

Efficient curing of polymethylsilane by borazine and reaction mechanism study

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Abstract

An efficient way to improve the low ceramic yield and poor processability of PMS as a SiC precursor utilizing high levels of Si–H, was developed by simply modifying at 70 °C for 1 to ~3 h in presence of 1 wt.% borazine. The ceramic yield was significantly enhanced from 35 to 87 wt.% and molecular weight increased from 740 to 3554. It is believed that these benefits are due to dehydrocoupling of Si–H of the PMS with N–H of the borazine to form $\equiv\text{Si}-\text{N}=\text{}$ units, and of Si–H with itself to form $\text{Si}-(\text{MeSi})=\text{Si}_2$ units. The structure evolution of the PMS during treatment was thoroughly studied using TGA, GPC, ²⁹Si CP/MAS-NMR, ¹H-NMR, IR and GC-MS. Furthermore, the processability of the PMS was improved controllable by alteration either the content of borazine added or heating time. Green fibers were readily prepared by hand-drawing the improved PMS solution; these were characterized by SEM.

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1. Introduction

Polymethylsilane (PMS), synthesized by dehalocoupling of dichloromethylsilane or by catalytic dehydrocoupling of MeSiH₃, is a very important precursor of SiC ceramics because of 1/1 ratio of C/Si and rich Si–H bonds [1–8]. The PMS is potentially useful in preparation of high-temperature resistant ceramics, such as fibers, coating, bulk materials and composites [1–3,7,8]. However, the PMS suffers from low ceramic yield and poor processability [1,2,7,9], e.g. poor spinability for fibers. Many studies have been undertaken to resolve these problems. Iseki et al. [10] and Narisawa et al. [7] improved the ceramic yield by reflux heat-treatment and γ -ray curing. Boury et al. [9] employed organoborate

additives such as B[OSi(CH₃)₃]₃ at 230 °C to improve the ceramic yield of PMS. Seyferth et al. [11–16] modified the PMS by hydrosilylation with organic or organosilicon compounds, such as divinylbenzene and polybutadiene. Moreover, transition metals, such as Ru₃(CO)₁₂ and Cp₂ZrH₂, were also found to promote the ceramic yield of PMS. In our previous work [17], we improved the ceramic yield by heat-treatment with polyborazine (PBN) at 70 °C for 10 h, but did not perform a mechanistic study.

In this paper, we report upon a much more efficient way of improving PMS, for high ceramic yield and controllable processability, by adding only 1 wt.% of borazine monomer at 70 °C for 1 to ~3 h; and interpret its structural evolution. In contrast with the methods reported by other researchers, this modification is achieved by using very gentle reaction conditions, i.e. a low temperature and a short time, and therefore, the process system requirements have a lower cost base. An additional benefit of this process is that the method does not introduce molecularly bound oxygen or carbon,

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which could cause high temperature instability, into the final product. This is particularly important in the case of the high temperature stability requirements of ceramic products.

2. Results and discussion

The oily white PMS feed stock became a low viscosity fluid at 70 °C without boiling; while the PMS was heated with 1 wt.% borazine at 70 °C in a small closed pressure reactor, the rigorous formation of bubbling, probably induced by gas by-products, was observed. Within 3 h, the low viscosity fluid gradually become a yellow solid, and the reactor pressure had increased. In contrast, when PMS was heated PMS alone no observable phenomena occurred at under the same conditions.

Fig. 1 shows thermal properties of PMS samples as determined by TGA. PMS feed stock gave only a 34% ceramic yield at temperatures up to 1000 °C and significant weight loss between room temperature and 300 °C, probably due to the presence of a volatile low molecular weight fraction, as reported previously [9,10,17]. While treatment with 1 wt.% borazine at 70 °C for 1 h, the ceramic yield increased to 72%, and when treated for 3 h this reached 87%, which is higher than the achieved 78% by the modified PMS by 1 wt.% polyborazine at the same temperature for 10 h [17]. On the other hand, the PMS heated at 70 °C for 10 h without borazine showed no change in the ceramic yield.

Table 1 and Fig. 2 show the molecular weight distributions of various PMS. The oily PMS feed stock had a low molecular weight, i.e. $M_n = 740$, $M_w = 1456$, but after treatment with 1 wt.% borazine at 70 °C for 1 h, the M_n and M_w increased to 2206 and 9309, respectively, and in 3 h these reached 3554 and 17397, respectively; the polydispersity also increased at 3 h to 4.22 and 4.89, respectively. It is significantly distinguished that the PMS without borazine exhibited no change at the same conditions. It should be mentioned that the use of borazine as a promoter of PMS was

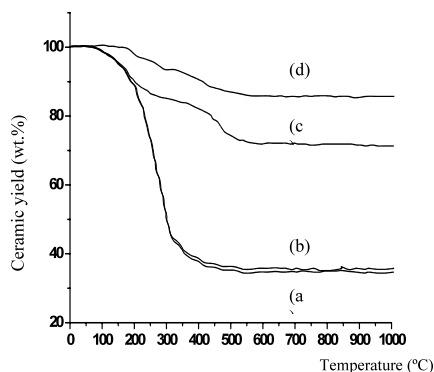


Fig. 1. TGA of (a) PMS feed stock, (b) heated at 70 °C for 10 h and treated by 1 wt.% borazine at 70 °C for (c) 1 h and (d) 3 h.

significantly more efficient than polyborazine. In addition, the UV maximum absorption wavelength λ_{\max} showed a shift to longer wavelength from an initial 360 nm for the PMS feed stock to 370 nm for a borazine treated PMS sample heated at 70 °C for 1 h, and to 375 nm after 3 h. This indicates increased numbers of PMS repeating units in the borazine treated PMS, which is consistent with the literature [18].

Fig. 3 shows the ^{29}Si CP MAS-NMR of the PMS feed stock and of PMS heated with 1 wt.% of borazine at 70 °C for 3 h. The spectrum of the PMS feed stock consisted of partly overlapping peaks: -45 to -75 ppm was assigned to $\text{Si}-(\text{MeSiH})-\text{Si}$ and -65 to ~ -75 ppm to the $\text{Si}-(\text{MeSi})=\text{Si}_2$ unit [7,19–23]. After heat-treatment with 1 wt.% borazine for 3 h, the NMR spectrum clearly changed in two ways, i.e., first, new signals obviously arose in the -28 to 15 ppm range, and secondly the main peak was visibly broadened from -75 to -85 ppm and the signal centered at -34 ppm was enhanced. Formation of $\text{Si}-\text{N}$ by reaction between the $\text{Si}-\text{H}$ in PMS and the $\text{N}-\text{H}$ in borazine (Scheme 1) could have been responsible for the former signals in the range -28 to 15 ppm. [24,25] Assignment can be partly made by referring to chemical shifts in series of organosilicon compounds with substituted N atoms; $(\text{CH}_3)_4\text{Si}$ at 0ppm, $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$ at 5.9 to ~ 6.9 ppm, $(\text{CH}_3)_2\text{Si}(\text{N}(\text{CH}_3)_2)_2$ at -1.30 to ~ -1.85 ppm, $\text{CH}_3\text{Si}(\text{N}(\text{CH}_3)_2)_3$ at -16.30 to ~ -17.50 ppm and $\text{Si}(\text{N}(\text{CH}_3)_2)_4$ at -28.1 to ~ -28.6 ppm [24,25]. As the ^{29}Si chemical shift is affected by not only the nearest-neighbor atoms but also the next-nearest-neighbor atoms in the presence of B atom as adjacent atoms of N atom, which may have caused the observed peak broadening. Moreover, the $\text{Si}-\text{N}$ bonds formed by dehydrocoupling between polyvinylsilane (PVS) containing $-\text{SiH}_3$ or polyphenylsilane (PPS) and PBN were observed by liquid phase ^{29}Si -NMR [26]. IR absorption of $\text{Si}-\text{N}$ (870 cm^{-1}) was difficult to be distinguished due to overlapping with CH_3 (867 cm^{-1}). However, the peak at -28 to 15 ppm cannot be assigned to $\text{C}-(\text{MeSiH})-\text{C}$ or SiC_4 structural units, because carosilane units are usually formed at temperatures of 370 °C or higher by Kumada rearrangement [27–30]. On the other hand, it is believed that the peaks at -75 ppm to ~ -85 ppm, and centered at -34 ppm, are attributable to the formation of the $\text{Si}-(\text{MeSi})=\text{Si}_2$ units promoted by borazine as another route to enhance PMS. It is supposed that borazine catalyzes the disproportionation reaction between $\text{Si}-\text{Si}$ and $\text{Si}-\text{H}$, and/or the dehydrocoupling of $\text{Si}-\text{H}$ with itself, which leads to the formation of new $\text{Si}-\text{Si}$ bonds. Similar chemistry has been well-documented in the organosilicon chemistry literature [32,34]. Boury et al. [9] investigated the disproportionation of $\text{Si}-\text{Si}$ and $\text{Si}-\text{H}$ reaction in PMS using $\text{B}[\text{OSi}-(\text{CH}_3)_3]_3$ as a catalyst. Ring et al. [33,34] and Abedini et al. [35] also studied the

Table 1
Molecular weight of various PMS samples

	PMS	PMS+1 wt.% borazine (70 °C, 1 h)	PMS+1 wt.% borazine (70 °C, 3 h)	PMS+1 wt.% PBN (70 °C, 10 h)
Mn	740	2206	3554	3400
Mw	1456	9309	17 379	16 000
Pd	1.97	4.22	4.89	4.70

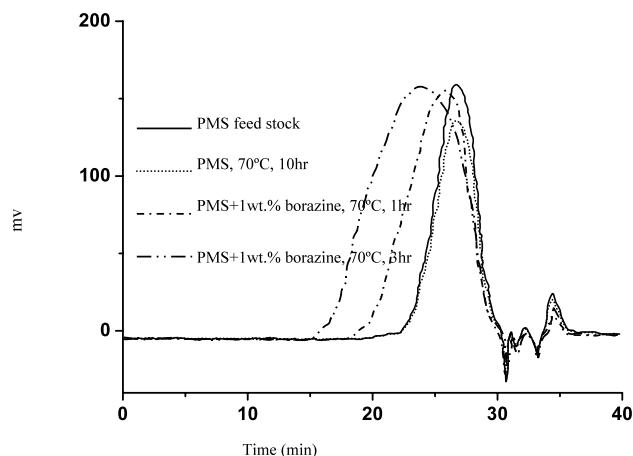


Fig. 2. Molecular weight distribution of various PMS.

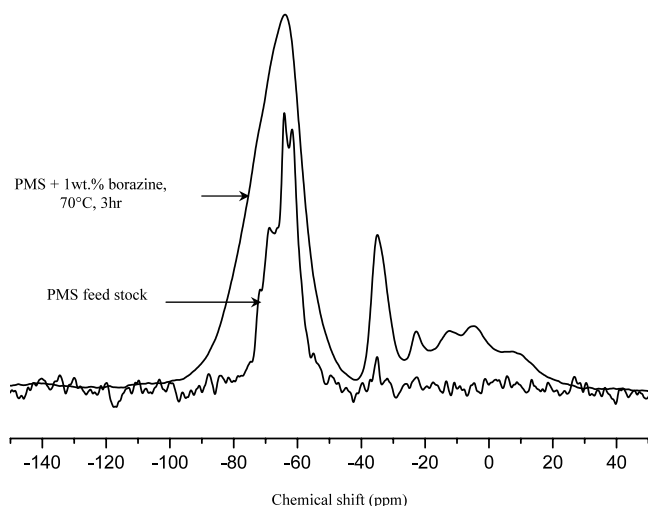


Fig. 3. ^{29}Si CP MAS-NMR of PMS before and after modification with 1 wt.% borazine at 70 °C for 3 h.

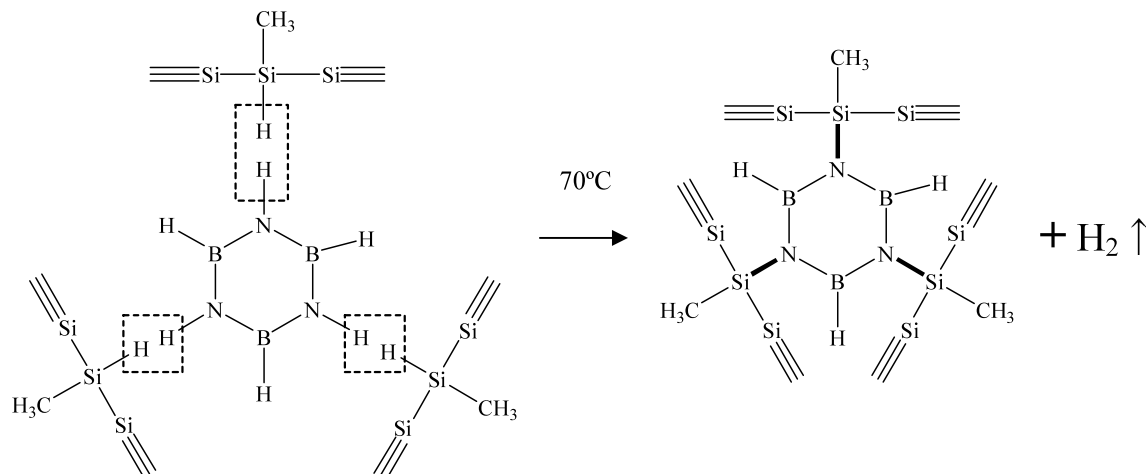
redistribution of Si–Si and Si–H bonds. In the synthesis of Yajima Mark III PCS [36], it was observed that the dehydrocoupling of Si–H led to the formation of Si–Si bonds in presence of polyborodiphenylsiloxane (PBDPSO). It is also interesting that PMS ‘enhanced’ by γ -ray treatment was also involved formation of Si–(MeSi)=Si₂ units as reported by Narisawa et al. [7].

In the ^1H -NMR spectrum of soluble compounds, the groups of resonances in the ranges 5.3 to \sim 5.75 ppm and 3.75 to \sim 5.1 ppm were assigned to N–H and B–H in borazine, respectively [37]. The latter resonance was

partly overlapped with that of Si–H; observed at 3.4 to \sim 4.1 ppm; on the scale the chemical shift due to C–H was in the range of 0 to \sim 0.7 ppm [17,37]. According to Table 2, when a mixture of PMS–borazine (10/2) was heated at 70 °C, the ratios of B–H/C–H, N–H/C–H and Si–H/C–H decreased. In particular, these decreased Si–H/C–H and N–H/C–H ratios were attributed to the consumption of Si–H and N–H to form units of $\equiv\text{Si}-\text{N}=\text{}$ and Si–(MeSi)=Si₂. Meanwhile, the self-polymerization of borazine by dehydrogen coupling between N–H and B–H was probably negligible due the 35 to \sim 40 h required for recognizable polymerization at 70 °C [38]. In addition, IR spectrum presented that relative intensity of the Si–H peak (2100 cm⁻¹) to the Si–CH₃ peak (1250 cm⁻¹) of the mixture of PMS even with 1 wt.% borazine was obviously lower than that of PMS feed stock.

Fig. 4 presents the relative partial gas pressures of the gases that evolved during the borazine treatment of PMS as a function of the heating time. Various gases were produced during the reaction, and no gases were detected in the absence of borazine except N₂. The increased emission of hydrogen at the extended PMS with borazine reaction time suggests the dehydrocoupling of Si–H in PMS with N–H in borazine to form $\equiv\text{Si}-\text{N}=\text{}$ units, and of Si–H with itself to form Si–(MeSi)=Si₂ units. Moreover, increased relative partial pressures of both methylsilane (MeSiH₃) and dimethylsilane (Me₂SiH₂) were also identified at the longer reaction time. It is believed that these two silanes were formed by a disproportionation reaction between Si–Si and Si–H bonds or by the dehydrocoupling of Si–H, as described by Boury et al. [9], Ring and coworkers [31,33] and Abedini and McDarmird [35], who observed similar silane byproducts during the treatment of PMS in the presence of other boron derivatives. In this case, the nitrogen detected in the accumulated gaseous species must be from the atmosphere in glove-box where the PMS and borazine samples were charged. Therefore, the relative partial pressure decreased with increasing reaction time, whereas the partial pressures of the other gases increased with time. A small amount of borazine must be evaporated from the added one.

In order to determine thermolysis chemistry of the PMS, with or without borazine, the gases evolved in both cases were identified by GC-MS as samples were gradually heated to 500 °C. In the chromatograms of the



Scheme 1. Proposed dehydrocoupling reaction between PMS and borazine to form Si–N bonds, which cured PMS.

Table 2
¹H-NMR integration ratios for various samples

	B–H/ N–H	B–H/ C–H	N–H/ C–H	Si–H/ C–H
Borazine	1.00	–	–	–
Borazine, 70 °C, 2 h	0.94	–	–	–
PMS feed stock	–	–	–	0.29
PMS/borazine = 10/2 mixture	1.96	0.16	0.08	0.28
PMS/borazine = 10/5, 70 °C, 2 h	2.19	0.11	0.05	0.20

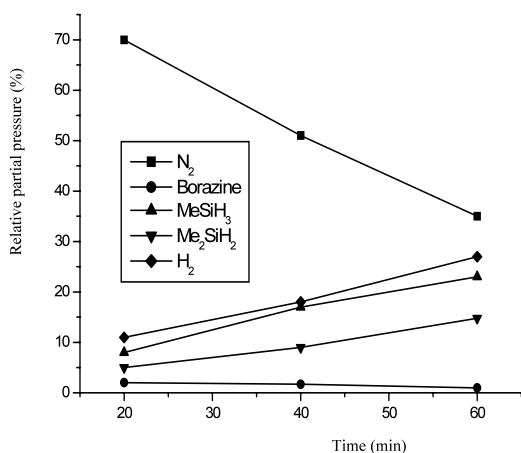


Fig. 4. The relative partial pressure of gases evolved during heat-treatment of PMS by 1 wt.% borazine at 70 °C, as function of heating time.

total gas evolved from the PMS feed stock and the pre-treated sample produced at 70 °C for 3 h. Generally, the PMS feedstock was found to emit much more gas than the borazine modified PMS, especially in the temperature range 200 to ~450 °C. This result is consistent with the TGA result, which showed a major mass loss in this temperature range. This result indicates that the dehydrocoupling of PMS occurs primarily during the treatment of PMS at 70 °C for 3 h in the presence of borazine. The highly cured PMS structure produced under these conditions showed higher thermal stability and lower weight loss while the less cured PMS feed stock was vulnerable to thermal decomposition. In contrast to the total amount of gas evolved, the amount of hydrogen evolved from the borazine treated PMS was higher than that evolved from the PMS feed stock, and showed a strong emission peak at around 350 °C, as shown in Figs. 5 and 6. These results suggest that the dehydrocoupling reactions occur continuously at over 70 °C, and that this eventually leads to the formation of a ceramic phase.

Finally, the processability of PMS was improved by the borazine treatment to a level suitable for spinning into green fibers. Fig. 7 illustrates the typical surface morphology of the modified PMS-derived green fibers produced. These self-supporting green fibers, 25 cm in length and 30 μm in diameter were easily obtained by hand drawing. In contrast, the PMS feed stock never could be spun into fibers due to low viscosity. There is a possibility that ceramic fibers can be formed from these green fibers by pyrolysis at elevated temperatures without additional curing if the molecular weight of the base is high enough. Furthermore, it is under report that the obtained ceramic fibers could be oxygen free and dense due to the sintering aid B and N induced inherently, as we reported previously sintered ceramic fibers [29,39].

3. Conclusion

The modification of PMS with 1 wt.% borazine at 70 °C for 1 to ~3 h presents a highly efficient way of dramatically improving the molecular weight, ceramic yield and processability of PMS. The white oily PMS was transformed into a yellow powdery solid by this

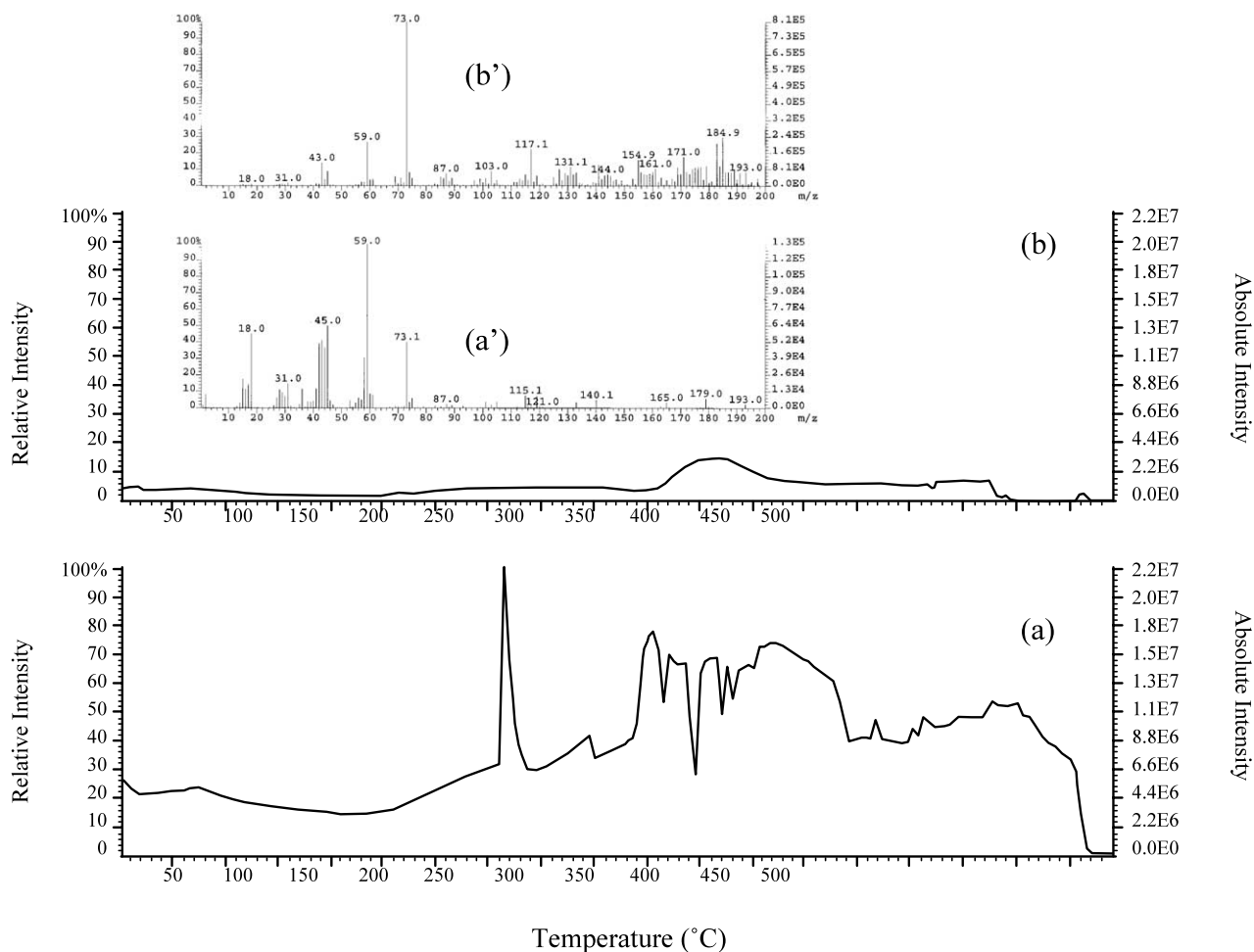


Fig. 5. Chromatogram of total gas evolved from (a) PMS feed stock and (b) treated PMS with 1 wt.% of borazine at 70 °C for 3 h, respectively, and heated to 500 °C. Insert: average mass spectrum of the gases evolved at the temperature from 200 to 220 °C by samples (a) and (b), respectively.

process, so improving the PMS ceramic yield from 35 to 87 wt.% and enhancing the molecular weight from 740 to 3554. ^{29}Si CP/MAS-NMR, ^1H -NMR and GC-MS results suggest that the dehydrocoupling of Si–H in PMS with the N–H of the borazine to form $\equiv\text{Si}-\text{N}=\text{}$ units, and of the dehydrocoupling of Si–H with itself to form $\text{Si}-(\text{MeSi})=\text{Si}_2$ units, which are believed responsible for the promotion mechanism of PMS. Furthermore, the processability of the PMS was improved to a level that allowed it to be spun into green fibers.

4. Experimental

4.1. Materials

To avoid oxygen and moisture contamination, all samples described in this investigation were manipulated in nitrogen. Hexane as a solvent was purified by distillation with sodium. The transparent colorless borazine liquid was synthesized by using a modification of Sneddon's procedure, as described in our previous

reports [17,37,40,41]. Oily white PMS was synthesized by the Würtz condensation of dichloromethylsilane with sodium, as previously reported [17].

4.2. Processing

In a typical reaction, 2 g of PMS and 0.02 g of borazine were charged into a dried 20 ml glass pressure reactor (Ace Glass Co.) equipped with a degassing system, a magnetic stirrer, a thermometer and a pressure gauge for determination of total pressure. The borazine was homogeneously blended with the PMS by stirring. The mixture was then heated to 70 °C with an oil bath. The vessel was degassed hourly, during which the reactor was cooled in ice water. The gas produced during the reaction was accumulated using a glass gas connector (Ace Glass Co.) vacuumed in advance. In order to study the reaction mechanism the PMS was heat-treated with borazine at different weight ratios (10/3 and 10/2 etc.) using the conditions described above.

Solid PMS modified with 1 wt.% borazine at 70 °C for 3 h was spun into green fibers by hand drawing. Viscous

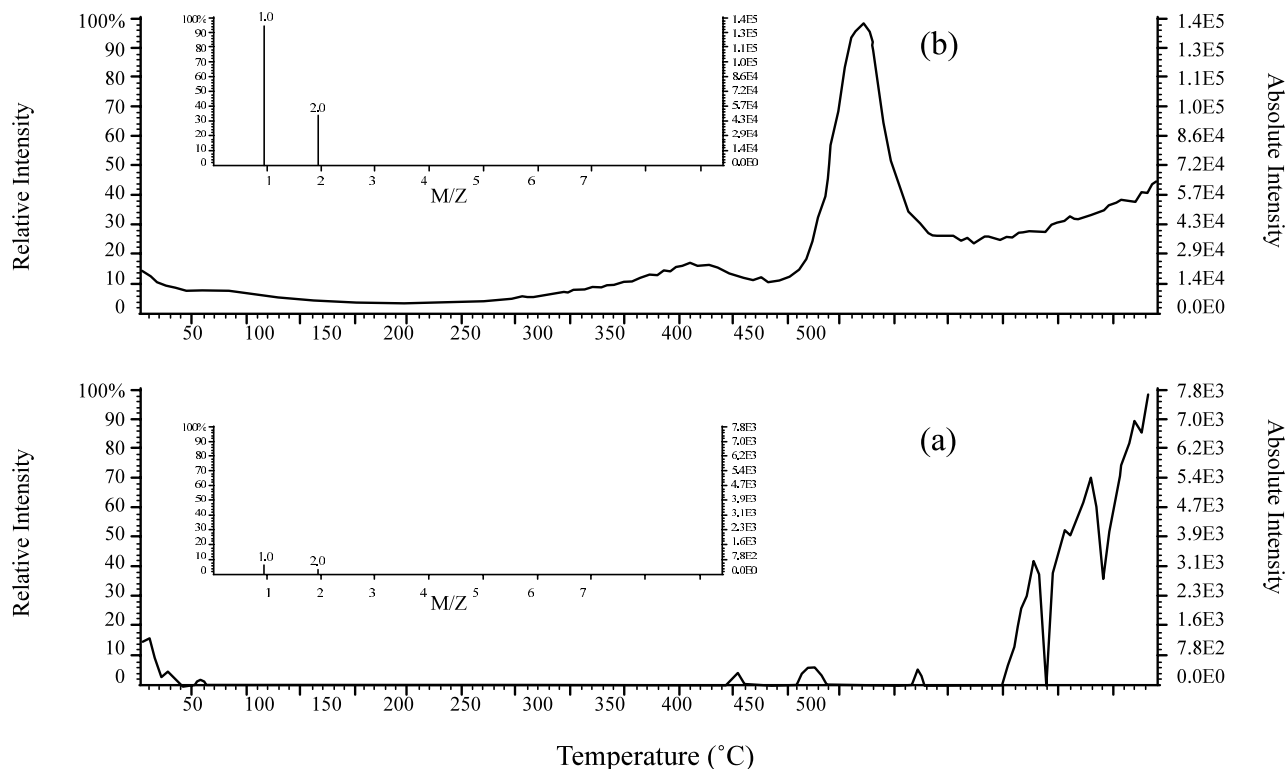


Fig. 6. Chromatogram of hydrogen evolved from (a) PMS feed stock and (b) treated PMS with 1 wt.% of borazine, respectively, and heated to 500 °C. Insert: average mass spectrum of the gases evolved by samples (a) and (b), respectively.

solutions for the fiber-spinning process were obtained by dissolving 2 g of the solid PMS in about 0.5 ml THF. The solution was allowed to age overnight to remove bubbles. As described by Yajima et al. [42,43], green fibers greater than 20 cm in length were prepared by drawing the viscous solution.

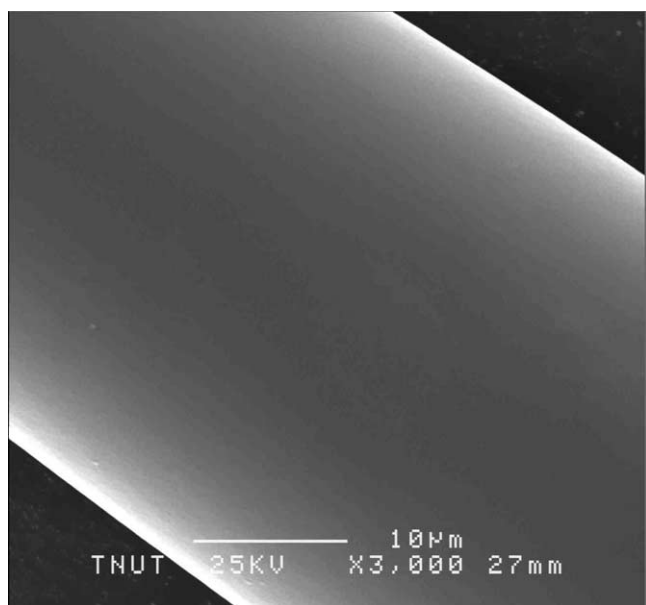


Fig. 7. The typical morphology of the modified PMS-derived green fiber.

4.3. Analytical techniques

All $^1\text{H-NMR}$ (Varian Unity 400MHz) experiments were performed using CDCl_3 as the solvent and all ^{29}Si CP/MAS-NMR (Bruker Solid State NMR Spectrometer DSX400MHz) experiments were carried out using tetramethylsilane (TMS) as a reference. Molecular weight distributions were determined by GPC (gel permeation chromatography, Waters) equipped with s-Styragel columns calibrated with polystyrene standards. THF was used as the eluent at a flow rate of 0.5 min^{-1} . Thermogravimetric analysis (TGA; TA Instrument 2950) was performed at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ to $1000 \text{ }^\circ\text{C}$ in a N_2 atmosphere. A Hitachi 3500 double-beam spectrophotometer was used to record the UV absorption spectra at room temperature, by dissolving a sample in hexane at a concentration of 2–3 wt.%. Gases evolved during the modification of PMS by 1 wt.% borazine were analyzed by gas chromatography/mass spectrometry (GC/MS, Finnigan MAT 271, Germany) to determine the amount of H_2 evolved. The pressure of H_2 was determined using a reference gas sample. Other components in the gaseous by-products were also investigated by GC/MS (HP5890/5971) equipped with a HP-5 capillary column ($25 \text{ m} \times 0.20 \text{ mm} \times 0.25 \text{ } \mu\text{m}$). The relative partial pressure was estimated according to the integrated area of every peak in the chromatograph spectrum. On the other

hand, the PMS modified at 70 °C for 3 h with 1 wt.% borazine was heated in a fused silica capillary column to 500 °C, and the total gas evolved was analyzed using a HP 5890 gas chromatograph coupled to a VG 70-VSE mass spectrometer (GC/MS); controlled by a VGOPUS data system running on a VAX station 3100-computer. The chromatograms and mass spectra of the constituent ionizable gases were obtained using a 70-eV electron beam; data-acquisition was performed at 3 °C internals.

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