Thermal Stability and Mechanical Property of Vinyl-Functionalized Polyborosiloxane and Silicone Rubber

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Abstract. In this study, under solvent-free condition, the vinyl-functionalized polyborosiloxane (BSiO Vi) was synthesized by reacting triethoxyvinylsilane (VTEOS) and boric acid (BA) and the chemical structures were characterized by GPC and FT-IR. The results indicated that the BSiO Vi containing Si-O-B bonds and vinyl groups was successfully synthesized. Moreover, the thermal stability and compressive strength after heat treatment were studied. TG-DTG result indicated that the BSiO Vi with more Si-O-B high energy bonds possessed the better thermal stability than that of silicone rubber only possessing Si-O-Si bonds. The results of mechanical property of BSiO Vi showed that the BSiO Vi after heat treatment possessed the higher compressive strength than that of silicone rubber. This is because that the polymerization of Si-CH=CH 2 groups could improve the crosslinking density, and the ceramic transformation of BSiO Vi after heat treatment tend to the formation of dense SiBOC nanocomposites. We believed that the BSiO Vi could be effectively served high temperature resistant matrix resin for ceramic matrix.

1. Introduction
In present study, under solvent-free condition, the vinyl-functionalized polyborosiloxane (BSiO Vi) is prepared with low reaction temperature and short reaction time by aqueous sol-gel method. The silicone rubber is prepared by vinyl silicone oil (vinyl content=0.06%), vinyl MQ silicone resin (vinyl content=0.98%) and hydrogenated silicone oil (hydrogen content=0.77%) under the catalysis of Pt. The monomer structure is characterized by a HW-2000 Gel permeation chromatography (GPC) and the Fourier transform infrared spectroscopy (FT-IR). Moreover, the compressive strength and thermal stability of BSiO Vi and silicone rubber after different heat treatment temperature are compared.

2. Experimental

2.1. Synthesis of BSiO Vi
Typical experiment process, 0.2 mol triethoxyvinylsilane (VTEOS) and 0.1 mol boric acid (BA) are taken in a three necked round bottom flask under the catalysis of HCl in nitrogen atmosphere. The mixtures keep continuous mechanical stirring in oil bath at 80 °C for 0.5 hour. Then, the mixtures are cooled to 25 °C. A small amount of borate ester and almost ethanol acted as the by-products, is distilled off by flash evaporation method. Finally, the transparent yellow liquid resin, labeled as BSiO Vi, is obtained. The yellow liquid BSiO Vi is provided for GPC and FT-IR testing. The solid BSiO Vi cured at 100 °C for 12 h is used for TGA analysis and mechanical performance test.

2.2. Preparation of Silicone Rubber
A certain amount of vinyl silicone oil and vinyl MQ resin is putted in dispersion machine for 10 min at a room temperature. Then, a certain quality of hydrogenated silicone oil, catalyst and inhibitor are
poured into the above mixture and keep stirring for 2 min. Finally, the mixtures are poured into a PTFE mould and remove bubbles under reduced pressure condition. Finally, the mixtures are cured at room temperature for 24 h. thus, the silicone rubber is obtained. The mass ratio of vinyl silicone oil, vinyl MQ resin and hydrogenated silicone oil is 75:20:5.

3. Results and Discussion

3.1. Characterization of BSiO\textsuperscript{Vi}

Fig 1 (a) showed the molecular weight data and GPC curves of BSiO\textsuperscript{Vi}. For BSiO\textsuperscript{Vi}, it could be seen that the high molecular weight peak appears at 8.5-9.5 min; the low molecular weight peak of BSiO\textsuperscript{Vi} appears at 9.5-10 min. The major molecules of BSiO\textsuperscript{Vi} contribute to the high molecular weight peak in GPC curve. The low molecular weight peak for BSiO\textsuperscript{Vi} is attributed to the borate ester, which is formed by the reaction between -OC\textsubscript{3}H\textsubscript{3} and B-OH and/or oligomeric fractions [1, 3]. Moreover, the area ratio of BSiO\textsuperscript{Vi} between high molecular weight and low molecular weight is about 1:0.31. Interestingly, the molecular weight for BSiO\textsuperscript{Vi} that synthesized under solvent-free condition is larger than that of resins synthesized under solvent condition [2]. The result indicates that the existence of solvents has a significant effect on the molecular weight during reaction process for BSiO\textsuperscript{Vi}. Under solvent-free system, it is easier for the reactants to form the higher molecular weight polymers than that of solvent system. Fig 1 (b) showed the FT-IR spectra of BSiO\textsuperscript{Vi}. The bonds appeared at 1080 cm\textsuperscript{-1} (Si-O) and 762 cm\textsuperscript{-1} (Si-O-Si) is related to Si-O bonds [3]. The appearance of Si-O-Si bonds indicates that the BSiO\textsuperscript{Vi} contains siloxane linkages in its body. The bonds appeared at 1601 cm\textsuperscript{-1} is related to C=C bonds and the peak appeared at 1278 cm\textsuperscript{-1} are attributed to the C-C bonds, which suggest that the existence of C=C groups in BSiO\textsuperscript{Vi} [1]. The peak at 2980 cm\textsuperscript{-1} (C-H) and 968 cm\textsuperscript{-1} (C-H) indicate that the BSiO\textsuperscript{Vi} resin also contains unreacted ethoxy groups. Moreover, the peaks appeared at 1406 cm\textsuperscript{-1} (B-O) are attributed to the B-O bonds. The peaks appeared at 3222 cm\textsuperscript{-1} is related to the B-OH groups [4-7]. The absorptions appeared at 884 cm\textsuperscript{-1} and 673 cm\textsuperscript{-1} is related to the Si-O-B and Si-O-B bonds. Based on the above results, it can be known that the Si-O-Si, Si-O-B, B-OH and unreacted ethoxy bands exist in BSiO\textsuperscript{Vi}.

![Figure 1. Characterizations of BSiO\textsuperscript{Vi} by (a) GPC and (b) FT-IR curves.](image)

3.2. Thermal Stability of BSiO\textsuperscript{Vi} and Silicone Rubber

Fig 2 (a) and (b) showed the TG-DTG results of BSiO\textsuperscript{Vi} and silicone rubber, respectively. The DTG curves of BSiO\textsuperscript{Vi} showed in Fig 2 (a) indicate that the existence of two degradation stages during pyrolysis process. The initial degradation temperature for BSiO\textsuperscript{Vi} is 141 °C; the 5 wt.% weight loss is about 256.4 °C and 10 wt.% weight loss is about 507.3 °C. The first degradation stage appears from 140 °C to 380 °C and the weight loss is about 7.25wt.%. The second degradation appears from 380 °C to 700 °C and the weight loss is about 9.64wt.%. Moreover, the residual mass of BSiO\textsuperscript{Vi} at 800°C is

| Rank | Mw | Mp | Mn | PDI | Area (%) |
|------|----|----|----|-----|---------|
| Area-I | 1845 | 1267 | 1572 | 1.17 | 76.2 |
| Area-II | 710 | 714 | 689 | 1.02 | 23.8 |

- **Figure 1.** Characterizations of BSiO\textsuperscript{Vi} by (a) GPC and (b) FT-IR curves.
about 82.4%. The two degradation stages of polymer indicate that the two different kinds of degradation mechanisms occur during the pyrolysis process. The weight loss of low molecular products, such as water and ethanol formed by the -OC₂H₅ groups and residual -OH, related to the first degradation stage [8]. The weight loss of low molecular weight hydrocarbons and hydrogen is due to the decomposition of the BSiO₆ molecular main chains, which contributed to the occurrence of the weight loss of the second degradation stage [9-11]. For silicone rubber, as shown in Figure 2(b), the initial degradation temperature is about 340 °C and the residual weight at 800 °C is only 11.4%. This is due to the lack of high-energy chemical bonds, because the silicone rubber only possesses the Si-O-Si bonds in its molecular backbone. However, the BSiO₆ possesses large amount of Si-O-B bonds in its molecular. The bond energy of Si-O bond is 422.5 KJ/mol and the B-O bond is about 537.6 KJ/mol. Thus, the BSiO₆ with more Si-O-B bonds possess better thermal stability. Moreover, the silicone containing boron can convert into siliconboronoxycarbide (SiBOC) ceramics nanocomposites. [1] Thus, the BSiO₆ possesses the higher residual mass than that of silicone rubber.

![Figure 2. TGA analysis of (a) BSiO₆ and (b) silicone rubber.](image)

3.3. Compressive Strength
The mechanical property of BSiO₆ and silicone rubber after different heat treatment are showed in Fig 3. All samples are kept at 100 °C, 400 °C and 800 °C for 2 h, respectively. It can be seen that the BSiO₆ possesses the better mechanical property than that of silicone rubber after heat treatment by high temperature. The maximum value of these two kinds of samples appears at 100 °C, which is contributed to the good thermal stability of silicone containing materials. However, with the increase of the heat treatment temperature, the compressive strength of silicone rubber decreases sharply. This is because that the main chains of silicone rubber molecule are thermally decomposed, which lead to the reduce of structural strength. As for BSiO₆, the compressive strength doesn’t decline significantly. It can be seen that the compressive strength still remains at 3.8MPa while the heat treatment temperature increase to 800 °C. The high compressive strength after heat treatment may be caused by the polymerization of vinyl groups during heat treatment process, which contributed to the increasing of crosslinking density [2]. From the result of TGA test, it can be concluded that the weight loss of the low molecular weight products is attributed to the small molecule products, water and ethanol, which are formed by the reactions between -OH and -OC₂H₅ groups in BSiO₆ before 400 °C. The first degradation stage of BSiO₆ can lead to the increase of crosslinking density for polymer matrix. The occurrence of Si-CH=CH₂ groups polymerization can further improve the crosslinking density of BSiO₆. The high crosslinking density will contribute to the high mechanical strength. Moreover, the formation of dense SiBOC nanocomposite caused by ceramic transformation of BSiO₆ after heat treatment may also promote this result. [1, 2].
4. Conclusion
In this work, under solvent-free condition, the BSiOVi was prepared. The BSiOVi was characterized by GPC and FI-IR. The GPC results showed that the high molecular weight polymers were easier formed under solvent-free system than that of solvent system. The FT-IR result indicated that the Si-O-Si, Si-O-B, B-OH and unreacted ethoxy groups were existed in BSiOVi. The TGA result indicated that the BSiOVi with more Si-O-B bonds possess better thermal stability than that of silicone rubber only possessing Si-O-Si bonds. Moreover, the results of compressive strength of BSiOVi and silicone rubber after different heat treatment indicated that the polymerization of Si-CH=CH2 groups will improve the crosslinking density, and the ceramic transformation of BSiOVi after heat treatment tend to form the dense SiBOC nanocomposites. Thus, the BSiOVi after heat treatment possessed the higher compressive strength than that of silicone rubber.

5. References
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