stability and ceramic residue (~74%) at 900°C.

### 3.3.3 Solventless synthesis of borosiloxane oligomers in the absence of catalyst from different alkoxysilanes

#### 3.3.3.1 Borosiloxane oligomer from PTMOS

Boric acid and PTMOS were reacted in the absence of solvent and catalyst at 150-160°C for 3 h to obtain a resinous material which is referred to as BSiPh-12. It has a viscosity of 5100 cps at 30°C. It is soluble in toluene, methanol,
chloroform, THF, diglyme and dioxane. BSiPh-12 shows a broad molecular weight
distribution (Fig. 3.3.5) and has $\bar{M}_w$ of 15,530 and $\bar{M}_n$ of and 3,970.

![Fig. 3.3.5. GPC curve of BSiPh-12](image)

The IR spectrum of BSiPh-12 is shown in Fig. 3.3.6. It shows characteristic absorption peaks due to Si-O-B at 884 and 696 cm$^{-1}$, due to stretching and deformation vibrations respectively. The broad peak at 1060 cm$^{-1}$ is due to Si-O-Si stretching vibration. The peak at 1134 cm$^{-1}$ is due to Si-OMe. Absorptions at 1595 and 1431 cm$^{-1}$ are due to Si-Ph units.

The $^1$H-NMR spectrum of BSiPh-12 is shown in Fig. 3.3.7. $^1$H-NMR spectrum shows a sharp peak at 3.7 ppm corresponding to protons of Si-OMe present in unreacted PTMOS. A broad peak observed in the region 3 to 3.9 ppm is attributed to unreacted Si-OMe groups present in the oligomer. A broad peak observed in the region 6.5 to 8.3 ppm is assigned to protons of Si-Ph groups. Based on the intensity of the above two peaks, it is inferred that for each phenylsiloxy unit incorporated in the oligomer, 2.54 Si-OMe groups have undergone reaction resulting in the formation of Si-O-B or Si-O-Si bonds. $^{13}$C-NMR spectrum of BSiPh-12 also indicates the presence of unreacted Si-OMe groups.

The $^{29}$Si-NMR spectrum of BSiPh-12 is shown in Fig. 3.3.8. Peaks observed at -67, -71 and -79 ppm are attributed to $T_1$, $T_2$ and $T_3$ structures respectively. The ratio of $T_3:T_1+T_2$ structures is 1:0.36. It is interesting to note that this ratio is close to the value obtained for BSiPh-1 (synthesized from PTMOS in
diglyme using HCl catalyst) and BSiPh-9 (synthesized from PTMOS in the absence of solvent using HCl catalyst). This observation suggests that for the borosiloxane oligomers synthesized from PTMOS which is a highly reactive monomer, the ratio of $T_3:T_1+T_2$ is not influenced by the reaction conditions.
3.3.3.2 Borosiloxane oligomer from PTEOS

Boric acid and PTEOS were reacted in 1:2 mole ratio without using any solvent or catalyst at 150°C and the oligomer obtained is referred to as BSiPh-15. The viscosity of the oligomer is 2600 cps at 30°C. The GPC curve of this oligomer (Fig. 3.3.9) shows a monomodal molecular weight distribution. $\bar{M}_n$ and $\bar{M}_w$ values of this oligomer are 1580 and 960 respectively.
The $^1$H-NMR spectrum of BSiPh-15 is shown in Fig. 3.3.10. Sharp peaks are observed at 1.4 and 3.9 ppm and these peaks are due to CH$_3$ and CH$_2$ protons of Si-OEt group of unreacted PTEOS present along with the oligomer. The broad peaks observed in the regions 0.9 to 1.6 ppm and 3.6 to 4.2 ppm are attributed to CH$_3$ and CH$_2$ protons respectively of unreacted Si-OEt group present in the oligomer. A broad peak observed in the region 6.8 to 8.2 ppm is due to protons of Si-Ph group. Based on the intensities of the peaks corresponding to aromatic and aliphatic protons, the ratio of Si-Ph:Si-OEt ratio is calculated to be 1:0.93. This implies that for each phenylsiloxy repeating unit, 2.07 Si-OEt groups have reacted. Comparison of $^1$H-NMR spectrum of BSiPh-15 with that of BSiPh-12 suggests that under identical experimental conditions, the reaction between boric acid and PTMOS proceeds to a higher extent than of boric acid and PTEOS.

![Fig. 3.3.10. $^1$H-NMR spectrum of BSiPh-15](image)

The $^{13}$C- and $^{29}$Si-NMR spectra of BSiPh-15 are shown in Figs. 3.3.11 and 3.3.12 respectively. $^{13}$C-NMR spectrum also shows the presence of unreacted Si-OEt groups. The peaks observed in the region 17.0 to 18.1 ppm and 58.7 to 59.3 ppm are due to Si-OCH$_3$CH$_3$ and Si-OC$\text{H}_2$CH$_3$ carbons respectively. Peaks due to aromatic carbons are observed in the region 127.6 to 134.7 ppm. In the $^{29}$Si-NMR spectrum, the peak at -67 ppm is attributed to T$_1$ structure and the peaks at -71 and -73 ppm are due to T$_2$ structures. The peaks at -77 and -80 ppm
are assigned to $T_3$ structures. The ratio of $T_3:T_1+T_2$ is 1:0.44. It is interesting to note that while the experimental conditions do not influence the ratio of $T_3:T_1+T_2$ for PTMOS based systems, considerable change in the ratio is observed for PTEOS-based systems. The ratio of $T_3:T_1+T_2$ is 1:1.24 for BSiPh-10, the oligomer synthesized from PTEOS in the absence of solvent using HCl as catalyst. Thus, it is evident that when the reaction of boric acid and PTEOS is carried out in the absence of both solvent and catalyst, the formation of $T_3$ structures, i.e., more branched structures, are favored.

![Fig. 3.3.11. $^{13}$C-NMR spectrum of BSiPh-15](image)

![Fig. 3.3.12. $^{29}$Si-NMR spectrum of BSiPh-15](image)
Modification of polyimide film with borosiloxane oligomer: Aromatic polyimide films are well known for their outstanding thermal stability, radiation resistance, electrical insulation, mechanical properties and can withstand the harsh space environmental conditions and hence, they have been widely used for many space applications. Research efforts have been put forth to prepare modified polyimide and polyimide composites that exhibit specific properties. For example, polyimides were modified with siloxane to provide materials with excellent adhesion to micro electronic devices. Polyimide-siloxanes might be able to provide AO resistance as their surface can be converted into silica through the reaction with AO. Polyimide films containing dispersed metals and metal complexes have been reported. Electrochemical behavior and electrical conductivity of polyimide film have been modified by incorporating phthalocyanine octacarbonitrile and polymeric copper phthalocyanine. Recently, for certain electronic applications, silica-incorporated polyimide organic-inorganic composite films were prepared from polyamic acid and TEOS via sol-gel reaction with water followed by thermal imidization.

Sol-gel process is a convenient method for the synthesis of organic-inorganic hybrid polyimide. Functional groups can be introduced into both the organic and inorganic precursors through which grafting can be carried out where a continuous interconnected organic and inorganic network can be obtained. Preparation and properties of polyimide/SiO$_2$ films from functionalized alkoxysilane via sol-gel process have been reported. The borosiloxane oligomer can be conveniently used for modifying polyimide film for the following reasons:

(i) The hydroxyl functional group present in the oligomer can react with -COOH group of polyamic acid thereby providing the chemical link between the organic and inorganic phase.

(ii) Unreacted Si-OEt groups present in the oligomer can undergo sol-gel reaction resulting in the formation of silica network structure and

(iii) The incorporation of boron and silicon is expected to impart certain interesting properties to polyimide film.

This section presents the results on the modification of polyimide film with borosiloxane oligomer. The mechanical properties and thermal stability of the
unmodified and modified films were evaluated. In the present study, for the preparation of modified polyimide films, polyamic acid (10% solution in DMAc, prepared by reacting pyromellitic dianhydride with 4,4'-diamino diphenyl ether) was reacted with borosiloxane oligomer (BSiPh-15) followed by thermal imidization. The borosiloxane oligomer is expected to react with -COOH group of polyamic acid thereby establishing a chemical link between the inorganic oligomer and the organic polymer. This modified polyamic acid on thermal imidization is expected to give polyimide film in which the borosiloxane oligomer is attached to the polyimide backbone. The reaction scheme for the above approach is given in Scheme 3.3.1.

Scheme 3.3.1. Modification of polyimide film with borosiloxane oligomer.
The hybrid films are translucent. IR spectra of the unmodified (Film-UM) and borosiloxane modified (Film-M) polyimide film are almost alike and show peaks corresponding to imide group at 1710 cm$^{-1}$ and 1780 cm$^{-1}$. IR spectrum of borosiloxane-modified sample does not show peaks corresponding to borosiloxane oligomer and this may be due to the very low concentration of oligomer (~1%) in the film. The TG curves of unmodified and the modified films are compared in Fig. 3.3.13. It is observed that there is a marginal improvement (~5%) in the overall thermal stability when the polyimide film is modified with borosiloxane oligomer.

![Fig. 3.3.13. TG curves of unmodified and borosiloxane oligomer modified polyimide films](image)

The mechanical properties of unmodified and the modified polyimide film described above are given in Table 3.3.1.

<table>
<thead>
<tr>
<th>Film</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (%)</th>
<th>Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified</td>
<td>106</td>
<td>20</td>
<td>2400</td>
</tr>
<tr>
<td>Modified</td>
<td>97</td>
<td>12</td>
<td>3021</td>
</tr>
</tbody>
</table>

Modification of the polyimide film with the borosiloxane oligomer results in a significant increase in the modulus and a decrease in elongation, probably because of the incorporation of rigid inorganic network into the film. The tensile
strength decreases by about 9% when the film is modified with borosiloxane oligomer. Probably, the inorganic network is not present as a co-continuous phase in the organic phase and this can lead to stress concentration at the organic-inorganic interface giving rise to low tensile strength.

### 3.3.3.3 Borosiloxane oligomer from VTEOS

Vinyl-functionalized borosiloxane oligomer, BSiVi-6 was obtained by reacting boric acid and VTEOS in 1:2 mole ratio at 150°C in the absence of both solvent and catalyst for 3 h. The oligomer underwent gelation when flash evaporation was attempted at 120°C under vacuum to remove unreacted monomer and the by-product ethanol. In order to overcome this problem, the reaction mixture was subjected to flash evaporation at 80°C instead of 120°C and the resinous product obtained is designated as BSiVi-7.

The GPC curve of BSiVi-7 is shown in Fig. 3.3.14. The oligomer has $\overline{M}_w$ of 5310 and $\overline{M}_n$ of 1450 with a broad molecular weight distribution.

![Fig. 3.3.14. GPC curve of BSiVi-7](image)

$^1$H-, $^{13}$C- and $^{29}$Si-NMR spectra of BSiVi-7 are shown in Figs. 3.3.15, 3.3.16 and 3.3.17 respectively. The $^1$H-NMR spectrum shows peaks corresponding to Si-CH=CH$_2$ at 5.8 to 6.2 ppm and the peaks in the region 3.7 to 4 ppm and 1.1 to 1.3 ppm are due to methylene and methyl protons respectively of Si-OCH$_2$CH$_3$ group. The peak at 3 ppm is attributed to B-OH group. Based on the intensity of vinyl and aliphatic protons, the ratio of vinylsilox to Si-OEt units is calculated to be 1:2.21. Comparison of $^1$H-NMR spectral data of BSiPh-12, BSiPh-15 and BSiVi-7 suggests that the reactivity of PTMOS, PTEOS and VTEOS towards boric acid in the absence of solvent and catalyst follows the trend, PTMOS > PTEOS > VTEOS.
Solventless synthesis

The $^{13}$C-NMR spectrum (Fig. 3.3.16) shows peaks at 136 and 130 ppm due to Si-CH=CH$_2$ and Si-CH=CH$_2$ carbons. The peaks at 17.3, 18.1 and 18.4 ppm are due to Si-O-CH$_2$-CH$_3$ carbon and the peaks at 58.5 and 59.0 are due to Si-O-CH$_2$-CH$_3$ carbon. The multiplicity of the peaks observed for CH$_2$ and CH$_3$ carbons arises probably due to the presence of Si-OCH$_2$CH$_3$ in different structural units (T$_1$ and T$_2$).

The $^{29}$Si-NMR spectrum (Fig. 3.3.17) shows peaks corresponding to T$_1$ at -68 ppm and T$_2$ at -73 and -74 ppm. T$_3$ structures are observed at -79 and -81 ppm. The ratio of T$_3$:T$_1$+T$_2$ structures is 1:0.53.
As VTEOS-based oligomer has a tendency to undergo premature gelation, it is desirable that ethyl alcohol formed as a by-product is not completely removed. The resin gives a solid content of 58% and the viscosity of the solution is 150 cps at 30°C. TG curve of BSiVi-7 (after complete removal of alcohol) suggests that the oligomer is stable up to 500°C. It gives a ceramic residue of 86% at 900°C.

### 3.3.3.4 Borosiloxane oligomer from GPTMOS

In the previous chapter, the effect of solvent and the monomer feed ratio on BSiEp oligomers was discussed. It is observed that all the oligomers except for the one synthesized from boric acid:GPTMOS mole ratio 1:1.5 got gelled while attempting to remove the solvent and unreacted GPTMOS from the reaction mixture and the gelation is attributed to some side reactions, which may be taking place during processing. Though a processable oligomer is obtained when the monomer feed ratio is 0.5:1.5, the boron content is less and for some application such as preparation of mixed non-oxide ceramics, it is desirable to have higher amount of boron. But the TGA studies of the gelled material synthesized from the monomer feed ratios (boric acid:GPTMOS) 0.5:1 and 1:1 suggest that the former one has better thermal stability than the latter. The lower thermal stability of the latter has been attributed to the presence of unreacted boric acid or its derivatives.
Thus, it would be interesting to investigate the synthesis of BSiEp oligomers using the monomer feed ratio 0.5:1 for the solventless synthesis. The reaction was carried out for the monomer feed ratio 0.5:1 at 120°C for 3 h and the by-product, methanol, formed was not removed from the system in order to avoid premature gelation. The oligomer (BSiEp-6) was characterized by GPC, IR and $^1$H-, $^{13}$C- and $^{29}$Si-NMR spectra. The GPC curve of BSiEp-6 is given in Fig. 3.3.18.

![Fig. 3.3.18. GPC curve of BSiEp-6](image)

The oligomer has $\bar{M}_w$ of 4070 and $\bar{M}_n$ of 1600. $\bar{M}_w$ of BSiEp-6 is close to that of the flash-dried sample (BSiEp-3A) and more than that of the freeze dried sample (BSiEp-3B) prepared using the monomer feed ratio 0.5:1.5 (boric acid:GPTMOS) in dioxane (Chapter 3.2). Probably, increasing the mole ratio of boric acid:GPTMOS from 0.5:1.5 to 0.5:1 is expected to increase the extent of reaction of Si-OEt and B-OH groups resulting in increase in molecular weight. The solvent used for the synthesis of the oligomer may also affect the molecular weight build-up. BSiEp-6 has epoxy value of 4.4 eqv/kg and solid content of 83.1%.

The IR, $^1$H- and $^{13}$C-NMR spectra of BSiEp-6 are similar to those of epoxy containing borosiloxane oligomers discussed in Chapter 3.2. $^{29}$Si-NMR spectrum of BSiEp-6 is shown in Fig. 3.3.19. The peaks observed at -41.79, -50, -55 and -59 ppm are assigned to $T_0$, $T_1$, $T_2c$ and $T_2$ respectively. The peaks at -65 and -68 ppm are due to $T_3$ structures. The presence of $T_8$ (cage structure) cannot be ruled out.
Characterization of crosslinked oligomer/gelled material obtained from BSiEp-6: The oligomer obtained by the solventless process is a low viscous liquid. However, the liquid becomes more viscous when methanol is distilled off and finally it gels. During processing of the resin, probably the epoxy groups react with unreacted B-OH groups resulting in the formation of a crosslinked product. The gelled material was subjected to flash drying to remove residual volatile matter. The IR spectra of BSiEp-6 before and after gelation are compared in Fig. 3.3.20.
It is observed that the intensity of the peaks at 1256, 909 and 834 cm\(^{-1}\) due to epoxy group reduces considerably when the resin undergoes gelation. TGA studies indicates that the crosslinked polymer is stable up to 380 °C and undergoes degradation above this temperature leaving behind a ceramic residue of 42% at 600 °C.

### 3.3.3.5 Borosiloxane oligomer from GPTMOS and VTEOS

In an attempt to synthesize borosiloxane oligomer containing both vinyl and epoxy functional groups boric acid, GPTMOS and VTEOS were reacted in 1:1:1 mole ratio in the absence of solvent and catalyst at 150 °C for 3 h. The oligomer was characterized by GPC, IR and \(^1\)H-, \(^{13}\)C- and \(^{29}\)Si-NMR spectra. The GPC curve of the oligomer is given in Fig. 3.3.21.

![Fig. 3.3.21. GPC curve of BSiEpVi-5](image)

The oligomer has \(M_w\) and \(M_n\) of 3460 and 1110 respectively. IR spectrum indicates the presence of vinyl and epoxy groups. \(^1\)H- and \(^{13}\)C-NMR spectra show signals corresponding to epoxy, vinyl, methoxy and ethoxy groups. The ratio of epoxy and vinyl groups as estimated from \(^1\)H-NMR spectrum is 1:0.9. The \(^{29}\)Si-NMR spectrum of BSiEpVi-5 is shown in Fig. 3.3.22. It shows a large number of peaks corresponding to different structural units containing glycidoxypropylsiloxo and vinylsiloxo groups. A detailed discussion on different structural units present in BSiEpVi systems are given in chapter 3.2.
Curing of BSiEpVi-5 oligomer with tertiaryamine catalyst: As the epoxy group can be cured at room temperature by using a suitable catalyst, in the present study, attempt has been made to obtain a crosslinked oligomer by curing BSiEpVi-5 with a tertiaryamine, 2,4,6-tris-(N,N-dimethylaminomethyl)phenol (HY 960). The curing was carried out at room temperature for one day and a yellow coloured solid was obtained which is insoluble in common organic solvents. The cured product was characterized by IR and TGA. Comparison of IR spectra of cured and as synthesized resin suggests that on curing with HY 960, the peak at 920 cm\(^{-1}\) disappears suggesting that epoxy group has undergone curing. The thermograms of the cured and the uncured resins are compared in Fig. 3.3.23.
It is observed that the overall thermal stability and ceramic residue of the cured resin are higher than that of the uncured resin. This improvement is attributed to crosslinks resulting from the curing of epoxy groups.

3.3.4 Conclusions

Borosiloxane oligomers were synthesized by reacting boric acid with PTMOS, PTEOS, VTEOS, GPTMOS and a mixture of VTEOS and GPTMOS (boric acid:alkoxysilane=1:2) without using any solvent and catalyst. For PTMOS and PTEOS-based systems the solventless synthesis was carried out in the presence of catalyst, HCl. The oligomers were characterized by GPC, IR, $^1$H-, $^{13}$C- and $^{29}$Si-NMR spectra and TGA. Based on the results presented in this chapter, following conclusions have been drawn:

i) The solventless synthesis of borosiloxane oligomers in the presence of catalyst shows that the oligomer synthesized from PTMOS has higher molecular weight and thermal stability compared to the oligomer synthesized from PTEOS. This is attributed to the higher reactivity of PTMOS compared to PTEOS. The effect of reaction time for the reaction of boric acid with PTEOS shows that even though there is an increase in the molecular weight, there is no improvement in thermal stability.

ii) Resinous products were obtained when the oligomers were synthesized in the absence of catalyst whereas when catalyst was used the oligomers were obtained as powdery material. This is a major advantage as the oligomers obtained in the resinous form can be directly used as matrix resins for CMCs and as infiltrating resins.

iii) Solventless process provides the scope for synthesizing vinyl/epoxy functionalized borosiloxane oligomers soluble in common organic solvents which is difficult to achieve when the synthesis is carried out in the presence of solvent.

iv) NMR spectral studies of the oligomers synthesized in the absence of catalyst indicate the presence of appreciable amount of unreacted alkoxy groups.
v) The viscosity of the resins can be varied from 150 cps to 6000 cps at 30°C by controlling the quantity of the by-product distilled out from the system.

References


Chapter 3.4

Ceramic conversion studies of borosiloxane oligomers

This chapter presents the ceramic conversion studies of some typical borosiloxane oligomers, discussed in the previous chapters and a decaborane(14)-based borosiloxane oligomer having high boron content. These oligomers were heat treated at 900, 1400 and 1600°C in argon atmosphere and the ceramics obtained were characterized by IR and XRD.

*Part of the results presented in this chapter has resulted in a patent application:

3.4.1 Background

In recent years, considerable interest is shown on the pyrolysis of preceramic organometallic compounds with a view to synthesizing new inorganic materials. The main objective of this preceramic process route is to build-up novel materials from molecular units. The first step in this approach is to synthesize preceramic polymers from monomer units. The preceramic networks obtained by crosslinking will be transformed into amorphous materials by pyrolysis. Further increase of heat treatment temperature yields thermodynamically metastable and/or stable crystalline phases.

The transformation of inorganic and organometallic compounds into ceramic materials by thermal treatment in a controlled atmosphere is fairly a new and simple process for forming new type of inorganic materials. The general idea behind this concept is that organometallic precursor molecules i.e., oligomers/polymers, are designed to contain structural units of the residual inorganic materials from which they are derived. By thermolysis the preceramic polymers provide a novel path for controlling composition, homogeneity, atomic distribution and microstructure of the ceramic. The flow chart for the conversion of preceramic polymers to ceramics is shown in the Scheme 3.4.1.

Since the first proposal of this concept by Popper\textsuperscript{1}, several research groups worldwide have been working in this field. The synthetic approaches
adopted for the preparation of preceramic polymers, their characterization, controlled pyrolysis to ceramics and their end-uses have been reported in the literature.\textsuperscript{2-8} 

The following aspects make the preceramic route the most attractive one for the development of new ceramic materials and components:

i) With this technique one can produce amorphous materials eventually well away of those known from thermodynamically stable stoichiometric compounds, with compositions not obtainable by conventional synthetic routes.

ii) Because of the low mobility in predominantly covalent bonded materials, the amorphous stage can be thermally stable to very high temperature before transforming into crystalline phases.

iii) One can control the thermal activation in the amorphous stage for material transport mechanisms. This gradually provides the means for the kinetic stabilization of less stable phases and microstructures with morphologies not possible by common synthetic routes.

iv) Taking advantage of the various fabrication capabilities of polymer process engineering, ceramic fibers, coatings and complex-shaped bulk parts can be produced in an easy manner.

The conversion of the amorphous ceramic to crystalline one is known to depend on the elemental composition of the polymer.\textsuperscript{8} Polysilanes and polycarbosilanes containing only silicon as heteroatom yield SiC ceramic at around 1400°C. On the other hand, when the preceramic polymers contain both silicon and boron, the crystallization temperature increases considerably and they yield mixed non-oxide ceramics.\textsuperscript{8} Thus, it would be of interest to study the ceramic conversion of borosiloxane oligomers containing heteroatoms, Si, B and O.

### 3.4.2 Ceramic conversion studies of borosiloxane oligomers

Ceramic conversion studies have been carried out only for representative samples from selective systems since each ceramic conversion study consumes considerable amount of time.
**Borosiloxane oligomer from PTEOS:** Ceramic conversion of one of the borosiloxane oligomers, BSiPh-7 was carried out by heating the oligomer at three different temperatures, 900, 1400 and 1600°C as explained in the experimental section. The IR spectra of BSiPh-7 heat-treated at 900, 1400 and 1600°C are shown in Fig. 3.4.1.

![IR spectra of BSiPh-7 heat-treated at 900, 1400 and 1600°C](image)

Fig. 3.4.1. IR spectra of BSiPh-7 heat-treated at 900, 1400 and 1600°C

It is seen from the IR spectrum of the oligomer heat-treated at 900°C that four peaks are observed at 1550, 1320, 1070 and 490 cm\(^{-1}\). The peaks at 1070 and 490 cm\(^{-1}\) are due to Si-O-Si linkage. The presence of peaks at 1550 and 1320 cm\(^{-1}\) is probably due to residual organic moieties/partially degraded organic moieties present in the pyrolyzed sample suggesting that the pyrolysis is incomplete at 900°C. It is worth noting that the IR spectrum of the sample heat-treated at 1400°C shows a major peak at 1070 cm\(^{-1}\) and the other two peaks at 1550 and 1320 cm\(^{-1}\) seen in IR spectrum of the pyrolyzed sample disappear, suggesting that the organic moieties have reacted with Si and B present in the oligomer resulting in the formation of a ceramic. The sample heat-treated at 1600°C, shows a broad peak at 823 cm\(^{-1}\) and this is attributed to the conversion of amorphous ceramic to crystalline SiC.\(^9\) The broadness of the peak is probably due to presence of amorphous glassy phase (SiOC or SiOCB).

The XRD patterns of BSiPh-7 heat-treated at 900, 1400 and 1600°C are shown in Fig. 3.4.2. The samples heat-treated at 900 and 1400°C show peaks due
to amorphous phase whereas the sample heat-treated at 1600°C shows peaks at 2θ = 36, 61 and 72.5 corresponding to 111, 220 and 311 planes of β-SiC respectively (Table 3.4.1).  

![XRD patterns of BSPh-7 heat-treated at 900, 1400 and 1600°C](image)

Table 3.4.1. Cubic β-SiC XRD characteristics

<table>
<thead>
<tr>
<th>Angle (2θ)</th>
<th>Intensity (%)</th>
<th>Value of d (Å)</th>
<th>Diffraction plane</th>
</tr>
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<td>(200)</td>
</tr>
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<td>(220)</td>
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<tr>
<td>72.97</td>
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<td>(311)</td>
</tr>
<tr>
<td>75.78</td>
<td>5</td>
<td>1.25</td>
<td>(222)</td>
</tr>
</tbody>
</table>

Lattice parameters obtained for cubic SiC: \(a=b=c=4.358\) Å and \(\alpha=\beta=\gamma=90^\circ\)
Peaks corresponding to B<sub>2</sub>C are not observed which may be due to low concentration of boron (~ 2% by wt.) in the oligomer. It is observed that when preceramic polymers containing only silicon is heat-treated at 1400°C in inert atmosphere, crystalline β-SiC is formed. On the other hand, borosiloxane oligomer (BSiPh-7) affords crystalline ceramic only when it is heat-treated at 1600°C. This clearly suggests that the presence of boron and oxygen in the oligomer suppresses the crystallization.

**Borosiloxane oligomer from VTEOS:** Ceramic conversion of vinyl functionalized borosiloxane oligomer (BSiVi-6) was carried out following a similar procedure as in the case of BSiPh-7. The IR spectra and XRD patterns of the heat-treated samples are shown in Figs. 3.4.3 and 3.4.4 respectively.

![Fig. 3.4.3. IR spectra of BSiVi-6 heat-treated at 900, 1400 and 1600°C](image)

The results obtained are by and large similar to that of BSiPh-7. The conversion of BSiVi-6 to ceramics has taken place only at 1600°C. IR spectrum of the heat-treated sample at 1600°C shows a peak at 814 cm<sup>-1</sup> and a shoulder peak at 880 cm<sup>-1</sup>. The peak at 814 cm<sup>-1</sup> is due to SiC and the reason for the appearance of the shoulder peak is not clearly understood.

The XRD patterns suggest that the samples heat-treated at 900 and 1400°C are amorphous in nature as evidenced from broad peaks. XRD pattern of
the sample heat-treated at 1600 °C shows sharp peaks corresponding to β-SiC. In addition to the sharp peaks low intensity peaks adjacent to β-SiC peaks are observed. These peaks are probably due to the formation of small amount of α-SiC (rhombohedral).

![XRD patterns of BSiVi-6 heat-treated at 900, 1400 and 1600 °C](image)

Fig. 3.4.4. XRD patterns of BSiVi-6 heat-treated at 900, 1400 and 1600 °C

The presence of α-SiC may be the reason for the appearance of shoulder peak at 880 cm⁻¹ in the IR spectrum. Comparison of XRD patterns of BSiPh-7 and BSiVi-6, heat-treated at 1600 °C, suggests that the amorphous phase which is present in the former is absent in the latter. BSiPh-7 is synthesized from PTEOS whereas BSiVi-6 is synthesized from VTEOS and hence, the carbon content in BSiPh-7 is more than that in BSiVi-6. Presence of excess carbon in BSiPh-7 is probably responsible for the amorphous phase.

**Borosiloxane oligomer from PTMOS and VTEOS mixture:** Ceramic conversion of BSiPhVi-4 was also carried out following the procedure similar to that of BSiPh-7 and BSiVi-6. IR spectra and XRD patterns of the heat-treated samples are shown in Figs. 3.4.5 and 3.4.6 respectively.
Fig. 3.4.5. IR spectra of BSiPhVi-4 heat-treated at 900, 1400 and 1600 °C

They are similar to those of BSiVi-6 heat-treated samples. Comparison of XRD patterns of BSiPh-7, BSiVi-6 and BSiPhVi-4 suggests that crystallization of ceramic takes place to a higher extent when vinyl group is present in borosiloxane oligomer.

Fig. 3.4.6. XRD patterns of BSiPhVi-4 heat-treated at 900, 1400 and 1600 °C
Borosiloxane oligomer from TEOS: BSiT-2 and BSiT-4, containing 5 and 10.9% carbon respectively, were heat-treated at 900, 1400 and 1600°C under argon atmosphere. Unlike the other borosiloxane oligomers synthesized from organoalkoxysilanes, in BSiT-2 and BSiT-4, the carbon is not directly attached to silicon and is present as -OEt groups. These -OEt groups would be knocked off when heat-treated at 900°C. If this does not happen, carbon present in the samples would react with Si and B at high temperatures forming the corresponding carbides. Thus, it would be of interest to study the heat-treatment of these two oligomers.

The samples of BSiT-2 heat-treated at 900 and 1400°C are powdery in nature, where as a molten material, which is black in colour is formed at 1600°C. The IR spectra (Fig. 3.4.7) show peaks corresponding to SiO$_2$ and B$_2$O$_3$ and the peak assignments are given in Table 3.4.2.

The XRD patterns (Fig. 3.4.8) of BSiT-2 heat-treated at 900, 1400 and 1600°C reveal that the samples are amorphous in nature. It is observed that the ceramic obtained at 1600°C is more amorphous than that formed at 1400°C. This may be due to the formation of glass when heat-treated at 1600°C.
<table>
<thead>
<tr>
<th>Wave number (cm⁻¹)</th>
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<th>Wave number (cm⁻¹)</th>
<th>Assignment</th>
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<tr>
<td>3400</td>
<td>Si-OH stretching</td>
<td>800</td>
<td>Si-O-Si bending</td>
</tr>
<tr>
<td>1397</td>
<td>B-O stretching</td>
<td>670</td>
<td>Si-O-B bending</td>
</tr>
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<td>1087</td>
<td>Si-O-Si stretching</td>
<td>470</td>
<td>-O-Si-O- deformation</td>
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<tr>
<td>905</td>
<td>Si-O-B bending/ Si-OH stretching</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.4.2. IR spectral assignments of the heat-treated borosiloxane oligomer, BSiT-2

![XRD patterns of BSiT-2 heat-treated at 900, 1400 and 1600°C](image)

Fig. 3.4.8. XRD patterns of BSiT-2 heat-treated at 900, 1400 and 1600°C

In order to understand the effect of heat treatment of the oligomer in air, BSiT-2 was heat treated at 1000°C and characterized by IR and XRD. The IR spectrum of the sample is similar to that of BSiT-2 heat treated at 900°C in argon atmosphere. The formation of SiOH is more in the former case where the heat
treatment was carried out in the presence of air. The XRD pattern (Fig. 3.4.9) of the heat-treated sample in air at 1000°C reveals the presence of amorphous phase similar to that of the sample heat-treated at 1600°C in inert atmosphere.

Fig. 3.4.9. XRD pattern of BSiT-2 heat-treated at 1000°C in air

BSiT-4 synthesized in the absence of catalyst contains 10.9% of carbon. Thus, it would be of interest to investigate the ceramic conversion of this oligomer to see if any carbide is formed. The IR spectra of BSiT-4 heat treated at 900, 1400 and 1600°C are similar to that obtained for the corresponding heat-treated samples of BSiT-2. The XRD pattern of BSiT-4 heat-treated at 1600°C is given in Fig. 3.4.10.

Fig. 3.4.10. XRD pattern of BSiT-4 heat-treated at 1600°C
The XRD pattern suggests that the sample is amorphous in nature. The absence of peaks corresponding to SiC implies that the ethoxy groups were knocked off during the early stages of heat treatment.

3.4.3 Ceramic conversion studies of decaborane(14)-based oligomer with high boron content

The borosiloxane oligomers obtained through the reaction of boric acid and organoalkoxysilanes contain boron in the range of 2-7%. As discussed earlier, XRD studies of borosiloxane oligomers indicated the formation of mainly β-SiC. The presence of B₄C was not detected by XRD though elemental analysis indicated the presence of boron to the extent of 2-3% by weight in the heat-treated samples.

In order to obtain mixed non-oxide ceramics from boron and silicon containing polymers, it is necessary that both boron and silicon are present in appreciable concentration in the starting preceramic polymer. One way of increasing the boron content in the oligomer is to use cage-type boron hydride monomers. Considerable amount of literature is available on carborane-siloxane polymers, which contain boron in appreciable concentration. A brief account of this development is given in section 1.3.2. In fact, carborane (C₂B₁₀H₁₂) itself is synthesized from decaborane(14) involving multiple synthetic steps. Thus, it would be advantageous if boron and silicon containing polymers are synthesized directly from decaborane than from carborane. As discussed earlier, decaborane forms adducts with bidendate ligands resulting in the formation of polymeric Lewis base adducts of decaborane. In order to incorporate decaborane adduct units into borosiloxane oligomer, the adduct should contain functional groups, capable of reacting with boric acid, like alkoxy group. Ambadas reacted decaborane with 3-aminopropyltriethoxysilane to obtain an adduct, B₁₀H₁₂[H₂N-(CH₃)₃-Si(OEt)₃]₂ which on standing resulted in the formation of a crosslinked polymer presumably due to the reaction of -OEt groups with moisture.

In variation to this study, in the present work, decaborane was reacted with 3-aminopropylmethyldiethoxysilane (APMDEOS) to obtain a stable adduct.
The -OEt group present in the adduct was made use of for reacting with boric acid as shown in Scheme 3.4.2. It is noticed that the adduct obtained by reacting decaborane and APMDEOS is soluble in THF, whereas the product obtained after the reaction with boric acid is insoluble in organic solvents and this is attributed to crosslinking. The product (BSiDB-1) was characterized by IR and TGA.

The IR spectrum of BSiDB-1 is shown in Fig. 3.4.11. The peak at 1417 cm\(^{-1}\) is due to B-N linkages.\(^{17}\) The peaks at 1082 and 781 cm\(^{-1}\) are attributed to siloxane linkages. The B-H stretching vibration, which appears around 2500-2550 cm\(^{-1}\) is not so prominent in the spectrum, but a peak at 925 cm\(^{-1}\) is present which is probably due to B-H wagging vibration. The peak at 641 cm\(^{-1}\) shows the presence of Si-O-B. The broad absorption in the region 2800-3400 cm\(^{-1}\) is attributed to the presence of residual N-H and C-H bonds present in the polymer.
The TG curve (Fig. 3.4.12) of BSiDB-1 shows a sudden weight loss (~7%) in the region 175-230 °C. In this region, probably the aliphatic linkages present in the adduct undergoes degradation resulting in low molecular volatile products. Only a gradual weight loss occurs in the region 350-500 °C and this is attributed to the loss of organic moieties. Above this temperature, practically no weight loss is noticed. A ceramic residue of 68% is obtained at 900 °C.
Ceramic conversion of BSiDB-1 was carried out by heating it at three different temperatures, 900, 1400 and 1600°C as explained in the experimental section. The IR spectra of the heat-treated samples are shown in Fig. 3.4.13.

![IR Spectra of BSiDB-1](image)

Fig. 3.4.13. IR spectra of BSiDB-1 heat-treated at 900, 1400 and 1600°C

All the samples show a peak at 1194 cm\(^{-1}\) corresponding to bending vibration of B-OH group. This peak is absent in the IR spectrum of the virgin polymer. Probably, during heat treatment B\(_2\)O\(_3\) is formed that would have got converted into B-OH by reacting with moisture. It is observed that the peaks at 2237 (due to B-OH), 641 (B-OH bending), 547 (Si-O-Si) and 460 cm\(^{-1}\) (O-Si-O bending) present in the IR spectra of the samples heat-treated at 900 and 1400°C are absent in the IR spectrum of the sample heat-treated at 1600°C. The broadness of the peak around 830 cm\(^{-1}\) reduces with the increase in heat treatment temperature and a peak at 817 cm\(^{-1}\) due to SiC is observed in the IR spectrum of the sample heat-treated at 1600°C. The peak at 1379 cm\(^{-1}\) is due to BN\(^{17}\) and the broadness of this peak also decreases with the increase in heat treatment temperature. The above observations suggest that Si-O-Si and B-OH/ B-O-B linkages get converted to SiC and BN when the heat treatment temperature is increased to 1600°C.
The XRD patterns of the polymer heat-treated at 1400 and 1600°C are compared in Fig. 3.4.14. The sample heat-treated at 1400°C shows mainly two sharp peaks at \(2\theta = 14.6\) and 27.9° corresponding to (420) and (310) planes of \(B_2O_3\). The XRD pattern of the sample heat treated at 1600°C shows peaks due to \(\beta\)-SiC, h-BN and \(B_2O_3\). The BN and SiC crystal characteristics are given in Tables 3.4.3 and 3.4.4. The broad peak centered around \(2\theta = 20°\) is due to SiO\(_2\)-B\(_2\)O\(_3\) glassy phase.

![Fig. 3.4.14. XRD of BSIDB-1 heat-treated at 1400°C and 1600°C](image)

It is found that the decaborane-based polymer has higher boron content than that of boric acid based polymers. The boron content decreases from 17.5% in the virgin sample to 16.7% in the pyrolyzed one and to 12.5% in the sample heat treated at 1600°C. This is probably due to the fact that part of boron present in the system gets converted to \(B_2O_3\) which evaporates off during heat treatment at 1600°C.

The crystalline structure of the BN formed is hexagonal and the lattice parameter is \(a_0 = b_0 = 2.5\) Å, \(c_0 = 6.66\) Å; \(\alpha = \beta = 90°\), \(\gamma = 120°\) whereas that of SiC is cubic with lattice parameter, \(a_0 = b_0 = c_0 = 4.358\) Å and \(\alpha = \beta = \gamma = 90°\). The particle size
of BN formed is 25.7 nm and that of SiC is 53.9 nm as calculated from XRD. It is interesting to note that BSiDB-1 on heat treatment at 1600 °C does not give \( \text{B}_4\text{C} \). This is attributed to the absence of direct B-C bond in the oligomer where boron atom of decaborane is directly attached to only the nitrogen atom of Lewis base.

Table 3.4.3. Hexagonal BN XRD characteristics

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Table 3.4.4. Cubic β-SiC XRD Characteristics

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<td>1.26</td>
<td>12.6</td>
<td>75.54</td>
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3.4.4 Conclusions

Representative borosiloxane oligomers synthesized from boric acid and PTEOS, VTEOS, TEOS and a mixture of PTMOS and VTEOS were heat-treated at 900, 1400 and 1600 °C in inert atmosphere. In addition, decaborane(14)-based borosiloxane oligomer having high boron content was synthesized and converted into ceramic by heat treatment. The ceramic residues were characterized by IR and XRD. Based on the results presented in this chapter, the following conclusions have been drawn:
i) $\beta$-SiC was obtained at 1600°C for the borosiloxanes based on alkoxy silane except for TEOS-based ones. On heat treatment at 900°C and 1400°C, only amorphous ceramic was obtained for all the systems. The increase in the crystallization temperature is attributed to the presence of boron. XRD does not show the presence of $B_4C$ and this is attributed to the low concentration of boron (2-3%).

ii) Amorphous ceramic was obtained for TEOS-based systems, irrespective of the heat treatment temperature. This may be due to the absence of carbon atom directly attached to the Si atom. The ceramic conversion studies of TEOS-based oligomers with two different carbon content reveals the fact that the presence of unreacted alkoxy group does not influence the nature of the ceramic formed.

iii) Decaborane(14)-based borosiloxane oligomer on heat treatment at 1600°C gives $\beta$-SiC and h-BN ceramics, having particle size of 53.9 and 25.7 nm respectively.

References

End uses of borosiloxane oligomers

This chapter reports the end-uses of the borosiloxane oligomers as oxidation resistant coating for C-C composite and matrix resins for C-SiC ceramic matrix composite. This chapter also deals with a high temperature glass coating prepared from tetraethoxysilane-based borosiloxane oligomer. The coatings were subjected to oxidation resistance test at 1000°C in air. The mechanical properties of C-SiC composites, prepared using borosiloxane oligomer-addition curable phenolic resin blend as precursor matrix, were evaluated.

*Part of the results presented in this chapter has resulted in a patent application:
3.5.1 Background

Preceramic polymers find wide range of applications as high temperature polymers, high temperature rubbers, thermal protection systems, oxidation resistant coatings, matrix resins for ceramic matrix composites, precursors for ceramic fibers, binders for making ceramic components and precursors for obtaining ultra-fine ceramic powders. A brief account of the end-uses of preceramic polymers was given in the introduction. As the present chapter focuses on the enduses of borosiloxane oligomers as oxidation resistant coatings, glass coating and matrix resin for CMCs, the developments relating to these applications are presented in some detail in this section.

Oxidation resistant coatings for C-C composites: Advanced C-C composites have attractive properties such as high strength up to 2200°C in inert atmosphere, low density, low coefficient of thermal expansion and thermal shock resistance.¹ For the above reasons, they are considered as the most suitable candidate for hot structures such as nosecone and leading edges of reentry vehicles and reusable space shuttles. However, in an oxidizing environment, they undergo degradation above 500°C, which drastically brings down their properties. Hence, they need protection against oxidation if they are to be used for the above applications.

Multilayered oxidation resistant coating is the popular choice for the protection of C-C composites against oxidation.¹,² The multilayer coating is a three-part system consisting of an initial sealant layer applied to the substrate by either slurry painting, spraying and/or CVD followed by a primary oxidation barrier applied by CVD, consisting of near-stoichiometric SiC or siliconized SiC. Because of the thermal expansion mismatch between the fiber-reinforced substrate and the primary oxidation barrier, a network of cracks develops within the coating upon cooling down from the CVD coating deposition temperature. Higher the deposition temperature, wider the cracks that are developed and these cracks provide paths for the diffusion of oxidizing species to the substrate.² In order to seal the cracks
End uses of borosiloxane oligomers

on SiC coating, in the last step of the coating process borosilicate glass coating is
applied by painting, spraying or impregnation.

In recent years, preceramic polymers have emerged as a promising
candidate for the protection of C-C composites. The advantages of preceramic
polymeric systems are the following: (i) most of the preceramic polymers/oligomers undergo melting and in the molten condition they can be used
for protecting the composites, (ii) it is possible to use solution infiltration or
brushing technique when the precursor polymer/oligomer is not meltable, but at
the same time soluble in organic solvents, (iii) conversion to ceramics takes place
at relatively low temperatures, thereby preventing the damage of the
reinforcements and (iv) the composition of the preceramic polymer can be
controlled thereby providing the scope for combining different ceramic materials in
a single system and (v) short processing time, ability to form coatings on complex
shaped objects and ability to apply multiple coatings with relative ease are the
additional advantages. In view of the above advantages, preceramic polymers find
application as protective coatings for a variety of substrates including
carbon/carbon composites, carbon/graphite fibers, ceramic fibers, CMCs, metals
and metal oxides.\textsuperscript{3,4}

Polycarbosilane obtained from polydimethylsilane was used as a
precursor for obtaining SiC coating to protect carbon-based objects, metals or
ceramic against high temperature oxidative deterioration.\textsuperscript{5-8} Polysilazanes,\textsuperscript{9,10}
boron containing polymers\textsuperscript{11} and boron and silicon containing polymers\textsuperscript{12-16} were
used to obtain ceramic coatings on C-C articles and carbon fibers used in fiber
reinforced SiC composites to prevent them against oxidative degradation.

In recent years, there have been extensive studies relating to the use of
B and Si containing preceramic oligomers as precursors for oxidation resistant
coatings. The choice of such oligomers is justified from the fact that on heat
treatment at high temperatures, they would form mixed non-oxide ceramics,
having better thermooxidative stability than simple non-oxide ceramics.\textsuperscript{17-20} On
oxidation the mixed non-oxide ceramics would form borosilicate glass which can
melt and flow into the cracks thereby sealing the pathways for oxygen entry.\textsuperscript{21-23}
In addition, presence of boron in molecularly dispersed state in the polymer network is expected to improve the sintering characteristics of the coating.

**Glass coating:** Another area of application of preceramic polymers particularly for borosiloxane oligomers is that they can be used as precursors for high temperature glass coating. As discussed earlier, in order to seal the cracks which are formed on SiC coating, glass coating is applied over SiC coating using B_2O_3-SiO_2 mixture with suitable additives. In borosiloxane oligomers, B and Si are distributed in the atomic level and hence such oligomers can give glass coating with uniform composition.

**Matrix resin for CMCs:** Yet another important area of application of preceramic polymers is as matrix resins for CMC. In CMCs, to achieve good mechanical properties, it is necessary that the interaction between ceramic fibers and ceramic matrix should be bare minimum. This is achieved by giving BN or pyrolytic carbon coating onto C-fiber. In addition, it is desirable to process the composite in a temperature range, which does not cause fiber degradation. Low temperature processing of CMCs can be achieved by employing preceramic polymers as the matrix resin.

A survey of pertinent literature on CMCs suggests that glasses, metal oxides, and non-oxide ceramics such as SiC, B_4C, BN and Si_3N_4 can be used as matrix material for CMCs. In recent years, considerable interest is shown towards using non-oxide ceramics as matrix materials as they possess excellent thermal stability, abrasion resistance, thermal shock resistance and superior thermooxidative stability. Among all the non-oxide ceramic systems, SiC ceramic is by far the widely studied one. Besides other reasons, the choice of SiC is probably due to the fact that it is synthesized from elemental silicon and carbon, which are abundantly available in nature. In the case of polymer matrix composites (PMCs), the weight percent of the fabric/fiber is around 60% whereas it is the reverse in the case of CMC. Hence, it is desirable to develop a cost-effective method for making SiC matrix. Carbon fiber reinforced silicon carbide composites (C/SiC) were made by Krukonis et al. and Zheng et al. by using polycarbosilane as matrix resin. Zheng et al. further reported that boron addition to carbon fiber/polycarbosilane-derived SiC composite improved oxidation
resistance due to the formation of B$_2$O$_3$ which sealed the pores in the composite. Hoshii and Kojima used polyborodiphenylsiloxane as a matrix resin for making C/SiC composites.\textsuperscript{30} The composite exhibited good oxidation resistance at high temperature due to the formation of vitreous film of B$_2$O$_3$ on the surface.

Kotani et al.\textsuperscript{31} developed SiC fiber reinforced SiC matrix composite (SiC/SiC composite) by polymer impregnation and pyrolysis (PIP) method. CMCs such as SiC/SIOC and Si$_3$N$_4$/SiOC were prepared by Schiavon\textsuperscript{32} using polysiloxane, SiC and Si$_3$N$_4$ inert fillers. The polysiloxane not only acted as a binder for ceramic particles, but also as a precursor for the ceramic phase thereby controlling the shrinkage and the porosity of CMCs. They also introduced boron in polysilazane by hydroboration process. The SiBCN ceramic produced from the polymer showed low crystallization rate at higher temperatures, when compared to the corresponding glass without boron.\textsuperscript{32}

This chapter deals with the end-uses of borosiloxane oligomers, prepared in the present investigation, as precursors for oxidation resistant coating and high temperature glass coating and as matrix resins for CMCs.

### 3.5.2 Oxidation resistant coating for C-C composites

#### 3.5.2.1 Preparation of SiC coating

Borosiloxane oligomers synthesized in the present investigation give reasonably high ceramic residue (> 70%) and hence, they can serve as precursors for ceramics. Usually, for preparing a SiC coating formulation, SiC powder is added as an additive in order to increase the ceramic content of the final coating and also to prevent cracks formed due to loss of volatiles resulting from the degradation of preceramic polymer. When attempts were made to prepare oxidation resistant coating from borosiloxane-SiC powder blend, the adhesion of the precursor coating onto C-C composite was poor. In order to overcome this problem, borosiloxane oligomer, BSiPh-1, was blend with addition curable phenolic resin, PF-AC developed by Nair et al.\textsuperscript{33,34}, instead of conventional phenolic resin as the former gives higher carbon content when compared to that of the latter. As PF-AC on pyrolysis gives carbon, it is necessary to use elemental
silicon powder in the coating formulation to convert pyrolytic carbon to SiC. After carrying out a number of trials on the composition of preceramic polymer blend and other additives, a suitable formulation of the precursor coating was arrived at, which was able to give adherent SiC coating onto C-C composite. As the coating formulation is a proprietary one, exact composition of the coating could not be disclosed in the thesis.

The addition curable phenolic resin used in the present study is synthesized by Nair et al.\textsuperscript{33,34} by reacting novolac resin with propargyl bromide. This resin undergoes curing through the involvement of propargyl group as shown in Scheme 3.5.1.

![Scheme 3.5.1. Curing of addition-curable phenolic resin](image)

As PF-AC is used as one of the ingredient in the coating formulation, it is essential to ensure that the carbon residue obtained from PF-AC is converted to SiC under the experimental condition used for sintering of the coating. The cured resin gives a char residue of 62.3% at 900°C. Based on the carbon content of the pyrolyzed product, the quantity of silicon metal required was calculated. Required quantity of silicon metal powder was mixed with PF-AC and cured at 185°C for 2 h. The cured product was pyrolyzed at 900°C and then sintered at 1400°C in argon atmosphere. The ceramic obtained was characterized by wet analysis,
IR and XRD. Wet analysis indicates that the ceramic contains 98% SiC and about 2% SiO₂ as impurity. The IR spectrum and XRD pattern of the sintered product are shown in Figs. 3.5.1 and 3.5.2 respectively.

![Fig. 3.5.1. IR spectrum of the sintered sample of PF-AC and elemental silicon blend](image1)

![Fig. 3.5.2. XRD pattern of the sintered sample of PF-AC and elemental silicon blend](image2)
The IR spectrum of the sintered sample shows two peaks due to SiC and SiO$_2$ at 847 and 1092 cm$^{-1}$ respectively. The peaks observed at $2\theta = 35.79, 41.48, 60.19, 71.92$ and 75.68 in XRD correspond to 111, 200, 220, 311 and 222 planes respectively of $\beta$-SiC. The preparation of SiC coating on C-C composite involves multiple steps as shown in the flow chart (Scheme 3.5.2).

3.5.2.2 Evaluation of oxidation resistance of SiC coated C-C composite

SiC coated C-C composite of dimension, 25.34 x 26.03 x 11.02 mm$^3$ and uncoated C-C composite of dimension, 24.99 x 23.55 x 11.36 mm$^3$ were exposed to oxidizing environment at 1000°C. This experiment was carried out using a muffle furnace maintained at 1000°C. The samples were placed side by side on an alumina tile and kept in the furnace for 5 min. At regular time intervals (every one minute), the furnace door was opened and closed to admit fresh air. The samples were removed at regular time intervals (5 min) and weighed to find out the weight loss. The samples were exposed to the oxidizing environment for a total period of 50 min. This exposure is a severe test as the sample is taken to high temperature rapidly and brought back to room temperature suddenly which would cause thermal shock.
The mass loss vs. exposure time for uncoated C-C composite and SiC coated C-C composite is given in Fig. 3.5.3. It is interesting to note that SiC coated C-C composite loses only 0.915 mg/cm$^2$ whereas uncoated C-C composite loses 3.94 mg/cm$^2$ in 5 min. The mass loss of uncoated C-C composite is about 4 times higher than that of SiC coated C-C composite. With increase in exposure time the mass loss increases both for uncoated C-C composite and SiC coated C-C composite and the increase in mass loss is more for uncoated C-C composite. After 50 min of exposure to the oxidizing environment, SiC coated C-C composite loses 45.77 mg/cm$^2$ whereas uncoated C-C composite loses 197.05 mg/cm$^2$. It is noticed that while the dimension of the sample remained the same in the case of SiC coated C-C composite, for uncoated C-C composite the dimension of the sample decrease continuously on exposure to oxidizing environment. Hence, the dimension of uncoated C-C composite was measured after each exposure and this data was used for calculating the mass loss/cm$^2$.

Fig. 3.5.3. Cumulative mass loss per unit area of C-C composite and SiC coated C-C composite on exposure to oxidizing environment at $1000^\circ$C for 50 min

The oxidation resistance test suggests that SiC coating certainly offers protection to C-C composite. If protection by SiC coating is perfect, there should be no mass loss for SiC coated C-C composite. The mass loss of 45.77 mg/cm$^2$
after 50 min of exposure for SiC coated C-C composite suggests that there are certain defects in the SiC coating through which oxygen gets entry to C-C composite causing erosion. SEM studies which will be discussed in the later part of this section would throw some light on this aspect.

The protection offered by SiC coating to C-C composite would be further exemplified by comparing the percentage mass loss and percentage volume change (Fig. 3.5.4) of uncoated and SiC coated C-C composite samples after 50 min of exposure to oxidizing environment.

![fig3_5_4](image)

**Fig. 3.5.4.** (a) Percentage mass loss and (b) Percentage volume remaining of uncoated and SiC coated C-C composites after 50 min exposure at $1000^\circ$C

From Fig. 3.5.4a it is noticed that SiC coated C-C composite loses 9.71% of its weight even though there is no change in the dimension of the sample. This observation suggests that the SiC coating has certain defect sites or pores through which oxygen gets entry to C-C composite causing mass loss. As the
mass loss is probably from the interior of the composite, the overall dimension remains the same. In the case of uncoated C-C composite, as the surface is not protected erosion takes place predominantly from the surface causing reduction in the dimension of the sample.

Scanning electron micrographs of uncoated C-C composite and SiC coated C-C composite before and after exposure to oxidizing environment are shown in Figs. 3.5.5 and 3.5.6 respectively.

![Fig. 3.5.5. SEM of a) C-C composite and b) SiC coated C-C composite before exposure to oxidizing environment](image1)

![Fig. 3.5.6. SEM of a) C-C composite and b) SiC coated C-C after exposure to oxidizing environment](image2)

From the micrographs it is quite evident that the uncoated C-C composite undergoes extensive surface erosion leading to degradation of both the matrix and the reinforcement. No such surface erosion is noticed on the SiC coated C-C composite. As discussed earlier, about 9.71% mass loss is noticed for the coated composite on exposure to oxidizing environment. A closer look at the SEM of SiC
coated C-C composite before exposure to oxidizing environment reveals the presence of micro cracks. These cracks were probably formed when the sample was allowed to cool after sintering. Though the cooling rate was slow (3°C/min) the formation of cracks could not be eliminated probably due to the thermal expansion mismatch of C-C composite and SiC coating and also due to the shrinkage caused by the evolution of volatiles from borosiloxane oligomer and addition curable phenolic resin.

A closer view of the SiC coating exposed to oxidizing environment is shown in Fig. 3.5.7.

Fig. 3.5.7. SEM of SiC coated C-C composite exposed to oxidizing environment (Two views)

From Fig. 3.5.7a it is seen that the crack propagates deep into the coating through which oxygen gets easy access to the substrate. Fig. 3.5.7b shows the texture of SiC coating.

### 3.5.3 Glass coating from borosiloxane oligomers

From the foregoing discussion it is obvious that the cracks on SiC coating are to be sealed in order to make the coating impermeable to oxygen. SiC coating is usually meant for use in the temperature region 1400-1700°C. When SiC coated C-C composites are subjected to such high temperatures during reentry, cracks can develop due to thermal expansion mismatch between SiC coating and C-C composite. The glass coating that is applied over SiC coating should be capable of sealing the cracks which are formed during the processing of the coating and also the cracks which are formed during the flight. Thus, it is
necessary that the glass coating should melt at a slightly lower temperature than
the service temperature. Then only the glass coating can melt and flow into the
cracks. Thus, if SiC coating is targeted for use at 1400-1700°C, the glass coating
should melt around 1400°C. In addition to sealing the cracks, the glass coating
offers yet another advantage viz., protection against moisture absorption by SiC
coating and by the component.\textsuperscript{24,25,35-37} If glass coating is not applied over SiC
coating, it would absorb moisture and the moisture absorbed at the interface
between the SiC coating and the substrate would form water vapour/steam when
heat load is applied onto the substrate.\textsuperscript{38} This will result in development of internal
pressure at the interface causing peeling of the coating from the substrate when
the SiC coated composite experiences higher temperatures. Thus, it is essential to
provide glass coating over SiC coating.

Glass coating is usually obtained from SiO$_2$-B$_2$O$_3$ flux or by sol-gel
process.\textsuperscript{39-48} In the present investigation, attempts have been made to get glass
coating from borosiloxane oligomers synthesized from boric acid by non-aqueous
sol-gel process. An important criterion to obtain glass coating from borosiloxane
oligomer is that it should not contain organic moieties attached to silicon atom in
order to prevent the formation of non-oxide ceramics. The formation of glass
coating onto C-C composite should be done in inert atmosphere in order to
prevent any damage to C-C composite due to the oxygen entry. This implies that
the borosiloxane oligomers or polymers should be devoid of carbon or if carbon is
present, it should be knocked off completely during heat treatment. Borosiloxane
oligomers based on phenylalkoxysilane and VTEOS, discussed in detail in
chapter 3.4, give SiC non-oxide ceramics on heat treatment under inert
atmosphere. So they are not suitable for obtaining glass coating. The borosiloxane
oligomer (BSIT-2), synthesized from boric acid and TEOS (monomer feed ratio-
1:1.5) in diglyme using HCl as catalyst was used for preparing glass coating. In a
preliminary study, the oligomer was taken in a graphite crucible and heated to
1600°C under inert atmosphere. The oligomer melted and the inside of the
crucible was coated with a hard black colored glaze coating. Visual observation
indicated that the coating is intact, uniform and crack-free. The scanning electron
micrographs of the glass coating formed on the graphite substrate are shown in Fig. 3.5.8.

![Fig. 3.5.8. SEM of glass coating from BSiT-2](image)

It is seen that even at higher magnifications the glass coating is smooth and free from cracks. The oxidation resistance of the coating was evaluated by subjecting a part of the crucible coated with the glass coating in a muffle furnace at 1000°C in air for 50 min. SEM of the coating after exposure to oxidizing environment is shown in Fig. 3.5.9. SEM of a portion of the unprotected area of the crucible which was subjected to a similar test is shown in Fig. 3.5.10.

![Fig. 3.5.9 SEM of glass coating from BSiT-2 exposed to air at 1000°C for 50 min](image)

No cracks are seen in the glass coating exposed to oxidizing environment. However, some blisters are seen and the reason for the formation of such blisters is not clearly understood. From Fig. 3.5.10 it is seen that the unprotected graphite surface is attacked by oxygen resulting in extensive erosion.
3.5.4 Ceramic matrix composites

Besides other end uses, preceramic polymers serve as matrix resins for CMC and a brief account of this is given in the background of this chapter. As in the case of SiC coating process, a blend of borosiloxane oligomer and PF-AC along with additives such as SiC and elemental silicon was used as the precursor matrix. The flow chart for the preparation of the CMC is given in Scheme 3.5.3.

Unlike in polymer matrix composite, in CMC the interaction between the fiber and matrix should be weak in order to facilitate fiber pull-out. Giving an interfacial coating onto the fiber/fabric facilitates the fiber pull-out. Such a coating involves a process requiring CVD coating facility. In recent years, preceramic polymers are also used for such interfacial coating. In the present study, attempts have been made to use C-fabric without any protective coating for the preparation of CMC. This approach was adopted in order to know whether the preceramic oligomer used in the preceramic blend itself gives protection to the fabric.
In the present investigation, rayon-based C-fabric and PAN-based carbon fabric (T-300) were used as reinforcements. The porous C-SiC composite obtained by pyrolysis as shown in flow chart (Scheme 3.5.3) was infiltrated with borosiloxane oligomer (BSiPh-1) and then subjected to pyrolysis. This process was repeated until there was no further increase in density. Finally, the composite was sintered at 1400°C following the procedure described earlier.

### 3.5.5 Mechanical properties of CMCs prepared using rayon-based carbon fabric and different precursor compositions

Two different formulations were tried for making CMC using rayon fabric. The details regarding the formulation and the properties obtained are given in Table 3.5.1. Both the composites exhibit very poor tensile strength (1.5-3 MPa). This shows that there is strong interaction between the brittle matrix and the fiber. It is seen from Table 3.5.1, that when SiC content in the formulation is increased, the flexural as well as compressive strength of the composite decreases.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Formulation (g)</th>
<th>Mechanical Properties (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BSiPh-1</td>
<td>PF-AC</td>
</tr>
<tr>
<td>CMC-5</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>CMC-6</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Probably, with increase in SiC content, the sintering of the matrix is incomplete. The scanning electron micrographs of CMC-5 and CMC-6 are compared in Fig. 3.5.11. CMC-5 did not show any fiber-pullout whereas fiber-pullout is observed in CMC-6. As discussed earlier, CMC-6 has higher SiC particulate content and hence, sintering may be less effective which probably favors fiber-pull out.
As PAN-based carbon fabric is known to have better mechanical property than rayon-based carbon fabric attempts were made to study the mechanical properties of the CMC prepared using carbon fabric T-300. Two different formulations with higher amount of SiC than in the earlier formulations were tried and the mechanical properties obtained are given in Table 3.5.2.

Table 3.5.2. Mechanical properties of CMCs prepared using different precursor composition with PAN-fabric

<table>
<thead>
<tr>
<th>Composite</th>
<th>Formulation (g)</th>
<th>Mechanical Properties (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BSiPh-1</td>
<td>PF-AC</td>
</tr>
<tr>
<td>CMC-7</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>CMC-9</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

It is observed that in both cases, the tensile strength obtained is higher than that of rayon-based composites. However, similar improvement is not noticed in flexural and compressive strength. Even though SiC loading in CMC-7 and CMC-9 is higher than that of CMC-6, the flexural strength of CMC-7 and CMC-9 is double than that of CMC-6. This is attributed to the higher mechanical properties of carbon T-300 compared to that of rayon-based carbon cloth. However, the compressive strength of CMC-9 is lower than that of CMC. This is probably due to improper sintering due to higher SiC loading.
CMC prepared using carbon T-300 fabric and cotton gauze cloth:

In CMCs, it is known that the carbon reinforcement hinders the sintering. The poor mechanical properties of CMCs investigated in the present investigation supports the above inference. In order to improve the mechanical properties, it may be necessary to bring down the volume fraction of the reinforcement. This has been achieved by using cotton gauze cloth along with carbon T-300 fabric. Preceramic polymer slurry coated gauze cloth was sandwiched between preceramic slurry coated C-fabric. The gauze cloth would ensure maximum pick-up of preceramic slurry and would hold the major part of the precursor slurry during consolidation and curing. Having higher quantity of precursor matrix between the reinforcement would probably ensure good sintering. As the precursor slurry can flow easily through the gauze cloth, continuity of the ceramic matrix after sintering is ensured. The above factors are expected to contribute towards the improvement in mechanical properties of CMC. It is observed that CMC prepared by the above approach (CMC-10) has tensile, flexural and compressive strength of 16, 23 and 40 MPa respectively. Considerable improvement in tensile strength is observed for CMC-10 compared to that of CMC-7 and CMC-9, though a similar improvement is not noticed for flexural and compressive strength.

The scanning electron micrographs of the fractured surface of CMC-10 tensile test coupon after testing are shown in Fig. 3.5.12. No fiber pull-out is seen whereas a sintered ceramic matrix is visibly seen. Thus, it can be inferred that the improvement in tensile strength is probably due to a well sintered ceramic matrix.

Fig. 3.5.12. SEM of fractured surface of CMC-10 test coupon
3.5.6 Conclusions

Based on the results presented in this chapter, the following conclusions have been drawn:

i) SiC coating prepared from borosiloxane oligomer and addition curable phenolic resin blend offers protection to C-C composites against oxidation. Uncoated C-C composite has a mass loss of 40.15% whereas the coated one has 9.71% mass loss of its weight.

ii) SEM studies of uncoated C-C composite indicate extensive erosion of both the C-matrix and the C-reinforcement. No such erosion is observed with SiC coated C-C composite. SEM studies of SiC coated C-C composite indicate the presence of microcracks, which are formed probably during sintering and/or oxidation resistance test resulting from thermal expansion mismatch between SiC coating and C-C composites.

iii) A glass coating on graphite substrate was prepared by heat treatment at 1600°C of borosiloxane oligomer, synthesized from boric acid and TEOS. The SEM studies suggest that the coating is free from cracks. The oxidation resistance test of a graphite substrate coated with a glass coating suggests that it offers good protection to the substrate.

iv) Evaluation of the mechanical properties of C-SiC composites prepared using borosiloxane-PF-AC blend suggests that there is strong interaction between the matrix and the fiber resulting in poor mechanical property. Improvement in tensile strength has been achieved by using alternate layers of carbon T-300 fabric and cotton gauze cloth and this improvement is attributed to better sintering of the matrix.

References


Part B

Polysilahydrocarbons
Chapter 3.6

Thermal degradation kinetics of polysilahydrocarbons

This chapter deals with the thermal degradation kinetics of polysilahydrocarbons synthesized from diorganodichlorosilanes and styrene under dechlorination conditions and polycarbosilanes derived from polysilahydrocarbons by heat treatment. The thermal degradation studies were carried out by non-isothermal TGA studies. Four different kinetic methods were applied for the kinetic study and activation energy and pre-exponential factor were calculated. It was found that all the four methods gave almost the same value for the activation energy and pre-exponential factor. The activation energy and pre-exponential factors vary depending on the type of the structural units present in the polymers.

* The results presented in this chapter have been published and presented in the following National and International Symposia

3.6.1 Background

Polysilahydrocarbons, containing Si-C grades repeating units (where x ≥ 2) in the polymer backbone, were synthesized through the dechlorination of different diorganodichlorosilanes with styrene under dechlorination conditions using sodium in toluene.\(^1\)\(^-\)\(^7\) The polysilahydrocarbons have very poor thermal stability. Thermally unstable polysilahydrocarbons can be converted to thermally stable polycarbosilanes by heat treatment at temperatures above 400°C in a partially confined environment.\(^3\) It is observed that the thermal stability and the ceramic residue of the polycarbosilanes obtained from polysilahydrocarbons very much depend on the temperature at which the thermal conversion of polysilahydrocarbons is carried out.\(^3\) Thus, it would be of interest to study the thermal stability and thermal degradation kinetics of polysilahydrocarbons and the polycarbosilanes obtained from polysilahydrocarbons by heat treatment at different temperatures and correlate the results with the microstructure of starting polysilahydrocarbons and polycarbosilanes.

3.6.2 Kinetic Equations

Thermal analysis is one of the most versatile techniques universally applicable in materials characterization and is utilized in almost every area of technology.\(^8\)\(^,\)\(^9\) Thermal analysis is defined as a group of techniques in which a physical property of a substance and/or its reaction products is measured as a function of temperature while the substance is subjected to a controlled temperature program, in a specified atmosphere.\(^8\)\(^,\)\(^9\)

Kinetic investigations are one of the most important applications of thermal analysis. A common goal of kinetic studies is to define the time-temperature dependence of conversion, \(\alpha = f(t, T)\) where \(t\) refers to time and \(T\) refers to temperature. Kinetic analysis includes determination of the reaction mechanism or appropriate kinetic equation for the system being analyzed and measurement of Arrhenius and activation parameters viz., reaction order, activation energy and pre-exponential factor of the specified reactions. Conversion of data from TG curves into kinetic parameters is based on the utilization of
Thermal degradation kinetics...

classical laws of kinetics. Various thermal methods of analysis have been used for the study of thermal behavior of substances. These methods can be divided into two categories: static and dynamic. The static method itself can be classified into isobaric and isothermal. In isobaric method, changes in the equilibrium property of a substance are measured as a function of time at constant pressure while in the isothermal method, changes in the property are measured as a function of time at constant temperature. Dynamic method consists of measurement of properties under a programmed temperature condition. Isothermal methods generally give a more accurate and reliable description of cure reactions. Non-isothermal methods include single and multiple heating rate methods. The single heating rate methods give quick and valuable comparative studies, although the reproducibility is lower than that of isothermal methods. The multiple heating rate methods give reliable estimates of activation energy for most of the reactions without requiring knowledge of the reaction mechanism.

All kinetic models start with the basic rate equation which relates the rate of conversion at constant temperature, \( \frac{d\alpha}{dt} \) to a function of the concentration of reactants, \( f(\alpha) \), through a rate constant, \( k \).

\[
\frac{d\alpha}{dt} = kf(\alpha) \quad \text{Eq. (1)}
\]

where \( \alpha \) is the fractional conversion, \( k \) is the rate constant, and \( f(\alpha) \) is assumed to be independent of temperature.

For reactions following \( n^{th} \) order kinetics, the rate of conversion is proportional to the concentration of unreacted material (reactant concentration), expressed as:

\[
\frac{d\alpha}{dt} = k(1-\alpha)^n \quad \text{Eq. (2)}
\]

where \( n \) is the reaction order.

The dependence of temperature on the rate constant is given by the Arrhenius equation,

\[
k = A e^{\left(-\frac{E}{RT}\right)} \quad \text{Eq. (3)}
\]

where \( A \) is the Arrhenius or pre-exponential factor (1/s), \( E \) is the activation energy (J/mol), \( R \) is the universal gas constant (8.314 J/mol/K) and
T, the absolute temperature (K). Equations 2 and 3 when combined give the complete rate equation for $n^{th}$ order reactions:

$$\frac{d\alpha}{dt} = Ae^{\left(\frac{-E}{RT}\right)}(1-\alpha)^n$$

Eq. (4)

There are two basic approaches in solving the rate equation:

i) Mechanism invoking method which gives the physicochemical description of the process, proposed on the basis of certain models.

ii) Mechanism non-invoking method which is a general kinetic study based on the simple extension of homogeneous kinetics to solid state (usually heterogeneous) kinetics.

3.6.2.1 Isothermal kinetics

Isothermal kinetics is the conventional method for the evaluation of kinetic parameters. It is based on the observation of a reaction at constant temperature, the determination of the rate equation for the reaction course and the determination of the dependence of rate constants on temperature under static conditions. In isothermal kinetics, the kinetic parameters are evaluated using the rate equation 2. The dependence of the rate constant on temperature is given by the Arrhenius equation 3.

It is often difficult to follow solid state reactions isothermally due to the temperature lag between the sample and the furnace. The variable thermal conductivities of the solid reactants and products lead to this temperature lag. For maintaining a constant temperature, a furnace of large mass is required which usually takes a long time for heating. A sizeable fraction of the reaction could be completed before the sample attains the temperature of the furnace by heat transfer.

3.6.2.2 Non-isothermal kinetics

The main advantage of non-isothermal techniques is obtaining kinetic values from a single measurement for the whole temperature range. For a linear heating rate ($\phi = dT/dt$), the rate equation (2) becomes:

$$\frac{d\alpha}{dT} = \left(\frac{A}{\phi}\right)e^{\left(\frac{E}{RT}\right)}(1-\alpha)^n$$

Eq. (5)
Equation 5 may be considered as a general equation relating the parameters $A$, $E$ and $n$. Different authors\textsuperscript{10,11} have given solutions of this equation in simpler and more practically useful forms for calculating kinetic parameters. These methods fall into two distinct categories, viz., the differential method and the integral method. Using these methods, there are a number of equations derived by different authors\textsuperscript{10,11} Some of the important methods, especially that are used in this work, are reviewed in section 3.6.2.4.

3.6.2.3 Comparison of isothermal and non-isothermal methods

The isothermal or static method is the determination of the degree of transformation at constant temperature as a function of time, while the non-isothermal or dynamic method is the determination of degree of transformation as a function of time, during a linear increase of temperature. According to Blazek,\textsuperscript{12} the isothermal method is more suitable for obtaining information about slow processes, and also the reaction order and reaction mechanism while the non-isothermal method is more suitable for obtaining data on the reaction kinetics from a single curve for the whole temperature range. Advantages of non-isothermal methods\textsuperscript{10} are the following: i) considerably fewer data are required, ii) the kinetics can be calculated over an entire temperature range in a continuous manner, iii) when a sample undergoes considerable reaction during the temperature being raised to the required level, the results obtained by an isothermal method are often questionable and iv) a single sample is sufficient to scan the entire temperature range, whereas for isothermal methods a new sample is needed for each experiment.

According to Bagchi and Sen,\textsuperscript{13} the explicit advantages of non-isothermal method is that it is possible to determine the reaction onset temperature ($T_i$) very precisely which is almost impossible by isothermal technique. In addition, in non-isothermal methods the time error in measuring the mass is absent. However, there are some disadvantages of non-isothermal methods. They are i) The reaction mechanism cannot be usually determined and one gets only overall kinetic expression, whereas many of the solid state reactions follow more than one
kinetic law and ii) The greater susceptibility to procedural factors such as sample mass, heating rate, particle size, etc.\textsuperscript{14,15}

3.6.2.4 Different methods for the determination of kinetic parameters using non-isothermal kinetic methods

**Differential method:** Freeman Carroll method is the most widely used differential method for the evaluation of kinetic parameters. It uses $T_{\text{max}}$, the DTG peak temperature where the decomposition rate is maximum. But recently the most widely used ones are the integral methods where accurate results are obtained.\textsuperscript{16-18}

**Integral methods:** Integral methods are generally accepted as the most accurate among the methods available for the determination of kinetic parameters from TG data.\textsuperscript{19,20} Different authors have employed different techniques for the evaluation of the exponential integral. These techniques fall into three distinct groups (i) approximation methods, (ii) series expansion method and (iii) numerical solution method, using tabulated values. The present study makes use of more widely used methods which are described below:

i) **Horowitz-Metzger method**\textsuperscript{21} is an approximation method which uses the inflection temperature, $T_s$, for calculation. The equation is given as:

$$
\ln(g(\alpha)) = \ln \left( \frac{A R T}{\phi E} \right) - \frac{E}{R T_s} + \frac{E \theta}{R T_s^2}
$$

Eq. (6)

The major disadvantage of this method is its dependence of $T_s$, which is influenced by procedural factors such as sample mass and heating rate.

ii) **Coats-Redfern Equation**\textsuperscript{22} falls under the series expansion method and takes the form as given below.

$$
\ln \left( \frac{g(\alpha)}{T^2} \right) = \ln \left( \frac{A R}{\phi E} \right) \left( \frac{1 - 2RT}{E} \right) - \left( \frac{E}{RT} \right)
$$

Eq. (7)

The authors have also recommended a trial and error method for determining the form of $g(\alpha)$, i.e., the value of 'n' is determined by trial and
This drawback has been overcome by the use of iteration methods to get best-fit value of n with the aid of a computer.

iii) Madhusudanan-Krishnan-Ninan Equation\textsuperscript{23} falls under the series expansion method and takes the form as follows:

\[
\ln \left( \frac{g(\alpha)}{T^{1.9215}} \right) = \ln \left( \frac{AE}{\phi R} \right) + 3.7721 - 1.9215 \ln(E) - 0.12039 \frac{E}{T} \quad \text{Eq. (8)}
\]

iv) MacCallum-Tanner method\textsuperscript{24} falls under the category of numerical solution method. In this method, the order of the reaction is determined by trial and error or by iteration.

\[
\log g(\alpha) = \log \left( \frac{AE}{\phi R} \right) - 0.483E^{0.435} - (0.449 + 0.217E) \left( \frac{10^3}{T} \right) \quad \text{Eq. (9)}
\]

where \( g(\alpha) = -\ln(1 - \alpha) \) for \( n=1 \); \( g(\alpha) = \left[ \frac{1 - (1 - \alpha)^{1+n}}{1 - \alpha} \right] \) for \( n \neq 1 \)

\( \alpha \) - fractional conversion; \( A \) - pre-exponential factor; \( n \) - order of the reaction; \( t \) - time; \( E \) - apparent activation energy, \( R \) - universal gas constant, \( T_s \) - DTG peak temperature, \( \phi \) - heating rate, \( \theta \) - \((T-T_s)\) and \( T \) - temperature

3.6.3 Poly(dimethylsilylene-co-styrene) and Poly(methylphenylsilylene-co-styrene)

3.6.3.1 Composition of the copolymers

Poly(dimethylsilylene-co-styrene) (PDMSS) and poly(methylphenylsilylene-co-styrene) (PMPSS) copolymers synthesized by Ambadas et al.\textsuperscript{25} from dimethyldichlorosilane (DMDCS) and styrene and from methylphenyldichlorosilane (MPDCS) and styrene respectively in different mole ratios, were used in the present investigation. Based on \(^{13}\text{C}\)- and \(^{29}\text{Si}\)-NMR spectra the composition of PDMSS and PMPSS copolymers was calculated and the results are given in Tables 3.6.1 and 3.6.2 respectively along with the GPC data.
A detailed discussion on the microstructure and mechanism of formation of these copolymers is given elsewhere. Based on the spectral studies, the probable structural units of the copolymers can be represented as given in structure 1:

\[
\begin{align*}
\text{Structure 1} \\
\text{where } R = \text{Me or Ph}
\end{align*}
\]

All the copolymers show bimodal molecular weight distribution which is common with most of the polysilanes prepared by Wurtz-type reaction. The low molecular weight fraction increases with increase in the amount of styrene in the feed. As the concentration of styrene is increased, the number of initiating species and consequently propagating chains increase resulting in higher proportion of low molecular weight compounds. The increase in low molecular weight fraction with the increase in styrene concentration in the monomer feed is more pronounced for PDMSS system than for PMPSS system and this observation is attributed to the lower reactivity of silyl radical anion produced from DMDCS with styrene when compared to that of silyl radical anion produced from MPDCS with styrene.

3.6.3.2 Thermal properties

The TG curves of PDMSS copolymers and polystyrene are given in Fig. 3.6.1 and those of PMPSS copolymers are given in Fig. 3.6.2. Initial decomposition temperature ($T_i$), maximum decomposition temperature ($T_{\text{max}}$) and final decomposition temperature ($T_f$) and the ceramic residue at 900°C of PDMSS and PMPSS systems are given in Tables 3.6.3 and 3.6.4 respectively. It is observed that polystyrene is stable up to 380°C and undergoes degradation in the temperature range 400-450°C leaving behind no char residue. The copolymers have higher thermal stability when compared to polystyrene and this is attributed to the presence of C-Si linkages in the copolymers. Comparison of TG curves of PDMSS and PMPSS systems reveals that the TG curve of PMPSS-II is distinctly different from the rest of the TG curves. $T_i$, $T_{\text{max}}$, $T_f$ and ceramic residue values
are the highest for PMPSS-II. The higher thermal stability of this copolymer is attributed to the presence of alternating units of di(methylphenylsilylene) and styryl. Interestingly, such improvement in thermal stability is not observed for PDMSS-I (synthesized from DMDCS:styrene monomer feed ratio, 1:0.5) which also contains alternating units of di(dimethylsilylene) and styryl.

Fig. 3.6.1. TG curves of PDMSS copolymers

Table 3.6.3. Comparison of thermal properties and ceramic residue for PDMSS copolymers

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Decomposition temperature (°C)</th>
<th>Ceramic residue at 900°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_i$</td>
<td>$T_{\text{max}}$</td>
</tr>
<tr>
<td>PDMSS-I</td>
<td>380</td>
<td>455</td>
</tr>
<tr>
<td>PDMSS-II</td>
<td>370</td>
<td>460</td>
</tr>
<tr>
<td>PDMSS-III</td>
<td>370</td>
<td>455</td>
</tr>
</tbody>
</table>

$T_i$ - initial decomposition temperature; $T_{\text{max}}$ - maximum decomposition temperature; $T_f$ - final decomposition temperature
Fig. 3.6.2. TG curves of PMPSS copolymers

Table 3.6.4. Comparison of thermal properties and ceramic residue of PMPSS copolymers

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Decomposition temperature(°C)</th>
<th>Ceramic residue at 900°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_i$</td>
<td>$T_{max}$</td>
</tr>
<tr>
<td>PMPSS-I</td>
<td>385</td>
<td>430</td>
</tr>
<tr>
<td>PMPSS-II</td>
<td>445</td>
<td>470</td>
</tr>
<tr>
<td>PMPSS-III</td>
<td>400</td>
<td>445</td>
</tr>
<tr>
<td>PMPSS-IV</td>
<td>380</td>
<td>445</td>
</tr>
<tr>
<td>PMPSS-V</td>
<td>360</td>
<td>450</td>
</tr>
</tbody>
</table>

$T_i$: initial decomposition temperature; $T_{max}$: maximum decomposition temperature; $T_f$: final decomposition temperature

For PDMSS systems, PDMSS-II (synthesized from DMDCS:styrene monomer feed ratio 1:1), containing styryl block in addition to alternating units of disilyl and styryl, has the highest thermal stability. Studies on the thermal conversion of PDMSS and PMPSS copolymers to polycarbosilanes by heat treatment in inert atmosphere at temperatures above 400°C, suggest that
phenylene ring gets inserted into the disilyl linkage, thereby rendering the polycarbosilane thermally more stable and such phenylene insertion reactions are probably more favored when methylphenylsilyl units are present. This may be the reason for the higher thermal stability of PMPSS-II compared to that of PDMSS-I. For PDMSS system, the overall thermal stability follows the trend, PDMSS-II > PDMSS-I > PDMSS-III and for PMPSS system, the trend is PMPSS-II > PMPSS-III > PMPSS-IV > PMPSS-I > PMPSS-V. For PMPSS system, it is observed that the incorporation of polysilyl blocks (as in the case of PMPSS-I) or polystyryl blocks (as in the case of PMPSS-III, PMPSS-IV and PMPSS-V) in the polymer backbone containing alternating units of di(methylphenylsilylene) and styryl reduces the overall thermal stability.

### 3.6.3.3 Thermal degradation kinetics

The TGA studies indicate that the overall thermal stability and the ceramic residue are influenced by the composition and structure of the copolymers. Thus, it is expected that the thermal degradation kinetics would also be influenced by above such factors.

Using the TG curves, the kinetics of thermal degradation of the copolymers was carried out by the following four methods: Horowitz-Metzger method (H-M)\textsuperscript{21}, Coats-Redfern method (C-R)\textsuperscript{22}, Madhusudhanan-Krishnan-Ninan method (MKN)\textsuperscript{23} and Mac Callum-Tanner method (M-T)\textsuperscript{24}. The order of thermal degradation reaction (n) was determined, by iterating the TGA data using one of the methods (C-R method). Different n values were substituted in the equation and \( \ln \left( \frac{g(\alpha)}{T^2} \right) \) was plotted against \( \left( \frac{1}{T} \right) \times 10^3 \) for different n values ranging from 0.1 to 3 with an increment of 0.1; where \( g(\alpha) = -\ln(1-\alpha) \) for \( n=1; \ g(\alpha) = \left[ \frac{1-(1-\alpha)^{1-n}}{(1-n)} \right] \) for \( n \neq 1. \) The n value that gave the best fit (having the maximum correlation coefficient, 0.99 or above) was taken as the order of the reaction. The order of the reaction (for the best fit) along with the correlation coefficient values for polystyrene (PS), PDMSS-I to PDMSS-III and PMPSS-I to PMPSS-V are given in the Tables 3.6.5 and 3.6.6. A typical kinetic plot of PDMSS-II is shown in Fig. 3.6.3.
Fig. 3.6.3. Coats-Redfern kinetic plot for different values of n for PDMSS-II

Table 3.6.5. Order and correlation coefficient of PDMSS system

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Reaction order (n)</th>
<th>Correlation coefficient (r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMSS-I</td>
<td>0.5</td>
<td>0.9987</td>
</tr>
<tr>
<td>PDMSS-II</td>
<td>0.5</td>
<td>0.9990</td>
</tr>
<tr>
<td>PDMSS-III</td>
<td>0.1</td>
<td>0.9985</td>
</tr>
<tr>
<td>PS</td>
<td>0</td>
<td>0.9871</td>
</tr>
</tbody>
</table>

Table 3.6.6. Order and correlation coefficient of PMPSS system

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Reaction order (n)</th>
<th>Correlation coefficient (r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMPSS-I</td>
<td>2.0</td>
<td>0.9936</td>
</tr>
<tr>
<td>PMPSS-II</td>
<td>2.0</td>
<td>0.9869</td>
</tr>
<tr>
<td>PMPSS-III</td>
<td>1.4</td>
<td>0.9987</td>
</tr>
<tr>
<td>PMPSS-IV</td>
<td>1.2</td>
<td>0.9975</td>
</tr>
<tr>
<td>PMPSS-V</td>
<td>0.8</td>
<td>0.9982</td>
</tr>
</tbody>
</table>
It is found that the n value for PDMSS-I and PDMSS-II is 0.5 and for PDMSS-III, the value is 0.1. For PMPSS-I and PMPSS-II the n value is 2.0 and the value decreases gradually with the increase in styrene concentration. The n value is 0.8 for PMPSS-V system. Though PDMSS-I and PMPSS-II have almost the same ratio of disilyl unit to styryl unit, the order is 0.5 for PDMSS whereas it is 2 for PMPSS. Another interesting observation is that with the increase in styryl unit to dimethylsilyl unit ratio of 0.8 for PDMSS-II to 1.3 for PDMSS-III, the order decreases from 0.5 to 0.1, approaching that of polystyrene. On the other hand, for PMPSS system, with the increase in the ratio of styryl unit to methylphenylsilyl unit from 0.74 to 2.56 the order decreases from 1.4 to 0.8. Thus, for PMPSS system the order value does not approach that of polystyrene even when polystyryl blocks are present in higher concentration when compared to that of PDMSS system. It is worth mentioning that for poly(methylvinylsilylene-co-styrene) which will be discussed in the next section (Section 3.6.4), the ‘n’ value shows an increasing trend with increase in concentration of styrene in the copolymer system. Unlike, PDMSS and PMPSS systems which are linear copolymers, PMVSS copolymers contain crosslinks due to the participation of vinyl group in the polymerization. From the above observation, it is clear that the order of thermal degradation depends on the nature of the silyl group present in the copolymer. It is noticed that the E and A values decrease with the increase in concentration of styryl units in PDMSS and PMPSS copolymers. (Tables 3.6.7 and Table 3.6.8)

Table 3.6.7. Kinetic parameters for the thermal degradation of PDMSS copolymers

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Activation energy/Pre-exponential factor</th>
<th>Kinetic equations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>M-T</td>
</tr>
<tr>
<td>PDMSS-I</td>
<td>E(kJ/mol) 150.92</td>
<td>169.01</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹) 3.09 x 10⁸</td>
<td>6.31 x 10⁸</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.55 x 10⁸</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.38 x 10⁸</td>
</tr>
<tr>
<td>PDMSS-II</td>
<td>E(kJ/mol) 123.99</td>
<td>143.56</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹) 3.02 x 10⁸</td>
<td>7.76 x 10⁷</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.58 x 10⁸</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.38 x 10⁸</td>
</tr>
<tr>
<td>PDMSS-III</td>
<td>E(kJ/mol) 91.18</td>
<td>113.50</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹) 8.51 x 10³</td>
<td>3.63 x 10⁶</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.78 x 10³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.07 x 10³</td>
</tr>
<tr>
<td>PS</td>
<td>E(kJ/mol) 93.65</td>
<td>133.72</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹) 20.89 x 10³</td>
<td>39.81 x 10⁶</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14.12 x 10³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.30 x 10³</td>
</tr>
</tbody>
</table>
PMPSS-II is an exception with very high E and A values. As explained earlier, PMPSS-II contains alternating units of di(methylphenylsilyl) and styryl units and has higher thermal stability when compared to other polysilahydrocarbons. This difference in thermal stability is probably responsible for the higher E and A values of PMPSS-II.

From the Tables 3.6.7 and 3.6.8 it can be seen that except for Horowitz-Metzger method,\textsuperscript{21} E and A values are very close. Some what higher values of E and A obtained by Horowitz-Metzger method when compared to those obtained by other three methods may be due to the fact that the H-M method is an approximation method whereas the other three methods are integral methods.\textsuperscript{27}

### Table 3.6.8. Kinetic parameters for the thermal degradation of PMPSS copolymers

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Activation energy/Pre-exponential factor</th>
<th>Kinetic equations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>M-T</td>
</tr>
<tr>
<td>PMPSS-I</td>
<td>E(kJ/mol)</td>
<td>237.62</td>
</tr>
<tr>
<td></td>
<td>A(s(^{-1}))</td>
<td>2.75 x 10(^{15})</td>
</tr>
<tr>
<td>PMPSS-II</td>
<td>E(kJ/mol)</td>
<td>365.96</td>
</tr>
<tr>
<td></td>
<td>A(s(^{-1}))</td>
<td>2.19 x 10(^{23})</td>
</tr>
<tr>
<td>PMPSS-III</td>
<td>E(kJ/mol)</td>
<td>166.28</td>
</tr>
<tr>
<td></td>
<td>A(s(^{-1}))</td>
<td>7.2 x 10(^{9})</td>
</tr>
<tr>
<td>PMPSS-IV</td>
<td>E(kJ/mol)</td>
<td>178.35</td>
</tr>
<tr>
<td></td>
<td>A(s(^{-1}))</td>
<td>7.1 x 10(^{10})</td>
</tr>
<tr>
<td>PMPSS-V</td>
<td>E(kJ/mol)</td>
<td>140.52</td>
</tr>
<tr>
<td></td>
<td>A(s(^{-1}))</td>
<td>1.02 x 10(^{8})</td>
</tr>
</tbody>
</table>

#### 3.6.4 Poly(methylyvinylsilylene-co-styrene)

Polysilahydrocarbons described earlier give very poor ceramic residue as they are linear polymers. It is reported that the ceramic residue of such polymers can be improved by incorporating branching or crosslinking sites in the polymer chain.\textsuperscript{28,29} Schilling et al.\textsuperscript{5-7,30,31} reported that under dechlorination conditions
methylvinylidichlorosilane (MVDSC) behaves as a tetrafunctional monomer and gives a highly crosslinked polymer. In order to improve the thermal stability of polysilahydrocarbons, Ambadas et al. synthesized poly(methylvinylsilylene-co-styrene) copolymers (PMVSS) through the dechlorination of MVDSC in presence of styrene. The copolymers were synthesized using varying monomer feed ratios and they were found to be thermally more stable than PDMSS and PMPSS copolymers. Unlike PDMSS and PMPSS, PMVSS copolymers are insoluble in organic solvents.

The composition of the copolymers (Table 3.6.9) was calculated based on the pyrolysis gas chromatography data and ratio of absorbance (A) of Si-Me (of methylvinylsilylene units) and phenyl group (styryl units) and the details are given elsewhere.29

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Mole ratio of styrene to MVDSC in the monomer feed</th>
<th>Mole ratio of styryl to MVS units in the copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMVSS-I</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>PMVSS-II</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>PMVSS-III</td>
<td>1.00</td>
<td>1.10</td>
</tr>
<tr>
<td>PMVSS-IV</td>
<td>3.00</td>
<td>1.80</td>
</tr>
<tr>
<td>PMVSS-V</td>
<td>7.00</td>
<td>2.80</td>
</tr>
</tbody>
</table>

The copolymers were insoluble in organic solvents and hence, their microstructure could not be elucidated. Detailed microstructural analysis of the polysilahydrocarbons obtained by the dechlorination of DMDCS, MPDCS or a mixture of DMDCS and MPDCS in presence of styrene suggests that the polymer backbone contains alternating units of disilyl and styryl.25 The copolymers synthesized with diorganodichlorosilanes to styrene feed ratio of 2 contain alternating units of disilyl and styryl while the copolymers synthesized with the monomer feed ratios greater than 2 and less than 2 contain polysilyl and polystyryl blocks respectively in addition to the alternating units of disilyl and styryl. Thus, it
is expected that the microstructure of the copolymers synthesized from styrene and MVDCS, a diorganodichlorosilane monomer whose reactivity is expected to fall between DMDCS and MPDCS, will be similar to the ones synthesized from DMDCS and MPDCS. However, the polysilahydrocarbons synthesized from styrene and MVDCS would have a highly crosslinked structure as the vinyl group takes part in the polymerization. The participation of the vinyl group in the polymerization resulting in a crosslinked product is evident from the highly insoluble nature of the copolymers obtained. Based on the above discussion, the reaction scheme for the synthesis of poly(methylvinylsilylene-co-styrene) can be depicted as shown in Scheme 3.6.1.

![Scheme 3.6.1. Synthesis of poly(methylvinylsilylene-co-styrene)](image)

**3.6.4.1 Thermal properties**

The TG curves of PMVS (homopolymer) and the copolymers, PMVSS-I to PMVSS-V are compared in Fig. 3.6.4 and the DTG curves of PMVS, PMVSS-I and PMVSS-II are compared in Fig. 3.6.5. $T_i$, $T_{\text{max}}$, and $T_r$ and the ceramic residue
at 900°C of the copolymers and PMVS are summarized in Table 3.6.10. PMVS has the highest thermal stability which is clearly understood from \( T_i \) (435°C) and \( T_f \) (595°C).

![Fig. 3.6.4. TG curves of PMVS (homopolymer) and copolymers PMVSS-I to PMVSS-V](image1)

![Fig. 3.6.5. DTG curves of PMVS, PMVSS-I and PMVSS-II](image2)
In the case of copolymers, PMVSS-I to PMVSS-V, $T_i$, $T_{\text{max}}$ and $T_f$ are found to decrease with the increase in the concentration of styrene. The DTG curve of PMVS shows a single peak at 559°C. As PMVS (structure 2) contains only polysilyl linkages, the decomposition at 559°C is attributed to the degradation of these linkages. Linear polysilanes normally degrade at a relatively lower temperature. The higher $T_{\text{max}}$ for PMVS is due to the presence of extensive crosslinks resulting from the participation of vinyl group in the polymerization.

Table 3.6.10. Comparison of thermal properties of PMVSS (insoluble fraction) and PMVS (homopolymer) and ceramic residue obtained at 900°C

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Decomposition temp.(°C)</th>
<th>Ceramic residue at 900°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_i$</td>
<td>$T_{\text{max}}$</td>
</tr>
<tr>
<td>PMVS</td>
<td>435</td>
<td>559</td>
</tr>
<tr>
<td>PMVSS-I</td>
<td>420</td>
<td>460</td>
</tr>
<tr>
<td>PMVSS-II</td>
<td>400</td>
<td>457</td>
</tr>
<tr>
<td>PMVSS-III</td>
<td>395</td>
<td>445</td>
</tr>
<tr>
<td>PMVSS-IV</td>
<td>390</td>
<td>438</td>
</tr>
<tr>
<td>PMVSS-V</td>
<td>380</td>
<td>429</td>
</tr>
</tbody>
</table>

$T_i$-initial decomposition temperature; $T_{\text{max}}$-maximum decomposition temperature; $T_f$-final decomposition temperature

The DTG curve of PMVSS-I shows two peaks at 460°C and 545°C whereas in the case of PMVSS-II the second peak is not well resolved. The peak at 460°C for PMVSS-I and the peak at 457°C for PMVSS-II are attributed to the degradation of -Si-Si-CH$_2$CH(Ph)- repeating units (alternating units of disilyl and
Thermal degradation kinetics.....

styril) present in the copolymers. In the case of PMVSS-I, in addition to the above repeating units, polysilyl blocks are also present. By comparing the DTG curve of PMVSS-I with that of PMVS, it can be concluded that the second peak at 545°C for PMVSS-I is due to the degradation of polysilyl linkages. The higher decomposition temperature for polysilyl linkages when compared to that of Si-Si-CH$_2$-CH(Ph) linkages is understood in view of the higher extent of crosslinking present in the case of the former. It is observed that the second peak is practically absent in the DTG curves of the copolymers, PMVSS-III, PMVSS-IV and PMVSS-V. It is also noticed that $T_{\text{max}}$ gradually decreases with the increase in styrene concentration in the monomer feed suggesting that the incorporation of styril blocks in the polymer backbone decreases the overall thermal stability.

Comparison of TG curves (Fig. 3.6.4) suggests that PMVS has the highest overall thermal stability and the incorporation of styril moieties by way of copolymerization decreases the thermal stability. This is understood in view of the fact that the incorporation of styril units results in reduction of concentration of methylvinysilyl units which in turn results in reduction of crosslinking. Though it is expected that the overall thermal stability and ceramic residue should gradually decrease while going from PMVSS-I to PMVSS-V, the thermograms of PMVSS-I and PMVSS-II are significantly different from that of PMVSS-III to PMVSS-V. The marked difference in the ceramic yield at 900°C and the lower thermal stability of PMVSS-III to PMVSS-V compared to that of PMVSS-I and PMVSS-II are consistent with the gross difference in their structure with respect to the concentration of polystyryl blocks present in them, the former set of polymers having high concentration of polystyryl blocks and the latter having very little polystyryl blocks as reported elsewhere.$^{29}$

3.6.4.2 Thermal degradation kinetics

The compositional analysis by pyrolysis gas chromatography reveals that the copolymers differ in their composition.$^{29}$ PMVSS-I contains appreciable amount of polysilyl block while PMVSS-III, PMVSS-IV and PMVSS-V contain polystyryl blocks and the concentration of such blocks increases with the increase in concentration of styrene in the monomer feed. TG studies indicate that the
overall thermal stability and the ceramic residue at 900°C are influenced by the composition and structure of the copolymers. Thus, it is expected that the thermal degradation kinetics would also be influenced by such factors.

Using TG curves, the thermal degradation kinetics of the copolymers was carried out as explained in section 3.6.3.3. The order of the reaction (for the best fit) along with the correlation coefficient values for PMVSS-I to PMVSS-V and PMVS are given in the Table 3.6.11.

Table 3.6.11. Order and correlation coefficient of PMVSS copolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Reaction order (n)</th>
<th>Correlation coefficient (r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMVS</td>
<td>0.1</td>
<td>0.9908</td>
</tr>
<tr>
<td>PMVSS-I</td>
<td>1.0</td>
<td>0.9978</td>
</tr>
<tr>
<td>PMVSS-II</td>
<td>2.0</td>
<td>0.9989</td>
</tr>
<tr>
<td>PMVSS-III</td>
<td>2.0</td>
<td>0.9996</td>
</tr>
<tr>
<td>PMVSS-IV</td>
<td>2.0</td>
<td>0.9982</td>
</tr>
<tr>
<td>PMVSS-V</td>
<td>2.0</td>
<td>0.9984</td>
</tr>
</tbody>
</table>

It is found that the best-fit values for PMVS and PMVSS-I are 0.1 and 1 respectively and for all the others it is 2. Thus, it is seen that PMVS, which contains only polysilyl linkages with extensive crosslinks resulting from the participation of vinyl groups, shows close to zero order for thermal degradation. In the case of PMVSS-II to PMVSS-V, which contain alternating disilyl and styryl units in the backbone and practically no polysilyl blocks, the order is found to be 2. The presence of linear polystyryl blocks in PMVSS-III to PMVSS-V does not alter the order, whereas for PMVSS-I, where polysilyl blocks are present in addition to the basic copolymer structure, the order is 1 which is in between that of homopolymer and the copolymers. Using these n values, E and A values for the thermal degradation of all the polymers were calculated by the four different methods and the results are given in Table 3.6.12. It is observed that the E and A values increase with the increase in concentration of styryl units in the copolymer or in other words with the decrease in crosslinking density.
Table 3.6.12. Kinetic parameters for the thermal degradation of PMVS and copolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Activation energy/Pre-exponential factor</th>
<th>Kinetic Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M-T</td>
<td>H-M</td>
</tr>
<tr>
<td>PMVS</td>
<td>E(kJ/mol)</td>
<td>50.82</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹)</td>
<td>2.69</td>
</tr>
<tr>
<td>PMVSS-I</td>
<td>E(kJ/mol)</td>
<td>64.93</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹)</td>
<td>57.54</td>
</tr>
<tr>
<td>PMVSS-II</td>
<td>E(kJ/mol)</td>
<td>106.1</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹)</td>
<td>1.09 x 10⁵</td>
</tr>
<tr>
<td>PMVSS-III</td>
<td>E(kJ/mol)</td>
<td>119.3</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹)</td>
<td>1.41 x 10⁶</td>
</tr>
<tr>
<td>PMVSS-IV</td>
<td>E(kJ/mol)</td>
<td>131.1</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹)</td>
<td>1.58 x 10⁷</td>
</tr>
<tr>
<td>PMVSS-V</td>
<td>E(kJ/mol)</td>
<td>169.9</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹)</td>
<td>2.57 x 10¹⁰</td>
</tr>
</tbody>
</table>

3.6.5 Polycarbosilanes from polysilahydrocarbons

The earlier section (section 3.6.4) dealt with thermally stable polysilahydrocarbons obtained through the dechlorination of MVDSC in presence of styrene. Though these polymers gave good ceramic residue, they are insoluble due to crosslinking resulting from the participation of vinyl group during dechlorination.

Linear polysilahydrocarbons such as poly(dimethylsilylene-co-styrene) and poly(methylphenylsilylene-co-styrene) on heat treatment at temperatures above 350°C are expected to undergo thermal rearrangement resulting in the formation of thermally stable polycarbosilanes. As these polymers contain disilyl
linkages during heat treatment methylene and phenylene insertion reactions are expected to take place.

In order to minimize the carbon content, it is desirable to synthesize polysilahydrocarbons with maximum silicon content. In other words, the quantity of styrene used should be such that polysilyl linkages are present in appreciable concentration. Ambadas et al. synthesized PSH-I through the dechlorination of DMDCS in presence of styrene and PSH-II through the dechlorination of a mixture of DMDCS and MPDCS in presence of styrene. The quantities of styrene used were such that the composition of PSH-I and PSH-II (Si and C content) is close to each other and at the same time having predominantly polysilyl linkages. Ambadas et al. studied the micro structural changes that take place during heat treatment of PSH-I and PSH-II and investigated the role played by the heat treatment condition on the molecular weight and processability.

In the present thesis, thermal stability and thermal degradation kinetics of polycarbosilanes obtained from PSH-I and PSH-II at different experimental conditions are dealt with. The structure of PSH-I (Structure 3) and PSH-II (Structure 4) as elucidated by $^1$H-, $^{13}$C- and $^{29}$Si-NMR are given below:

\[
\begin{align*}
\text{Structure 3} & \\
\left[ \begin{array}{c}
\text{Me} & \text{Me} & \text{Me} \\
\text{Si} & \text{Si} & \text{CH}_2
\end{array} \right]_n & \begin{array}{c}
\text{Me} & \text{Me} \\
\text{Si} & \text{Si} & \text{Ph}
\end{array}
\end{align*}
\]

\[
\text{Structure 4} & \\
\left[ \begin{array}{c}
\text{Me} & \text{Me} & \text{Me} & \text{Me} \\
\text{Si} & \text{Si} & \text{Si} & \text{Si}
\end{array} \right]_n & \begin{array}{c}
\text{Me} & \text{Me} & \text{Me} & \text{Me} & \text{Me} & \text{Me} \\
\text{Si} & \text{Si} & \text{CH}_2 & \text{CH} & \text{Ph}
\end{array}
\]

The basic difference between the polysilahydrocarbons, (PSH-I and PSH-II) being dealt in the present chapter and the polysilahydrocarbons, PDMSS
and PMPSS described in section 3.6.3 is that the latter ones contain mainly disilyl linkages alternating with styryl units whereas PSH-I and PSH-II mainly contain polysilyl linkages.

### 3.6.5.1 Thermal properties of polycarbosilanes obtained by heat treatment of PSH-I and PSH-II

As described earlier, PSH-I was converted to polycarbosilane PCS-400, PCS-420 and PCS-460 by heat treatment at 400°C, 420°C and 460°C respectively in a partially confined environment (pressure range: 2.4-2.7 kg/cm²). It is noticed that PCS-400 and PCS-420 were soluble in organic solvents such as chloroform, toluene and xylene, and PCS-460 is insoluble in organic solvents. When PSH-I is heat treated at 400°C, the molecular weight ($M_w$) decreases from 68,000 to 10,000 and it further decreases to 5,000 when the temperature of heat treatment is raised from 400 to 420°C. The above results suggest that the increase in heat treatment temperature enhances the thermolytic cleavage of the polymer chains. The insolubility of PCS-440 and PCS-460 indicates that extensive crosslinking reactions take place when the heat treatment temperature is raised above 420°C. Even though PCS-460 has the highest thermal stability (as would be discussed in the latter part of the section) among all the polycarbosilanes obtained by heat treatment it is insoluble in organic solvents. Hence, attempts were made to synthesize a soluble polycarbosilane by heat treatment of PSH-I at 460°C without letting off the volatiles at a uniform heating rate of 4.8°C/min. As the volatiles were not let off, the heat treatment chamber pressure went up to 3.4 kg/cm². The polycarbosilane obtained by this process is designated as PCS-460C and it is soluble in organic solvents such as chloroform, toluene and xylene. It has $M_w$ of 55,000 and $M_n$ of 3100 with a polydispersity of 17.5. TG curves of PSH-I and the corresponding polycarbosilanes are compared in Fig. 3.6.6. When the heat treatment temperature is increased from 420 to 460°C it is observed that the ceramic residue and, $T_r$, $T_{\text{max}}$, and $T_f$ values increase drastically. It is worth noting that though PCS-460C has higher ceramic residue compared to PCS-460, it is soluble in common organic solvents. Confining the volatiles during the heat treatment results in increased methylene and phenylene insertion and extensive
branching as evidenced by $^{13}$C- and $^{29}$Si-NMR spectral studies. The thermal stability and char residue of the polymers follow the trend given below:

$$\text{PSH-I} < \text{PCS-400} < \text{PCS-420} < \text{PCS-460} < \text{PCS-460C}$$

Fig. 3.6.6. TG curves of PSH-I and the polycarbosilanes obtained by heat treatment

Spectral studies$^{3,25}$ reveal that the structure of polycarbosilanes obtained by heat treatment of PSH-I consists of linear, ring and branched/crosslinked structures. Different rearrangement reactions taking place during the conversion of polysilanes to polycarbosilanes by heat treatment have been dealt in detail by Hasegawa and Okamura$^{32}$ and by Yajima et al.$^{33}$ Similar rearrangement reactions are expected to take place during the heat treatment of polysilahydrocarbons.

**Methylene insertion:** Methylene insertion results from the recombination of Si-methylene and hydrogen radicals. The Si-methylene radicals are formed by the attack of hydrogen radicals on Si-methyl units as given in equations 10 and 11.

$$\text{Si} - \text{H} \xrightarrow{\Delta} \text{Si}^+ + \text{H}^+ \quad \text{Eq. (10)}$$

$$\text{Si} - \text{CH}_3 + \text{H}^+ \rightarrow \text{Si} - \text{CH}_2 + \text{H}_2 \quad \text{Eq. (11)}$$
Thermal degradation kinetics...

The Si-Me unit undergoes scission and forms a methyl radical which induces the cleavage of a CH bond of another Si-Me unit resulting in the formation of Si-CH$_2$ radicals (Eq. 12, 13).

\[
\begin{align*}
-\text{Si}-\text{CH}_3 & \xrightarrow{\Delta} -\text{Si}^* + \text{CH}_3 & \text{Eq. (12)} \\
-\text{Si}-\text{CH}_3 + \text{CH}_3 & \rightarrow -\text{Si}-\text{CH}_2 + \text{CH}_4 & \text{Eq. (13)}
\end{align*}
\]

The Si radicals (Eqs. 10 and 12) combine with Si-CH$_2$ radical (Eqs. 11 and 13) leading to the formation of -SiCH$_2$Si- units (Eq. 14).

\[
\begin{align*}
-\text{Si}^* + \cdot \text{CH}_2 - \text{Si}^- & \xrightarrow{\Delta} -\text{Si}-\text{CH}_2 - \text{Si}^- & \text{Eq. (14)}
\end{align*}
\]

Recombination of two Si-CH$_2$ radicals may also take place resulting in the formation of -SiCH$_2$CH$_2$Si- unit (Eq. 15).

\[
\begin{align*}
-\text{Si}-\text{CH}_2 + \cdot \text{CH}_2 - \text{Si}^- & \rightarrow -\text{Si}-\text{CH}_2 - \text{CH}_2 - \text{Si}^- & \text{Eq. (15)}
\end{align*}
\]

In addition to the above reactions, phenylene insertion as shown below can also take place.

\[
\begin{align*}
-\text{Si}-\text{CH}_2 - \text{CH} - \text{Si}^- & \xrightarrow{\Delta} -\text{Si}-\text{CH}_2 - \cdot \text{CH}^- - \text{Si}^- + \cdot \text{O} & \text{Eq. (16)} \\
-\text{Si}^* + \cdot \text{O} & \rightarrow -\text{Si} - \text{O} & \text{Eq. (17)}
\end{align*}
\]

\[
\begin{align*}
-\text{Si}^* + \cdot \text{Si}^- & \rightarrow -\text{Si} - \text{Si}^- + \text{H}^* & \text{Eq. (18)}
\end{align*}
\]

Studies on the effect of heat treatment temperature, pressure and composition on the conversion of PSH-I to polycarbosilane suggest that the nature of the polycarbosilane and the ceramic residue obtained can be controlled by
proper choice of heat treatment conditions. Higher heat treatment temperature increases the ceramic yield of polycarbosilane formed. But, the improvement is usually at the cost of processability. It is felt that a combination of suitable pressure, heat treatment temperature and heating rate profile may give a processable polycarbosilane capable of giving higher ceramic yield.

In the preparation of PCS-460C volatiles were not let off and the pressure in the chamber was 3.4 kg/cm$^2$. PCS-460C shows a broad bimodal molecular weight distribution. Due to the above experimental conditions, inspite of the rearrangement reactions leading to methylene (Eq. 14 and 15) and phenylene (Eq. 16-18) insertion, branching resulting from dehydrogenative coupling (Eq. 19 - 21)$^{33}$ may take place to a greater extent in PCS-460C resulting in the increase in molecular weight.

\[
\begin{align*}
\text{CH}_2 & \quad \text{Si-CH}_3 + \text{H-Si-CH}_3 \rightarrow \text{H-Si-CH}_2\text{Si-CH}_3 \\
\text{CH}_2 & \quad \text{Si-CH}_3 + \text{H-Si-CH}_3 \rightarrow \text{H-Si-CH}_2\text{Si-CH}_3 \\
\text{H} & \quad \text{Si-CH}_3 + \text{H-Si-CH}_3 \rightarrow \text{H-Si-CH}_2\text{Si-CH}_3
\end{align*}
\]

Eq. (19)

\[
\begin{align*}
\text{CH}_2 & \quad \text{Si-CH}_3 + \text{H-Si-CH}_3 \rightarrow \text{H-Si-CH}_2\text{Si-CH}_3 \\
\text{CH}_2 & \quad \text{Si-CH}_3 + \text{H-Si-CH}_3 \rightarrow \text{H-Si-CH}_2\text{Si-CH}_3 \\
\text{H} & \quad \text{Si-CH}_3 + \text{H-Si-CH}_3 \rightarrow \text{H-Si-CH}_2\text{Si-CH}_3
\end{align*}
\]

Eq. (20)

or

\[
\begin{align*}
\text{CH}_2 & \quad \text{Si-CH}_3 + \text{H-C} \rightarrow \text{CH}_3\text{Si} \quad \text{H} \\
\text{CH}_3 & \quad \text{Si} \quad \text{H-C} \rightarrow \text{CH}_3\text{Si} \quad \text{H} \\
\text{H} & \quad \text{Si-CH}_2\text{Si-CH}_3
\end{align*}
\]

Eq. (21)
PSH-II was converted to polycarbosilane TPPCS-400 and TPPCS-420 by heat treatment at 400 and 420°C in a partially confined environment (at a pressure of 2.4 kg/cm²). The polycarbosilanes, TPPCS-400 and TPPCS-420 are found to be soluble in organic solvents. Detailed characterization of TPPCS-400 and TPPCS-420 are described elsewhere.³

The TG curves of PSH-II, TPPCS-400 and TPPCS-420 are compared in Fig. 3.6.7. The TGA studies reveal that the overall thermal stability and char residue of the polymers follow the trend, PSH-II<TPPCS-400<TPPCS-420. ¹³C-NMR studies suggest that with the increase in heat treatment temperature from 400°C to 420°C, the extent of methylene and phenylene insertion increases, which in turn contributes towards the increase in thermal stability and char residue.²⁵

![Fig. 3.6.7. TG curves of PSH-II and the polycarbosilanes obtained by heat treatment](image)

The thermal properties of PSH-I, PSH-II and the heat-treated polymers are compared in Table 3.6.13. It is noticed that TPPCS-400 and TPPCS-420 have much higher thermal stability compared to the corresponding...
polycarbosilanes (PCS-400 and PCS-420) obtained from PSH-I. In PSH-II system, in addition to styryl units flanked by silyl units, silyl units with pendant phenyl groups are present. Thus, in the case of PSH-II, phenylene insertion can occur due to the insertion of phenyl group of styryl units (as shown in Eq. 16-18) and also from Si-Ph units as shown below:

Eq. (22)

Hence, it is expected that the extent of phenylene insertion would be more in the case of PSH-II than in PSH-I. $^{13}$C-NMR spectral studies of polycarbosilane derived from PSH-I and PSH-II support this conclusion. $^{3,25}$ Higher extent of phenylene insertion taking place in the case of PSH-II-based polycarbosilanes is responsible for their higher thermal stability and ceramic residue compared to that of PSH-I-based polycarbosilanes.

Table 3.6.13. Comparison of thermal properties of PSH-I and PSH-II and the polycarbosilanes derived from them

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Decomposition temperature ($^{\circ}$C)</th>
<th>Ceramic residue at 900$^{\circ}$C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_i$</td>
<td>$T_{max}$</td>
</tr>
<tr>
<td>PSH-I</td>
<td>400</td>
<td>433</td>
</tr>
<tr>
<td>PCS-400</td>
<td>400</td>
<td>448</td>
</tr>
<tr>
<td>PCS-420</td>
<td>405</td>
<td>454</td>
</tr>
<tr>
<td>PCS-460</td>
<td>450</td>
<td>518</td>
</tr>
<tr>
<td>PCS-460C</td>
<td>470</td>
<td>521</td>
</tr>
<tr>
<td>PSH-II</td>
<td>400</td>
<td>425</td>
</tr>
<tr>
<td>TPPCS-400</td>
<td>390</td>
<td>430</td>
</tr>
<tr>
<td>TPPCS-420</td>
<td>405</td>
<td>583</td>
</tr>
</tbody>
</table>
3.6.5.2 Thermal degradation kinetics

The kinetics of thermal degradation of PSH-I and PSH-II and the polycarbosilanes derived from them was carried out using the TG curves, by four methods as explained in the section 3.6.4.2 The order of the reaction along with the correlation coefficient values for these systems are given in the Table 3.6.14.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Reaction order (n)</th>
<th>Correlation coefficient (r)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSH-I</td>
<td>1.3</td>
<td>0.9964</td>
</tr>
<tr>
<td>PCS-400</td>
<td>1.4</td>
<td>0.9950</td>
</tr>
<tr>
<td>PCS-420</td>
<td>1.5</td>
<td>0.9988</td>
</tr>
<tr>
<td>PCS-460</td>
<td>1.6</td>
<td>0.9993</td>
</tr>
<tr>
<td>PCS-460C</td>
<td>2.0</td>
<td>0.9999</td>
</tr>
<tr>
<td>PSH-II</td>
<td>0.5</td>
<td>0.9988</td>
</tr>
<tr>
<td>TPPCS-400</td>
<td>1.0</td>
<td>0.9959</td>
</tr>
<tr>
<td>TPPCS-420</td>
<td>1.0</td>
<td>0.9885</td>
</tr>
</tbody>
</table>

As discussed earlier, the structure of PSH-II is similar to that of PSH-I except for the presence of methylphenylsilyl units to the extent of 0.6 mole%. Though both of them contain predominantly polysilyl linkages, the order of the reaction is not the same. This is also true for the heat-treated polymers obtained from them.

The E and A values for PSH-I and PSH-II-based systems (Table 3.6.15 and Table 3.6.16) were calculated using the n values given in Table 3.6.14. It is observed that for PSH-II, E and A follow the trend PSH-II > TPPCS-400 > TPPCS-420. Similar trend is observed for PSH-I for heat treatment up to 420°C. However, increase in both E and A values are observed for PCS-460 and PCS-460C. The reason for this observation is not clearly understood.
### Table 3.6.15. Kinetic parameters obtained from various kinetic analysis for PSH-I system

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Activation energy/Pre-exponential factor</th>
<th>Kinetic equations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>M-T</td>
</tr>
<tr>
<td>PSH-I</td>
<td>E(kJ/mol)</td>
<td>193.06</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹)</td>
<td>1.4 x 10¹²</td>
</tr>
<tr>
<td>PCS-400</td>
<td>E(kJ/mol)</td>
<td>144.57</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹)</td>
<td>1.4 x 10⁸</td>
</tr>
<tr>
<td>PCS-420</td>
<td>E(kJ/mol)</td>
<td>128.57</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹)</td>
<td>6.7 x 10⁶</td>
</tr>
<tr>
<td>PCS-460</td>
<td>E(kJ/mol)</td>
<td>147.46</td>
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<tr>
<td></td>
<td>A(s⁻¹)</td>
<td>3.0 x 10⁷</td>
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<tr>
<td>PCS-460C</td>
<td>E(kJ/mol)</td>
<td>200.91</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹)</td>
<td>1.3 x 10¹¹</td>
</tr>
</tbody>
</table>

### Table 3.6.16. Kinetic parameters obtained from various kinetic analysis for PSH-II system

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Activation energy/Pre-exponential factor</th>
<th>Kinetic equations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>M-T</td>
</tr>
<tr>
<td>PSH-II</td>
<td>E(kJ/mol)</td>
<td>159.8</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹)</td>
<td>4.5 x 10⁹</td>
</tr>
<tr>
<td>TPPCS-400</td>
<td>E(kJ/mol)</td>
<td>69.5</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹)</td>
<td>4.4 x 10⁶</td>
</tr>
<tr>
<td>TPPCS-420</td>
<td>E(kJ/mol)</td>
<td>46.8</td>
</tr>
<tr>
<td></td>
<td>A(s⁻¹)</td>
<td>2.2</td>
</tr>
</tbody>
</table>
In general it is noticed that the E and A values are lower for PSH-II-based systems compared to PSH-I-based systems. In the case of PSH-II the extent of phenylene insertion reaction is more as evidenced by spectral studies.\(^3\) With increase in phenylene insertion the extent of volatilization comes down as indicated by high char residue for PSH-II-based systems. This may be the reason for the lower E and A values for PSH-II-based systems.

### 3.6.6 Conclusions

The thermal degradation kinetics of polysilahydrocarbons and polycarbosilanes derived from certain selected polysilahydrocarbons was studied and attempts have been made to correlate the reaction order (n), activation energy (E) and pre-exponential factor (A) with the structure of the polymers. Based on this study the following conclusions have been drawn:

i) The thermal degradation kinetic study of the polysilahydrocarbons containing dimethylsilyl and methylphenylsilyl groups in the polymer backbone suggests that the order for thermal degradation is influenced by increase in styrene concentration and for a given styrene concentration, the values are higher for phenyl-substituted polymers than for methyl ones.

ii) In the case of PDMSS and PMPSS copolymers, the E and A values decrease with the increase in the concentration of styryl units.

iii) Unlike in the case of PDMSS and PMPSS copolymers, for the polysilahydrocarbons synthesized from MVDCS and styrene (PMVSS) the E and A values increase with increase in the concentration of styryl units in the copolymer. PMVSS is a crosslinked system whereas PDMSS and PMPSS are linear polysilahydrocarbons and probably this difference is responsible for the above observation.

iv) Linear polysilahydrocarbons, PSH-I and PSH-II on heat treatment (400°C and above) in a partially confined environment results in the formation of thermally stable polycarbosilanes.

v) Studies on the effect of heat treatment temperature, pressure and composition on the conversion of PSH-I to polycarbosilane suggest that the nature of polycarbosilane and the ceramic residue obtained depend
on the heat treatment conditions. With the increase in heat treatment temperature the extent of methylene and phenylene insertion reaction increases which in turn contributes towards the increase in thermal stability and char residue.

vi) Under identical heat treatment conditions, the polycarposilanes obtained from PSH-II have higher thermal stability and give higher ceramic residue compared to that of polycarposilanes obtained from PSH-I. The presence of methylphenylsilylene units in PSH-II increases the extent of phenylene insertion reaction and this is responsible for the higher thermal stability and ceramic residue of polycarposilanes derived from PSH-II.

vii) The E and A values of polycarposilanes are found to be less than that of polysilahydrocarbons from which they are derived. These values are lower for PSH-II-based systems compared to that of PSH-I-based ones. PSH-II-based systems contain more of phenylene moieties which probably reduce the extent of degradation and this may be the reason for the observed trend.

References


<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Mole ratio of styrene to DMDCS in the monomer feed</th>
<th>Mole ratio of styryl to DMS units in the copolymer</th>
<th>a**</th>
<th>b**</th>
<th>High molecular weight fraction</th>
<th>Low molecular weight fraction</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a*</td>
<td>b**</td>
<td>$M_w \times 10^5$</td>
<td>$M_n \times 10^4$</td>
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<td>PDMSS-I</td>
<td>0.5</td>
<td>0.5</td>
<td>0.1</td>
<td>0.09</td>
<td>1.31</td>
<td>6.86</td>
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<td>0</td>
<td>0.4</td>
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<td>PDMSS-III</td>
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<td>0</td>
<td>1.3</td>
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<td>6.87</td>
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</table>

a** The ratio of silyl units present as polysilyl blocks to silyl units present as disilyl linkages

b** The ratio of $\text{(styryl)}_n$ to Si-styryl units determined from $^{13}$C-NMR spectra
Table 3.6.2. Composition and GPC data of the PMPSS copolymers

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Mole ratio of styrene to MPDCS in the monomer feed</th>
<th>Mole ratio of styryl to MPS units in the copolymer</th>
<th>a*</th>
<th>b**</th>
<th>High molecular weight fraction</th>
<th>Low molecular weight fraction</th>
<th>Wt. %</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\bar{M}_w \times 10^5)</td>
<td>(\bar{M}_n \times 10^5)</td>
<td>(\bar{M}_w / \bar{M}_n)</td>
</tr>
<tr>
<td>PMPSS-I</td>
<td>0.33</td>
<td>0.37</td>
<td>0.32</td>
<td>0.09</td>
<td>1.40</td>
<td>1.12</td>
<td>1.24</td>
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<tr>
<td>PMPSS-II</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0.18</td>
<td>1.26</td>
<td>1.01</td>
<td>1.25</td>
</tr>
<tr>
<td>PMPSS-III</td>
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<td>0.74</td>
<td>0</td>
<td>0.46</td>
<td>1.38</td>
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<tr>
<td>PMPSS-IV</td>
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<td>1.74</td>
<td>1.49</td>
<td>1.16</td>
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</table>

*a* The ratio of silyl units present as polysilyl blocks to silyl units present as disilyl linkages

*b** The ratio of (styryl)_n to Si-styryl units determined from \(^{13}\)C-NMR spectra
Chapter 3.7

Polysilahydrocarbons as atomic oxygen resistant coatings

This chapter deals with polysilahydrocarbons, namely, poly(tetramethyldisilylene-co-styrene), poly(methylphenylsilylene-co-styrene) and poly(dimethylsilylene-co-methylphenylsilylene-co-styrene) as atomic oxygen (AO) resistant coatings for substrates such as polyimide film, C-polyimide composite and glass polyimide composite which are susceptible to AO attack. The AO resistance of the above polymers has been compared with siloxane-imide-epoxy resins and phosphazene-based polymers.

*The results presented in this chapter form the basis for the following patent applications, publications in International journals and presented in National and International Symposia:

3.7.1 Background

The spacecraft materials in the Low Earth Orbit (LEO) are vulnerable to atomic oxygen (AO) attack. The combined effects of thermal cycling, far UV radiation, high vacuum, micrometeoroid and debris impact, charged particle bombardment, spacecraft charging and AO are a severe threat to the space station in LEO. Among these, AO formed in the upper atmosphere by the photodissociation of molecular oxygen, is the most severe threat. The presence of various atmospheric gases in different altitudes is shown in Fig. 3.7.1. The high orbital velocity of 8 km/s accelerates degradation by increasing the energy of AO impact with the spacecraft surface. At orbital altitudes, the neutral atmosphere consists primarily of 80% AO and 20% molecular nitrogen. Since AO is formed by photodissociation, its concentration depends strongly on solar activity and position. The AO number density varies from $10^9$ to $10^8$ atoms/cm$^3$ over an altitude range of 300-500 km during conditions of high solar activity. As space stations and LEO satellites/spacecrafts operate in this altitude range advanced composites and engineering thermoplastic materials used in their construction are susceptible to surface recession due to interaction with AO. Thus, there is an urgent need of a protective coating which would limit the interaction between AO and the surface of the materials.

There are several approaches to protective coatings for AO. Metal oxide coatings have negligible erosion rates since they are completely oxidized already. The coatings, however, lack flexibility, require elaborate sputtering techniques for application on complex shapes and are susceptible to pin hole defects caused by shadowing of dust particles. They also crack easily on thermal cycling since the substrates, usually polymers, have much higher thermal expansion coefficients.

Inorganic and organometallic polymers are capable of overcoming these problems. These polymers on exposure to AO will form a thin oxide layer, preventing further reaction of the coating with AO. Even if, AO penetrates into the next layer due to surface defects, the unoxidized virgin polymer underneath the oxide layer would provide self-healing. The thermal expansion coefficients of the
virgin polymer and the polymeric substrate are usually close to each other which implies that the crack formation on the surface of the coating would be prevented.  

Inorganic and organometallic polymers such as polysilanes, polyimides, polysiloxanes, siloxane-epoxies, siloxane-imides, poly(carborane-siloxane) decaborane-based polymers and phosphorus-containing polyarylene ethers have been evaluated as AO resistant coatings. These polymers on reaction with AO form a protective oxide layer on the surface of the coating, which prevents further reaction of the coating with AO.

Polydisilahydrocarbons, containing alternating units of disilyl and styryl units, are of particular interest as they exhibit good film forming characteristics. The disilyl linkages present in polydisilahydrocarbons can trap AO resulting in the formation of siloxane linkage which on further interaction with AO would result in the formation of silica layer on the surface, preventing further oxidation of the coating. The present chapter deals with the evaluation of the following polysilahydrocarbons containing disilyl linkages as AO resistant coatings for polyimide film, C-polyimide and glass-polyimide composites: (i) poly(tetramethyl-disilylene-co-styrene) (ii) poly(methylphenylsilylene-co-styrene) and (iii) poly(di-
methylsilylene-co-methylphenylsilylene-co-styrene). The AO resistance of these polymers has been compared with siloxane-imide-epoxy resin and phosphazene-based polymers.

3.7.2 Poly(tetramethyldisilylene-co-styrene) (PTMDSS) as AO resistant coating

3.7.2.1 Synthesis of PTMDSS

PTMDSS was synthesized by reacting DMDCS and styrene in 2:1 mole ratio under dechlorination condition using sodium in refluxing toluene following the procedure of Packirisamy et al.\textsuperscript{28} It was characterized by GPC, \textsuperscript{1}H-, \textsuperscript{13}C- and \textsuperscript{29}Si-NMR spectra. The GPC curve of the copolymer shows a bimodal molecular weight distribution which is common with most of the polysilanes prepared by Wurtz-type polymerization.\textsuperscript{29} The copolymer contains about 20 wt\% of low molecular weight fraction. The high molecular weight fraction has $\bar{M}_w$ of 1,25,900 and $\bar{M}_n$ of 1,00,700 and the low molecular weight fraction has $\bar{M}_w$ of 6,350 and $\bar{M}_n$ of 3,300.

The composition of the copolymer, as evaluated from \textsuperscript{1}H-NMR spectrum on the basis of the relative intensities of the aromatic and aliphatic resonances is 0.5. The \textsuperscript{29}Si-NMR spectrum of the copolymer (Fig. 3.7.2) obtained shows signals at -11.42, -15.43 and -15.77 ppm.

![Fig. 3.7.2. \textsuperscript{29}Si-NMR spectrum of PTMDSS](image-url)
Available literature data suggest that substituents on β-carbon affect the chemical shift of silicon only marginally.\textsuperscript{30} Thus, two distinguishable Si atoms are present in the copolymers viz., -Si-Si-CH(Ph)CH\textsubscript{2} and -Si-Si-CH\textsubscript{2}CH(Ph)-. Based on the observed de-shielding of phenyl substituent on α-carbon,\textsuperscript{30} the resonance at -11.42 ppm was assigned to -Si-Si-CH(Ph)- and the resonances at -15.43 and -15.77 ppm were assigned to -Si-Si-CH\textsubscript{2}- moiety. The multiplicity of signals in the up-field arises from the two possible stereochemical arrangements. A detailed microstructural analysis of poly(tetramethyldisilylene-co-styrene) is discussed elsewhere.\textsuperscript{28, 29} Si-NMR spectral studies unambiguously suggest that disilyl linkages alternate with styryl units.

In the $^{13}$C-NMR spectrum (Fig. 3.7.3) of the copolymer, methyl carbons show a large number of resonances in the region -2 to -6 ppm and this can be attributed to the presence of different neighbouring groups (CH and CH\textsubscript{2}) as well as to the sensitivity of stereochemical environment.

![Fig. 3.7.3. $^{13}$C-NMR spectrum of PTMDSS](image)

Based on off-resonance decoupling experiments, the resonances at 15.18 and 30.4 ppm are assigned to methylene (SiCH\textsubscript{2}) and methyne (SiCH) carbons respectively. The distinct feature of the spectrum in the aromatic region is the absence of a signal at 125.6 ppm corresponding to C\textsubscript{4} carbon of styryl units of polystyrene and the presence of a signal at 124.4 ppm which is assigned to C\textsubscript{4} carbon of styryl units flanked by disilyl moieties. Thus, $^{13}$C-NMR rules out the presence of polystyryl blocks and supports the presence of alternating units of disilyl and styryl linkages in the copolymer.
The structure of the copolymer as elucidated by $^1$H-, $^{13}$C- and $^{29}$Si- NMR spectral studies is shown in structure 1.

\[
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\text{Si} - \text{Si} - \text{CH} - \text{CH}_2 \\
\text{CH}_3 \quad \text{CH}_3 \quad \text{Ph} \\
\end{array}
\]

Structure 1

### 3.7.2.2 AO exposure studies

PTMDSS coated quartz plate, aluminized Kapton® film (125 µm) (coating applied on the unaluminized side), glass-polyimide and C-polyimide composites were exposed to AO in a plasma barrel system along with the corresponding uncoated samples and Kapton® film (125 µm). As explained in the experimental section, the uncoated Kapton® film was used as the standard for calculating the AO fluence.

**PTMDSS-coated quartz plate:** Before using any polymer as AO resistant coating it is essential to find out whether this polymer is resistant to AO. For this purpose the polymer was coated on quartz plate and exposed to AO. As quartz is resistant to AO attack, mass loss if any would be due to degradation of the polymer. A typical graph showing the mass loss vs fluence of Kapton® film and PTMDSS-coated quartz plate is shown in Fig. 3.7.4.

It is observed that the uncoated Kapton® film loses 6.37 mg/cm$^2$ on exposure to AO fluence of $2.1 \times 10^{21}$ atoms/cm$^2$ whereas PTMDSS coating on quartz loses only 0.03 mg/cm$^2$. PTMDSS contains disilyl linkages and on exposure to AO, it is expected that insertion of oxygen to disilyl linkages would take place resulting in the conversion of disilyl linkage to siloxane linkage. On further exposure to AO, the coating would undergo oxidation resulting in the formation of silica layer. The silica layer formed on the surface of the coating would prevent further attack of the coating by AO and thus protect the substrate from AO attack. From this graph it is clear that PTMDSS has excellent résistance to AO. Hence,
it can be used as AO resistant coating for substrates which are susceptible to AO attack.

![Graph showing Mass loss vs. fluence of Kapton® film and PTMDSS coated quartz](image)

**Fig. 3.7.4.** Mass loss vs. fluence of (■) Kapton® film and (●)PTMDSS coated quartz

**PTMDSS-coated aluminized Kapton®**: High performance polymeric films are being extensively used in aerospace systems for various applications. Kapton®, an organic polyimide film, is being used as a flexible substrate for light weight, high power solar arrays because of its inherent strength, thermal stability, excellent insulation properties, UV stability, IR transparency, radiation resistance and good space heritage. Aluminized Kapton® is used as an external thermal control material on almost every satellite. In this configuration aluminum in the back surface acts as a reflector and Kapton® is used to limit the emittance of light. Although the Kapton® film performs fairly well under extreme conditions, its long-term stability in LEO environment is a major concern. Hence, it is preferable to protect the Kapton® film from AO attack in LEO. As aluminum is resistant to AO attack, the unaluminized side of the films would be susceptible to AO attack and hence, this side of the aluminized Kapton® film was coated with PTMDSS.
Fig. 3.7.5 presents the mass loss vs. fluence for uncoated and coated aluminized Kapton®. It is observed that PTMDSS coated aluminized Kapton® loses 0.14 mg/cm² when exposed to an AO fluence of $2.1 \times 10^{21}$ atoms/cm² whereas the uncoated aluminized Kapton® loses 6.35 mg/cm² when the sample was exposed to AO fluence of $1.6 \times 10^{21}$ atoms/cm². This suggests that PTMDSS offers good protection to Kapton® against AO attack. Scanning electron micrographs of the uncoated and coated samples exposed to AO are given in Fig. 3.7.6. It is observed that the uncoated sample is completely damaged due to erosion by AO whereas in the coated sample no such damage is observed.

Fig. 3.7.5. Mass loss vs. AO fluence of (■) Kapton® film and (●) PTMDSS-coated Kapton® film

Fig. 3.7.6. SEM of (a) uncoated aluminized Kapton® film and (b) PTMDSS-coated aluminized Kapton® film exposed to AO
PTMDSS-coated C-polyimide and glass-polyimide composites:
Advanced composites are extensively used for spacecraft structural, power and thermal subsystem applications. Of the various composite materials, polymer matrix composites are preferred for spacecraft applications because of their combination of lightweight, dimensional stability, high structural rigidity and low thermal expansion. In the fabrication of polymer matrix composites, a variety of epoxies, polyimides, polysulfones and phenolics are used as matrix resins and glass, aramid, graphite/carbon and boron fibers are used as reinforcements. Typical applications of polymer composites for spacecraft structures include primary truss assemblies, core structures, boom, sandwich panels, bulkheads and stiffeners. Advanced composites, due to their dimensional stability, are used as payloads in spacecrafts which include communication antenna reflectors, radio frequency components, optical telescope components, space-based radar and precision mounting pay load platforms and support structures. Nowadays, rigid structural support for photovoltaic solar arrays and solar dynamic power system concentrators also utilize composites.

The high energy AO interacts with both matrix resin and reinforcements resulting in the formation of volatile oxides on the surface, that leads to surface erosion. These effects are mainly responsible for reduction of mechanical strength and changes in surface morphology and optical and thermal properties. In the present work, for the AO exposure studies, C-polyimide and glass-polyimide composites have been chosen.

Fig. 3.7.7 presents the mass loss vs fluence of uncoated and PTMDSS-coated C-polyimide composite. It is interesting to note that the uncoated composite undergoes mass loss of 63.64 mg/cm² on exposure to an AO fluence of $1.8 \times 10^{21}$ atoms/cm² and the composite was to be removed from the plasma chamber as it got completely damaged. On the other hand, PTMDSS-coated composite loses only 0.21 mg/cm² even after exposure to an AO fluence of $2.1 \times 10^{21}$ atoms/cm².

The scanning electron micrographs of uncoated and coated C-polyimide composites exposed to AO are given in Fig. 3.7.8. It is observed that in the case
of the uncoated sample, the matrix resin is eaten away and the C-fabric is badly damaged. In contrast to the above observation, for the coated sample no such damage is observed. The mass loss data and SEM studies suggest that PTMDSS coating offers excellent protection to C-polyimide composite against AO attack. SEM studies reveal the presence of cracks in certain areas of the coating on C-polyimide composite through which AO could get access to the substrate causing erosion (Fig. 3.7.9).

![Graph showing mass loss vs. AO fluence](image)

Fig. 3.7.7. Mass loss vs. AO fluence of (■) uncoated and (●) PTMDSS-coated C-PI composite

![SEM images](image)

Fig. 3.7.8. SEM of (a) uncoated C-polyimide composite (b) PTMDSS-coated C-polyimide composite exposed to AO
Fig. 3.7.9. SEM of a defect site of PTMDSS-coated C-polyimide composite exposed to AO.

Fig. 3.7.10 presents the mass loss vs. fluence of uncoated and PTMDSS-coated glass-polyimide composite. The uncoated composite undergoes mass loss of 14.89 mg/cm$^2$ on exposure to an AO fluence of $1.4 \times 10^{21}$ atoms/cm$^2$ and the composite has to be removed from the plasma chamber as it got completely damaged. On the other hand, PTMDSS-coated composite loses only 0.17 mg/cm$^2$ even after exposure to an AO fluence of $2.1 \times 10^{21}$ atoms/cm$^2$.

Fig. 3.7.10. Mass loss vs. AO fluence of (■) uncoated and (●) PTMDSS-coated GI-PI composite.

* Sample was removed as it was badly damaged.
The scanning electron micrographs of uncoated and PTMDSS-coated glass-polyimide composite exposed to AO are given in Fig. 3.7.11. It is clearly seen that in the former case the matrix resin is completely eaten away by AO resulting in the pull-out of loose fibers while in the latter case no visible damage is observed. When compared to carbon fiber, glass fiber is not susceptible to AO attack. Thus, the mass loss observed in the case of C-polyimide is due to the degradation of both the matrix and the fiber, whereas for glass-polyimide composite the mass loss is mainly due to the degradation of matrix resin.

3.7.3 Poly(methylphenylsilylene-co-styrene) (PMPSS) as AO resistant coating

3.7.3.1 Synthesis of PMPSS

PTMDSS has offered excellent protection against AO attack to substrates such as aluminized polyimide film, C-polyimide composite and glass-polyimide composite. However, the coating is somewhat tacky and for practical applications it is desirable that the coating is free from this problem. In an attempt to overcome this problem, a polysilahydrocarbon viz., poly(methylphenylsilylene-co-styrene) containing disilyl linkages was synthesized by reacting MPDCS and styrene in 1:0.5 mole ratio under dechlorination condition using sodium in refluxing toluene following the procedure of Ambadas. The copolymer was obtained as a white powder and is soluble in organic solvents such as toluene, xylene, chloroform, benzene, THF and dioxane. GPC curve of the copolymer shows a bimodal
molecular weight distribution. The copolymer contains about 20 wt% of low molecular weight fraction. The high molecular weight fraction has $\bar{M}_w$ of 238020 and $\bar{M}_n$ of 41710 and the low molecular weight fraction has $\bar{M}_w$ of 1610 and $\bar{M}_n$ of 480.

The $^1$H-NMR spectrum of the copolymer shows resonance peaks in the region -0.6 to 1.1 ppm and these peaks are assigned to the methyl protons attached to silicon. The methylene and methyne protons of styryl units present in the copolymers are observed at 1.2 and 2.1 ppm respectively. A broad aromatic peak observed in the region 7.2 to 8.2 ppm is attributed to the phenyl groups of methylphenylsilylene and styryl units. Due to the presence of large number of protons and due to their spatial arrangements, the proton NMR shows splitting with large number of peaks. Chemical shifts observed for PMPSS at -14.84 and -16.15 ppm in the $^{29}$Si-NMR spectrum (Fig. 3.7.12) are assigned to silicon attached to -CH(Ph)- group and the peaks centered around -18.52 ppm are assigned to silicon attached to -CH$_2$- group of styrene. Thus, the $^{29}$Si-NMR spectral studies confirm the presence of disilyl linkages separated by styryl units. The absence of signal around -40 ppm rules out the presence of polysilyl linkages.

Fig. 3.7.12. $^{29}$Si-NMR spectrum of PMPSS
In the $^{13}$C-NMR spectrum of PMPSS, methyl carbons show a large
number of resonances in the region -2 to -6 ppm and this can be attributed to the
presence of different neighbouring groups (CH and CH$_2$) as well as to the
sensitivity of stereochemical environment. The resonances at 15.18 and 30.4 ppm
are assigned to methylene (SiCH$_2$) and methyne (SiCH) carbons respectively. The
aromatic peaks are observed in the region 124 to 145 ppm. A detailed account of
the microstructural analysis of PMPSS is discussed elsewhere.$^{33}$

Based on $^1$H, $^{13}$C- and $^{29}$Si-NMR spectral studies, the structure given below
(Structure 2) is proposed for PMPSS.

\[
\text{Structure 2}
\]

3.7.3.2 AO exposure studies

PMPSS-coated quartz plate, aluminized Kapton® film (coating applied on
the unaluminized side), glass-polyimide and C-polyimide composite were exposed
to AO in a plasma barrel system along with the corresponding uncoated samples
and uncoated Kapton® film.

**PMPSS-coated quartz plate:** The polymer was coated on quartz plate
and exposed to AO. It is observed that the uncoated Kapton® film loses
4.0 mg/cm$^2$ whereas PMPSS coating on quartz loses only 0.15 mg/cm$^2$ on
exposure to AO fluence of 1.3 x$^{21}$ atoms/cm$^2$. A graph depicting the mass loss
vs. fluence of Kapton® film and PMPSS-coated quartz plate is shown in
Fig. 3.7.13. Though PMPSS film was tack free, visual observation of the coating
after exposure to AO indicated that it had a tendency to flake off from the
substrate. Thus, the performance of PMPSS differs from that of PTMDSS. In
PMPSS, phenyl group is present in appreciable concentration and it would
undergo oxidation on reaction with AO, resulting in the formation of CO, CO$_2$ and
H$_2$O.$^{34-36}$ Such oxidation reaction probably causes blisters and cracks resulting
from the shrinkage of the coating.
PMPSS-coated aluminized Kapton®: It is observed that the coated aluminized Kapton® loses 0.55 mg/cm² whereas the uncoated aluminized Kapton® loses 4 mg/cm² when they were exposed to AO fluence of $1.3 \times 10^{21}$ atoms/cm². The exposure to AO was not continued further as the visual observation of the coating indicated the formation of cracks and blisters. SEM of PMPSS-coated sample on exposure to AO is given in Fig. 3.7.14. It is observed that the coating has developed cracks on exposure to AO. Some portion of the coating has flaked off from the substrate and in some locations blisters are also seen. SEM studies suggest that PMPSS based coating has a tendency to embrittle on exposure to AO.

PMPSS-coated C-polyimide and glass-polyimide composites: The uncoated and PMPSS-coated C-polyimide composites undergo mass loss of 25 mg/cm² and 1.16 mg/cm² respectively on exposure to an AO fluence of $1.3 \times 10^{21}$ atoms/cm². SEM of PMPSS-coated C-polyimide composite (Fig. 3.7.15) exposed to AO reveals the presence of cracks and blisters throughout the coating and through these locations AO gets entry to the substrate causing erosion.
In the case of glass-polyimide composite, the uncoated composite undergoes mass loss of 12.66 mg/cm$^2$ whereas PMPSS-coated composite loses 1.90 mg/cm$^2$ on exposure to AO fluence of $1.3 \times 10^{21}$ atoms/cm$^2$. The scanning electron micrographs of PMPSS-coated glass-polyimide composite exposed to AO are given in Fig. 3.7.16. In addition to the formation of cracks and blisters, in some locations the coating has flaked off from the substrate thereby rendering the substrate vulnerable to AO attack.

**3.7.4 Poly(dimethylsilylene-co-methylphenylsilylene-co-styrene) (PSH-TER) as AO resistant coating**

**3.7.4.1 Synthesis of PSH-TER**

The evaluation of PTMDSS and PMPSS as AO resistant coatings suggest that the performance of PTMDSS is better than that of PMPSS. However, its tacky
nature makes it susceptible to dust accumulation. In order to overcome this problem, PTMDSS was modified by incorporating methylphenylsilylene units. This was achieved by carrying out terpolymerization of DMDCS, MPDCS and styrene using the monomer feed ratio 1:0.1:0.55 following the procedure of Ambadas. The concentration of MPDCS is chosen in such a way that the tackiness of the film is eliminated without deteriorating the AO resistance of the coating. This terpolymer (PSH-TER) is soluble in organic solvents such as toluene, xylene, chloroform and partially soluble in THF. It was characterized by GPC, $^1$H-, $^{13}$C- and $^{29}$Si-NMR spectra. PSH-TER shows bimodal molecular weight distribution. The high molecular weight fraction has $M_w$ of 209850 and $M_n$ of 78540 and the low molecular weight fraction has $M_w$ of 6710 and $M_n$ of 2250.

The $^1$H-NMR spectrum of the terpolymer shows resonance peaks in the region -0.6 to 1.1 ppm and these peaks are assigned to the methyl protons attached to silicon. The methylene and methyne protons of styryl units present in the copolymers are observed at 1.2 and 2.1 ppm respectively. A broad aromatic peak observed in the region 7.2 to 8.2 ppm is attributed to the phenyl groups of methylphenylsilylene and styryl units.

The $^{29}$Si-NMR shows sharp characteristic resonance peaks at -11.58, -15.55 and -15.81 ppm. In addition to these peaks, another peak is observed at -18.6 ppm which is absent in the $^{29}$Si-NMR spectrum of PTMDSS but present in the $^{29}$Si-NMR spectrum of PMPSS. By comparing the chemical shifts of PSH-TER with that of PTMDSS and PMPSS, the resonance peak at -11.58 ppm is assigned to $\text{Si-Me}_2-\text{CH(Ph)}$- and the resonance peaks at -15.55 and -15.81 ppm are assigned to $\text{-Si(Me)}_2\text{-Si(Me)}_2\text{-CH}_2$-.$^2$ The resonance at -18.6 is assigned to $\text{-Si(Me)}_2\text{-Si(Me)}_2\text{(Ph)}\text{-CH}_2$-.

In the $^{13}$C-NMR spectrum of PSH-TER the signals in the region -3 to -5 ppm are assigned to Si-Me carbon atom. The splitting of the signals in this region is due to the different stereochemical arrangements caused by the neighbouring methylene and methyne groups. The signals due to Si-CH$_2$- and Si-CH- carbons are observed at 14.1 ppm and 30.9 ppm respectively.

Based on $^{13}$C- and $^{29}$Si-NMR spectral studies the structure of PSH-TER can be represented as given in structure 3.
3.7.4.2 AO exposure studies

PSH-TER-coated quartz plate, aluminized Kapton® film and glass-polyimide and C-polyimide composites were exposed to AO in a plasma barrel system along with uncoated samples and uncoated Kapton® film.

**PSH-TER-coated quartz plate:** It is observed that the uncoated Kapton® film loses 6.37 mg/cm² on exposure to AO fluence of $2.1 \times 10^{21}$ atoms/cm² whereas PSH-TER coating on quartz loses only 0.018 mg/cm² for the same extent of exposure. The above mass loss data suggest that PSH-TER can serve as an excellent AO resistant coating. Visual observation of the coating after exposure to AO suggests that the coating is free from cracks and blisters.

The mass loss of PSH-TER, PTMDSS and PMPSS coatings on quartz on exposure to AO is compared in Fig. 3.7.17 for AO fluence level of $1.3 \times 10^{21}$ atoms/cm², the maximum fluence level at which the mass loss of PMPSS system could be studied.

![Fig. 3.7.17. Comparison of mass loss of different polysilahydrocarbons on exposure to AO](image)
It is noticed that the mass loss of PSH-TER is the lowest followed by PTMDSS. Incorporation of methylphenylsilylene units (0.1mol%) in PTMDSS not only reduces the tackiness but also improves its AO resistance. This is probably due to the improved film forming characteristics of PSH-TER compared to that of PTMDSS.

**PSH-TER-coated aluminized Kapton®, C-polyimide and glass-polyimide composites:** It is observed that coated aluminized Kapton® loses 0.17 mg/cm² when exposed to an AO fluence of 2.1x10²¹ atoms/cm² whereas the uncoated aluminized Kapton® loses 6.35 mg/cm² when the sample was exposed to the same AO fluence. In the case of C-polyimide composite, the uncoated one loses 63.64 mg/cm² and PSH-TER-coated composite loses only 0.12 mg/cm² on exposure to an AO fluence of 1.8x10²¹ atoms/cm². On further exposure of the coated sample to an AO fluence of 2.1x10²¹ atoms/cm², it undergoes an additional mass loss of 0.01 mg/cm². For glass-polyimide composite, it is observed that the uncoated composite undergoes a mass loss of 16.04 mg/cm² on exposure to an AO fluence of 1.3x10²¹ atoms/cm² and the composite has to be removed from the plasma chamber as it got completely damaged. On the other hand, PSH-TER-coated composite loses 0.053 mg/cm² for the same extent of AO exposure. On further exposure of the coated sample to an AO fluence of 2.1x10²¹ atoms/cm² an additional mass loss of 0.047mg/cm² is noticed. The mass loss data of aluminized Kapton®, C-polyimide composite and glass polyimide composite coated with different polysilahydrocarbons on exposure to AO fluence of 1.3x10²¹ atoms/cm² are compared in Fig. 3.7.18.

![Fig. 3.7.18. Comparison of mass loss of substrates coated with different polysilahydrocarbons on exposure to AO](image-url)
It is observed that the performance of PSH-TER as AO resistant coating is marginally better than that of PTMDSS and remarkably different from that of PMPSS. SEM studies of PSH-TER-coated samples exposed to AO fluence of $2.1 \times 10^{21}$ atoms/cm$^2$ also reveal that the coating is free from cracks and blisters.

3.7.5 Comparison of AO resistance of PSH-TER with other AO resistant materials

Survey of literature on AO resistant materials suggests that inorganic and organometallic polymers can serve as AO resistant materials as they form protective oxide layer on exposure to AO. Preceramic Polymers Laboratory in the Vikram Sarabhai Space Centre is working on the development of various inorganic and organometallic polymers as AO resistant materials and the author of the thesis is actively involved in such developments. Besides polysilahydrocarbons, siloxane-imide-epoxy resin and phosphazene-based polymers have been evaluated as AO resistant materials. Among polysilahydrocarbons studied as AO resistant materials, the performance of PSH-TER as AO resistant material surpasses that of PTMDSS and PMPSS. Thus it would be interesting to compare PSH-TER with other inorganic and organometallic polymers evaluated by the author of the thesis in an attempt to understand the factors which contribute to AO resistance.

Siloxane-imide-epoxy resin: The siloxane-imide-epoxy resin (SIE) was synthesized by reacting siloxane-imide-epoxy prepared by epoxidation of siloxane containing diimide-diacid, 1,3-bisglycidoxypropyltetramethyldisiloxane, 3-aminopropylterminated polydimethylsiloxane and 1,3-bis(3-aminopropyl)tetramethyldisiloxane in THF followed by curing at 120°C as described elsewhere.$^{13,16,37}$ The structure of the resin is shown in Fig. 3.7.19.

Phosphazene-based polymers: Phosphazene-based polymers such as, cyclomatrix phosphazene-bismaleimide, cyclomatrix phosphazene-triazine-bismaleimide and a vinylic polymer containing fluoroalkoxy-substituted phosphazene as pendant groups were evaluated as AO resistant materials. Cyclomatrix phosphazene-bismaleimide polymer (PZ-BMM) was synthesized by the Alder-ene reaction between tris(2-allylphenoxy)triphenoxycyclotriphasphazene
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(TAP) and bis(4-maleimidophenyl)methane (BMM). TAP was synthesized from hexachlorocyclotriphosphazene by sequential reaction with sodiumphenolate and sodium (2-allylphenolate). Cyclomatrix phosphazenetriazine-based polymers (PZ-TZ-BMM) with varying bismaleimide content were synthesized by co-curing a blend of TAP and tris(2-allylphenoxy)triazine (TAT) (1:1 mole ratio) with bis-(4-maleimidophenyl)methane (BMM) by the method of Nair and Ninan. The phosphazene-based film prepared from TAP and bis(4-maleimidophenyl)methane (BMM) with allyl to maleimide content 1:2.5 is referred to as PZ-BMM-25 and cyclomatrix phosphazene-triazine-based ones with allyl to maleimide content 1:1.5 and 1:2.5 are referred to as PZ-TZ-BMM-15 and PZ-TZ-BMM-25 respectively. The structures of phosphazene- and phosphazenetriazine-based polymers are given in Figs. 3.7.20 and 3.7.21 respectively. A vinylic polymer, VCP-1, in which fluoroalkoxy-substituted phosphazene is present as pendant group, was synthesized by Chandrasekhar and Athimoolam from \( \text{N}_3\text{P}_3\text{Cl}_5(\text{OC}_6\text{H}_4-p-\text{CH}=\text{CH}_2) \) and sodium trifluoroethanolate following the procedure of Inoue et al. and is used for evaluation of AO resistance. The structure of VCP-1 is given in Fig. 3.7.22.
Fig. 3.7.20. Structure of phosphazene based polymer (PZ-BMM)

Fig. 3.7.21. Structure of phosphazene-triazine-based polymers (PZ-TZ-BMM)

Where, \( R = \) 

(for allyl/ BMM = 1/2)
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Fig. 3.7.22. Structure of vinylic phosphazene based polymer (VCP-1)

The mass loss of PSH-TER is compared with that of siloxane-imide-epoxy resin and phosphazene-based polymers in Fig. 3.7.23.

![Bar chart showing mass loss comparison](image)

From the above figure, it is evident that PSH-TER has better AO resistance when compared to other systems. The AO resistance of the polymeric systems compared in Fig. 3.7.23 follows the trend, PSH-TER>SIE>VCP-1>PZ-TZ-BMM-15>PZ-BMM-25>PZ-TZ-BMM-25. The observed trend can be explained by considering the heteroatom content of the polymers (Table 3.7.1).
Table 3.7.1. Phosphorus/silicon content of the polymers

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>Silicon Content (%)</th>
<th>Phosphorus content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSH-TER SIE</td>
<td>25.5</td>
<td>-</td>
</tr>
<tr>
<td>VCP-1</td>
<td>-</td>
<td>11.3</td>
</tr>
<tr>
<td>PZ-BMM-25</td>
<td>-</td>
<td>4.5</td>
</tr>
<tr>
<td>PZ-TZ-BMM-15</td>
<td>-</td>
<td>3.4</td>
</tr>
<tr>
<td>PZ-TZ-BMM-25</td>
<td>-</td>
<td>2.4</td>
</tr>
</tbody>
</table>

From Table 3.7.1, it is observed that PSH-TER has the highest silicon content followed by siloxane-imide-epoxy. Among the phosphorous containing polymers, VCP-1 has the highest phosphorous content (11.3%) and this polymer has better AO resistance when compared to other phosphazene-based polymers which have much lower phosphorous content (2.4-4.5%). Thus, it is evident that the amount of silicon/phosphorous present in the polymer backbone is the main factor which contributes to AO resistance.

In the case of PZ-BMM and PZ-TZ-BMM polymers, AO resistance is found to depend on both the structure and phosphorus content of the polymer (Table 3.7.1). It is interesting to note that PZ-TZ-BMM-15 which has less phosphorus content (3.4 %) has better AO resistance compared to that of PZ-BMM-15 which has higher phosphorus content (4.5%) and this observation is attributed to the presence of triazine moieties in the former. PZ-TZ-BMM-15 has better AO resistance compared to that of PZ-TZ-BMM-25. Both these polymers have the same amount of triazine moieties and better AO resistance of PZ-TZ-BMM-15 is attributed to higher phosphorus content (3.4%) when compared to that of PZ-TZ-BMM-25 (phosphorus content, 2.4 %).

3.7.6 Conclusions

Atomic oxygen resistance of polysilahydrocarbons synthesized by reacting diorganodichlorosilanes with styrene under dechlorination condition was
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evaluated using a plasma barrel system. The mass loss with respect to atomic oxygen fluence was determined for uncoated and polysilahydrocarbon-coated substrates. The uncoated and coated substrates before and after exposure to atomic oxygen was characterized by SEM. Based on these investigations the following conclusions have been drawn:

i) Poly(tetramethyldisilylene-co-styrene) (PTMDSS) in which disilyl and styryl units alternate with each other was evaluated as AO resistant coating. This copolymer exhibited excellent resistance to AO attack and offered very good protection to substrates such as polyimide film, C-polyimide composite and glass-polyimide composite. However, PTMDSS-based coating is somewhat tacky in nature.

ii) In order to overcome this problem a polysilahydrocarbon (PMPSS) was synthesized from methylphenyldichlorosilane and styrene. The coating-based on this copolymer was found to be brittle and flaked off from the substrate during evaluation.

iii) PTMDSS was modified by incorporating methylphenylsilyl units (mole ratio of dimethylsilyl:methylphenylsilyl units, 1:0.1). The modified polymer (PSH-TER) was tack-free and offered excellent resistance to the substrates from atomic oxygen attack

iv) The performance of PSH-TER was compared with siloxane-imide-epoxy and phosphazene-based polymers. PSH-TER has better AO resistance than the other two systems and this has been attributed to higher silicon content in the former system.

References


40. V. Chandrasekhar and A. Athimoolam, VCP-1 polymer was prepared by this research group of IIT, Kanpur under ISRO Respond Program, 1999.