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Synthesis and characterization of polyvinylsilazane as a precursor for Si_3N_4 based ceramic materials

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Abstract This investigation focused on the synthesis and characterization of a polyvinylsilazane (PVSZ) polymer. This material shows promise as a precursor for silicon nitride/silicon carbide based ceramic materials. The polymer was synthesized via the ammonolysis of vinyltrichlorosilane (VTS) in tetrahydrofuran (THF). The polymer was characterized using Fourier Transform Infrared (FT-IR) spectroscopy, $^{1}H/^{13}C$ nuclear magnetic resonance (NMR) spectroscopy, and gel permeation chromatography (GPC). This polymer was found to have a molecular weight of around 880 g/mol, as determined by GPC. Thermal cross-linking, up to 1500 °C in an inert atmosphere, produced a ceramic material with a char yield of around 85%. The gas by-products from the partial decomposition of the polymer to a ceramic material were characterized using residual gas analysis (RGA). The crystallite phases of the ceramic char, pyrolyzed in different atmospheres, were determined by X-ray powder diffraction (XRD). Lastly, the ability of the polymer to form a free standing monolithic structure as well as the ability to be drawn into fibers was evaluated.

Introduction

Preceramic polymers play a vital role in the processing of different ceramic materials [1–5]. One of the primary objectives in polymer synthesis is developing resin systems that are inexpensive and produce ceramic material with high ceramic char yields. SiC and Si_3N_4 ceramic material derived from polycarbosilane and polysilazane preceramic polymers have recently received increasing attention [1–7]. Commercially available polymers such as S200 produced by COI Ceramics, Inc., which utilizes a hydridopolysilazane (HPZ) [8] system or Ceraset® Polysilazane 20 developed by KiON® [9] are either hard to manufacture or difficult to obtain. These polysilazane polymers produce Si_3N_4/SiC materials when pyrolyzed under inert atmospheres with char yields between 60 and 82% [8, 9].

One of the major goals of this study was to develop a simple procedure to synthesize a SiC/Si_3N_4 based preceramic polymer utilizing low cost starting materials while maintaining a high ceramic yield. Based on these requirements, the starting precursor chosen for this study was a vinylsilane. Vinyltrichlorosilane is an inexpensive precursor that has been previously used by Gregori [10] and Seryferth [1] as part of a co-ammonolysis procedure with favorable results. In this study vinyltrichlorosilane was not only used to provide the vinyl group for cross-linking, but also the silicon moiety for the backbone of the polymer. Previous studies have shown that the absence of a vinyl group on the polymer backbone yielded a material that required higher cross-linking temperatures and/or a stronger catalyst [1]. The polyvinylsilazane synthesized in this paper can be easily cross-linked at around 180 °C in an inert atmosphere or by the use of a radical initiator at room temperature in an inert atmosphere. Cross-linking is one of many mechanisms which decrease decomposition during pyrolysis thus increasing ceramic yield and reducing volume contraction [1, 11–13]. Other polysilazane systems that lack vinyl substituents require a strong base (like KH) to accomplish cross-linking between hydrogen functional

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groups [1]. Dicumyl peroxide is a more practical cross-linking agent than hydrides for use in industry [14]. However, due to the reactivity of vinyl side groups [15], cross-linking at elevated temperature under inert conditions was all that was necessary for this PVSZ system.

The PVSZ polymer can be synthesized via the ammonolysis reaction of vinyltrichlorosilane in THF. This reaction follows the general equation described in the literature for the ammonolysis of other similar silane precursors [1, 7]. The proposed reaction is described below (Fig. 1) and results in a linear polyvinylsilazane network.

Experimental

Synthesis

The PVSZ polymer was synthesized via the ammonolysis of reagent grade vinyltrichlorosilane (Gelest, Inc.) dissolved in reagent grade tetrahydrofuran (Alfa Aesar®). To synthesize the polymer, THF was first added to a 2 L Erlenmeyer flask equipped with a two hole rubber stopper which housed the injector and exhaust tubes. Both the injector and exhaust tubes were 9 mm fused silica tubes (see Fig. 2).

Ultra high purity (UHP) nitrogen (Airgas) was first introduced into the flask in order to purge any residual air from the reactor. THF was then added to the flask under anhydrous conditions, followed by the addition of an appropriate amount of vinyltrichlorosilane (10:1 volumetric ratio of solvent to precursor) at 0 °C with an ice bath. Anhydrous ammonia (Airgas) gas was then bubbled into the solution via the quartz tube accompanied by high speed magnetic stirring. A separate flow of UHP nitrogen was used to dilute the ammonia and prevent the exhaust tube from clogging up with ammonia chloride. The ammonia flow was periodically interrupted to insure that the reaction proceeded at a controlled rate. The resulting mixture was filtered to remove any by-products formed from the reaction. The by-product (NH_4Cl) was removed via a vacuum filtration system, which consisted of a 1 L Erlenmeyer vacuum flask and a 600 mL Büchner funnel equipped with a 4–5 μm ceramic frit. Prior to the filtration, the funnel was rinsed several times with THF to remove any absorbed moisture in the frit. The reaction mixture was poured into the filter to separate the solid ammonium chloride from the PVSZ/THF solution. If the filter became clogged, this meant that the reaction did not go to completion and the mixture had to be placed back into the reactor to be further ammonolyzed. Once the solid ammonium chloride was separated from the PVSZ/THF solution, the solvent was removed via a rotary evaporator to yield a pale yellow viscous liquid. The density of the polymer was determined using a 10 mL pycnometer. The shelf life of this polymer was found to be limited (1 day). Therefore, a small amount of THF was introduced back into the vessel containing the PVSZ polymer. In this fashion, the shelf life of the polymer was considerably extended. In addition, the PVSZ/THF solution was always kept under a nitrogen atmosphere and in a freezer when not being used.

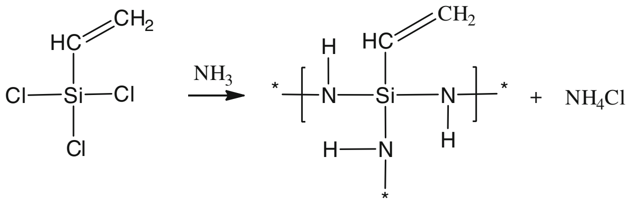

Fig. 1 Proposed structure of the PVSZ polymer resulting from the ammonolysis of vinyltrichlorosilane in THF

Solid puck and fiber formation

A solid puck was fabricated by placing approximately 60 mL of the liquid PVSZ polymer into a 100 mL beaker

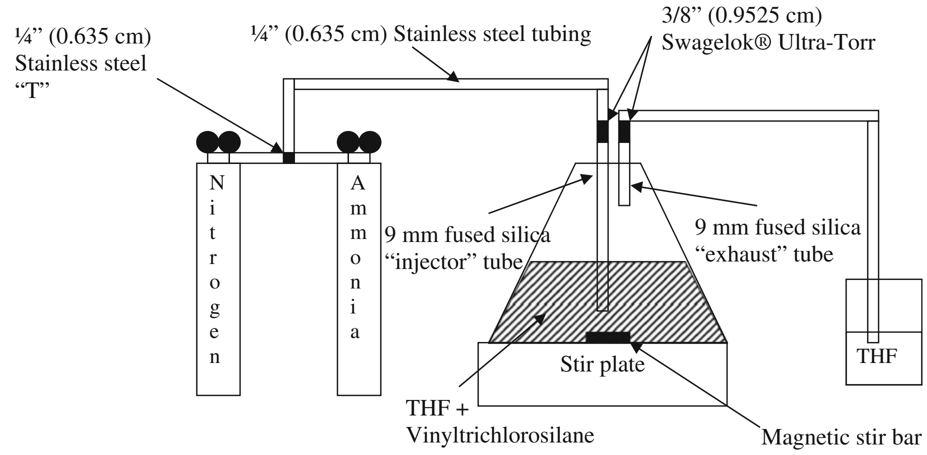

Fig. 2 Reaction vessel designed and built to synthesize the PVSZ polymer from the vinyltrichlorosilane precursor

with 1% (by mass) of the catalyst dicumyl peroxide (99.9% Sigma-Aldrich™). This beaker was placed in a furnace under flowing UHP nitrogen and heated to 350 °C at a heating rate of 2 °C/min and a dwell time of 1 h. Fibers were drawn by dipping a glass pipette into a vial of the liquid PVSZ polymer and slowly drawing a fiber from the "neat" polymer. The fibers were then pyrolyzed by heating the fibers under flowing UHP nitrogen to a temperature of 1000 °C at a heating rate of 2 °C/min. The fibers were held at 1000 °C for 1 h.

Characterization

FT-IR characterization on the polymer was performed using a Nicolet 740 Magna FT-IR with a resolution of 4 cm^{-1}. ^{1}H/^{13}C NMR spectroscopy characterization on the polymer was conducted using a Bruker DXR-400. All NMR spectra were acquired using $CDCl_3$ as the solvent at operating frequencies of 400 MHz (^{1}H spectra) and 100 MHz (^{13}C spectra). The molecular weight of the polymer was determined using a GPC Viscotek MAX TDA 302 tetra-detector. Elemental analysis was carried out for C, N, and O by combustion and Si concentration by difference. Thermo-gravimetric analysis was carried out utilizing a SDT Q600 TGA. The TGA experiments were carried out by placing a small amount of liquid PVSZ polymer in an Al_2O_3 boat and heated to 1000 °C at 2 °C/min. The mineralized polymer was then heated to 1500 °C at a rate of 5 °C/min and held at temperature for 5 min. The whole process was carried out under flowing UHP N_2 gas. In order to determine the gaseous species evolved during the pyrolysis cycle a MKS Cirrus™ benchtop atmospheric residual gas analyzer was used. The analysis was performed by placing 1 g of the liquid PVSZ polymer in a quartz boat inside a hot-walled furnace. The reactor was heated from room temperature to 800 °C at a rate of 1 °C/min with a sampling rate of 20 cm^3/min. Prior to heating, a 3/8″ (0.9525 cm) Swagelok® Ultra-Torr vacuum fitting was connected to the end of the reactor which was connected to the RGA. Micrographs of the pyrolyzed material were obtained using a Zeiss DSM 982 Gemini field emission scanning electron microscope (FE-SEM) with a Schottky Emitter at an accelerating voltage of 2 kV. The ceramic powders produced for X-ray analysis were obtained by pouring liquid PVSZ polymer into a 50 mL alumina combustion boat and cured in five different atmospheres (UHP nitrogen, UHP argon, UHP helium, UHP hydrogen, and anhydrous ammonia) at a heating rate of 1 °C/min to 1600 °C and held at the final temperature for 1 h. The XRD patterns were obtained using a Scintag 2000 XDS instrument with a Cu Kα X-ray source with a beam voltage of 45 kV and 40 mA beam current. The scan was from 5° to 75° with a scan rate of 0.1°/min. X-ray diffraction patterns were verified by JCPDS cards and Jade™ X-ray software.

Results and discussion

Observations in synthesis

Prior to the introduction of ammonia gas into the THF/VTS solution, the solution was a faint yellow color. Once the ammonia gas was introduced, the color changed to milky white due to the formation of the byproduct ammonium chloride (NH_4Cl). During the first half of the synthesis process, the reaction vessel showed little to no variation in temperature. Throughout this process, the first and second chlorine atoms on the vinyltrichlorosilane were lost as reported by Matsumoto [9]. During the last half of the reaction, the reaction underwent an exothermic process causing an increase in temperature. This has been attributed to the removal of the third chlorine [9]. Midway through the reaction, the vessel was shaken several times to make sure that the entire VTS precursor had reacted with the ammonia to form the PVSZ polymer. Depending on the extent of conversion during the ammonolysis process, the vessel sometimes needed to be shaken to ensure the reaction went to completion. When the vessel was shaken, further exothermic reactions took place as well as a corresponding drop in pressure. For this reason, the exhaust line from the reactor was placed in THF to ensure that air was not sucked back into the reaction vessel. In addition, nitrogen was always kept flowing along with the ammonia during the shaking process. The reaction was considered completed, when the by-product (NH_4Cl) had the resemblance of "cottage cheese". The PVSZ polymer was pale yellow in color and had a density of approximately 1.0 g/cm^3.

Fourier transform infrared spectroscopy

FTIR spectroscopy was used to analyze the structure of the liquid PVSZ polymer (Fig. 1). The spectrum shown in Fig. 3 supports the presence of the specific bonds which correlates with the structure proposed in Fig. 1 [15, 16]. The spectrum shows a broad absorption band at 3380 cm^{-1} which is attributed to N–H bonds. The shoulders at 3480 and 3200 cm^{-1} indicate stretches corresponding to NH_2. The two nitrogen bonding environments support the presence of the linear structure seen in Fig. 1. The presence of Si–CH=CH_2 is seen at 3050, 1920, 1590, and 1400 cm^{-1}, which means that there is no degradation of the vinyl group during the ammonolysis process. Since the reaction was performed in THF, there are residual bands at 2980, 2870, 1450, 1070, and 1010 cm^{-1} which are from the solvent.

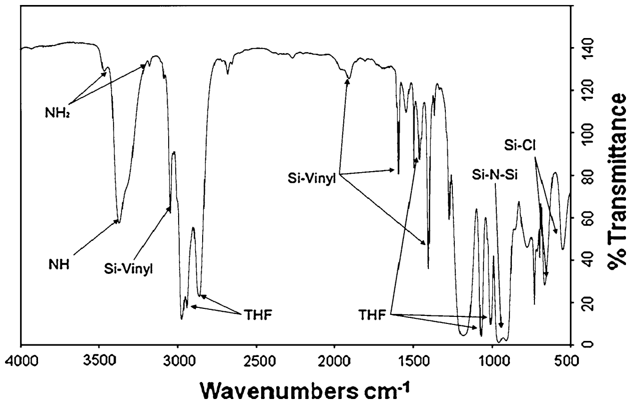

Fig. 3 Transmission FT-IR spectrum of the liquid PVSZ

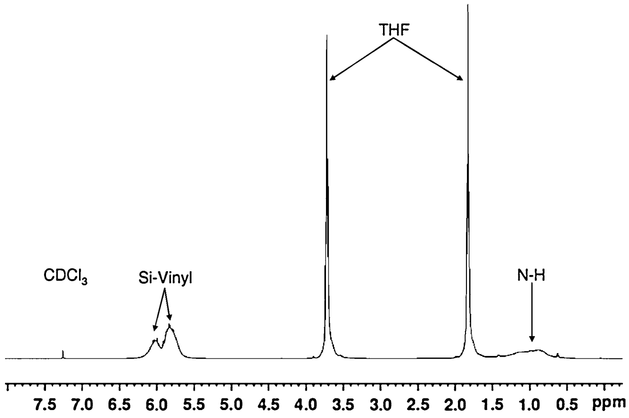

Fig. 4 ^{1}H NMR PVSZ polymer in $CDCl_3$

There is a broad peak around 1180 cm^{-1} representing the presence of Si–N–Si bonding in the polymer. Residual Si–Cl peaks are observed at 550 and 670 cm^{-1}.

Nuclear magnetic resonance

The structure of the synthesized PVSZ polymer was further characterized using ^{1}H/^{13}C NMR spectroscopy as seen in Figs. 4 and 5. In the ^{1}H NMR spectra, the THF peaks dominate the spectra with a triplet at 3.72 ppm and a quintet at 1.83 ppm. Between 1.46 and 0.67 ppm a broad peak appears which is attributed to coupling of the nitrogen proton to vinyl protons in different environments. The Si–vinyl peak is split into two multiplets at 6.02 and 5.84 ppm. This verifies the multiple bonding environments present in the Si–N–Si backbone.

To verify the environments determined from the ^{1}H spectra, ^{13}C NMR was utilized (Fig. 5). The peaks located at 66.2 and 25.8 ppm suggests the presence of residual THF in the polymer. The vinyl groups bound to the silicon can be seen at 140 and 132.3 ppm. The presence of two separate peaks in the ^{13}C NMR spectra verifies the existence of multiple environments in the polymeric backbone.

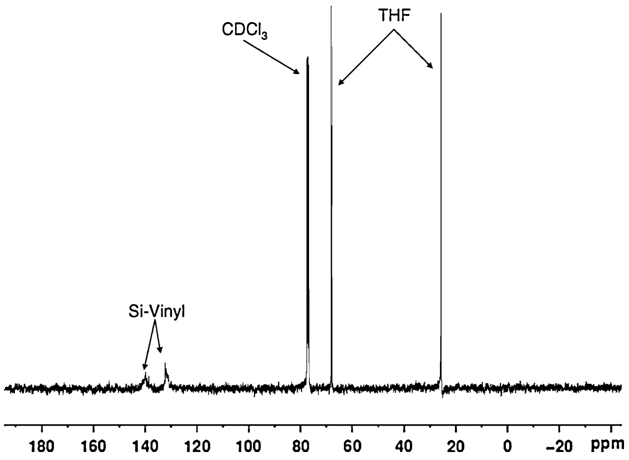

Fig. 5 ^{13}C NMR of PVSZ polymer in $CDCl_3$

Gel permeation chromatography

The average molecular weight of this polymer was found to be 880 g/mol by GPC. The instrument that was used to determine the molecular weight of the polymer has a lower limit of detection at around 1,000 g/mol. Therefore, our molecular weight is an average and will have a higher standard deviation of around 50 g/mol. This molecular weight is close in comparison to other commercially available polymer resins [8, 9].

Bulk ceramic composition

Compositional analyses of the ceramic char that was heat treated to 1100 °C in both argon and ammonia are presented in Table 1. Conversion of the polymer in both atmospheres resulted in a SiNC material. The silicon concentration was done by difference. Pyrolysis in ammonia resulted in a char with a higher nitrogen content and minimal carbon content. From the results of the analysis, there appears to be higher oxygen content in the material produced in the ammonia atmosphere than in the argon atmosphere. This may be due to the difference in the grade of gas used or the higher affinity for moisture that ammonia possesses over argon. In any case, it is unclear why there is such a difference in the oxygen composition between the two samples.

Table 1 Bulk composition of the pyrolyzed PVSZ in at.%

Pyrolyzing environment	Si	N	C	O
Argon	45.4	25.6	27.3	1.7
Ammonia	53.9	39.2	0.1	6.8

Thermogravimetric analysis and residual gas analysis

The results of the thermo-gravimetric analysis are shown in Fig. 6. From the analysis, the resulting char yield was greater than 85%. This conversion yield is consistent for these types of materials. For instance, the ceramic yield for Ceraset® Polysilazane 20 has been reported to be around 82% [9] and for HPZ the yield was around 60% [8]. In addition, the thermogram presented in Fig. 6 shows three mass loss events. The first event occurred below 250 °C, the second above 250 °C, and the final around 500 °C. In order to determine the chemical make up of the gaseous species evolved during these events, residual gas analysis was performed up to 800 °C in UHP helium.

Figure 7 presents the results of the RGA analysis that was performed in UHP helium. From room temperature up to 250 °C, species with a mass to charge ratio (*m*/*z*) ranging from 41 to 43 were detected. These evolved gases have been attributed to the decomposition of THF. The second stage ranged between 250 and 425 °C. During this stage, the major species detected was most likely due to NH_3 (17 *m*/*z*) and to a lesser extent, species with a mass to charge ratio of 15. These may be attributed to methyl radicals from the vinyl groups. The evolution of species with an *m*/*z* of 16 most likely originated from CH_4 or NH_2. As the temperature increased and the third stage was reached, the mineralization process began. In this third stage, the ammonia that was previously being evolved declined and the species with *m*/*z* ratios of 15 and 16 dominated the total amount of gases evolved during decomposition. Hydrogen was detected beginning near 500 °C. From the TGA results presented in Fig. 6, the continuing loss of mass from 800 to 1500 °C is most likely the result of hydrogen being evolved during the heat treatment. The phase of the resulting material from the RGA performed in UHP helium was confirmed to be α-SiC by XRD analysis (Fig. 8d).

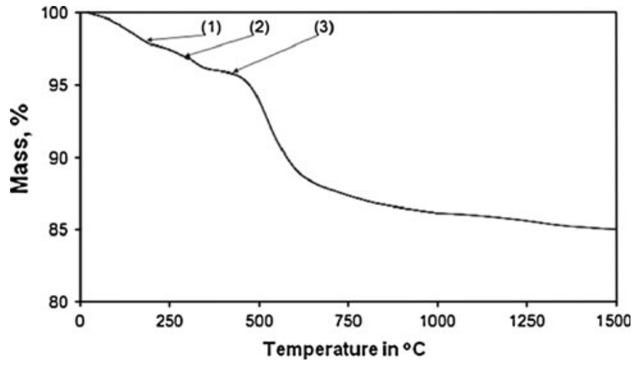

Fig. 6 TGA of the PVSZ polymer heat treated to 1500 °C under flowing UHP nitrogen gas. Note the three different mass loss events

X-ray powder diffraction

Figure 8 shows the XRD patterns for the polymer that was heat treated to 1600 °C in five different atmospheres. Figure 8a is the XRD pattern for the ceramic char that was heated in an anhydrous ammonia atmosphere. This heat treatment produced a white ceramic char that produced a very intense X-ray diffraction pattern. Comparison of the reflections and their intensities with the JCPDS cards and Jade™ X-ray software showed that the material was predominantly α-Si_3N_4 (JCPDS 41-360) with trace amounts of *β*-Si_3N_4 (JCPDS 33-1160). Figure 8b shows the XRD pattern for the ceramic char heated in the UHP nitrogen atmosphere. This material appeared as a dull black colored solid when removed at room temperature from the furnace. The X-ray diffraction pattern for this material also consisted of both the α-Si_3N_4 and the *β*-Si_3N_4 phases with the α-Si_3N_4 crystalline phase being the predominant phase. An interesting feature of this study was the lack of any SiC phase when heated in UHP nitrogen. This is contrary to XRD studies performed on KiON®'s polymers which showed a mixture a *β*-SiC, α-Si_3N_4, and *β*-Si_3N_4 (obtained from KiON®'s Technical Bulletin 1). The XRD pattern for the pyrolyzed PVSZ that was heat treated in argon is presented in Fig. 8c. The major crystalline phase shown in this figure was an α-SiC polytype (Moissanite-6H, JCPDS 29-1131). The minor phase was α-Si_3N_4. The presence of SiC in the ceramic char was not unexpected because there was an appreciable amount of carbon present in the polymer that was heat treated in argon (see Table 1). From the results shown in Fig. 8a, b, pyrolyzing the PVSZ polymer under either N_2 or NH_3 atmospheres yielded a char without reflections for SiC in the XRD patterns. This may be due to the reactivity of these two atmospheres at elevated

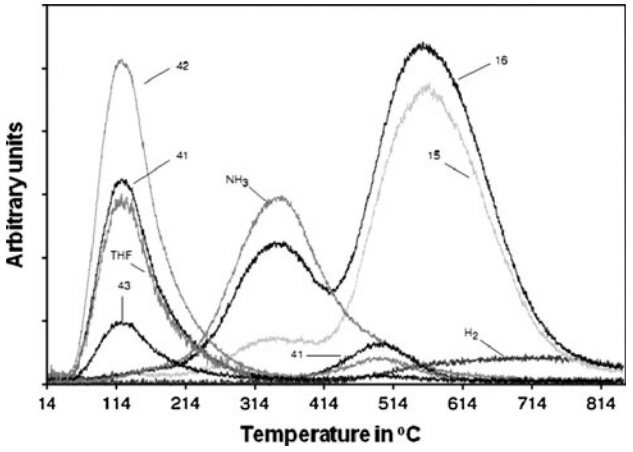

Fig. 7 Residual gas analysis of liquid PVSZ polymer heated to 800 °C in a UHP helium atmosphere. Note the three different regions

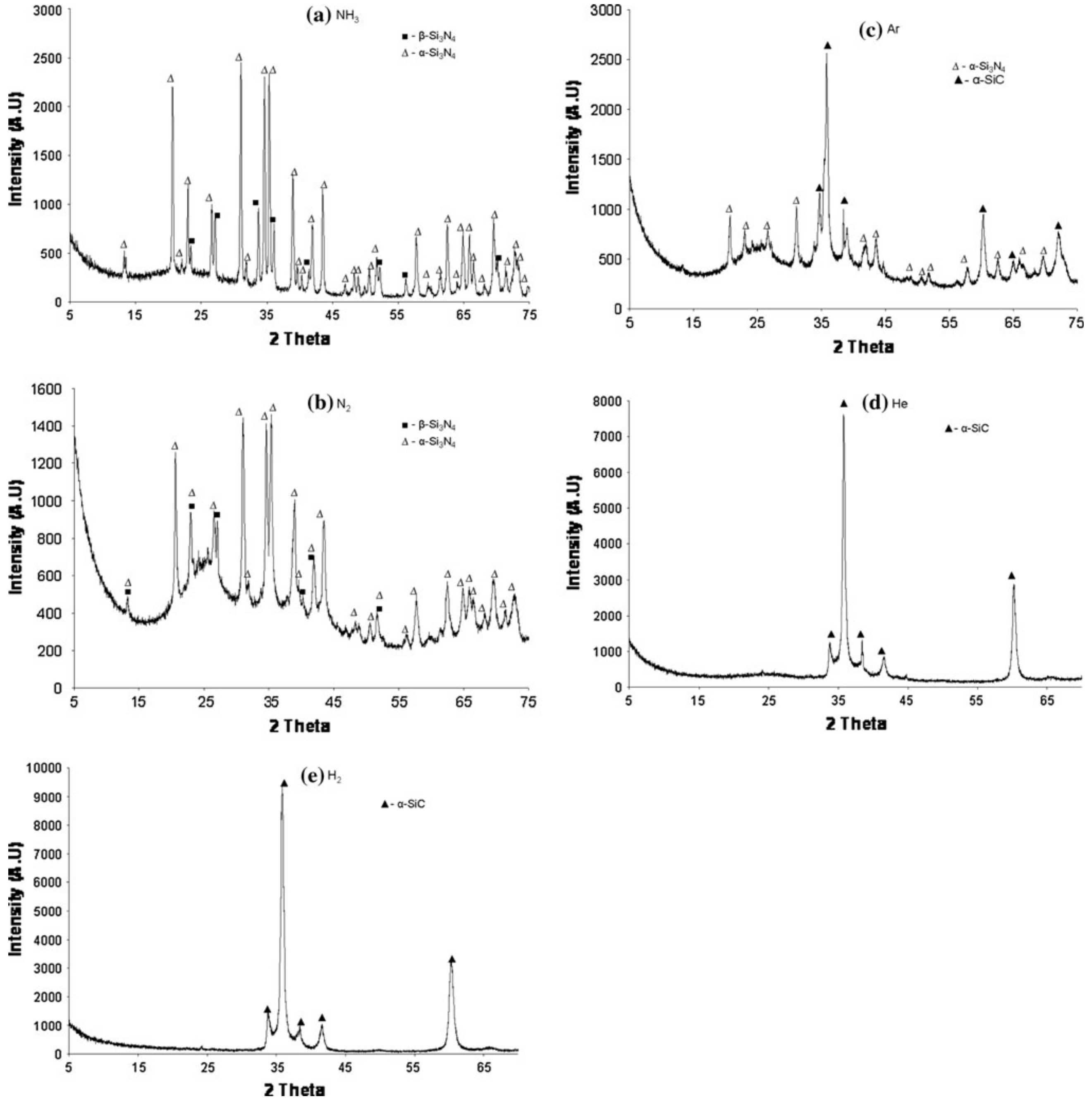

Fig. 8 X-ray diffraction patterns of the pyrolyzed PVSZ that was heat treated in different atmospheres to 1600 °C. **a** Ammonia, **b** Nitrogen, **c** Argon, **d** Helium, and **e** Hydrogen

temperatures. For the ammonia atmosphere, at elevated temperatures hydrogen may have reacted with the carbon in the partially pyrolyzed PVSZ to form methane. Under UHP nitrogen, the absence of carbon in the XRD pattern may be attributed to the reduction to an amorphous carbon. To further understand the phenomenon between the phase of the ceramic char and the pyrolyzing atmosphere, samples were pyrolyzed in UHP helium and UHP hydrogen. Figure 8d shows the XRD pattern for the ceramic char that was pyrolyzed in UHP helium atmosphere. The XRD pattern for the ceramic char that was pyrolyzed in UHP hydrogen atmosphere seen in Fig. 8e is similar to the ceramic char pyrolyzed in UHP helium (Fig. 8d). In these patterns only α-SiC was observed. An observation from the XRD study was proposed that using a nitrogen containing atmosphere (N_2 or NH_3) may have caused a cleavage of the carbon containing groups from the silicon during the pyrolysis process [1].

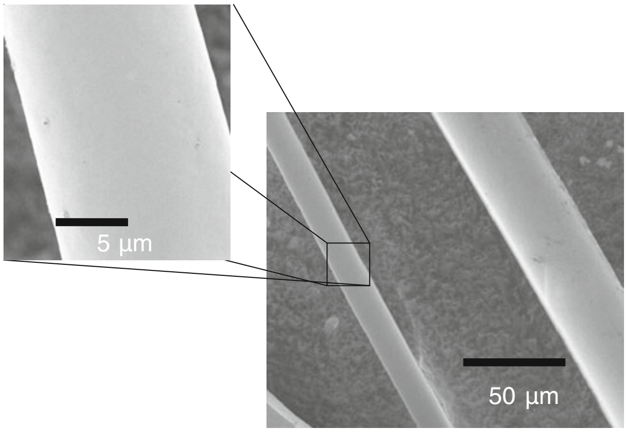

Fig. 9 FE-SEM micrograph of filaments that were drawn from the liquid PVSZ polymer and subsequently pyrolyzed to 1000 °C

PVSZ filaments and matrix material

The ability of this polymer to be used as a matrix material was investigated to see if the polymer had the ability to form a free standing monolithic structure and to examine the possibility of drawing fibers. A partially pyrolyzed PVSZ puck was formed after a 350 °C heat treatment in UHP nitrogen, yielding a pale yellow solid. Heat treatment in UHP nitrogen, greater than 500 °C, produced pucks that were black in color. While these observations are only at the beginning and middle of the pyrolysis cycle from polymer to ceramic, pucks made from commercially available polymers (Ceraset® Polysilazane 20 and S200) produced similar looking materials. This is a good indication that the PVSZ system would make an exceptional matrix material [17].

Figure 9 shows a FE-SEM micrograph of filaments that were drawn from the PVSZ polymer resin and pyrolyzed to 1000 °C. As shown in the micrograph, the fibers appear to have a relatively smooth surface (see inset) indicating that no surface defects were formed. FE-SEM analysis also showed that the filament diameter vary between 10 and 30 µm. Although commercially available fibers range from 10 to 15 µm [18, 19], the fact that these filaments could be drawn using a pipette gives credence to the use of this polymer to be fabricated into fibers.

Conclusions

This investigation focused on the synthesis of a polyvinylsilazane polymer. The polymer was synthesized via the ammonolysis of vinyltrichlorosilane in tetrahydrofuran. Thermogravimetric analysis showed that there was an 85% conversion of the polymer to a ceramic material up to 1500 °C. RGA analysis in a helium environment showed that the solvent, methane, ammonia, and hydrogen were the predominate species being evolved during the mineralization process. The polymer was also characterized by both FT-IR and NMR spectroscopy. XRD analysis showed that a crystalline material could be formed at 1600 °C. In addition, the results of the XRD analysis show the ability to tailor the crystallinity of the pyrolyzed PVSZ to Si_3N_4, SiC or a mixture of the two by changing the atmosphere used during the pyrolysis process. Finally, the ability of this polymer to form a free standing monolith and to be drawn into fibers was shown. In conclusion, this material shows promise as a precursor for silicon nitride/silicon carbide based ceramic materials.

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