Preparation of heat resistant boron-containing phenyl silicone oil and its initial degradation mechanism in air

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Abstract
Boron-containing phenyl silicone oil (BCPSO) with terminal boronic hydroxyl groups was synthesized by acid-catalyzed balance condensation polymerization using phenylboric acid, dimethylchlorosilane and diphenylchlorosilane as raw materials. The structure of BCPSO was characterized by 1H, 13C and 29Si nuclear magnetic resonance (NMR) and Fourier transform infrared spectrometry (FTIR). The thermal degradation behavior of BCPSO was tested by thermogravimetry-Fourier transform infrared spectrometry (TG-FTIR) analysis. The TG-FTIR results indicated that thermal decomposition of BCPSO had significant hysteresis over that of phenyl silicone oil. The empty electron orbital of boron atom could accept electron of peroxide free radical to generate conjugation effect at initial degradation stage of BCPSO, and this phenomenon was confirmed by 11B NMR, FTIR and Raman spectroscopies. As a result, temporarily stable intermediate was formed which increased the heat resistant of BCPSO.

1. Introduction
Phenyl silicone oil has good heat resistance and its oxidative degradation occurs only at temperatures above 250 °C [1]. With increase of phenyl mole fraction, high steric hindrance of phenyl group hinders breaking of Si-O skeleton, which greatly improves heat resistance of phenyl silicone oil [2]. However, high phenyl content causes phenyl silicone oil to lose fluidity, and it is impossible to increase heat resistance of phenyl silicone oil by merely increasing the content of phenyl group. Deshpande et al [3] used 29Si NMR to analyze pyrolyzed phenyl-containing polysiloxane copolymers and found that phenyl content influenced degradation of polysiloxane copolymers. Zhou et al [4] found that initial thermal stability of phenyl-containing polysiloxane began to fall in air when phenyl content exceeded 50%.

Introduction of boron, nitrogen and phosphorus into main chain can improve the heat resistance of phenyl silicone oil. Devapal et al [5] synthesized borosiloxane oligomers through condensation of boric acid with phenyltrimethoxysilane (PTMOS) and phenyltriethoxysilane, 5% mass loss temperature (Td5) in air was more than 500 °C. Chen et al [6] used small amount of platinum catalyst and aminopropyltriethoxysilane to improve thermal stability of silicone rubber. The 10% mass loss temperature (Td10) and residue at 900 °C in air were 473 °C and 68 wt%, respectively. Januszewski et al [7] synthesized polydimethylsiloxanes by using biphenyl phosphates, and subsequently cross linked with 1,1,3,3-tetramethyldivinylsiloxane. The Td10 and residue at 900 °C of functionalized silicone rubber in air were 358 °C and 41.2 wt%, respectively. The bond energy of B–O bond (537.6 kJ mol⁻¹) is much higher than that of Si–O bond (422.5 kJ mol⁻¹) [8], which made thermal decomposition of polyborosiloxane at higher temperature. Gao et al [9] synthesized a series of borosiloxane/polybenzoxazine hybrids. The Td5 of hybrid polymers were higher than 400 °C in air. Mosurkal et al [10] synthesized polyborosiloxanes with aminopropyl-terminated polydimethylsiloxane, phenylboronic acid and 4,4′-oxydiphthalic anhydride. The 20% mass loss temperature (Td20) in air was 431 °C.

The mechanism of thermal degradation of ordinary silicone oil in air has been extensively studied. Free radical oxidation decomposition and rearrangement degradation mechanism have been proposed [11–13]. The principle of rearrangement degradation is to form oligomeric rings after thermal fracture of the Si-O-Si main...
The methyl, phenyl or vinyl side chains of polysiloxane are easily oxidized to peroxides in air at high temperature, which result in free radical degradation \cite{14}. Camino et al \cite{15} found that polydimethylsiloxane thermally decomposed to cyclic oligomers through Si–O bond scission in a chain-folded cyclic conformation energetically favored by overlapping of empty silicon d-orbitals with orbitals of oxygen and carbon atoms. The oligomers produced by the thermal decomposition of polysiloxanes varied greatly with different heating rates. However, there are few reports on the thermal decomposition of polyborosiloxane in air.

In this work, heat resistant boron-containing phenyl silicone oil (BCPSO) was synthesized by one-pot balance condensation polymerization using phenylboronic acid, dimethyldichlorosilane and diphenyldichlorosilane as raw materials. And we propose to research initial thermal decomposition mechanism of BCPSO in air. The results indicated that empty electron orbital of boron atom could accept electron of peroxide free radical to generate conjugation effect at initial degradation stage of BCPSO, thermal decomposition of BCPSO had significant hysteresis over that of phenyl silicone oil.

### 2. Experimental

#### 2.1. Materials

Phenylboronic acid (PBA) was of analytical grade and supplied by Sigma-Aldrich Co. LLC. Dimethyldichlorosilane, diphenyldichlorosilane and diethylene glycol dimethyl ether were of analytical grade and purchased from Aladdin Industrial Corporation (China). Absolute ethanol, sulfuric acid and sodium carbonate were of analytical grade and obtained from Sinopharm Chemical Reagent Co. Ltd, (China). All reagents were used as received without any further purification.

#### 2.2. Synthesis of BCPSO

The synthesis route of BCPSO was shown in scheme 1. A certain amount of PBA (table 1) was dissolved by 100 ml diethylene glycol dimethyl ether. The solution was poured into a 250 ml three-necked flask fitted a reflux condenser and a mechanical stirrer, and 20 ml 60 wt% concentrated sulfuric acid was added as catalyst. Mixed silane (218.75 mmol dimethyldichlorosilane and 31.25 mmol diphenyldichlorosilane) were added dropwise through a dropping funnel at 60 °C, and the reaction continued for 2 h. Then reaction solution was warmed up to 120 °C and reacted for 2.5 h. The solution cooled to room temperature and poured into a separator funnel to

### Table 1. Sample formulation and its average molecular mass.

| Sample      | Phenyl silicone oil | BCPSO-1 | BCPSO-2 | BCPSO-3 |
|-------------|---------------------|---------|---------|---------|
| PBA (mmol)  | 0                   | 20.83   | 25      | 31.25   |
| Molar ratio of PBA to mixed silane | —       | 1:12    | 1:10    | 1:8     |
| Mn (g mol⁻¹) | 6460               | 6654    | 7011    | 7325    |
| Mw (g mol⁻¹) | 8905               | 9405    | 9638    | 9956    |
| Mw/Mn       | 1.38               | 1.41    | 1.38    | 1.35    |
separate oil phase and aqueous phase. The saturated sodium carbonate solution was slowly added to oil phase to adjust the pH value to 7, and then oil phase was washed with 100 ml absolute ethanol three times each. Finally, the oil was dried by vacuum oven at 70°C for 12 h. Phenyl silicone oil was synthesized by the same method without introducing PBA.

2.3. Characterization

2.3.1. Nuclear magnetic resonance spectroscopy (NMR)

$^1$H, $^{13}$C, $^{29}$Si and $^{11}$B NMR spectra of samples were recorded by using deuterochloroform (CDCl$_3$) as solvent on VNMR600 (Agilent, USA). The $^1$H, $^{13}$C and $^{29}$Si NMR spectra of samples were obtained using tetramethylsilane as a chemical shift reference compound and the $^{11}$B spectrum of sample was obtained using boron trifluoride etherate an external standard.

2.3.2. Fourier-transform infrared spectroscopy (FTIR)

FTIR spectra were collected with a spectral resolution of 2 cm$^{-1}$, the wavenumber range was from 500 to 4000 cm$^{-1}$ by coating samples on KBr chip in transmission mode, and 32 scans were always accumulated with a Nicolet 6700 (Nicolet, USA) at room temperature.

2.3.3. Thermogravimetric (TG)

TG of samples (10 mg) was carried out on a TG 209 F3 (Netzsch, Germany) in air atmosphere at a heating rate of 1 °C·min$^{-1}$.

2.3.4. Differential scanning calorimetry (DSC)

The glass transition temperature ($T_g$) of samples was characterized by differential scanning calorimetry (DSC, TA Q200). Samples were cooled from room temperature to $-150$ °C, then warmed up to room temperature and cooled to $-150$ °C with a heating and cooling rate of 10 °C·min$^{-1}$ in nitrogen atmosphere.

2.3.5. TG-FTIR

TG-FTIR was performed using a Pyris 1 thermogravimetric analyzer that was linked to a FT-IR spectrometer (PerkinElmer, USA). About 15 mg samples were heated from 50 °C to 700 °C at a heating rate of 5 °C·min$^{-1}$ in air atmosphere.

2.3.6. Raman spectroscopy

Raman spectroscopy was performed using a LabRAM HR Evolution (HORIBA Jobin Yvon). A solid-state laser source (785.1 nm/3 mW) was used. The spectral resolution was 2 cm$^{-1}$ and the wavenumber ranges were from 50 to 3200 cm$^{-1}$ at room temperature.
2.3.7. Gel permeation chromatography (GPC)

The number-average molecular weight \((M_n)\), weight-average molecular weight \((M_w)\) as well as the polymer dispersity index \((PDI)\) of the polymers were measured at 35 °C by a GPC instrument Waters 1515 (Waters, USA). Tetrahydrofuran was used as the eluent at a flow rate of 0.8 ml min\(^{-1}\), and a series of linearly narrow distribution polystyrene with different molecular weights were used as the standard samples.

3. Results and discussion

3.1. Heat resistant properties

The TG curves of BCPSO and phenyl silicone oil in air at heating rate of 1 °C·min\(^{-1}\) were shown in figure 1. From mass loss curves, introduction of boron increased thermal decomposition temperature of BCPSO. \(T_{d5}\), \(T_{d10}\) and residue at 700 °C of BCPSO and phenyl silicone oil were also summarized in table 2. The \(T_{d5}\) and \(T_{d10}\) of BCPSO were higher than that of phenyl silicone oil. BCPSO-2 had the highest \(T_{d5}\) \((347\ °C)\) and \(T_{d10}\) \((366\ °C)\).

Devapal et al\[5\] synthesized borosiloxane oligomers which were stable up to 500 °C and above this temperature borosiloxane oligomers underwent degradation when the temperature was higher than 500 °C. However, borosiloxane oligomers were solid and crosslinked. The thermal decomposition temperature of BCPSO did not increase with the increasing of boron content. Appropriate boron content could obtain the best heat-resistant modified silicone oil like BCPSO-2. Gao et al\[9\] got the best heat resistant hybrid sample when 25 wt% BSi-OH oligomer was added. The \(T_{d5}\), \(T_{d10}\), and residue at 700 °C of as-prepared sample reached 408 °C, 448 °C, and 65%, respectively. With increasing molar ratio of PBA to mixed silane increasing, residue at 700 °C of BCPSO was also increased. The residue was mixture of silica and boron oxide in BCPSO. We selected the best heat-resistant modified silicone oil of BCPSO-2 to analysis structure and initial thermal decomposition mechanism.

The DSC curve of BCPSO-2 was recorded in figure 2. As the curve shown, the \(T_g\) of BCPSO-2 was \(-108 °C\) while the \(T_g\) of ordinary polydimethylsiloxane was \(-130\ to \(-120 °C\). The reason might be that phenyl group of BCPSO-2 disturbed the regularity of main chain structure. However, phenyl groups were also symmetrically distributed on both sides of main chain, which made flexibility of main chain certain enhancement, and caused \(T_g\) increased a little\[16\]. There were no melting or crystalline peaks in figure 2, because small amount of phenyl groups effectively disrupted regularity of BCPSO-2 molecular chain\[17\].
3.2. Structure characterization
The structure of BCPSO-2 was characterized by NMR spectroscopy.\(^1\)H NMR spectrum was shown in figure 3. Strong resonance peaks of Si-CH\(_3\) in BCPSO-2 appeared at 0–0.2 ppm. Minor resonance at 7.59, 7.39 and 7.31 ppm peaks were identified to Si-C\(_6\)H\(_5\) group. Alongside with three characteristic peaks corresponding to B-C\(_6\)H\(_5\) group were at 7.60, 7.37 and 7.35 ppm, the peak at 3.69 ppm was assigned to B-OH bond \([9]\).

\(^{13}\)C NMR spectrum of BCPSO-2 was shown in figure 4. Strong resonance peaks of Si-CH\(_3\) group in BCPSO-2 appeared at 0.87 ppm. Minor resonance at 134.21, 129.65 and 127.43 ppm peaks were identified to Si-C\(_6\)H\(_5\) group. Three characteristic peaks corresponding to B-C\(_6\)H\(_5\) group were at 134.36, 129.70 and 127.48 ppm.

\(^{29}\)Si NMR spectrum of BCPSO-2 was shown in figure 5. Strong resonance peaks of Si-CH\(_3\) group in BCPSO-2 appeared at −21.9 ppm. Minor resonance at −19.9 ppm peak was identified to Si-O bond. Weak resonance peaks of Si-C\(_6\)H\(_5\) group were at −47.8 ppm \([18]\).

The FTIR spectrum of BCPSO-2 was shown in figure 6. The absorption peaks at around 855 and 701 cm\(^{-1}\) were attributed to a symmetric stretching vibration of the Si-O-B groups \([18]\). The presence of Si-O-Si bonds gave rise to strong bands at 1009–1124 cm\(^{-1}\) \([19]\). The peaks at 1586, 1498, and 1454 cm\(^{-1}\) were due to stretching vibration of phenyl skeleton and the peak at 3060 cm\(^{-1}\) was due to stretching vibration of unsaturated carbon-hydrogen bonds in phenyl group \([20]\). The peak at 1420 cm\(^{-1}\) was associated with the B-O group \([18]\).
The peaks at 2965, 2904 and 1273 cm\(^{-1}\) were due to Si-CH\(_3\) group \(^{21}\). The characteristic peaks at 800 cm\(^{-1}\) and 3700 cm\(^{-1}\) were attributed to Si-C group \(^{22}\) and B-OH bond \(^{23}\), respectively.

3.3. Initial degradation mechanism in air

The thermal degradation mechanism of BCPSO-2 in air was obtained by TG-FTIR and compared with that of phenyl silicone oil. The heating rate of test sample was set as 5 °C·min\(^{-1}\) \(^{15}\). The FTIR spectra of the evolved gas of phenyl silicone oil and BCPSO-2 were similar (figure 7). The peaks of Si-O-Si group at 1089, 1021 cm\(^{-1}\) and Si-CH\(_3\) group at 1264, 800 cm\(^{-1}\) in BCPSO-2 appeared at 400 °C (figure 7(b)), while those of phenyl silicone oil appeared at 350 °C (figure 7(a)). When heating temperature was higher than decomposition temperature, the main chain of two samples broke to generate a large number of cyclic oligomers. The content of alkane groups in phenyl silicone oil and BCPSO-2 were relatively few, which caused the absorption peak of CO\(_2\) to be inconspicuous, and even appeared inverted peak \(^{24}\).

Figure 8 showed absorbance of Si-O-Si group at 1021 cm\(^{-1}\) absorbance versus different temperature, which revealed that thermal decomposition of BCPSO-2 had significant hysteresis over that of phenyl silicone oil during the entire heating process.

According to previous study, two competitive mechanisms affected thermal decomposition of polydimethylsiloxane in air. One mechanism was Si-O-Si bond broke in main chain and generated cyclic siloxane oligomers \(^{25}\). The other mechanism was free radical degradation \(^{11}\). The alkyl groups on side chain
of polydimethylsiloxane were oxidatively decarboxylated to produce carbon dioxide and water. In initial period of thermal decomposition, ordinary polydimethylsiloxane mainly underwent free radical oxidative degradation. Methyl group in polydimethylsiloxane and oxygen combined to generate hydroperoxide and instable intermediate continued to react with oxygen to generate carboxylic acid as shown in scheme 2(a) [15]. The boron atom in BCPSO had an empty electron orbital, which could accept electron of peroxide free radical to generate conjugation effect as shown in scheme 2(b), so that BCPSO-2 obtained a temporarily stable intermediate. In addition, the strong steric hindrance of phenyl group also reduced reactivity of peroxide. As a result, the initial decomposition temperature of BCPSO-2 was increased.

3.4. Confirm the initial degradation mechanism
In order to conform initial degradation mechanism of BCPSO in air, the BCPSO-2 was heated to 350 °C (heated sample). The original and heated samples were tested at room temperature by $^{11}$B NMR, FTIR, and Raman spectroscopies. $^{11}$B NMR spectra was shown in figure 9. Chemical shift of boron atom shifted from 2.70 ppm to 5.72 ppm after heating. This phenomenon may due to that empty orbital of boron atom accepted electron of

Figure 7. FTIR spectra of evolved gas of samples at different temperature in air with heating rate at 5 °C·min$^{-1}$: (a) phenyl silicone oil, (b) BCPSO-2.

Figure 8. Absorbance of the Si-O-Si group at 1021 cm$^{-1}$ absorbance versus different temperature.
Scheme 2. Initial oxidation process of polydimethylsiloxane and BCPSO: (a)-ordinary polydimethylsiloxane, (b)-BCPSO.

Figure 9. $^{11}$B NMR spectra of two BCPSO-2 samples: (a)-original, (b)-heated.

Figure 10. Spectra of original and heated BCPSO-2 samples: (a)-FTIR, (b)-Raman spectroscopy.
peroxide free radical and formed intramolecular conjugation, which resulted in chemical shift to low field [26]. Kroeker et al [27] found that chemical shift in boron spectra increased with the increasing density of electron clouds around boron atoms.

The FTIR spectra was shown in figure 10(a). After heating, the peak of B-O bond had blue shift from 1408 to 1429 cm\(^{-1}\). After electron of peroxide free radical entered empty orbit of boron atom, the electro negativity of boron atom increased which resulted in the peak of B-O bond to move toward high wavenumber [28]. Cinquanta et al [29] reported effects of oxidation on \(sp\) and \(sp^2\)-hybridized carbon based on FT-IR spectra. They found that the peak of C-O bond had blue shift in FTIR spectrum as density of electron clouds around carbon atom increased. Raman spectroscopy also revealed that the peak of B-O bond had blue shift from 1405 to 1412 cm\(^{-1}\) in figure 10(b) [30]. O’Neill et al [31] used Raman spectroscopy to research a series of poly(pyridyl) complexes and found relative electron withdrawing effects of poly(pyridyl) ligand could make blue shift of Raman spectroscopy.

The results from \(^{11}\)B NMR, FTIR, and Raman spectroscopies analysis confirmed that an interaction existed between peroxide free radical and boron atom, which formed temporarily stable intermediate. This intermediate increased the heat resistant of BCPSO.

4. Conclusion

Heat-resistant BCPSO was prepared by one-pot balance condensation polymerization using phenylboronic acid, dimethyldichlorosilane and diphenyldichlorosilane as raw materials. At a heating rate of 1 °C-min\(^{-1}\) in air, Td\(_5\), Td\(_{10}\) and residue at 700 °C of BCPSO-2 were 347 °C, 366 °C and 42.22%, respectively. The thermal decomposition of BCPSO had significant hysteresis over that of phenyl silicone oil and the mechanism for initial decomposition of boron-containing phenyl silicone oil in air was proposed. The boron atom in BCPSO had an empty electron orbital, which could accept electron of peroxide free radical to generate conjugation effect, so that BCPSO obtained a temporarily stable intermediate. In addition, the strong steric hindrance of phenyl group also reduced the reactivity of peroxide. As a result, the initial decomposition temperature of BCPSO was increased.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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