

The Synthesis of SiCON Ceramics through Precursor Method

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ABSTRACT: A polymeric precursor, polysiloxazane (PSON), for SiCON ceramics has been synthesized by the partial hydrolysis of MeViSiCl₂, MeHSiCl₂, and MeSiCl₃ followed by ammonolysis reaction of the hydrolyzed intermediates with NH₃. The structure and thermal properties of the polymeric precursor were investigated by means of Fourier transfer infrared spectra (FTIR), ¹H-NMR, ²⁹Si-NMR, gel permeation chromatography, and thermogravimetric analysis. The structure of the SiCON ceramics

derived from the pyrolysis of PSON was characterized by FTIR and X-ray diffraction. The as-synthesized PSON produced mainly α -Si₃N₄ crystalline phase during pyrolysis at 1500°C under N₂ atmosphere, whereas when pyrolyzed at 1500°C under Ar atmosphere, crystalline phases of α / β -SiC and/or α -Si₃N₄ were detected. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: SiCON ceramics; precursor; pyrolysis

INTRODUCTION

Recently, ceramics of SiCON systems are a subject of increasing scientific interest because of their technological importance.^{1–3} They are very important structural and functional ceramic materials, which have very high-temperature strength, excellent oxidation resistance, lower expansion coefficient, high thermal shock resistance, and excellent resistance to nuclear damage, dielectric properties, and blocking metal diffusion.^{4–8} These inherent properties make them promising ceramic materials, which have been already widely used in fiber, film, and so forth.

SiCON ceramics were traditionally fabricated through inorganic solid reaction. However, there are some disadvantages in this method, such as high reaction temperature, long reaction time, and inhomogeneous reaction as well. Pyrolysis of polymeric precursor to obtain ceramics is emerging as a new method to prepare ceramics in recent years. Researchers have conducted extensive research on the pyrolysis of polycarbosilane (PCS), polysilazane, and polyborosilazane for ceramics; however, few works have discussed the synthesis and properties of polysiloxazane (PSON), which is a precursor for SiCON system ceramics.

Liu and Lu⁹ obtained SiCON ceramic fibers by ammonization of PCS fibers. The ammoniate process can be explained as a nucleophilic displacement of hydrogen and carbon by the attack of NH₂ radicals. The content of nitrogen in the samples varied with the ammoniating time, the concentration of ammonia, and ammoniating temperature. The tensile strength of the ceramic fibers prepared by this method reached to 3.2 GPa.

Schiavon et al.¹⁰ synthesized polycyclic silazane/siloxane networks via hydrosilylation reaction from [CH₂=CH(CH₃)SiNH]₃ and [CH₃(H)SiO]₄ with different Si–H:Si–vinyl molar ratios. The resultant polymers were pyrolyzed up to 1000°C in N₂ atmosphere, producing SiCON glasses, whereas when pyrolyzed at 1500°C, β -SiC and amorphous SiO₂ were produced. The final materials were identified as SiC/SiCON composites in nano/amorphous phases.

Pre-ceramic polymers play an important role in the processing of different ceramic materials, in which one of the primary objectives in polymer synthesis is to develop systems that are inexpensive and to produce ceramic materials with high ceramic yields. One of the major goals of the study is to develop a simple procedure to synthesize PSON polymer with high ceramic yield from low-cost starting materials. Based on these requirements, the raw materials for this study are MeViSiCl₂, MeHSiCl₂, and MeSiCl₃, which are commercially inexpensive. The polymer precursor for silicon oxynitride ceramics was prepared by the partial hydrolysis of MeViSiCl₂, MeHSiCl₂, and MeSiCl₃ followed by ammonolysis reaction of the hydrolyzed intermediates with NH₃. Then the

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pyrolysis of the polymer precursor resulted in SiCON ceramics. The prepared polymers were pyrolyzed at 1500°C, yielding SiC/SiCON composites and Si₃N₄/SiCON composites under different atmospheres, respectively.

EXPERIMENTAL

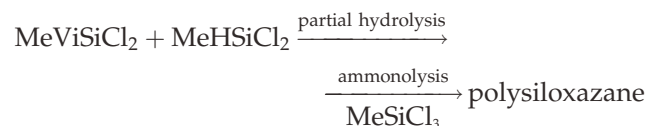
Raw materials

MeViSiCl₂, MeHSiCl₂, and MeSiCl₃ (Jilin Buddy Chemical, China) were distilled before use; dicumyl peroxide (DCP; Beijing Chemical Reagent, China) was recrystallized from ethanol before use; tetrahydrofuran (THF) and toluene (Beijing Chemical, China) were refluxed to dry using sodium before use; and deionized water was obtained from the Institute of Semiconductor, Chinese Academy of Sciences, Beijing, China.

Synthesis of the polymer precursors

A frozen circulation machine was used to control the temperature of the synthesis system. After the air in a three-necked flask was replaced with dry N₂ gas, MeViSiCl₂ and MeHSiCl₂ were mixed with different molar ratios into the flask in toluene as solvent. Then deionized water mixed with THF was slowly dropped into the stirred mixture, and after the addition of deionized water was complete, the mixture was kept stirring for a while. Then MeSiCl₃ was added into the system. After stirring for a while, NH₃ gas was introduced into this system accompanied by high-speed stirring. When the solution was alkaline, the system was purged continuously with ammonia for 2 h. Then the reaction mixture was filtered to remove ammonium chloride (NH₄Cl). When toluene in the filtrate was removed by vacuum, a viscous liquid, PSN, was obtained.

The as-synthesized three polymer precursors were indexed as PSN 1, PSN 2, and PSN 3, respectively. The synthesis procedure of the precursors can be expressed by the following formula, and the compositions of the raw materials for the polymeric precursors are listed in Table I.



Curing of the polymer precursors

To cure the PSN, 0.5 wt % DCP was added into the polymer precursor. Then the PSN was heated at 170°C for 2 h. After cooling down, a hard white bulk-cured PSN was obtained. The cured three precursors were indexed as PSN 1-C, PSN 2-C, and PSN 3-C, respectively.

TABLE I
The Synthesis Conditions of PSN 1, PSN 2, and PSN 3

Sample	PSN 1 (mol)	PSN 2 (mol)	PSN 3 (mol)
MeViSiCl ₂	0.2	0.2	0.2
MeHSiCl ₂	0.8	0.8	0.8
MeSiCl ₃	1.8	1.8	1.8
H ₂ O	0.1	0.3	0.5
Solvent	Toluene	Toluene	Toluene
Temperature (°C)	-20	-20	-20

Pyrolysis of the polymer precursors

The cured PSN was placed in an alumina crucible and pyrolyzed in a tube furnace in the presence of flowing nitrogen or argon. The pyrolysis process was conducted at a heating rate of 5°C/min with a dwelling time of 2 h at the highest pyrolysis temperature.

Characterization

Fourier transfer infrared spectra (FTIR) spectra were recorded on a Bruker Tensor-27 FTIR spectrometer in the wavenumber range of 4000–400 cm⁻¹ with KBr pellets. Average molecular weights of the polymeric precursor were estimated by gel permeation chromatography with polystyrene standard calibration using a Waters 1515 high-performance liquid chromatography pump equipped with four styragel columns (HR 0.5, HR 0.5, HR 1, and HR 2) and Waters 2414 refractive-index detector at 25°C in THF (1.0 mL/min).

The viscosity was measured by a Brookfield HADV-II viscometer at 31°C. Thermogravimetric analysis (TGA) was performed on a SII EXSTAR 6300 instrument heated from room temperature to 900°C at a heating rate of 10°C/min under nitrogen atmosphere at a flow rate of 200 mL/min. ¹H-NMR spectra were recorded in CDCl₃ solution with Bruker AVANCE 400 spectrometer. ²⁹Si spectra were recorded in CDCl₃ solution with Bruker AVANCE 300 spectrometer. X-ray diffraction (XRD) measurements were carried out on a Rigaku D/M4X 2500 diffractometer with Cu Kα radiation (λ = 1.5418 Å) using a continuous scanning mode with speed of 6°/min. Scanning electron microscopy (SEM) investigation was performed on a HITACHI JEOL s-4300 instrument.

RESULTS AND DISCUSSION

Characterization of the PSN

The molecular weight and viscosity of the synthesized three precursors are listed in Table II. The three precursors all presented low number-average molecular weight (*M_n*). The polydispersity indices

TABLE II
The Molecular Weight and Viscosity of PSON 1,
PSON 2, and PSON 3

Samples	M_n	M_w	M_w/M_n	Viscosity (Pa s)
PSON 1	586	3,079	5.25	28,044
PSON 2	451	1,615	3.58	14,757
PSON 3	797	3,248	4.08	8,975

(M_w/M_n) of the precursors ranged from 3.58 to 5.25. The viscosity of the precursors decreased with increasing content of the reactive water, because N—H and Si—H bonds in the polysilazane easily participate in crosslinking reaction. Of the three precursor polymers, PSON 1 has the largest number of Si—H and N—H bonds, and therefore, its viscosity is the highest.

Figure 1 shows the FTIR spectra of the synthesized PSON precursors, in which 3386 and 3047 cm^{-1} are assigned separately to the stretching of —NH₂ and =CH, and the stretching vibrations of C—H in —CH₃ and —CH₂— occur at about 2954 and 2897 cm^{-1} , respectively. The absorptions at 2150 and 1594 cm^{-1} are due to the stretching of Si—H and C=C bonds, respectively, and 1405 cm^{-1} is attributed to the in-plane bending vibration of C—H. The absorption at 1257 cm^{-1} is due to Si—CH₃ and at 1171 cm^{-1} is due to Si—NH—Si. The absorption at 1068, 944, and 767 cm^{-1} are separately due to Si—O—Si, Si—N—Si, and NSi₃, respectively.^{11,12} From the comparison of the three precursors, with water content increased in the raw materials, the intensity of Si—O—Si structure increased. This is because with increasing water in the system, more organochlorosilane will participate in the hydrolysis reaction in the first synthetic step.

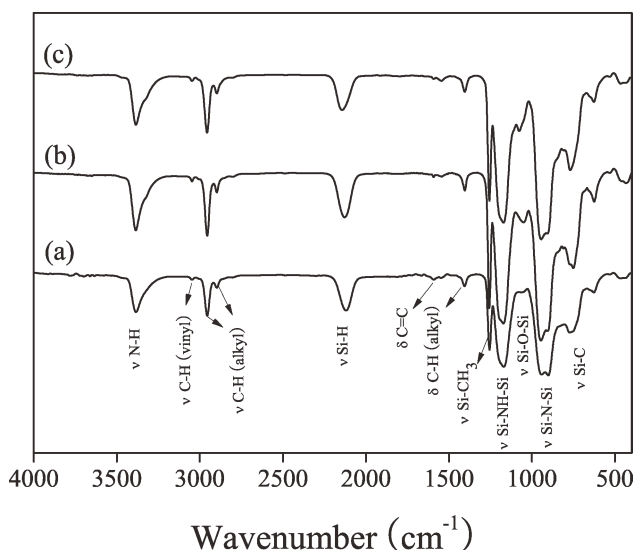


Figure 1 FTIR spectra of PSON 1 (a), PSON 2 (b), and PSON 3 (c).

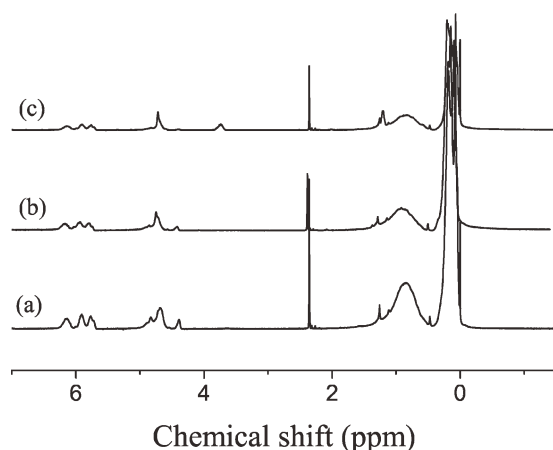
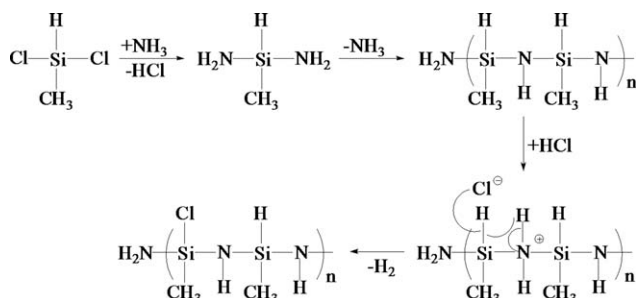


Figure 2 ¹H-NMR spectra (in CDCl₃) of PSON 1 (a), PSON 2 (b), and PSON 3 (c).

To better understand the structure of the products, ¹H-NMR of the polymeric precursors was examined. Figure 2 illustrates the ¹H-NMR spectra of the three precursors. In the ¹H-NMR spectra, the signals at 5.7–6 ppm are due to —CH=CH₂; the signals at 4.3–4.8 ppm are attributed to Si—H; the broad peak at 0.8–1.3 ppm arises from N—H; and the signals at 0–0.2 ppm are due to Si—CH₃. From the three ¹H-NMR spectra, it was found that the polymer synthesized under fewer water exhibits a higher intensity of Si—H; and although the molar ratio of Si—H/Si—Vi should be 4:1 according to the original raw material ratio, the practical ratio in the resultant polymer is lower than 4:1. The reason can be explained by the reaction shown in Scheme 1. HCl produced from the hydrolysis and ammonolysis will react with some Si—H fracture, generating some Si—Cl. As a result, the intensity of Si—H structure of the synthesized precursor will decrease with increasing water. Thus, the molar ratio of Si—H:Si—Vi should be lowered.¹³

The comparison of the ²⁹Si-NMR spectra of the three precursors is shown in Figure 3. Peaks at –15 to –18, –18 to –22, and –22 to –28 ppm in the ²⁹Si-NMR spectra are attributed to CH₃SiHN₂, CH₃ViSiN₂, and CH₃Si(N)₃, respectively.^{14,15} Broad peaks at –32 to –37 ppm are assigned to



Scheme 1 Possible reaction of MeHSiCl₂ during ammonolysis.

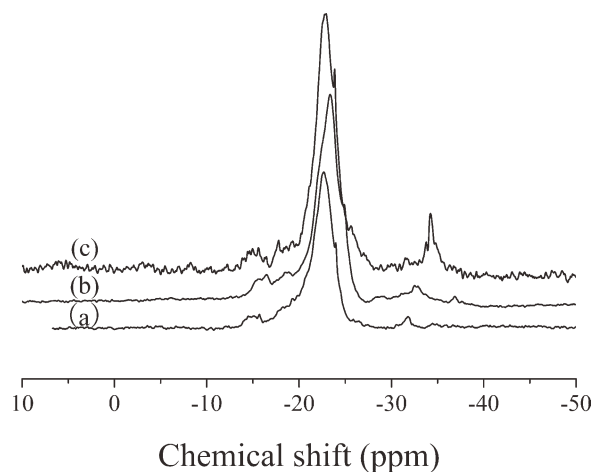


Figure 3 ^{29}Si -NMR spectra (in CDCl_3) of PSN 1 (a), PSN 2 (b), and PSN 3 (c).

$\text{CH}_3\text{VSiO}_2^{16}$ and $\text{CH}_3\text{HSiO}_2^{17}$ which can also reveal the complex chemical structure of the synthesized polymeric precursors.

TGA curves of the three cured precursors are shown in Figure 4. In this figure, it could be seen that the three precursors after curing are able to possess high ceramic yield above 70 wt % at 900°C (PSN 1 = 78.9%; PSN 2 = 75.5%; and PSN 3 = 74.2%). For comparison, the TGA curves of these three precursors in nitrogen are similar. All the three thermogravimetric profiles were observed to have two main degradation steps. The first step between 150 and 500°C corresponds to the evolution of ammonia through the reaction of transamination. The different weight loss (PSN 1 = 9%; PSN 2 = 11%; and PSN 3 = 12%) of the three precursors from room temperature to 500°C can be explained by the difference in the degrees of crosslinking due to the different numbers of N—H bond in the polysilazane, which can easily participate in the crosslinking

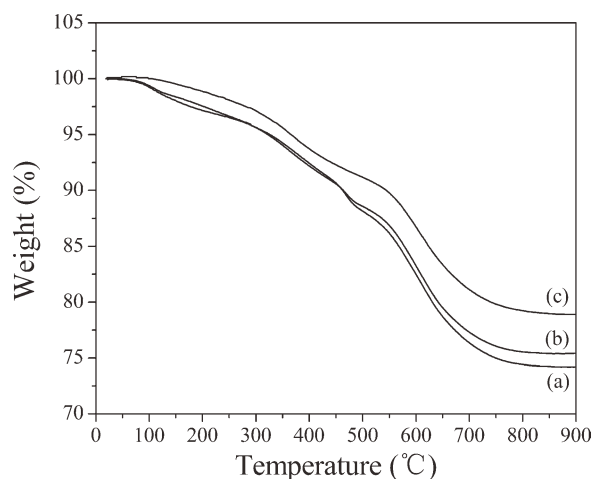


Figure 4 TGA curves of PSN 1-C (a), PSN 2-C (b), and PSN 3-C (c).

reaction. PSN 1 has the largest number of N—H bonds in the polymer, and therefore, its weight loss is the lowest. The second one between 500 and 850°C is due to the release of hydrocarbons and hydrogen, and the weight loss (PSN 1 = PSN 2 = PSN 3 = 13%) between 500 and 850°C for the three precursors are the same.^{18,19}

Conversion of PSN to SiCON ceramics

The pyrolysis behavior of the synthesized PSN was investigated by FTIR and solid ^{29}Si -NMR. To study the structural changes from the precursors to ceramics, the cured precursors (PSN 1-C, PSN 2-C, and PSN 3-C) were pyrolyzed at different temperatures. Based on the fact that PSN 1-C, PSN 2-C, and PSN 3-C are similar in structure, we just take PSN 2-C as an example. In its FTIR spectra shown in Figure 5, the intensity of N—H, Si—H and C—H, Si— CH_3 gradually decreases with the increasing treatment temperature. From Figure 5 (Curve c), it could be found that the peak of Si—H disappeared at 500°C , where the dehydrogenation reaction between Si—H, N—H and Si—H, Si—H took place. Besides, the intensity of N—H diminished, which was caused by the release of ammonia at about $150\text{--}500^\circ\text{C}$.²⁰ As shown in Figure 5 (Curve d), the intensity of Si— CH_3 decreased, and the peaks of — CH_3 and — CH_2 — disappeared due to the free radical reaction that occurred at the temperature of $400\text{--}800^\circ\text{C}$,²¹ whereas the peak of Si—H appeared again, which is probably owing to the decomposition of Si— CH_3 into Si—H.¹⁰ As shown in Figure 5 (Curve f), when the precursors were pyrolyzed at 1000°C , the

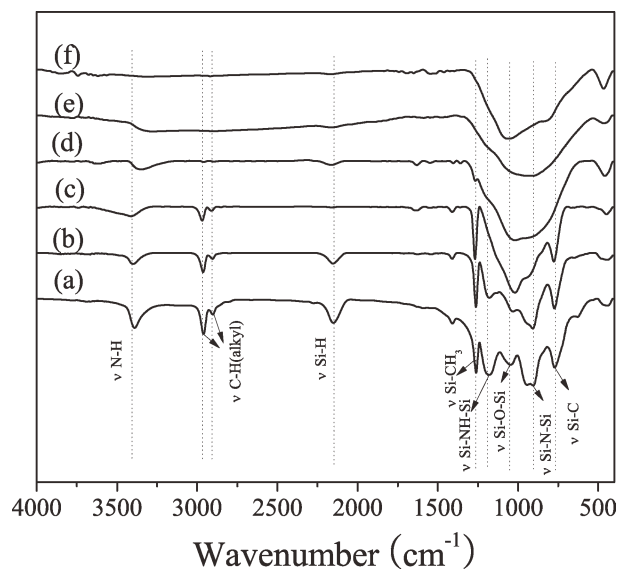


Figure 5 FTIR spectra of PSN 2-C (a) without pyrolysis and of the products from PSN 2-C pyrolyzed at 300 (b), 500 (c), 700 (d), 800 (e), and 1000°C (f) under Ar atmosphere.

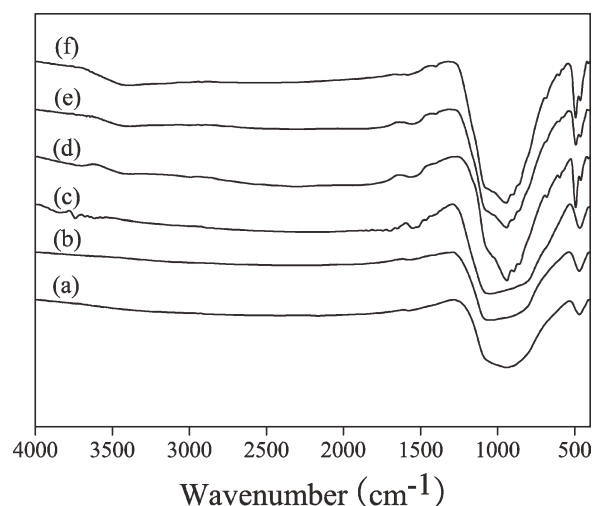


Figure 6 FTIR spectra of the products from PSON 1-C pyrolyzed at 1300°C (a), PSON 2-C at 1300°C (b), PSON 3-C at 1300°C (c), PSON 1-C at 1500°C (d), PSON 2-C at 1500°C (e), and PSON 3-C at 1500°C (f) under Ar atmosphere.

organic groups completely disappeared and the structure for ceramics was fully formed.

From Figure 6, when the precursors were pyrolyzed at the temperatures from 1300 and 1500°C, it could be seen that the organic groups such as Si–H, C=C, N–H, and C–H completely disappeared. When the precursors were pyrolyzed at 1300°C, the peaks of Si–N, Si–O, and Si–C overlapped in a very broad range of wavenumber, whereas when the precursors were pyrolyzed at 1500°C, the peaks became sharper because of the carbothermal reduction between the silica and the free carbon, as shown in Scheme 2.²² Therefore, the intensity of Si–O lowered and that of Si–C increased.

To further monitor the conversion process of the cured polymer to ceramics, ²⁹Si solid NMR spectroscopy was performed for samples obtained at different pyrolysis temperatures (Fig. 7). The assignment of the NMR resonance, especially the broad signals appearing in the NMR spectra of crosslinked polymers and amorphous materials, is difficult. We analyzed these data as reported in the literature. The ²⁹Si spectrum of PSON 2-C pyrolyzed at 400°C presents four peaks. Although the signal at –22 ppm was attributed to the silicon in (N)₃SiMe environment as presented in the liquid spectrum of the precursor, a new signal at –5 ppm appeared, which can be assigned to the silicon atoms in (N)₂Si(C^{sp3})₂ sites, denoting the crosslinking via hydrosilylation.¹⁴ The signal at –27.7 ppm was



Scheme 2 Carbothermal reduction of SiO₂.

attributed to the structure of SiMe(NH)₂O²³ and that at 1.9 ppm was assigned to NSi(Me)₃ sites, which was probably due to the modification of the polymer by the catalyst used.¹⁴ When the sample was pyrolyzed at 600°C, three peaks were distinguished in the spectrum, which were centered at –6.7, –22.8,

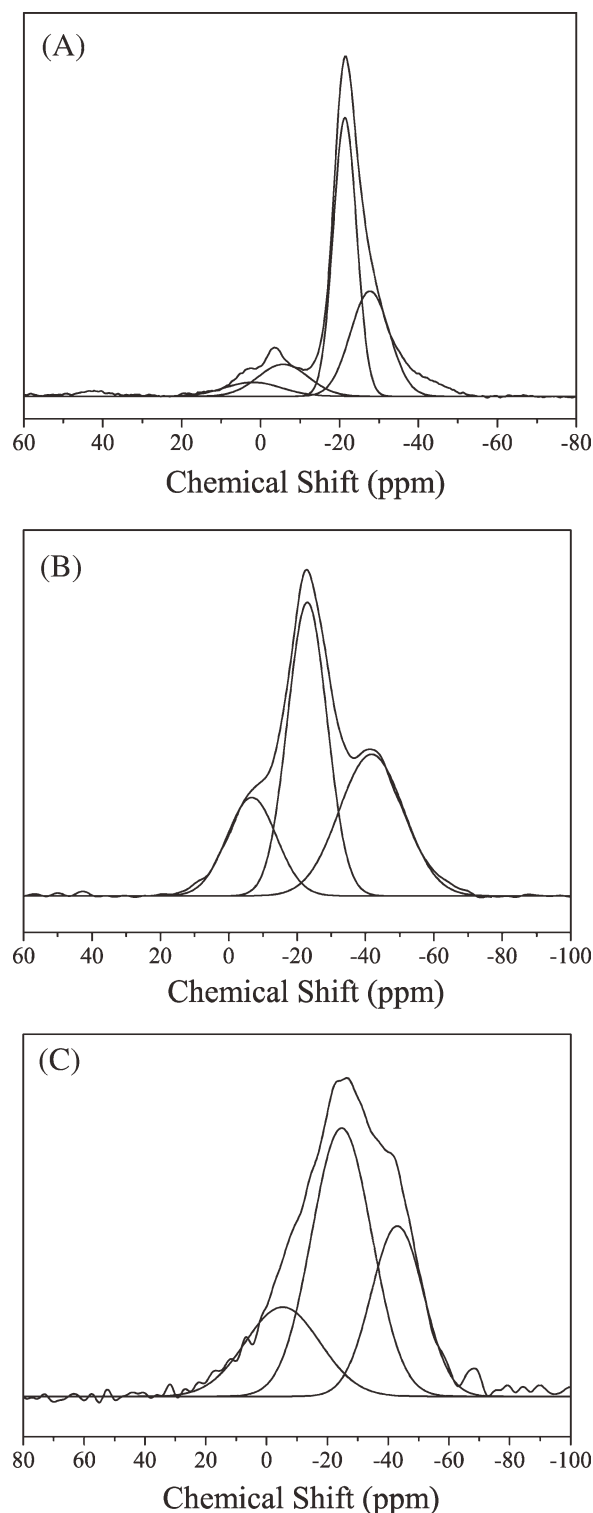


Figure 7 ²⁹Si-NMR of the products from PSON 2-C pyrolyzed at (A) 400, (B) 600, and (C) 800°C.

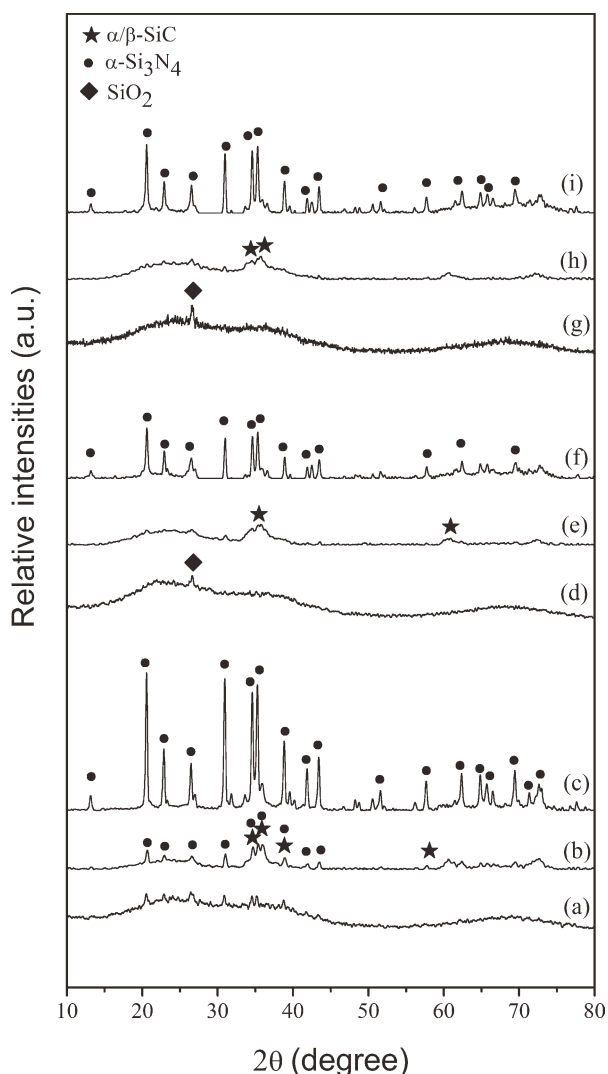


Figure 8 X-ray diffraction patterns of the pyrolytical products from PSN 1-C (a), PSN 2-C (d), and PSN 3-C (g) heated at 1300°C in Ar; PSN 1-C (b), PSN 2-C (e), and PSN 3-C (h) heated at 1500°C in Ar; and PSN 1-C (c), PSN 2-C (f), and PSN 3-C (i) heated at 1500°C in N₂.

and -42 ppm for the structures of $-\text{SiOC}_3-$, $-\text{SiN}_3\text{C}-$, and $-\text{SiN}_3\text{H}$, respectively.^{14,24} At higher temperature, the signals become broader and overlapped. When the sample was pyrolyzed at 800°C, there was a slight high-field shift of the peaks (-22.8 to -24.6 ppm and -42 to -43 ppm). The high-field shift of the peaks was in correspondence with the increase in the amount of Si–N bonds and decrease in that of Si–C bonds, probably due to the evolution of C-containing species.¹⁴

Crystallization behavior of PSN-derived ceramics

To investigate the evolution of PSN-derived ceramics at high temperature, the pyrolytical products obtained at different temperatures were analyzed

by XRD. Figure 8 illustrates the XRD patterns of the products from PSN 1-C, PSN 2-C, and PSN 3-C heated at 1300 and 1500°C in the atmosphere of Ar and at 1500°C in the atmosphere of N₂. After pyrolyzed at 1300 and 1500°C, a grayish black powder was obtained. For the product of precursor PSN 1-C pyrolyzed at 1300°C in the atmosphere of Ar, there were weak diffraction peaks of $\alpha\text{-Si}_3\text{N}_4$ and $\alpha\text{-SiC}$ with amorphous matrix. However, the diffraction peaks of SiO₂ emerged in the products obtained from PSN 2-C and PSN 3-C precursors. When the pyrolysis temperature reached up to 1500°C in Ar, the diffraction peaks of $\alpha\text{-Si}_3\text{N}_4$ and $\alpha/\beta\text{-SiC}$ in the product obtained from precursor PSN 1-C became more obvious. The weak diffraction of $\alpha\text{-SiC}$ appeared in the amorphous matrix, and the diffraction peaks of SiO₂ disappeared in the pyrolytical products obtained from precursors PSN 2-C and PSN 3-C, indicating that the crystallization degree of the pyrolytical products decreased with the increase of water content during the synthesis of the precursors. The diffraction peaks of SiO₂ disappeared due to the carbothermal

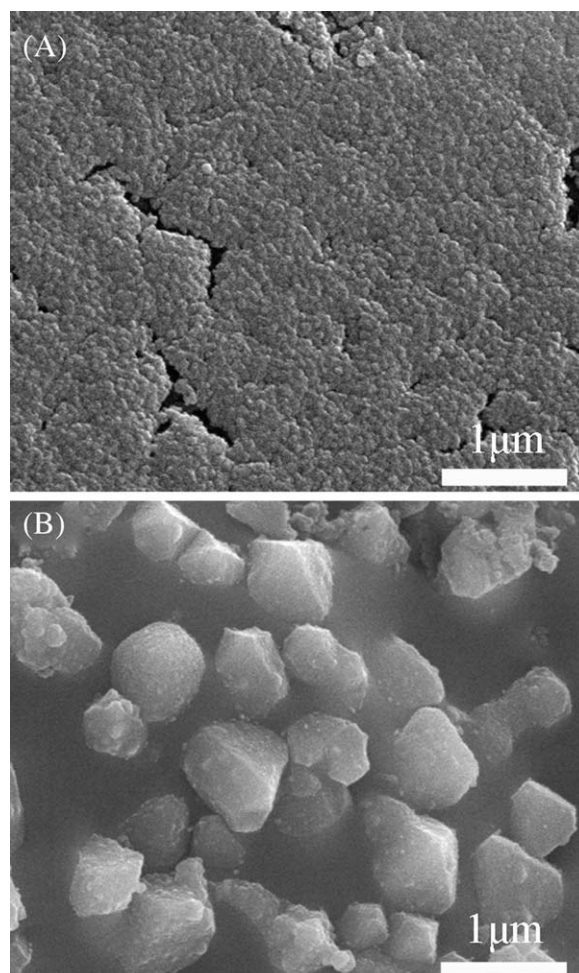


Figure 9 Scanning electron micrograph of the products from PSN 2-C pyrolyzed at 1500°C in the atmosphere of (A) Ar and (B) N₂.

reduction between the resultant silica and free carbon during pyrolysis, as shown in Scheme 2. The pyrolysis of the precursors at 1500°C in the atmosphere of N₂ resulted in the formation of crystalline α -Si₃N₄ within amorphous SiCON matrix for all three precursors.

Thus, the resultant ceramics of PSON 1-C can be described as a composite of Si₃N₄ and SiC/SiCON in a nano/amorphous phase, and those of PSON 2-C and PSON 3-C can be described as a composite of SiC/SiCON in a nano/amorphous phase.

The morphology of the obtained pyrolytical products was characterized by SEM. Based on the fact that the morphologies of the pyrolytical products from PSON 1-C, PSON 2-C, and PSON 3-C in the same atmosphere are similar, we just take PSON 2-C as an example. Figure 9 shows two typical SEM images of the products from PSON 2-C pyrolyzed at 1500°C in the atmosphere of Ar and N₂, respectively. In the products from PSON 2-C pyrolyzed at 1500°C in Ar, it was found that a large amount of amorphous nanoparticles with a size of 50–150 nm contacted each other very closely. The SEM image of the products from PSON 2-C pyrolyzed at 1500°C in N₂ show that some irregular nanoparticles distribute in the amorphous matrix, implying a better crystallization of the sample in N₂, which is consistent with the results of XRD.

CONCLUSIONS

The polymeric precursor for SiCON ceramic was prepared by the partial hydrolysis of MeViSiCl₂, MeHSiCl₂, and MeSiCl₃ followed by ammonolysis reaction of the hydrolyzed intermediates with NH₃. The effect of water content in the raw materials mixture on the structure and composition of the synthesized precursor was investigated. The ceramic yield of the precursor decreases with increasing content of the reaction water. The crystallization degree of the products from pyrolysis at the temperature between 1300 and 1500°C in Ar decreases with increasing content of the reaction water. In the product from precursor PSON 1-C pyrolyzed at 1500°C in Ar,

there exists α -SiC and Si₃N₄ phases in the matrix, whereas in those from PSON 2-C and PSON 3-C, only weak diffraction of α -SiC was observed within the resultant amorphous matrix. The pyrolysis at 1500°C in the atmosphere of N₂ resulted in α -Si₃N₄ within amorphous SiCON matrix for all the three precursors.

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