

Preparation and Properties of Borosiloxane Gels

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ABSTRACT: Hybrid gels were synthesized from modified silicon alkoxides ($R\text{-Si}(\text{OEt})_3$, $R = \text{H, Me, Vi}$) and triisobutylborate ($\text{B}(\text{O-R}')_3$, $R' = \text{isoBu}$). The obtained gels were characterized by Fourier-transform infrared (FTIR), nuclear magnetic resonance (NMR), elemental analyses, X-ray diffraction (XRD), and scanning electron microscopy (SEM). Boron atoms in the precursors were homogeneously dispersed in the siloxane network via Si-O-B bonds. The effect of the boron load on oxidation resistance of the gels, and the pyrolysis behavior of the borosiloxane gels with different

substituents on silicon, were investigated using various techniques. The experimental results suggest that the addition of a proper fraction of boron alkoxide to the precursors can improve the oxidation stability of the gels, and decrease the weight loss of the samples to 6.9 wt % at 1000°C under air. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 719–724, 2006

Key words: borosiloxane gels; boron load; TGA; oxidation stability; pyrolysis

INTRODUCTION

The sol-gel method is well-known as one of the usual processes to prepare oxide ceramics or composites from silicon alkoxides.¹ However, the method is often complicated by difficulty in that the hydrolysis of polyfunctional alkoxides is too fast to regulate the process, leading to gels or heterogeneous materials in the reaction process. $\text{SiO}_2\text{-B}_2\text{O}_3$ gels, obtained from tetrafunctional silicon alkoxides such as $\text{Si}(\text{OCH}_3)_4$ or $\text{Si}(\text{OCH}_2\text{CH}_3)_4$, and boric acid, have been extensively studied as precursors for borosilicate ceramics.^{2–7} Irwin and coworkers^{8,9} reported on the structural evolution of this system during the entire sol-gel process and clearly demonstrated that no B-O-Si bonds exist in the final gels. It is well known that addition of a third metal, which is boron, increases thermal stability of the ceramics; however, there is limited study on the effect of the addition of boron on the thermo-oxidation stability of gels in air.

In this work, we report on the preparation and properties of hybrid gels obtained from cohydrolysis and cocondensation of $R\text{-Si}(\text{OEt})_3$ ($R = \text{Me, H, Vi}$) and $\text{B}(\text{OR}')_3$ ($R' = \text{isoBu}$). This system has not been reported on earlier. Our interest for these materials is primarily related to the preparation of borosiloxane as precursors for composites with good high-temperature oxidation stability. This study shows that some borosiloxane bonds were retained in the hybrid gels

containing boron. The effect of boron load in the oxidation stability and the pyrolysis behavior of homogeneous borosiloxane gels containing B-O-Si bonds are also investigated.

EXPERIMENTAL

Materials

Modified silicon alkoxides, that is, methyltriethoxysilane (MeSi), triethoxysilane (HSi), and vinyltriethoxysilane (ViSi), were purchased from Wuhan University Silicone New Material Co. Ltd. Tri-isobutylborate (TIBB), hydrochloric acid (HCl), and methyl isobutylketone (MIBK) were obtained from Beijing Chemical Reagent Company. All the chemicals were used as received.

Preparation of borosiloxane precursors and gels

Water acidified with HCl ($\text{pH} = 1$) was used for hydrolysis. To minimize the residual amount of water after hydrolysis, and thus to increase the stability of B-O-Si bonds in the resulting precursors, an $\text{H}_2\text{O}:(\text{Si} + \text{B})$ molar ratio of 1.5 was used for all the preparations. The precursors were prepared according to the following procedure: The silicon alkoxide (MeSi, ViSi, or MeSi and HSi), tri-isobutylborate, and methyl isobutylketone were poured into a three-necked flask and magnetically stirred for 5 min at room temperature. The amount of MIBK was adjusted to give a molar ratio $\text{MIBK}/(\text{Si} + \text{B}) = 2$. Then the proper amount of water in MIBK ($\text{MIBK}/\text{H}_2\text{O}$ molar ratio of 2) was added dropwise to the mixture over a period of

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30 min with stirring. The solution was then heated to reflux for 40 min. The precursors were prepared with a fixed MeSi/HSi molar ratio of 4 and nominal B/Si atomic ratios of 0, 0.1, 0.2, 0.25, 0.33, 0.5, 0.8, and 1.0. Finally, the precursors were poured into molds for gelation. The gels were then dried at 60°C for 12 h.

Heat treatment of borosiloxane gels

Heat treatments of the gels were performed on the powders in air, using an SK-1-10 tube furnace at various temperatures between 200 and 900°C. All the pyrolysis treatments were performed on powders with a heating rate of 5°C/min holding at the maximum temperature for 1 h.

Measurements

Si and B contents of gel samples were determined by inductively coupled plasma atomic emission spectroscopy using a SEIKO ICP-AES, model SPS-7000. The liquid ^{29}Si -NMR spectra were recorded on a Bruker WM 300 spectrometer using acetone- d_6 as solvent. IR spectra were measured on a PE 2000 IR spectrometer using the KBr disk method. The differential scanning calorimeter/thermogravimetric analysis (DSC/TGA) was performed on a NETZSCH (model STA-409) DSC/TG, at a heating rate of 10°C/min $^{-1}$ under air, up to a maximum temperature of 1000°C. X-ray diffraction (XRD) diagrams were recorded on a powder diffractometer (Rigaku D/M4 \times 2500) using $\text{CuK}\alpha$ radiation. The morphology of the gels and pyrolysis products were observed on an S-530 scanning electron microscope (SEM).

In this article the samples will be designated as follows: (Me+H) SiB0.25 refers to the gel precursor prepared from MeSi, HSi, and TIBB with a B/Si ratio of 0.25.

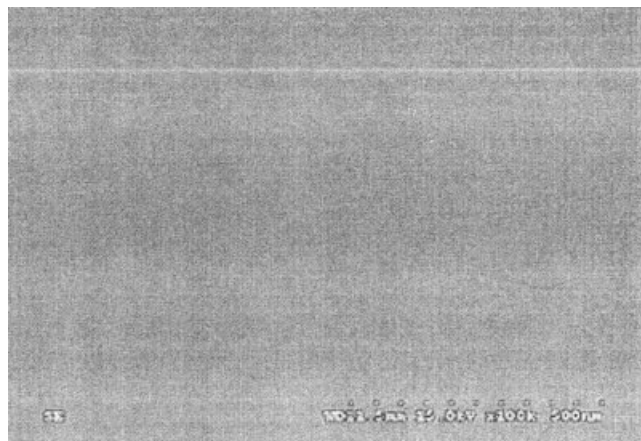


Figure 1 SEM image. Film of MeSiB0.25 on silicon wafer.

TABLE I
Elemental Analysis of the Gels

Sample	Composition (wt %)		B:Si (molar ratio) measured value
	Si	B	
MeSiB0.25	38.55	2.57	0.17
ViSiB0.25	32.77	2.53	0.2
(Me+H)SiB0.25	36.80	3.18	0.22
ViSiB0.1	33.72	1.32	0.10
ViSiB0.2	32.67	2.18	0.17
ViSiB0.33	30.36	3.58	0.30
ViSiB0.5	29.44	5.01	0.43
ViSiB0.8	27.17	7.22	0.68
ViSiB1	24.75	7.49	0.77

RESULTS AND DISCUSSION

Structural characterization of the precursors and gels

The precursor of MeSiB0.25 was dried at 60°C for 12h, and could be fabricated into uniform thin films by dipping or spin-coating. As shown in Figure 1, a film of MeSiB0.25 on a silicon wafer has good homogeneity. The same results, not reported here, can be obtained from other samples. It is indicated that addition of boron does not destroy the homogeneity of gels.

Elemental analysis results on the gels, prepared from the homogeneous precursors obtained by the reaction of silicon alkoxides and TIBB under different conditions, are summarized in Table I. The analyzed boron content is a little lower than the theoretical value. This behavior is ascribed to the evaporation of boron alkoxides during gelling and drying⁵ or experimental error. It has been infrequent that a higher fraction of boron atoms ($\text{B}:\text{Si} > 0.5$) was in the homogeneous precursor. In this work, we chose similar hydrolysis and condensation rates of silicon and boron alkoxides to obtain homogeneous precursors with higher boron content. The elemental analysis results of MeSiB0.25, ViSiB0.25, and (Me+H) SiB0.25 gels indicate that, for the same nominal boron loads ($\text{B}:\text{Si} = 0.25$), most boron is retained in the gel synthesized using MeSi and HSi.

Liquid ^{29}Si -NMR spectra, recorded on the precursors with the amount of boron ($\text{B}:\text{Si} = 0.25$ or 1.0), are reported in Figures 2 and 3. The ^{29}Si -NMR spectra show, for the four samples, the presence of one main peak at -64.7 , -79.3 , and -85.1 ppm, respectively, assigned to $\text{MeSiO}_{3/2}$, $\text{ViSiO}_{3/2}$, and $\text{HSiO}_{3/2}$ silicon units. The other small peaks, associated with some terminal Si-OEt or Si-OH groups, are also present in all the investigated precursors. The ^{29}Si -NMR spectra of the precursors are identical to that already published for the boron-free gel.¹⁰ As already reported in the literature,⁸ there is no chemical shift difference between Si-O-Si and Si-O-B bonds in the ^{29}Si -NMR

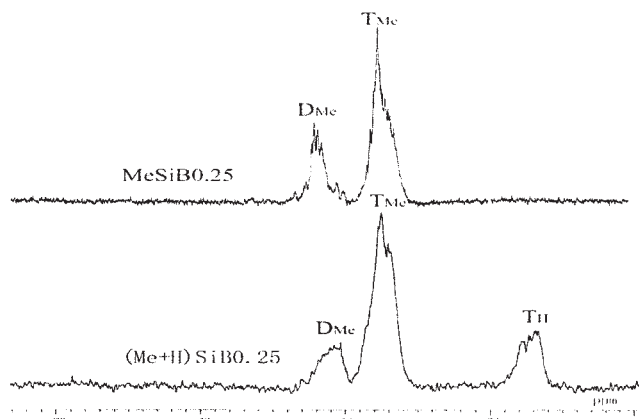


Figure 2 Liquid ^{29}Si NMR spectra of the (MeSi+HSi)-, ViSi-, and MeSi-derived precursors^a with B/Si = 0.25. $T_{(\text{Me}, \text{H}, \text{or Vi})}$ refers to the fully condensed formations. $D_{(\text{Me}, \text{H}, \text{or Vi})}$ refers to a resonance due to a silicon with one Si-OEt or Si-OH.

spectra. On the other hand, when the B:Si ratio is increased from 0.25 to 1, the formation of fully condensed ViSi is favored (see Fig. 3). It is indicated that the addition of boron alkoxide strongly modifies the hydrolysis and condensation degree of the silicon alkoxide.

The FT-IR absorption peaks of the boron-free ViSi gel and ViSiB0.2 gel are characterized by the typical bands associated with Si-O-Si bonds at 1120–1020, 840–790, and 460–400 cm^{-1} . Absorption peaks, at 3048, 3007, 1600, 1410, 1275, 970, and 770 cm^{-1} (Si-CH=CH₂),¹¹ are observed. Moreover, three new peaks, at 1500–1300 cm^{-1} (B-O), 892 cm^{-1} and 675 cm^{-1} (Si-O-B), are now visible in the FT-IR spectra of ViSiB¹² (see Fig. 4). The reason is that the boron is partially incorporated in the siloxane network via B-O-Si bridges. This can be verified from Figure 3 in that the intensity of the absorption peak at 892 cm^{-1} increases with the B/Si atomic ratio increasing from 0.2 to 0.5. These results show that some borosiloxane units

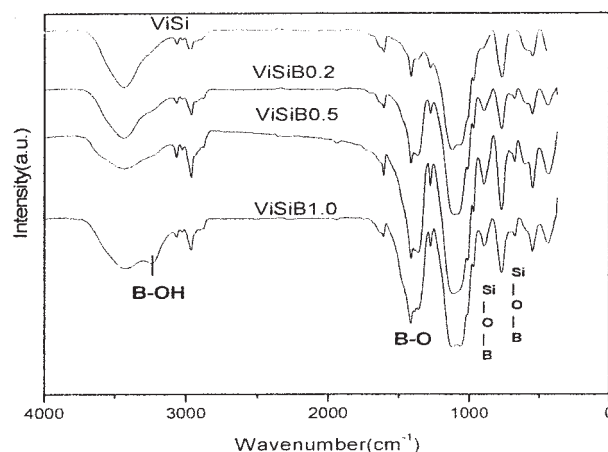


Figure 4 FT-IR spectra collected on ViSi-derived borosiloxane gels with different boron loads.

are retained in the gels. On the other hand, by increasing the boron content from B/Si = 0.5 to B/Si = 1, the intensity of the peaks related to the B-O-B and B-OH bonds increases (see Fig. 4).

The organic substituent on silicon influences the formation of borosiloxane bridges in the hybrid borosiloxane gels, as shown by the series of FT-IR spectra reported in Figure 5. The three samples, MeSi-, ViSi- and (MeSi+HSi)-derived gels, were obtained with a B/Si ratio of 0.25. The intensity of the band associated with the borosiloxane bridges at 880–890 cm^{-1} increases from MeSiB0.25 to ViSiB0.25 and to (Me+H)SiB0.25. These results can be related to the elemental analysis results.

XRD spectra, collected on selected MeSiB0.25, ViSiB0.25, and (Me+H)SiB0.25 borosiloxane gels obtained with B/Si = 0.25, are shown in Figure 6. The spectra show the SiO₂ amorphous hump centered at $2\theta = 22^\circ$, with two superimposed reflections at $2\theta = 15^\circ$ and 28° assigned to crystalline B(OH)₃.¹³ However, for such as the (Me+H)SiB0.25 sample, the peaks related to the boric acid phase are invisible.

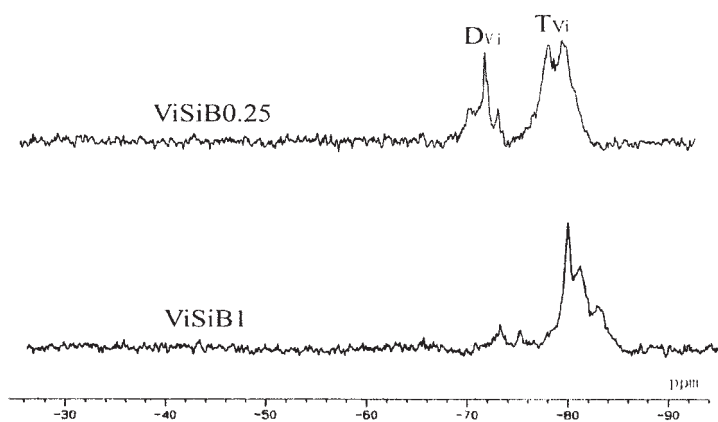


Figure 3 Liquid ^{29}Si NMR spectra collected on selected ViSi-derived precursors with two B/Si ratios (B/Si = 0.25 and 1).

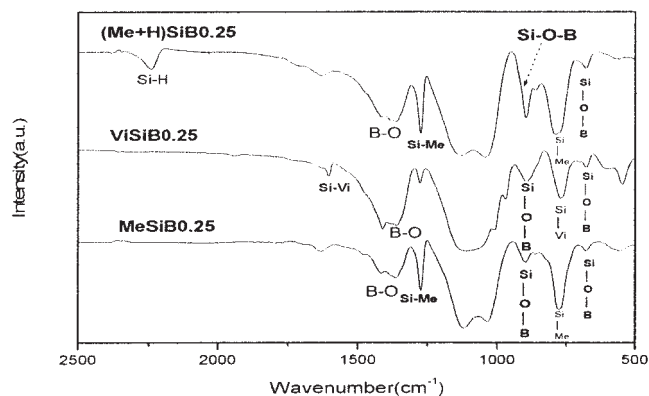


Figure 5 FT-IR spectra of the (Me+H)Si-, ViSi-, and MeSi-derived gels with B/Si = 0.25.

Indeed, as already indicated by the FT-IR analysis, the boron atoms in the (Me+H)SiB samples are mainly engaged in the formation of borosiloxane bridges, and the formation of $B(OH)_3$ is greatly hindered.

Oxidation stability of borosiloxane gels

Thermogravimetric curves are reported in Figure 7. The boron-free gel (ViSi) shows main decomposition between 200°C and 800°C, due to the evolution of silanes and organic/inorganic conversion of the system,¹⁴ under air. The total weight loss from 200 and 800°C is about 31.6%. Introduction of boron into the gel strongly modifies the pyrolysis pathway. Indeed, even for the gel with a nominal boron content of B/Si = 0.2, the main weight loss between 200°C and 800°C is 20%. Especially above 500°C, the weight loss of the borosiloxane gel (ViSiB0.2) is much lower than that of the boron-free gel (ViSi).

The precursor of MeSiB0.25 was dried at 60°C for 12h, and could be fabricated into uniform thin films by dipping or spin-coating. As shown in Figure 8, a film of MeSiB0.25 on silicon wafer remained homogeneous after pyrolyzing at 700°C under air. The same results,

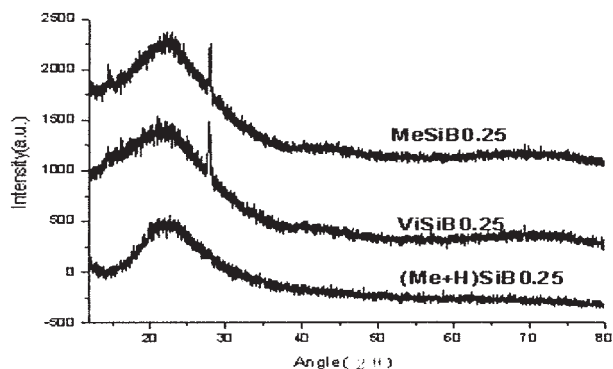


Figure 6 XRD spectra collected on selected (Me+H)Si-, ViSi-, and MeSi-derived gels with B/Si = 0.25.

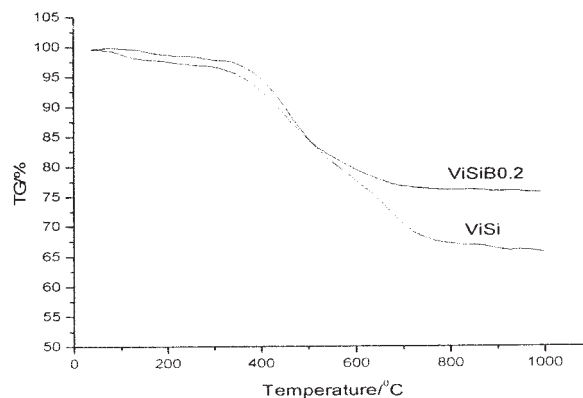


Figure 7 TG curves recorded on the ViSi-derived gels with B/Si = 0 or 0.2.

not reported here, can be obtained from the other samples and indicate that films of borosiloxane gels have good oxidation stability.

These results suggest that the addition of a proper amount of boron alkoxide to the precursor can enhance the thermo-oxidation resistance of the gels.

The effect of the B/Si atomic ratio

DSC analyses of the samples are reported in Figure 9. The results show that the first exothermic peaks of ViSiB0.2 and ViSiB0.5, due to oxidation of organic groups, are at 235.9°C and 403.2°C, respectively. Thus, the DSC study points out that the oxidation stability of the gels is enhanced with the B/Si atomic ratio increasing.

To illustrate the effect of the boron load in oxidation resistance of the gels, TG curves and results recorded on ViSi-derived gels are shown in Figure 10 and Table II for $0 \leq B/Si \leq 1$. As shown in Figure 10, it is observed that the total weight loss of the sample with $B/Si \leq 0.5$ decreases with boron load increasing, while for the sample with $B/Si > 0.5$, the weight loss in-

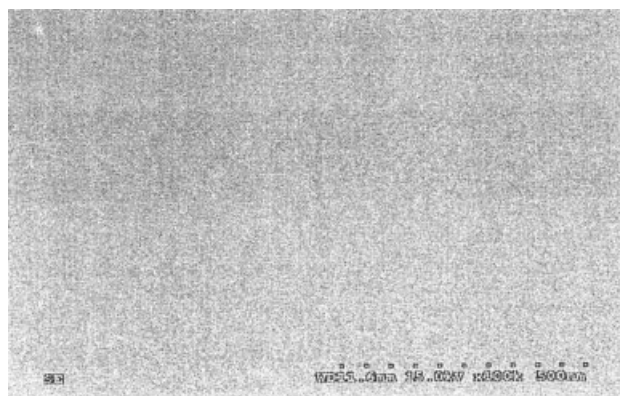


Figure 8 SEM image. Film of MeSiB0.25 on silicon wafer keeps pyrolyzed at 700°C under air.

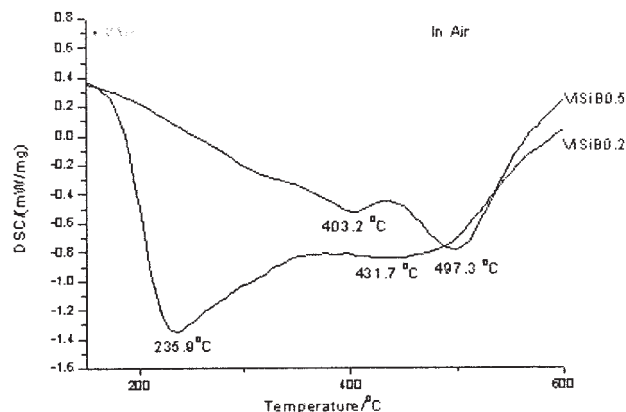


Figure 9 DSC curves recorded on the gel with the amount of boron ($B/Si = 0.2$ or 0.5).

creases. Similar conclusions can be easily extracted from Table II. As clearly shown in Figure 10 and Table II, the first weight loss step between room temperature and 200°C under air, assigned to the evaporation of water from the B-OH moieties,¹⁵ increases with the boron content in the samples ($B/Si > 0.5$). The first weight loss step of ViSiB1.0 is about 9%, which is half of the total weight loss. The second weight loss step, from 200 to 800°C under air, decreases with the boron load ($B/Si \leq 0.5$) increasing, and hardly changes in the gels with $B/Si > 0.5$. The third weight loss step (800 – 1000°C under air) does not show a strong difference for the gel composition, in the range of 0.3–1.5%. These results suggest that the number of stable borosiloxane bridges initially increases with the boron load up to a certain level, until a plateau is reached. Any further boron addition does not increase the amount of boron incorporated in the siloxane network but forms preferentially $\text{B}(\text{OH})_3$ in the samples with higher boron ($B:Si > 0.5$), in agreement with the former FT-IR study.

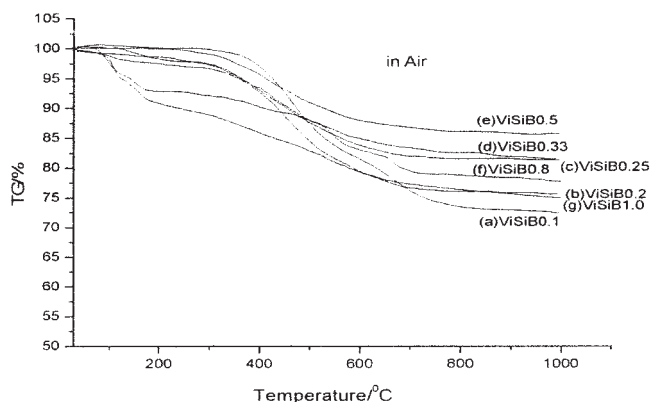


Figure 10 TG curves recorded on the ViSi-derived gels with various B/Si nominal ratios. $B/Si =$ (a) 0.1; (b) 0.2; (c) 0.25; (d) 0.33; (e) 0.5; (f) 0.8; and (g) 1.0.

TABLE II
Results of the Thermogravimetric Analysis for the Studied SiBOC Gels Under Air

Sample	Weight loss (%)			
	20/200	200/800	800/1000	20/1000
ViSi	1.1	31.6	1.4	34.1
ViSiB0.1	0.1	26.7	1.0	27.8
ViSiB0.2	0.9	22.6	0.5	24.0
ViSiB0.25	2.1	16.7	0.3	19.1
ViSiB0.33	1.4	16.0	1.1	18.5
ViSiB0.5	0.1	13.9	0.3	14.3
ViSiB0.8	7.1	14.1	1.1	22.3
ViSiB1.0	9.3	14.4	1.5	25.2
(Me+H)SiB0.25	0.4	6.4	0.1	6.9
MeSiB0.25	4.2	10.5	-	14.7

Pyrolysis behavior of borosiloxane gels with different substituents on silicon in air

From Figure 11 it is observed that the residual weight of borosiloxane gel containing Si- CH_3 and Si-H bonds can be increased up to 93% at 1000°C under air. Of the three samples, the weight loss of (Me+H) SiB0.25 is the lowest. In Table II, it is clearly shown that the first weight loss step of MeSiB0.25 is the highest, and is related to the fact that MeSiB0.25 does not easily form the Si-O-B bond but forms $\text{B}(\text{OH})_3$, which is in agreement with the former FT-IR and XRD studies. The second weight loss of ViSiB0.25 is about 16%, which is the highest of the three samples. The second weight loss step shows a strong dependence on the structure of the gels. This reason can be shown later in the next section.

The (Me+H)SiB0.25 and ViSiB0.25 gels were pyrolyzed in a tube furnace under air at different temperatures up to 900°C . The evolution of the FT-IR spectra recorded on these samples is reported in Figure 12. As shown in Figure 12A, by increasing the pyrolysis temperature, the peaks related to the Si-Vi bonds progres-

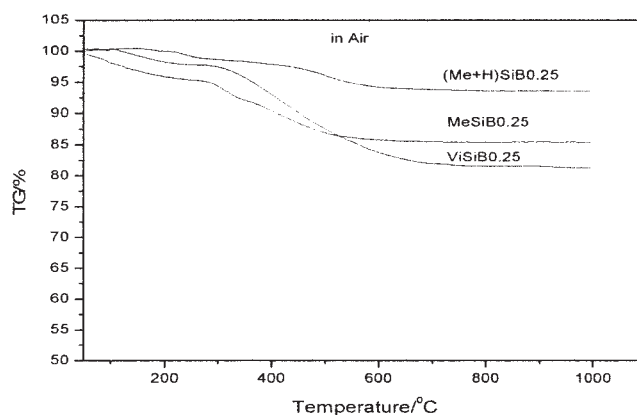


Figure 11 TG curves of the (MeSi+HSi)-, ViSi-, and MeSi-derived gels with $B/Si = 0.25$.

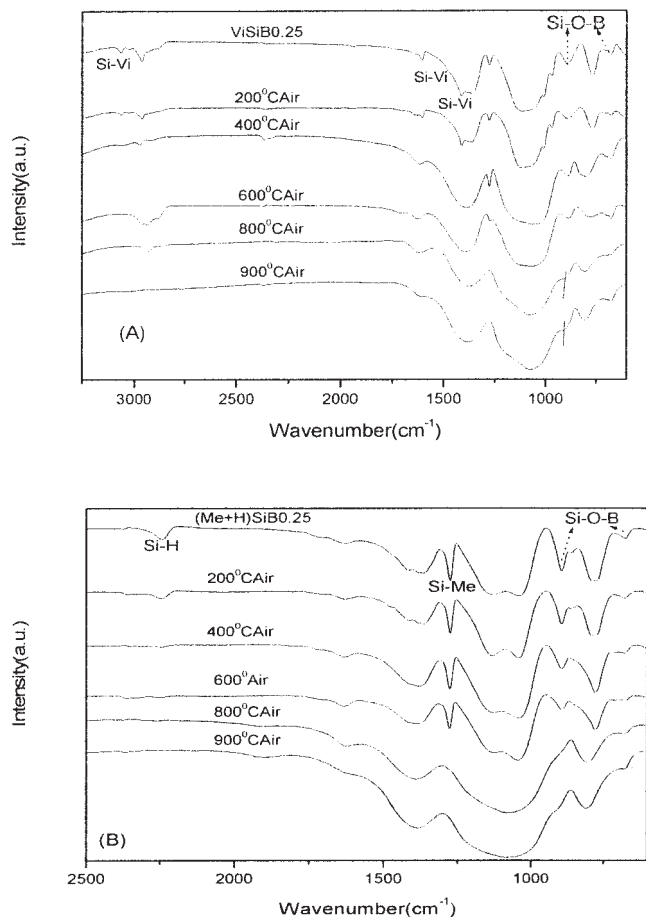


Figure 12 Evolution of the FT-IR spectra recorded on (a) ViSiB0.25 and (b) (Me+H) SiB0.25 gels pyrolyzed under air at different temperatures.

sively disappear due to the oxidation of the organic groups with the formation of new Si-O bonds. At the same time, it was observed that the band at 892cm^{-1} shifts (Si-O-B) toward higher wavenumbers and at 800°C reaches the value of 910cm^{-1} , reported in the literature for the B-O-Si bridge (obtained from tetra-functional silicon alkoxides and boric acid). This indicates that the organic substituent on silicon nearly disappears at 800°C under air. However, the band shift at 910cm^{-1} is hardly visible in (Me+H)SiB0.25 at 900°C (see Fig. 12B). It is also seen, from Figures 12A and B, that the Si-Vi group nearly disappears at 600°C , the Si-H group at 400°C , and the Si-Me group at 800°C , respectively. For the (Me+H)SiB0.25 from 200 to 400°C , a possible reaction could occur as condensation between residual B-OH or Si-OH and Si-H bonds forms new stable B-O-Si or Si-O-Si bonds, water, and hydrogen gas, or pyrolysis of the Si-H bond. Obviously, the pyrolysis behavior of the gels is very dependent on the organic substituent on silicon. On the

other hand, it is observed that the weight loss of (Me+H) SiB0.25 from 600 to 800°C , from its TG curve, is low, which is not in agreement with the results shown in Figure 12B. We tentatively assign the result to the larger mass of oxygen introduced; meanwhile, a detailed study is underway. However, it can be suggested that the organic substituent on silicon plays an important effect on pyrolysis under air.

CONCLUSIONS

Boron can be introduced into a siloxane network via the Si-O-B band by the cohydrolysis and cocondensation of $R\text{-Si}(\text{OEt})_3$ ($R = \text{Me}, \text{H}, \text{Vi}$) and $\text{B}(\text{OR}')_3$ ($R' = \text{isoBu}$) to give a borosiloxane homogeneous precursor for Si/C/O/B based compositions with good high-temperature performance. The identification of B-O-Si bridges in the borosiloxane gels is mainly based on the presence of an absorption peak at 890cm^{-1} in the FT-IR spectra.

This study has shown that a proper amount of boron can enhance the thermo-oxidation stability of the gel, and decrease the weight loss of the sample. The weight loss of borosiloxane gels decreases with boron load increasing ($\text{B}/\text{Si} \leq 0.5$) at 1000°C under air. On the other hand, the pyrolysis behavior of the gel is greatly dependent on the organic substituent on silicon. Notably, the weight loss of (Me+H)SiB0.25 is as low as 6.9% at 1000°C under air.

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