

Synthesis, Cure and Pyrolysis Behavior of Heat-Resistant Boron-Silicon Hybrid Polymer Containing Acetylene

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ABSTRACT: The synthesis and characterization of a novel heat-resistant boron-silicon hybrid polymer containing acetylene (PBSA) and its conversion to a highly cross-linked thermoset were discussed. The polymer was synthesized from phenylboron dichloride using Grignard reagent method. The structure of PBSA was characterized by using Fourier transform infrared spectra, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and gel permeation chromatography. PBSA was thermosetting, highly heat-resistant, high-viscous, orange liquid at room temperature and good solubility in common organic solvents. Differential scanning calorimetry and thermogravimetric analysis analyses showed that the PBSA had excellent thermal and oxidative stability and

the temperature of 5% weight loss (T_{d5}) were 650 and 638°C under nitrogen and air, respectively, and the residue at 1000°C were 93.3 and 91.3%, respectively, which indicated that the incorporation of boron and silicon into polymeric backbone was found to improve thermal and oxidative properties. X-ray diffraction and scanning electron microscope were also used to analyze the formation of pyrolytic products. The results showed that the pyrolysis of PBSA resin was made up of $\beta\text{-SiC}$ and graphite. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: high-temperature materials; thermal properties; curing of polymers; pyrolysis

INTRODUCTION

In recent years, polymers containing silicon and boron elements in the main backbone or side chains have received considerable interest in the field of the composite materials owing to their excellent inorganic and organic properties. Inorganic-organic hybrid materials play important parts in the development of heat-resistant materials, such as the aerospace, automotive, electronic industries, and even the household appliances.^{1–3} There are many reports in the literature on silicon-containing polymers composed of $[-\text{SiR}_2-\text{C}\equiv\text{C}-]$ (R = alkyl or phenyl) units. Itoh and Inoue⁴ synthesized a new poly(phenylsilyleneethynylene-1,3-phenyleneethynylene) $[-\text{Si}(\text{Ph})\text{H}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}-\text{C}-]_n$ (abbreviated as MSP) resin, which was prepared by the dehydrogenative coupling polymerization reaction between phenylsilane and *m*-diethynylbenzene in the presence of magnesium oxide. It was considered as a typically silicon-

containing polymer and the results showed that the polymer had an extremely high thermal stability.⁵ Craig et al.⁶ reported a linear silarylene-siloxane-diacetylene polymer which was prepared via polycondensation of 1,4-bis(dimethylaminodimethylsilyl)butadiyne with 1,4-bis(hydroxydimethylsilyl)benzene through the diacetylene groups above 300°C. The thermosetting property of this polymer was observed to exhibit long-term thermo-oxidative stability in air.

Up to now, many reports concerning the incorporation of inorganic elements into an organic polymeric system to enhance thermal and mechanical properties of the polymer materials have been published. Among all these inorganic elements, the addition of the boron element in the generation of new modified hybrid polymers will greatly enhance the thermal and oxidative properties of polymers.⁷ Pehrsson et al.⁸ mentioned that under high-temperature air atmosphere, the combination of the silicon and boron oxide layers provide the oxidation protection to more than 1000°C, whereas the unprotected carbons began to oxidize at about 500°C. Ohshita et al.^{9,10} found that the introduction of the silicon atom to the unsaturated $-\text{C}\equiv\text{C}-$ groups led to dense crosslinked networks and high heat-resistant properties. Deepa et al.¹¹ synthesized a kind of borosiloxane oligomers through the condensation of boric

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acid with phenyltrimethoxysilane and phenyltriethoxysilane in diglyme both in the presence and in the absence of hydrochloric acid as catalyst. The results showed that the oligomers give ceramic residue in the range of 64–75% (at 900°C in inert atmosphere). However, polymers containing the combination of Si,B and $-\text{C}\equiv\text{C}-$ units in the structure were rarely been reported.

Therefore, to improve and control the thermal and oxidative properties of inorganic–organic hybrid materials more precisely, it is a viable method to incorporation of Si,B and $-\text{C}\equiv\text{C}-$ units into polymer structures.¹² In a preliminary study from our laboratory, we reported the synthesis of a boron-silicon-acetylene hybrid polymer by the polycondensation reaction between phenylboric acid and diphenyldichlorosilane and then terminated by phenylacetylene which showed excellent properties.¹² In this article, we have successfully synthesized a novel heat-resistant boron-silicon hybrid polymer-containing acetylene (PBSA). The thermal curing behavior, the thermal and oxidative properties, and the formation of pyrolytic products were discussed to develop a new heat-resistant resin matrix.

EXPERIMENTAL

Materials

All syntheses were carried out at the atmosphere of dry nitrogen because the starting materials were sensitive to oxygen and moisture. The organic solvents used were dried and purified according to the standard procedures and stored under dry nitrogen. Tetrahydrofuran (THF) was distilled under a nitrogen atmosphere from sodium/benzophenone immediately before use. Dichloromethylsilane, phenylboron dichloride, and ethynylmagnesium bromide (0.5M solution in THF) were obtained from Aldrich Chemical Company (Shanghai, China). All other chemicals were received as reagent grade and used without further purification.

Instrumentation

Fourier transform infrared spectra (FTIR) were recorded on a Nicolet 5700 spectrometer from KBr pellets for solid samples and film deposited on NaCl plate for liquid samples.¹H-NMR and ¹³C-NMR spectra were obtained on a Bruker Avance 500 spectrometer (500 MHz for ¹H-NMR, 125.77 MHz for ¹³C-NMR). The chemical shifts were recorded relative to tetramethylsilane (d, 0.0 ppm) for ¹H-NMR and CDCl₃ (d, 77.7 ppm) for ¹³C-NMR. The molecular weight of the polymer was measured by gel permeation chromatography (GPC) (Waters 1515), THF used as eluent and polystyrene as the standard.

Differential scanning calorimetry (DSC) measurements were performed on NETZSCH DSC 200 F3 instrument at heating rate of 10°C/min using a nitrogen purge from room temperature to 300°C. Thermogravimetric analysis (TGA) curves were performed on PerkinElmer Pyris Diamond from room temperature to 1000°C at heating rate of 10°C/min under air or nitrogen atmosphere. The gas flowing rate was 20 mL/min. Td₅ was defined as the temperature resulting in 5% weight loss based on the initial weight and char yield referred to the final retention of the sample weight. The X-ray diffraction (XRD) patterns were carried out at room temperature on a Digaku D/max 2550 VB/PC diffractometer with CuK α radiation ($\lambda = 0.1542$ nm). The diffraction data were recorded from 3 to 80° with a scan speed of 4°/min. Scanning electron microscope (SEM) images were taken on a field-emission scanning electron microscope (FE-SEM S4800, Hitachi, Japan).

Synthesis of PBSA

A synthesis route to appropriate PBSA is shown in Scheme 1.

An organic magnesium reagent was prepared as follows: The ethynylmagnesium bromide (60 mmol) was injected into a flame-dried 250 mL three-necked flask under dry nitrogen gas atmosphere. Then, the solution was cooled down with a dry-ice/methanol bath and a THF solution containing dichloromethylsilane (30 mmol) was added dropwise. After completion of addition, the cold bath was removed and the mixture was then stirred at room temperature for 6 h. Meanwhile, the magnesium metal ribbon (2 g) was added into another flame-dried 250 mL three-necked flask equipped with a reflux condenser, a dropping funnel, and a stirred motor under dry nitrogen gas atmosphere. THF (20 mL), which had been dried over sodium and then distilled, was introduced into the flask, a small piece of iodine was added and the mixture was stirred to activate the reaction of magnesium. Then, a solution of 5 ml of ethyl bromide in THF (20 mL) was added at room temperature for about 0.5 h. The mixture then was refluxed for 2 h to produce ethylmagnesium bromide. To the reaction system a solution of product (3) was added in 30 mL THF dropwise at room temperature over 1 h with stirring and the reaction was continued for an additional 2 h at the refluxing condition to produce the intended and mixed organic magnesium reagents.

The polymerization reaction was subsequently performed. A solution of 5 g (30 mmol) of phenylboron dichloride in THF (20 mL) was dropwise added to the above flask at room temperature over a period of 50 min with stirring. Although the dimethyldichlorosilane was added, the white solid

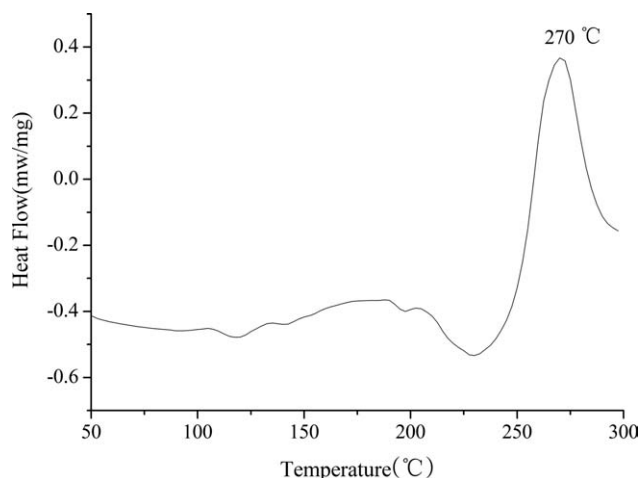


Figure 2 DSC curve of PBSA at heating rate of 10°C/min.

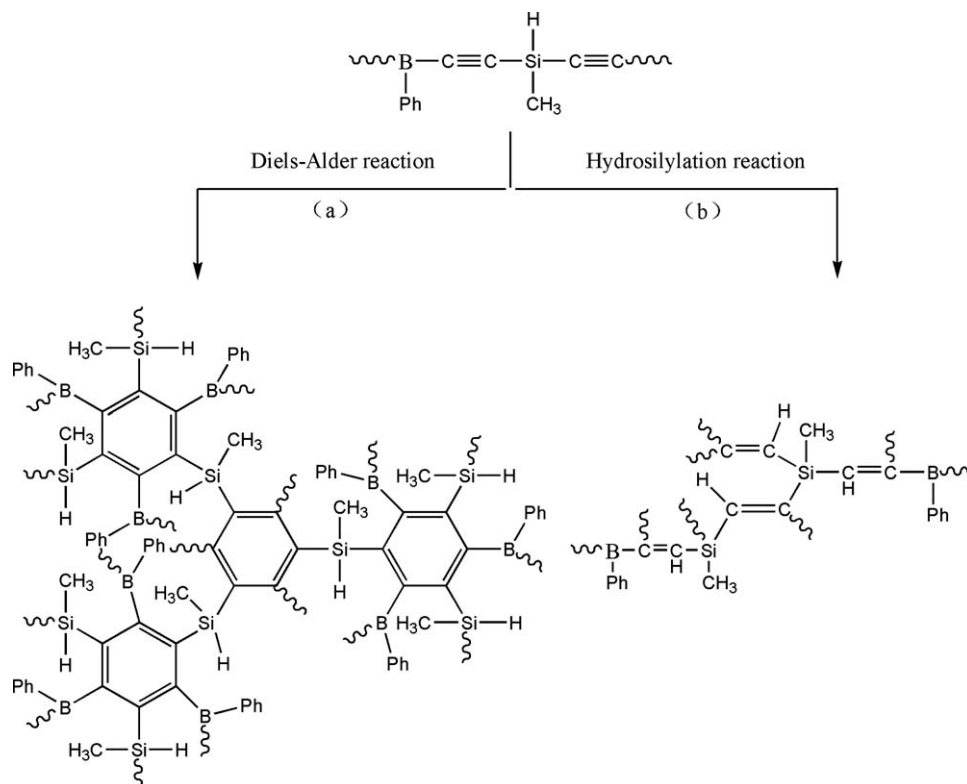
weight (Mn) was 2837 g/mol with a polydispersity value of 2.2.

Cure behavior of the resin and its thermal and oxidative properties

The DSC curve of the resin measured under nitrogen is shown in Figure 2. A broad exothermic peak during 150–225°C was corresponding to the reaction of Si–H bond to form the crosslink. There was a sharp

exothermic peak with the top temperature 270°C; this exothermic signal is typical of a crosslinking reaction between the secondary acetylene groups.⁶ When the resin was placed in a furnace and cured under nitrogen atmosphere, polymerization takes place through both hydrosilylation reaction between Si–H and C≡C bonds and Diels–Alder intermolecular cyclization involving two C≡C bonds without the formation or evolution of volatile by-products, which resulted in insoluble, void free, hard solid (Scheme 2).¹³ Inspection of the FTIR spectrum for thermoset [Fig. 1(b)] revealed the absorption at 2167 cm⁻¹ (Si–H) and 2039 cm⁻¹ (C≡C) completely disappeared, which indicated that under these conditions in an inert atmosphere both the hydrosilylation reaction and the Diels–Alder reaction had occurred.

The thermal and oxidative stability of cured PBSA resin was determined by using TGA study under a flow of nitrogen and air, respectively, as shown in Figure 3. The cured PBSA resin exhibited excellent heat-resistant properties both in nitrogen and in air. When heating rate was 10°C/min, the temperatures of 5% weight loss (Td₅) were 650 and 638°C under nitrogen and air, respectively, which were much higher than that of the MSP⁴ (The Td₅ of MSP under air was 567°C), and the residues at 1000°C were 93.3 and 91.3%, respectively, which was attributed to the synergistic effects obtained via the incorporation of silicon unit and boron unit into the molecular



Scheme 2 Possible curing mechanism of PBSA.

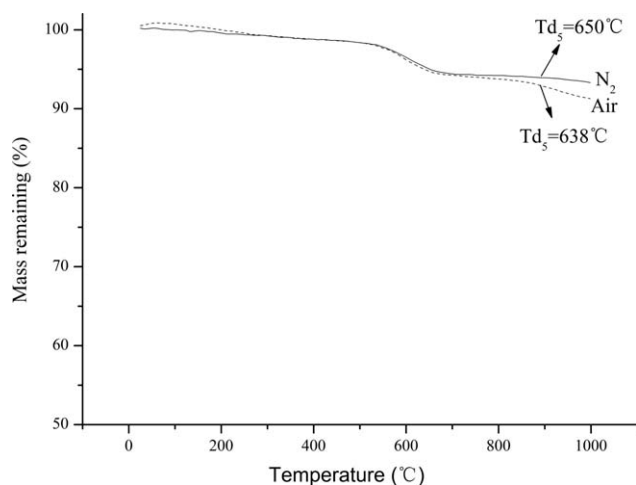


Figure 3 TGA curves of the cured PBSA resin in different atmospheres.

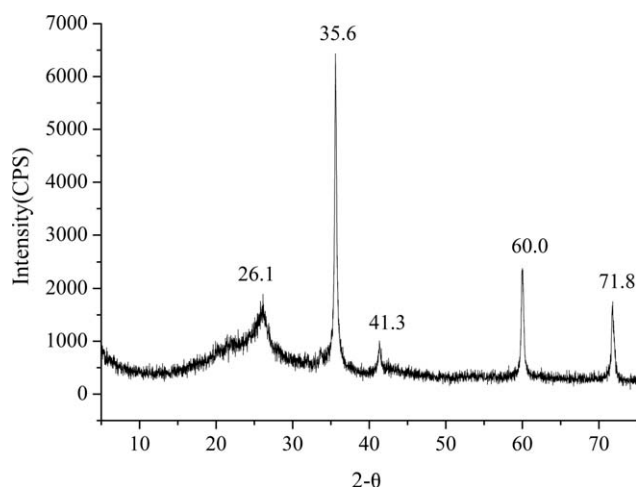


Figure 4 XRD patterns of pyrolysis PBSA resin.

structure. Both Si—H and the secondary acetylene linkages within the polymeric main chain that provided the opportunity to convert linear polymer into

thermoset. When heating up to 1000°C, the Si atom and B atom form thermally stable inorganic compounds such as SiC-B₄C or SiO₂-B₂O₃. These mixed inorganic compounds were reported to possess superior high-temperature properties, oxidation resistance, and thermal shock resistance compared to polymers containing only boron or silicon. From the above analysis, the cured PBSA resin exhibited excellent thermal and oxidative stability, which made it potentially useful as high-performance matrix resin and precursor for ceramics.

The formation of ceramics

The cured PBSA resin was sintered at 1450°C for 12 h in a typical stove under argon atmosphere and the ceramic was produced. XRD patterns of pyrolysis PBSA resin are shown in Figure 4. There were three sharp diffraction peaks at $2\theta = 35.6$, 60.0 , and 71.8° which were attributed to β -SiC at {111}, {220}, and {311}. Another two peaks appeared at $2\theta = 26.1$ and 41.3° corresponding to diffraction peak of graphite at {002} and {101}.¹⁴ Zaldiva¹⁵ reported that the incorporation of B atom into an organic polymeric system has the potential to improve the degree of graphitization, and hence there was no obvious diffraction peak of B₄C in the XRD spectra. These results showed β -SiC ceramic and graphite had formed after pyrolysis under a stream of argon.

SEM was performed in an attempt to characterize the morphology of the sintered resin. The images of a sample are shown in Figure 5. As shown in Figure 5, in the low magnification (3K) condition, the surface of the sintered resin was smooth and there was no obvious holes and cracks [Fig. 5(a)]. In a larger magnification (5K) condition, there were a lot of isolated spherical particles which were embedded in or grew out on the surface of the sintered resin orderly [Fig. 5(b)]. When the resin was exposed to an environment at elevated temperatures, a protective

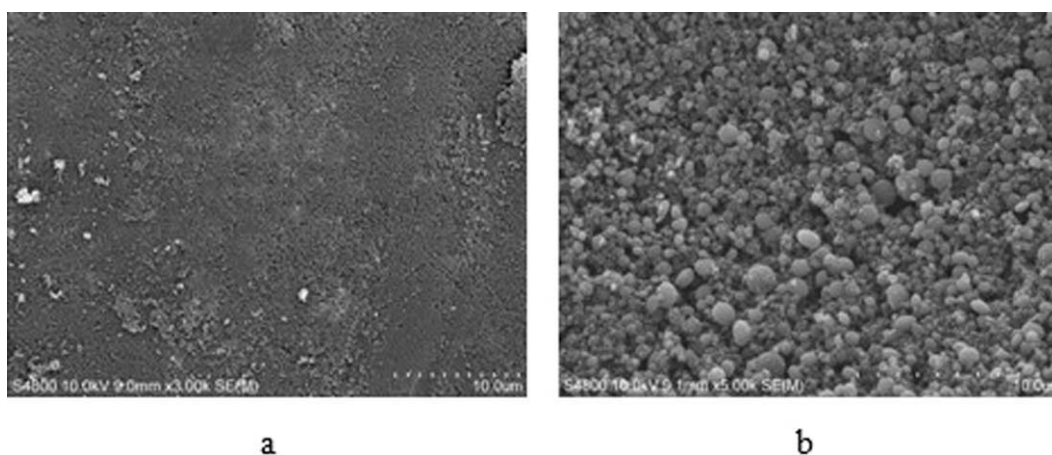


Figure 5 SEM microphotograph of the sintered resin.

passive borosilicate glassy layer was formed on the surface which prevented further oxidation of the protective coating and the substrate. The incorporation of B element into an organic polymeric system has greatly improved the thermal and oxidative properties. Further investigations are being undertaken.

CONCLUSIONS

A novel PBSA was synthesized by the condensation reaction between phenylboron dichloride, dichloromethylsilane, and organic magnesium reagent using Grignard reagent method. The resin can be easily cured at a relative low temperature and it exhibited excellent thermal and oxidative stability. The decomposition temperatures T_{d5} of the cured resin were 650 and 638°C under nitrogen and air, respectively, and the residues at 1000°C were 93.3 and 91.3%, respectively. The incorporation of boron and silicon into polymeric backbone was found to improve thermal and oxidative properties. XRD and SEM analysis showed that the pyrolysis of PBSA resin was made up of β -SiC and graphite. All of these showed that PBSA was a potential outstanding matrix material for high-temperature composite applications.

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