

## Preparation and Characterization of Polyborosiloxanes and Their Blends with Phenolic Resin as Shapeable Ceramic Precursors

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**Abstract** Two polyborosiloxanes (PBSis) with char yield up to 74.13% at 800 °C were synthesized by the direct polycondensation of boric acid with phenyltrimethoxysilane in diglyme. The PBSis were characterized by gel permeation chromatography, IR spectroscopy as well as <sup>1</sup>H-, <sup>29</sup>Si- and <sup>11</sup>B-NMR. PBSi modified phenol-formaldehyde resins (PBSi/PFs) were prepared at different PBSi/PF mass ratios and were cured at 150 °C. The PBSi/PFs were characterized by IR spectroscopy, scanning electron microscopy, thermogravimetric analysis and tensile test. The results revealed that the cured PBSi/PFs had sea-island morphology and higher char yield than the common PF. PBSi/PF blend with PBSi/PF mass ratio of 0.4:1 had char yield up to 70.83% at 800 °C. The PBSi/PFs had tensile strength similar to PF. The ceramization of PBSi/PFs was also studied. The silicon boron oxycarbide (SiBOC) ceramics formed were characterized by IR spectroscopy and elemental analysis. This method provided a valuable way to prepare easily shapeable polymer blends as ceramic precursors.

**Keywords:** Polyborosiloxane; Phenolic resin; Preparation; Ceramic precursors; SiBOC ceramics.

### INTRODUCTION

Polyborosiloxanes (PBSis) have been extensively explored as high temperature materials because of their high char yield. They can be used as active modifiers for thermosetting resins, non-halogenated flame retardants, heat resistant paintings and polymeric ceramic precursors<sup>[1, 2]</sup>. Several methods have been described to synthesize PBSis. A major synthesis method is a sol-gel route<sup>[3–7]</sup>. Sol-gel method involves hydrolysis and condensation of silicon alkoxides with triethylborate or boric acid (BA) in the presence of mineral acids and water. It often needs long aging time. The PBSis prepared are not stable to hydrolysis because B—O—Si bonds formed are susceptible to free water present, especially at the presence of mineral acids. They often hardly re-dissolve in organic solvents. Another method is a non-hydrolytic route, in which silicon compounds reacted directly with B(OH)<sub>3</sub> without any external addition of water. Yajima *et al.*<sup>[8]</sup> synthesized poly(borodiphenylsiloxane) through the reaction of BA and diphenyldichlorosilane. Hoshii *et al.*<sup>[9]</sup> prepared PBSi by reacting BA and diphenylsilanediol. Schiavon<sup>[10]</sup> reported PBSi synthesized through the reaction of BA with vinyltriethoxysilane and cyclotetrasiloxane. Packirisamy *et al.* synthesized borosiloxane oligomers by reacting BA with phenyltriethoxysilane, phenyltrimethoxysilane (PTMOS), or vinyltriethoxysilane in the presence or absence of the catalysis of HCl<sup>[11, 12]</sup>.

Phenolic resin (PF) is one of the important thermosetting resins. It is widely used in many fields especially as adhesives and coatings. Many methods have been developed to modify the toughness of PF, such as modified by butadiene-acrylonitrile rubber<sup>[13]</sup>, polyvinyl butyral<sup>[14]</sup> and polydimethylsiloxane<sup>[15]</sup>. Meanwhile, PF resins

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Received April 10, 2013; Revised June 8, 2013; Accepted June 13, 2013

doi: 10.1007/s10118-014-1393-1

have obviously higher char yields than common organic polymers. Several methods have been described to increase their char yields further, such as preparation of boron-containing<sup>[16–22]</sup>, silicon-containing<sup>[23, 24]</sup> and phosphorus-containing<sup>[25]</sup> PFs.

The non-hydrolytic synthesis route of PBSi from silicon alkoxides and  $B(OH)_3$  in the absence of any catalyst was especially attracting. And, the structure of the borosiloxane oligomers obtained by this way still remained uncertain. In this article, we synthesized two PBSi through a similar method by reacting BA with PTMOS directly without any catalyst. By combining PBSi with PF, several PBSi modified PF blends (PBSi/PFs) were prepared. The PBSi/PFs kept thermosetting characteristics and were used as shapeable polymeric ceramic precursors. The PBSi were characterized by gel permeation chromatography (GPC), IR spectroscopy as well as  $^1H$ -,  $^{29}Si$ -,  $^{11}B$ -NMR. The PBSi/PFs were characterized by scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and tensile test. The ceramization of PBSi/PFs was also studied. The silicon boron oxycarbide (SiBOC) ceramics formed were characterized by IR spectroscopy and elemental analysis.

## EXPERIMENTAL

### Materials

Boric acid was purchased from Beijing Chemical Reagent Company, China. Phenyltrimethoxysilane was purchased from Alfa Aesar Co. Ltd. Diglyme (DGM) was purchased from Tianjin Guangfu Fine Chemical Research Institute, China. Phenol was purchased from Tianjin Chemical Reagents Factory, China. Formaldehyde, 36 wt%, was purchased from Beijing Chemical Factory, China.  $Ba(OH)_2 \cdot 8H_2O$  was purchased from West Long Chemical Co. Ltd, China. Ethyl acetate and tetrahydrofuran (THF) were all purchased as chemical reagents and were used directly.

### Synthesis of PBSi

1.24 g (0.02 mol)  $H_3BO_3$  and 7.93 g (0.04 mol) PTMOS were dissolved in 10 mL diglyme in a 250 mL three necked flask equipped with a reflux condenser, a mechanical stirrer and a nitrogen inlet adapter. The system was slowly heated to 150 °C with an oil bath under stirring, and reacted at this temperature for 3 h, with concurrently removing by-product methanol. To increase molecular weight further, reaction was continued at reduced pressure of 4000 Pa until diglyme was completely removed, and the product became very viscous. Finally, the product was dried under vacuum at 60 °C for 20 h. The PBSi was obtained as white solid in 75% yield.

### Synthesis of PF

15 g (0.14 mol) phenol, 19.4 g 36 wt% (0.24 mol) formaldehyde and 0.25 g  $Ba(OH)_2 \cdot 8H_2O$  were taken into a 250 mL three necked flask equipped with a reflux condenser and a mechanical stirrer. The reaction mixture was slowly heated from 40 °C to 90 °C and kept 1.5 h. And then, water was completely removed under reduced pressure of 4000 Pa at 60 °C. The PF was poured out and cooled at room temperature. The obtained PF had  $M_n$  of 291,  $M_w$  of 368 and  $M_w/M_n$  of 1.26 detected by GPC.

### Preparation, Bonding and Curing of the PBSi Modified PF Resins

1 g PBSi-1 was dissolved in 2.5 mL ethyl acetate and then mixed with PF at room temperature to form a uniform mixture solution. The mass ratios of PBSi-1 to PF were 0.2:1, 0.4:1 and 0.6:1. The PBSi/PF resins were named as PBSi/PF-1, PBSi/PF-2 and PBSi/PF-3.

Two stainless steel plates were bonded with the PBSi/PF-1, PBSi/PF-2 or PBSi/PF-3 adhesives respectively at the joints and cured at 150 °C for 4 h.

### Characterization

$M_n$  and  $M_w$  were determined with a Waters GPC-515-2410 gel permeation chromatography equipped with HR1 and HR2 microstyragel columns and a refractive index detector at 25 °C. Polystyrene was used as standards, and THF was used as eluent at a flow rate of 1 mL/min.

The PBSi used for the FTIR and NMR detection were purified three times through dissolving-precipitation cycles using 20 mL THF as solvent and 200 mL petroleum ether as nonsolvent. The FTIR spectra were recorded

on a NICOLET 60SXB FT-IR spectrometer. The  $^1\text{H}$ -NMR spectrum was recorded on a Bruker AV-400 spectrometer using acetone- $\text{d}_6$  as solvent and tetramethylsilane as an internal standard. The solid  $^{29}\text{Si}$ -NMR spectrum was recorded on a Bruker AV-300 spectrometer. The  $^{11}\text{B}$ -NMR spectrum was recorded on a Bruker AV-400 spectrometer at 96.3 MHz. Deuterated dimethyl sulphoxide (DMSO) was used as solvent in the  $^{11}\text{B}$ -NMR detection and the chemical shifts were reported with boron trifluoride etherate as an external standard.

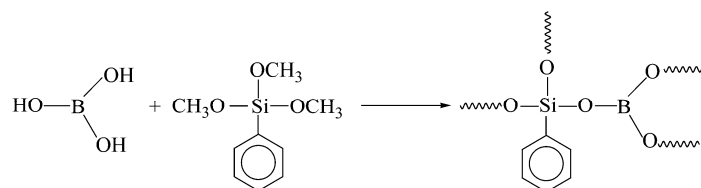
The thermogravimetric analysis was carried out by employing a TA TGAQ50 analyzer in the temperature range from 25 °C to 800 °C at a heating rate of 10 K/min under nitrogen atmosphere. The morphology of the fracture surface of PBSi/PFs was examined with an S-4700 scanning electron microscope. Samples were sputteringly coated with a thin gold layer under vacuum before measurements. The tensile tests were conducted on an Instron 1185 tensile testing machine with crosshead speed at 5 mm/min. Five measurements were performed for each sample, and the results were averaged to obtain a mean value.

The pyrolytic transformation from PBSi/PFs to SiBOC ceramics was studied with a TA TGAQ50 analyzer. In a typical procedure, 20 mg of powdered PBSi/PFs were loaded in an alumina crucible and heated at 10 K/min from room temperature to 800 °C under nitrogen (100  $\text{cm}^3/\text{min}$ ) with a holding time of 1 h at the maximum temperature. Elemental analysis of the SiBOC ceramics was performed by using an energy dispersive X-ray (EDX) spectroscopy (Gensis 60).

## RESULTS AND DISCUSSION

### Synthesis of the PBSis

Two PBSis were synthesized by the direct polycondensation of boric acid with PTMOS without any catalyst in diglyme. The synthesis reaction is shown in Scheme 1. The PBSis were synthesized at  $\text{H}_3\text{BO}_3/\text{PTMOS}$  molar ratio of 1:2. They were soluble in acetone, ethyl acetate, chloroform and tetrahydrofuran.



**Scheme 1** Synthesis reaction of PBSis

Table 1 shows the  $M_n$ ,  $M_w$  and  $M_w/M_n$  of PBSis detected by GPC method. PBSi-1 was directly synthesized at 150 °C for 3 h. It showed a major GPC peak having  $M_n$  of 3673 and  $M_w$  of 9228 with area ratio of 75.91% and a shoulder peak having  $M_n$  of 911 and  $M_w$  of 927 with area ratio of 24.09%. Maybe because  $\text{H}_3\text{BO}_3$  suffered from self condensation at high temperatures, B—OH groups conducted condensation with Si—OCH<sub>3</sub> as well as self condensation to form Si—O—B and B—O—B linkages. Two reaction modes led to wide molecular weight distribution with two GPC peaks emerged. One major peak had higher molecular weight and another shoulder peak had lower  $M_n$  and  $M_w$ . PBSi-2 was synthesized in the temperature range from 90 °C to 150 °C, *i.e.* 90 °C 1.5 h, 110 °C 1 h and 150 °C 3 h. Gradually increasing temperature suppressed self condensation of BA, and the B—OH groups just conducted condensation with Si—OCH<sub>3</sub> groups. So, PBSi-2 with one GPC peak having  $M_n$  of 1600 and  $M_w$  of 3912 was prepared. Table 1 also shows the char yields of PBSis at 800 °C under  $\text{N}_2$ . They all showed high char yields above 72.69%. From Table 1, it was also found that PBSis were all stable to hydrolysis. After they were laid aside for 1 year and immersed in water for 5 h or 24 h further, their solubility did not change, with  $M_n$  and  $M_w$  slightly decreased. They all showed good hydrolytic stability in storage.

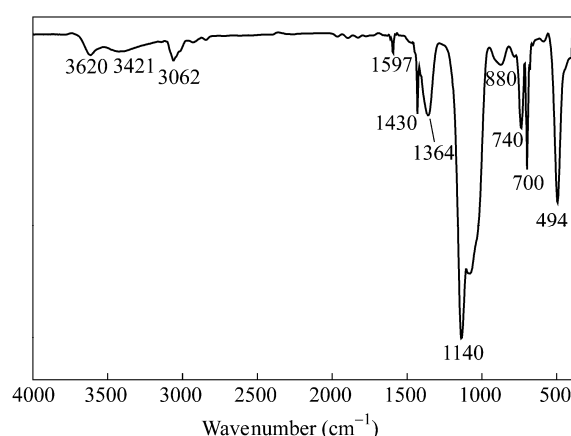
**Table 1.** Molecular weight, char yield and hydrolytic stability of PBSis synthesized at different conditions

| PBSis <sup>a</sup> | Synthesis temperature (time)                    | GPC determination <sup>b</sup> | $M_n$ (GPC) | $M_w$ (GPC) | $M_w/M_n$ (GPC) | Area ratio (%) (GPC) | Char yield at 800 °C (%) |
|--------------------|-------------------------------------------------|--------------------------------|-------------|-------------|-----------------|----------------------|--------------------------|
| PBSi-1             | 150 °C (3 h)                                    | I                              | 3673        | 9228        | 2.51            | 75.91                | 74.13                    |
|                    |                                                 |                                | 911         | 987         | 1.08            | 24.09                |                          |
|                    |                                                 | II                             | 3608        | 9276        | 2.57            | 77.12                |                          |
|                    |                                                 |                                | 896         | 1236        | 1.38            | 22.88                |                          |
|                    |                                                 | III                            | 3592        | 9051        | 2.52            | 77.02                |                          |
|                    |                                                 |                                | 786         | 881         | 1.28            | 22.98                |                          |
|                    |                                                 | IV                             | 3382        | 8943        | 2.64            | 77.61                |                          |
|                    |                                                 |                                | 711         | 869         | 1.22            | 22.39                |                          |
| PBSi-2             | 90 °C (1.5 h),<br>110 °C (1 h),<br>150 °C (3 h) | I                              | 1600        | 3912        | 2.44            | 100                  | 72.69                    |
|                    |                                                 | II                             | 1589        | 3899        | 2.45            | 100                  |                          |
|                    |                                                 | III                            | 1580        | 3839        | 2.43            | 100                  |                          |
|                    |                                                 | IV                             | 1520        | 3812        | 2.51            | 100                  |                          |

<sup>a</sup> H<sub>3</sub>BO<sub>3</sub>:PTMOS molar ratio = 1:2; in 10 mL of diglyme

<sup>b</sup> GPC determination: I, after preparation of PBSis; II, after 1 year; III, after 1 year and immersed in water for 5 h; IV, after 1 year and immersed in water for 24 h

The FTIR spectrum of PBSi-1 is shown in Fig. 1. The absorption peaks at 3421 and 3620 cm<sup>-1</sup> were assigned to the stretching vibration of the remaining B—OH groups. These —O—H signals in Fig. 1 were very weak. It indicated that most of H<sub>3</sub>BO<sub>3</sub> had participated in the polycondensation and was connected into the polymers with a little amount of B—OH groups left. These PBSis prepared without catalyst were obviously different from those obtained in the presence of catalyst. Packirisamy *et al.*<sup>[12]</sup> had reported PBSis synthesized at the same H<sub>3</sub>BO<sub>3</sub>/PTMOS molar ratio under the catalysis of aqueous HCl, whose IR spectra showed a very big and broad —O—H stretching vibration peak belonging to B—OH or Si—OH groups. Water added along with aqueous HCl resulted in serious hydrolysis of Si—OCH<sub>3</sub> to Si—OH groups, and many free B—OH and Si—OH groups were still left in those PBSis. In Fig. 1, the peak at 1140 cm<sup>-1</sup> was due to  $\nu$  (Si—O—Si) linkages, which were formed from the condensation between CH<sub>3</sub>O—Si— and HO—Si groups. The HO—Si groups might be formed from the hydrolysis of CH<sub>3</sub>O—Si— groups. Moisture or water formed from self condensation of boric acid caused the hydrolysis. The peaks at 1430 and 1364 cm<sup>-1</sup> corresponded to  $\nu$  (B—O) bonds in the B—O—B and B—O—Si linkages, respectively<sup>[2, 10, 26–28]</sup>. The peaks at 880 and 700 cm<sup>-1</sup> were due to  $\nu$  (Si—O—B) and  $\delta$  (Si—O—B) bridges. The peaks at 3062 and 1597 cm<sup>-1</sup> corresponded to  $\nu$  (H—C) and  $\nu$  (C=C) bonds in the phenyl groups.

**Fig. 1** FTIR spectrum of PBSi-1

The <sup>1</sup>H-NMR spectrum of PBSi-1 is shown in Fig. 2. The signals at  $\delta$  = 2.06, 3.63 and 7.28 belonged to the hydrogens in —B—OH (1), —OCH<sub>3</sub> (2) and phenyl groups (3), respectively. The peak corresponded to the

—OCH<sub>3</sub> groups was very weak. It meant that CH<sub>3</sub>O—Si groups had almost taken part in the polycondensation and were connected into PBSi through B—O—Si or Si—O—Si linkages. Diglyme was directly used as solvent without purification. It is soluble in water and may contain some moisture. Although PBSi was prepared at H<sub>3</sub>BO<sub>3</sub>:PTMOS molar ratio of 1:2, moisture in the solvent or from air and water formed from self condensation of BA caused the hydrolysis of CH<sub>3</sub>O—Si— to HO—Si groups, which reacted with other CH<sub>3</sub>O—Si— groups further to form Si—O—Si linkages. Si—O—Si linkages were very stable and feasible to be formed. The CH<sub>3</sub>O—Si— groups were almost consumed to react with HO—Si and B—OH groups, with Si—O—Si as well as B—O—Si linkages formed. So, few of CH<sub>3</sub>O—Si— groups were left in the PBSi prepared.

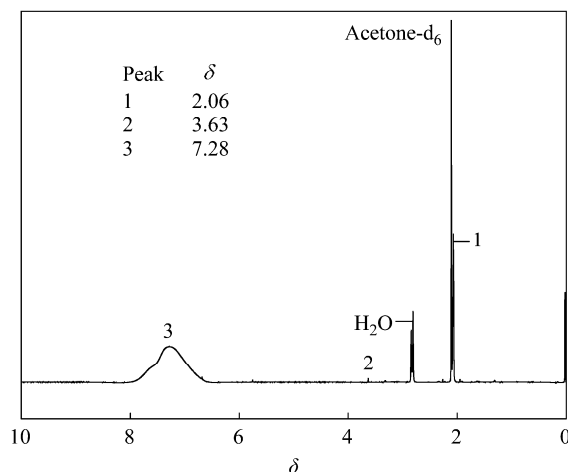
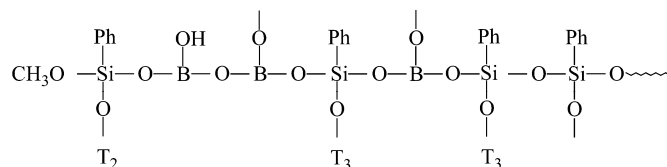


Fig. 2 <sup>1</sup>H-NMR spectrum of PBSi-1

The <sup>29</sup>Si-NMR spectrum of PBSi-1 is given in Fig. 3. Packirisamy *et al.*<sup>[12]</sup> studied in detail the <sup>29</sup>Si-NMR spectra of borosiloxane oligomers and assigned the chemical shifts to the structural units: T<sub>1</sub>, T<sub>2</sub> and T<sub>3</sub>. The T<sub>n</sub> denoted the unit structures of RSi(OSi)<sub>n</sub>(OR')<sub>3-n</sub> or RSi(OB)<sub>n</sub>(OR')<sub>3-n</sub> (n = 0–3). The Si—O—Si and Si—O—B bonds did not differ in their <sup>29</sup>Si-NMR chemical shifts. In Fig 3, the signals at  $\delta = -71.22$  and  $-78.58$  were assigned to T<sub>2</sub> and T<sub>3</sub> structures, respectively. It meant that the reaction of CH<sub>3</sub>O—Si groups was almost complete and there was no T<sub>1</sub> structure in the PBSi-1.

Packirisamy *et al.*<sup>[12]</sup> synthesized PBSis under the catalysis of aqueous HCl, whose <sup>11</sup>B-NMR spectra showed a strong signal at  $\delta = 20.89$  or  $20.91$ . Boric acid gave a signal at  $\delta = 19.6$ <sup>[10, 26]</sup>. Figure 4 showed the <sup>11</sup>B-NMR spectrum of PBSi-1 prepared without any catalyst. A signal at  $\delta = 20.15$  was found. From this observation, we suggested that chemical shifts of boron atoms were in the structural units like —B(OH)—O—B(OSi)—O or Si—O—B(OH)—O—Si. The reason maybe was that the PBSi was synthesized here in the absence of aqueous HCl, polycondensation between BA and PTMOS resulted in B—O—Si linkages. Meanwhile, reaction at 150 °C also led to self-condensation of BA, and some B—O—B linkages were formed. The borons in the B—O—B—O—Si and Si—O—B—O—Si linkages may have close environments, so they had the same chemical shift.

On the basis of the above analyses, the major polymer structure of PBSis was shown as follows:



The char yield of PBSi-1 was characterized by thermogravimetric analyses, and the result is shown in Fig. 5. PBSi-1 had high char yield. The TGA curve showed that the temperature at 5% weight loss (T<sub>5%</sub>) was

406 °C, and its char yield at 800 °C in N<sub>2</sub> was 74.13%. In the temperature range from room temperature to 450 °C, the weight loss was just about 6%. It was mainly caused by the release of small molecules such as water or methanol formed from the condensation of the remaining HO—B and CH<sub>3</sub>O—Si groups. As the amount of these groups was small, the weight loss in this period was small. After that, weight loss increased obviously from 450 °C to 710 °C, which was mainly caused by the loss of organic groups like phenyl groups at high temperatures.

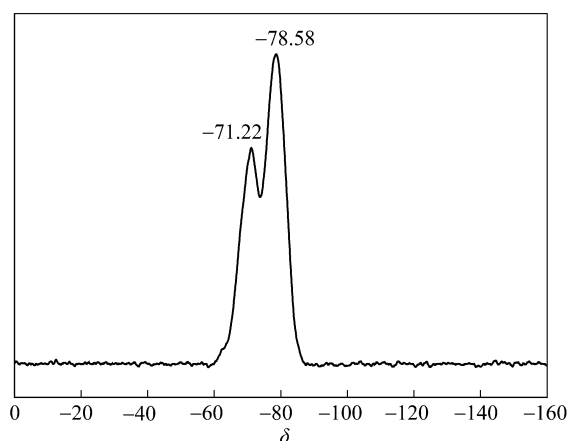


Fig. 3 Solid <sup>29</sup>Si-NMR spectrum of PBSi-1

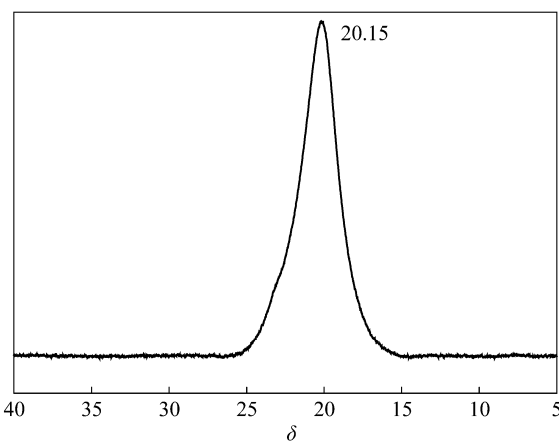


Fig. 4 <sup>11</sup>B-NMR spectrum of PBSi-1

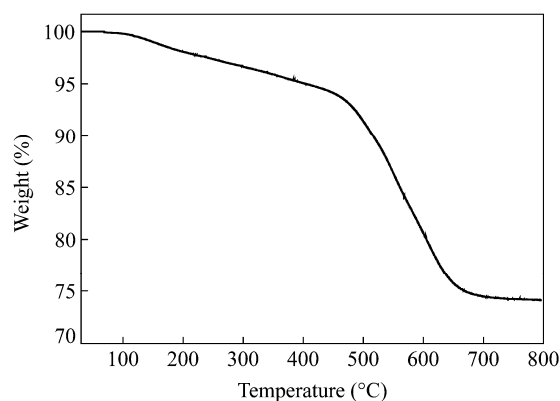


Fig. 5 The TGA curve of PBSi-1

#### Properties of the PBSi Modified PF Resins

PBSi-1 was mixed with PF resin in ethyl acetate at room temperature to form a uniform mixture solution. The PBSi modified PF resins named PBSi/PF-1, PBSi/PF-2 and PBSi/PF-3 were prepared at PBSi-1/PF mass ratios of 0.2:1, 0.4:1 and 0.6:1, respectively. They were used as adhesives to bond stainless steel plates and were cured at 150 °C for 4 h. Figure 6 shows the FTIR spectra of the cured PBSi/PF-1, PBSi/PF-2, PBSi/PF-3 and that of the common PF. In the IR spectrum of cured PF, the wide absorption peak at 3432 cm<sup>-1</sup> was assigned to the phenolic hydroxyl and the benzyl hydroxyl. The peak at 2911 cm<sup>-1</sup> corresponded to C—H stretching vibration of —CH<sub>2</sub>— groups. The peaks at 1600 cm<sup>-1</sup> and 1476 cm<sup>-1</sup> corresponded to the benzene ring skeleton C=C stretching vibration and the asymmetrical  $\delta$ (C—H) of —CH<sub>2</sub>— groups. The peak at 1050 cm<sup>-1</sup> corresponded to C—O stretching vibration of ether groups. This indicated that a large number of crosslinked structures had formed in the cured PF<sup>[29]</sup>. In the FTIR spectra of the cured PBSi/PF-1, PBSi/PF-2 and PBSi/PF-3, besides the absorption peaks of PF, new peaks at 1430, 1355, 1140 and 700 cm<sup>-1</sup> appeared, which corresponded to  $\nu$ (B—O) bonds in B—O—B and B—O—Si linkages, as well as  $\nu$ (Si—O—Si) and  $\delta$ (Si—O—B) bridges, respectively. This indicated the formation of PBSi/PF blends.

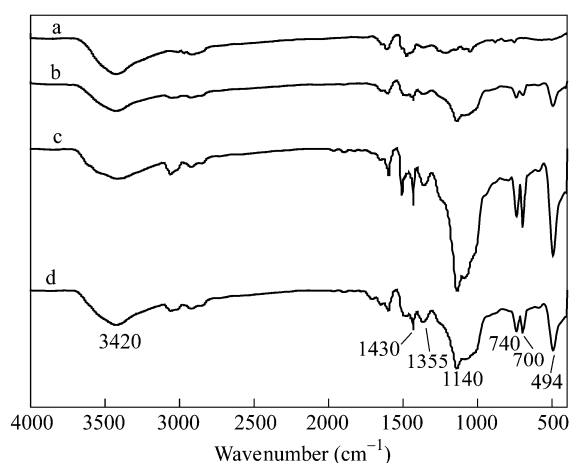


**Fig. 6** FTIR spectra of cured (a) PF, (b) PBSi/PF-1, (c) PBSi/PF-2 and (d) PBSi/PF-3

Figure 7 shows the fracture morphologies of the cured blends. The fracture surface of pure PF (Fig. 7a) was very smooth, but that of PBSi/PF blends (Figs. 7b, 7c and 7d) were rough. The cured PBSi/PF blends formed separated PBSi and PF phases. All the PBSi/PF blends in this study were heterogeneous. The PBSi phases were wrapped in PF phase and formed sea-islands structure. The reason might be that PBSis were prepared from PTMOS with less amount of BA. PBSis were surrounded by a lot of phenyl groups with little amount of B—OH groups left. PF had polar structure but PBSis didn't. Although they dissolved each other and formed a homogeneous phase in the presence of ethyl acetate before cured, after curing, difference of their polarity led to phase separation in microphotographs.

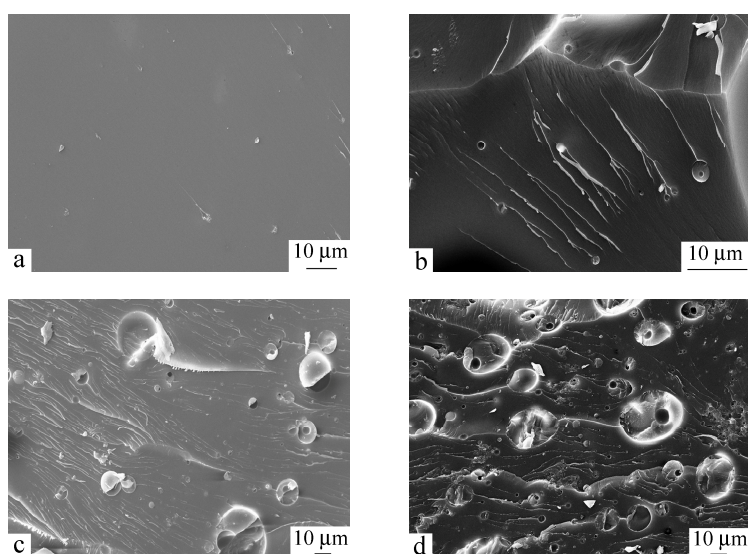


**Fig. 7** SEM morphologies of the fracture surface of cured (a) PF, (b) PBSi/PF-1, (c) PBSi/PF-2 and (d) PBSi/PF-3

The tensile testing data of cured PF and PBSi/PFs are shown in Table 2. The pure PF had tensile strength of 4.64 MPa, and PBSi/PF-1, PBSi/PF-2 as well as PBSi/PF-3 had tensile strength of 5.29, 4.57 and 4.28 MPa, respectively. The PBSi/PFs had similar tensile strength to PF, and PBSi/PF-1 had the highest. The major influencing factors on the fracture include the morphology of the blends, the amount of the modifier and the interfacial adhesion between the phases<sup>[30]</sup>. As PBSi/PF mass ratio increased from 0.2:1 to 0.6:1, the tensile strength of PBSi/PFs decreased. The reason might be that PBSi had obviously different polarity from PF. The

cured PBSi/PFs formed more obvious phase separation as the PBSi amount increased. Meanwhile, the PBSi had little amount of B—OH or CH<sub>3</sub>O—Si groups left to react with PF and form interfacial bonds between different phases. So the tensile strength decreased with the increase of PBSi/PF mass ratio. From Table 2, it was found that the pure PF had elongation at break of 5.70%, and the PBSi/PF-1, PBSi/PF-2 and PBSi/PF-3 had elongation at break of 5.61%, 4.70% and 4.43%, respectively. The elongation at break of the PBSi/PFs was slightly lower than that of pure PF. Introduction of PBSi into PF decreased the toughness of the blends. PBSi/PFs had sea-island morphologies and were lack of strong interfacial bonding between different phases, so increasing PBSi/PF mass ratios led to the decrease of toughness slightly.

**Table 2.** TGA<sup>a</sup> and tensile testing data of cured PF and PBSi/PF blends

| Adhesives | PBSi-1:PF<br>(mass ratio) | $T_{5\%}$<br>(°C) | Char yield at 800 °C<br>(%) | Tensile strength<br>(MPa) | Elongation at break<br>(%) |
|-----------|---------------------------|-------------------|-----------------------------|---------------------------|----------------------------|
| PF        | 0:1                       | 354               | 64.95                       | 4.64                      | 5.70                       |
| PBSi/PF-1 | 0.2:1                     | 345               | 66.19                       | 5.29                      | 5.61                       |
| PBSi/PF-2 | 0.4:1                     | 362               | 70.83                       | 4.57                      | 4.70                       |
| PBSi/PF-3 | 0.6:1                     | 339               | 65.95                       | 4.28                      | 4.43                       |

<sup>a</sup> Heating rate at 10 K/min in N<sub>2</sub> atmosphere

The char yields of PF and PBSi/PF blends were characterized through thermogravimetric analysis. The TGA curves of cured PF and PBSi/PF-1, PBSi/PF-2, PBSi/PF-3 are shown in Fig. 8. The  $T_{5\%}$  and the end mass loss were summarized in Table 2. The  $T_{5\%}$  of PF was 354 °C, and its char yield at 800 °C in N<sub>2</sub> was 64.95%. PBSi had higher char yield. Its  $T_{5\%}$  and char yield were 406 °C and 74.13%, respectively. By introducing some PBSi into PF (e.g. PBSi/PF-1, PBSi/PF-2, PBSi/PF-3), the char yields of them reached to 66.19, 70.83 and 65.95% respectively at 800 °C in N<sub>2</sub>, which were higher than that of PF but lower than that of PBSi. The PBSi/PF-2 had the highest char yield. As the PBSi amount increased from PBSi/PF mass ratio of 0.2 to 0.4, the char yield increased, because the char yield of PBSi was higher than that of PF. But increasing PBSi/PF mass ratio further to 0.6 led to the decrease of char yield like PBSi/PF-3. The reason maybe was that PBSis had different residue forming mechanism from PF. The PBSis formed final residue through formation of oxide ceramics, but PF through formation of graphitizing carbon. Introduction of too much PBSi might hamper the graphitizing of PF. It made the weight loss of the PF phase increased, so the char yield of PBSi/PF-3 with PBSi/PF mass ratio of 0.6 became lower than that of PBSi/PF-2. In Fig. 8, the thermal decomposition process of PBSi/PF was divided into two stages. In the temperature range from room temperature to 450 °C, PBSi/PFs had TGA curves similar to PF with weight loss less than 10%. Deepening crosslinking reaction and forming small molecules like water caused weight loss in this period. After that, weight loss increased obviously from 450 °C to 800 °C, which was mainly caused by the loss of organic groups like phenyl groups at high temperatures.

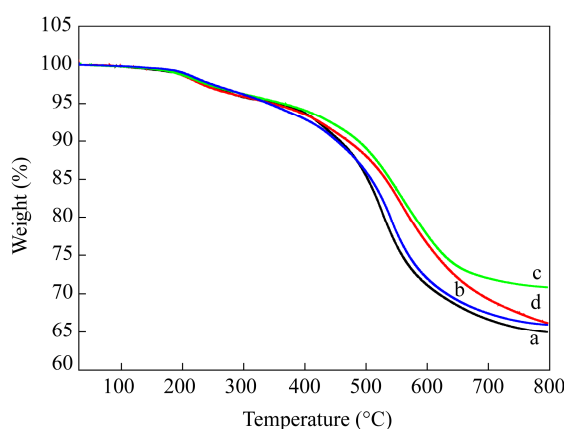


**Fig. 8** TGA curves of cured (a) PF, (b) PBSi/PF-1, (c) PBSi/PF-2 and (d) PBSi/PF-3

Introducing higher amount of PBSi in PBSi/PF-3 hampered the graphitizing of PF phase, so more organic groups like benzene rings were released as organic components and the char yield of PBSi/PF-3 decreased. Even so, PBSi/PFs still had higher char yields than pure PF.

The ceramization of PBSi/PFs was also conducted at 800 °C using TGA under N<sub>2</sub>. Figure 9 shows the FTIR spectra of the SiBOC ceramics obtained. The peak at 3434 cm<sup>-1</sup> corresponded to  $\nu$  (H—O) vibration. Peak at 1600 cm<sup>-1</sup> corresponded to  $\nu$  (C=C) vibration. Peaks at 1400, 1060 and 880 cm<sup>-1</sup> corresponded to  $\nu$  (B—O),  $\nu$  (Si—O—Si) and  $\nu$  (B—O—Si) vibrations, respectively. The peak at 800 cm<sup>-1</sup> corresponded to  $\nu$  (C—Si) vibration. Elemental analysis of the SiBOC ceramics is shown in Table 3. The ceramics consisted of Si, B, O and C elements. Formation of SiBOC ceramics was confirmed. High amount of C element was due to the graphitization of PF.

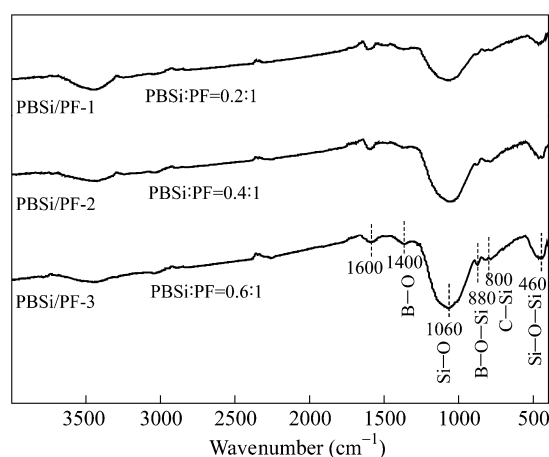


Fig. 9 FTIR spectra of the SiBOC ceramics formed through pyrolysis of PBSi/PFs at 800 °C under N<sub>2</sub>

**Table 3.** Elemental analysis of the SiBOC ceramics obtained at 800 °C under N<sub>2</sub>

| PBSi/PFs  | Composition (wt%) |      |       |       | Empirical formula                                       |
|-----------|-------------------|------|-------|-------|---------------------------------------------------------|
|           | Si                | B    | O     | C     |                                                         |
| PBSi/PF-1 | 17.52             | 1.24 | 21.46 | 59.79 | SiB <sub>0.18</sub> O <sub>2.12</sub> C <sub>6.83</sub> |
| PBSi/PF-2 | 20.61             | 1.81 | 20.76 | 56.82 | SiB <sub>0.21</sub> O <sub>1.78</sub> C <sub>6.48</sub> |
| PBSi/PF-3 | 23.81             | 1.77 | 18.40 | 56.02 | SiB <sub>0.19</sub> O <sub>1.35</sub> C <sub>5.49</sub> |

## CONCLUSIONS

Two polyborosiloxanes were synthesized by the direct polycondensation of boric acid with phenyltrimethoxysilane in diglyme without any catalyst. Characterization showed that PBSis obtained was constructed with B—O—B, B—O—Si and Si—O—Si linkages. PBSis had char yield up to 74.13% at 800 °C under N<sub>2</sub>. By introducing PBSi into common PF, PBSi/PF blends were formed. The cured PBSi/PFs had sea-island morphology, similar tensile strength to PF, and higher char yields than common PF. Among them, the PBSi/PF-2 with PBSi/PF mass ratio of 0.4:1 had char yield up to 70.83% at 800 °C. SiBOC ceramics were formed by ceramization of PBSi/PFs at 800 °C under N<sub>2</sub>. This method provided a valuable way to prepare easily shapeable polymeric ceramic precursors from polyborosiloxanes.

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