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Synthesis, characterization and ceramization of a novel vinyl-rich liquid precursor for Si(O)C ceramic

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Abstract

Polymethylsilane (PMS) was partially modified with 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane ($[CH_3(CH_2{=}CH)SiO]_4$, D4Vi) via conventional hydrosilylation. The as-synthesized vinyl-rich liquid precursor (V-PMS) was characterized by the viscosity test, gel-permeation chromatography, Fourier-transform infrared spectroscopy, nuclear magnetic resonances spectroscopy. The results indicate that the obtained precursor is well soluble in common solvents and exhibits a controllable viscosity of 326.9–714.6 mPa s at room temperature. The thermal properties of V-PMS were investigated by differential scanning calorimetry and thermogravimetric analysis. The V-PMS can be cured readily at 150 °C in inert atomosphere. The ceramic yield of V-PMS reaches 81% at 1200 °C, 38% higher than that of PMS. The final pyrolytic residue is hard, dense monolithic up to 1400 °C under Ar atmospheres. The controllable viscosity, excellent thermal curability and high ceramic yield enable the liquid precursor a promising material to shape various Si(O)C ceramic materials for high-temperature application.

Keywords: A. Precursor: organic; C. Thermal properties; D. SiC.

1. Introduction

Polymer-derived ceramics (PDCs) is a relatively new and promising technique for preparing advanced ceramics. The most competitive advantage of PDCs is that it can produce various complex shapes, such as ceramic fibers, coatings and composite materials, which is difficultly obtained by using the traditional powder technology [1,2]. In the past four decades, many advanced ceramic materials, such as SiC, SiOC and SiCN have been prepared via pyrolyzing preceramic polymer polycarbosilanes (PCS), polysiloxanes (PSO) and polysilazanes (PSZ) [3–6]. Among them, polymer-derived SiC ceramics has unusual high thermal stability, excellent chemical durability and outstanding mechanical properties, which are found to have various applications under stringent conditions, including aerospace, electronics, nuclear, and transportation industry fields [7–11].

Precursor synthesis is one of the key issues in the fabrication of PDCs, since the molecular structure of the precursor influences to a great degree of the composition and microstructure of the final ceramics. Thus, the chemical and physical properties of ceramics can be adjusted through the molecular design of the precursor. As an ideal precursor, the polymers should firstly possess a sufficiently high molecular weight to avoid volatilization of low weight fragments. Secondly, they should have appropriate rheological properties or solubility for the shaping process. Thirdly, they must exhibit latent reactivity (presence of functional groups) for the curing or cross-linking step. Moreover, polymeric structures with cages or rings are appreciated to survive a series of dramatic chemical reactions to the final ceramics [1,2,12]. Presently, PCS has been regarded as the most successful precursor for SiC [3,8,9,13]. However, the PCS encountered unavoidable drawbacks, such as high synthetic cost, low fluidability, foamable cure and low ceramic yield [14], which restrict its application in the fabrication of high performance SiC ceramics. STARFIRE SMP-10 by Starfire Systems Company is the only commercially available liquid precursor for SiC, but the cost is too high to be use for mass production [15]. Thus, new methods are highly appreciated for the synthesis of precursor for SiC ceramics.

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As another liquid precursor for SiC, polymethylsilane (PMS) has attracted substantial interest in the past years because of its stoichiometric composition (-$(SiH(CH_3))_n$-) and latent chemical activity [16–20]. However, the low ceramic yield restricts its application as a precursor for high performance SiC ceramic materials. As is known, a prerequisite for processing ceramic components by using liquid precursors is that the part needs to be transformed into thermoset which can retain the shape during ceramization. Therefore, the incorporation of suitable functional groups such as vinyl to PMS can enable the obtained precursor to form a thermoset via addition reaction that occurs spontaneously at a low temperature (typically, below 200 °C), with the additional benefit of increasing the ceramic yield and avoiding the evaporation of oligomers. Based on an overall consideration, we selected 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, ($[CH_3(CH_2{=}CH)SiO]_4$, D4Vi) as the curing agent to modify PMS.

In this work, the facile and cheap synthesis of a liquid precursor rich in vinyls was reported. The as-synthesized precursor, its polymerization and curing process were described. Additionally, the thermal properties, pyrolysis conversion, crystallization behavior and ceramic microstructure of this novel material were also investigated.

2. Experimental

2.1. Synthesis of the precursor

All reactions were carried out under N_2 atmosphere. PMS was synthesized as a yellow viscous liquid by a condensation reaction of methyl dichlorosilane (98%, Xinghuo, China, distilled before used) and metallic sodium (97%, Lingfeng Chemical Inc., China) as described previously [18]. PMS and D4Vi (98%, Shanghai Duolin Chemical Inc., purified by distillation) were first mixed, then heated at 120 °C for 3 h under a N_2 flow (heating rate: 3 °C/min), a liquid precursor (abbreviated as V-PMS) was then obtained.

2.2. Cross-linking and pyrolysis of the precursor

Thermal curing of V-PMS was performed under nitrogen atmosphere in a tube furnace. The furnace was heated from room temperature to 150 °C at a heating rate of 5 °C/min, and dwelled for an additional 2 h. Simply cooling the furnace to room temperature gives a pale yellow hard monolith.

Pyrolysis of the polymer was carried out in a high-temperature alumina tube furnace under ultra-high pure nitrogen atmosphere. The furnace was heated from room temperature to 400, 600, 800, 1000 and 1200 °C at a heating rate of 10 °C min^{-1}, dwelling for an additional 2 h, respectively. Additional heat treatments for the crystallization of the as-obtained ceramics were carried out in a flowing 99.999% ultra-high pure argon atmosphere in graphite furnace (AStro Furnace) using a graphite crucible heated to 1400, 1600 °C with a heating rate of 20 °C min^{-1} and held for an additional 2 h, respectively.

2.3. Characterization

The Gel-permeation chromatography (GPC) analysis was performed on a Waters 1515 apparatus using THF as eluent and polystyrene standards for calibration. The viscosity of the polymer was tested by NDJ-1 rotary viscometer at room temperature. Fourier-transform infrared (FTIR) spectra were obtained with a Nicolet Avatar 360 (Nicolet, Madison, WI) instrument from solid samples embedded in KBr pellets or from films deposited on KBr pellets in the case of liquid samples. ^1H NMR spectra of the polymers were acquired from solutions in $CDCl_3$ on a Bruker Advance 400 MHz instrument (Bruker, Germany). ^{29}Si-MAS-NMR spectra were measured with a Bruker AV 300NMR spectrometer (Bruker, Germany) 59.62 MHz. Quantitative analyses of carbon was measured in an Elemntar Vario EL, ELTRA CS-444 C/S analyzer, whereas O was measured in an IRO-I oxygen determinator. Si was quantified by means of ICP-AES in an Arl 3580B spectrometer. Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) was carried out on a NETZSCH STA449C (Netzsch STA449C, Netzsch, Germany) thermogravimetric analyzer at a heating rate of 10 °C/min with Ar flow rates of 100 cc/min. X-ray diffraction analysis was characterized by a Brucker ADVANCED X-ray diffraction analyzer (Bruker, Germany) with CuK_α radiation. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-5600 LV electron microscope.

3. Results and discussion

3.1. Synthesis and structure characterizations of V-PMS

The synthesis of V-PMS was based on a two-step reaction: a wurtz condensation between methyl dichlorosilane and metallic sodium to synthesize PMS, and a hydrosilylation addition between D4Vi and PMS to obtain V-PMS. The synthesis processes in this protocol are simple, cheap and easily controllable. The mass of the product V-PMS can easily be scaled to kilogram order, which is very promising for industry application.

A series of experiments was performed with good replicability using different weight ratios D4Vi to PMS, and the parameters and properties of the polymer were shown in Table 1. It is obvious that the weight-average molecular weights of the product increase remarkably with the rise of the weight ratio of D4Vi to PMS, from which we can speculate that vinyl groups in D4Vi have been successfully introduced into the backbone of PMS via hydrosilylation reaction. As a result, the viscosities of the polymers rose with the increasing of molecular weight.

Moreover, the as-synthesized V-PMS exhibits excellent solubility in most organic solvent, such as acetone, toluene, tetrahydrofuran, hexane, etc, and the viscosity at room temperature can be adjusted by changing the mass ratio PMS to D4Vi. Therefore, owing to its good solubility, suitable and controllable viscosity (326.9–714.6 mPa s at room temperature), the outstanding shaping properties of V-PMS can be expected.

The structure of V-PMS was investigated by means of FTIR. The spectra of V-PMS-3, PMS, and D4Vi are shown in Fig. 1. The main absorption peaks of V-PMS-3 can be assigned as follows: 3055/3016 cm^{-1}: $CH{=}CH_2$, 2961/2892 cm^{-1}: C–H, 2106 cm^{-1}: Si-H, 1597 cm^{-1}: C$=$C, 1407 cm^{-1}: Si–CH_3, 1260 cm^{-1}: Si–C, 1078 cm^{-1}: Si–O, and 1007/960 cm^{-1}: $SiCH{=}CH_2$. The hydrosilylation reaction between PMS and D4Vi was confirmed by the new peak in the spectrum of V-PMS-3 at 1132 cm^{-1}, the characteristic absorption of Si–CH_2–CH_2–Si [21]. It is reported that the crosslinking reaction occurs through the hydrosilylation reactions between the vinyl groups and the Si–H bonds via α- and/or β-addition mechanism (Scheme 1) [22]. Based on the FTIR results, we can speculate that the hydrosilylation reaction between D4Vi and PMS is dominated by β-addition mechanism. Besides, the Si–H bonds of PMS reacted partly with the $CH{=}CH_2$ moieties of D4Vi, which was proved by a diminution of Si–H peak at 2106 cm^{-1} and an intensification of the $CH{=}CH_2$ peaks at 3055, 3016, and 1597 cm^{-1}. The retained vinyl groups and Si–H bonds will be propitious to crosslink the precursor at a low temperature.

The synthesis process is also supported by the comparison of ^{1}H NMR spectra of PMS, V-PMS-3 and D4Vi, which are shown in Fig. 2. Resonances of V-PMS-3 are principally observed in four discrete regions, $\delta=0$–1, 1.2–1.7, 3.3–4.1, and 5.8–6.2 ppm, corresponding to CH_3,–CH_2–, Si–H, and $CH{=}CH_2$ functions, respectively. In V-PMS-3, the new peak at $\delta=1.6$ ppm can be assigned to the protons of Si–CH_2–CH_2–Si, which further confirms that the β-addition hydrosilylation between PMS and D4Vi.

Table 1
Properties of V-PMS and PMS.

Polymer	PMS (content/wt%)	D4Vi (content/wt%)	Yield (%)	Mn	Mw	Viscosity/mPa s
PMS	—	—	—	293	707	51.7
V-PMS-0	100	0	99.9	312	765	59.6
V-PMS-1	100	15	99.9	550	1695	326.9
V-PMS-2	100	25	99.8	1024	3309	597.5
V-PMS-3	100	50	99.9	1308	4360	714.6

3.2. Thermal properties of V-PMS

The incorporation of reactive vinyl groups into the backbone make it possible for the polymer to be cured readily, even under moderate conditions. Upon heating, the free-radical addition polymerization between vinyl groups and Si–H bonds results in the increase of the molecular weight of V-PMS, and thus avoid the evaporation of volatiles with formation of bubbles. This property is beneficial for making nonporous and dense monolithic ceramics from this precursor. As shown in Fig. 3 (DSC spectra of V-PMS-3), the thermal crosslinking reaction of V-PMS-3 initiated at about 140 °C, and the most dramatic process occurred at about 190 °C and completed at about 280 °C. Thus, all the synthesized three V-PMSs was cured at 150 °C for 2 h, since the curing mechanism was same. The reaction temperature is lower than that of PMS and PCS [14,16,23]. The lower thermal-crosslinking temperature imparts V-PMS with excellent processability, which makes it possible for making nonporous materials with diverse shapes.

In addition, it is essential for a liquid preceramic polymer to display high ceramic yield and excellent heat-resistance properties for high-temperature applications [24]. As revealed by the TGA results (Fig. 4), the ceramic yield of V-PMS-3 treated in Ar atmosphere up to 1200 °C was 81%, much higher than that of PMS under the same condition (38%). It should be noticed that the significantly mass loss (about 59%) of PMS occurred at 160~500 °C, which was probably due to the presence of low molecular weight fraction as reported previously [23]. For comparison, the mass loss of V-PMS starts at a higher temperature (340 °C) with a significantly lower weight loss of about 12% up to 500 °C. The significant difference in weight loss below 500 °C is responsible for the remarkable difference in the final ceramic yields in the two polymers. This is due to the hydrosilylation reaction with the introduction of reactive vinyl groups and the increase of the molecular weight in V-PMS. As a result, the volatilization of low weight molecular reduced and the ceramic yield was improved markedly.

To get a better understanding of the curing reaction and pyrolytic conversion, the structural evolution of V-PMS-3 treated under different temperature was investigated by FTIR (Fig. 5) and ^{29}Si-MAS-NMR (Fig. 6).

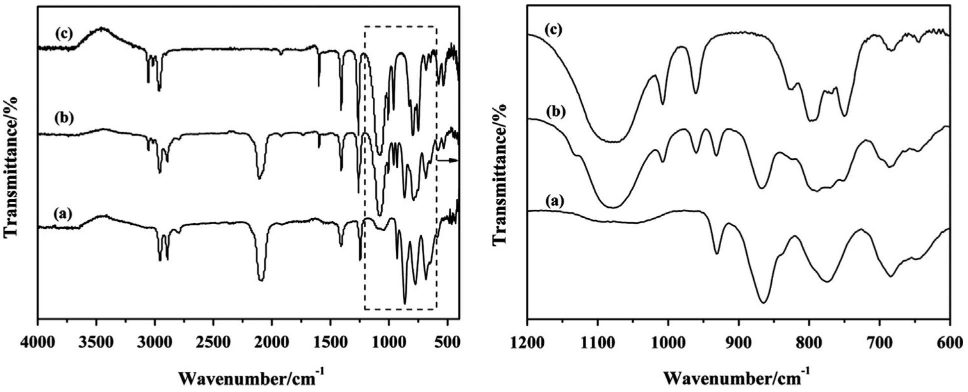
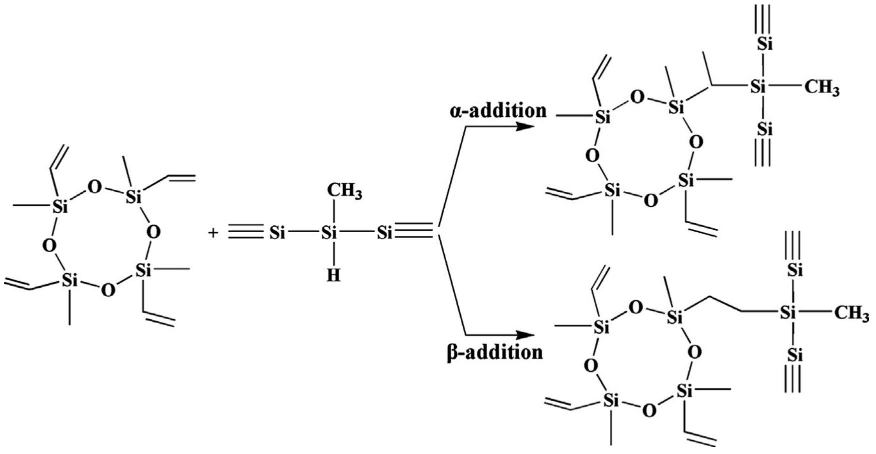


Fig. 1. FTIR spectra of (a) PMS, (b) V-PMS-3, and (c) D4Vi.



Scheme 1. Reaction between PMS and D4Vi.

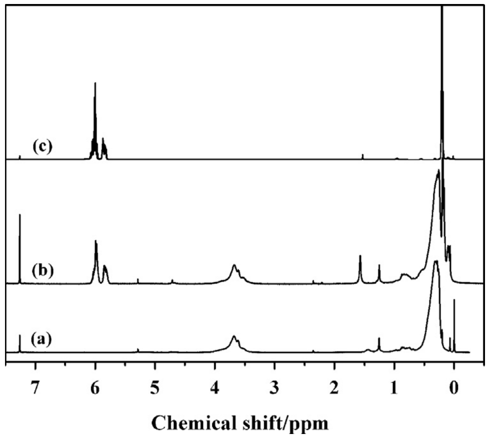


Fig. 2. 1H NMR spectra of (a) PMS, (b) V-PMS-3, and (c) D4Vi.

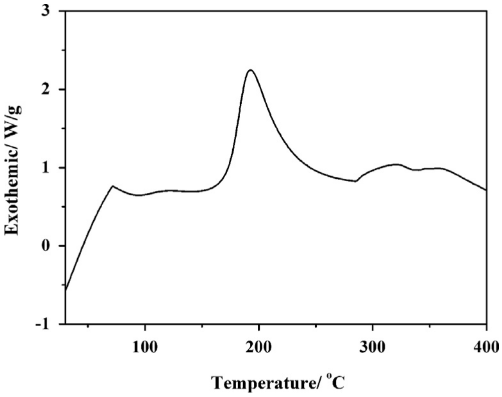


Fig. 3. DSC graph of V-PMS-3.

The absorption of Si–H groups markedly decreased and vinyl groups almost disappeared after curing at 150 °C for 2 h. This suggested that the hydrosilylation reaction between Si–H and vinyl groups was almost completed under such conditions. When treated at 400 °C for 2 h, the polymer exhibited a new peak at 1357 cm^{-1}, the characteristic peak of Si–CH_2–Si, and enhanced with the elevated treating temperatures, which may result from the thermal rearrangement of the Si–Si_3 to Si–CH_2–Si (Kumada rearrangement) [25]. In the spectrum of V-PMS-3 treated at 600 °C, the characteristic peak 2100 cm^{-1} of Si–H, 2961 and 2892 cm^{-1} of C–H almost disappeared due to further dehydrocoupling cross-linking. In addition, the decrease of the absorption of Si–CH_3 at 1250 cm^{-1} can be attributed to the decomposition of organic side groups. The vanish of the organic absorptions at 800 °C suggests the complete of the mineralization of the preceramic polymer. When treating the polymer at 1200 °C for 2 h, there are only two broad absorption peaks which could be assigned to Si–O (1090 cm^{-1}) and Si–C (810 cm^{-1}). The final pyrolysis product of V-PMS-3 was mainly composed of Si(O)C phase.

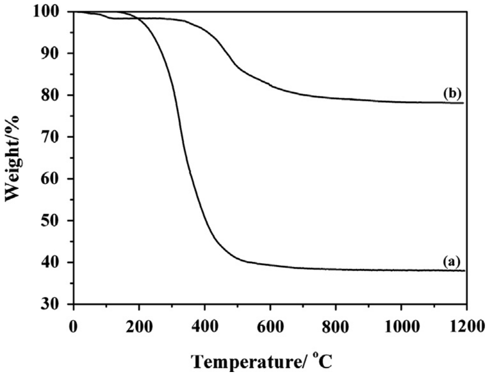


Fig. 4. TGA curves of (a) PMS, and (b) V-PMS-3.

The ^{29}Si-MAS-NMR spectra of V-PMS-3 heat-treated at different temperatures were shown in Fig. 6. V-PMS-3 heat-treated at 150 °C displayed spectra with a ^{29}Si resonance peaks in a broad range from 0 to−100 ppm, associated with a random distribution of the silicon sites, the peaks around −20 ppm, −32 ppm, −70 ppm can be assigned to SiC_2Si_2, SiC_2O_2, $SiCHSi_2$ respectively [23,26]. Increasing the temperature to 400 °C, the peak of $SiCHSi_2$ almost disappeared, and the peak of SiC_2Si_2 was enhanced and broaden, implying the conversion of $SiCHSi_2$ to SiC_3H (−18 ppm) and SiC_2Si_2 by Kumada rearrangement. This is consistent with the IR results. It should be noticed that the decrease of intensity of the peak −32 ppm and the appearance of the new peak −64 ppm (corresponding to $SiCO_3$ [27]) implied the conversion of

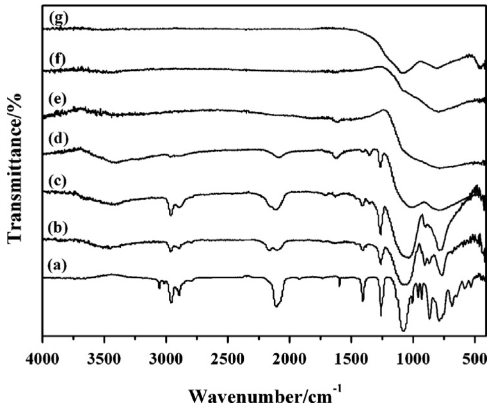


Fig. 5. FTIR spectra of V-PMS-3 heat-treated at different temperatures ((a) RT, (b) 150, (c) 400, (d) 600, (e) 800, (f) 1000, and (g) 1200 °C).

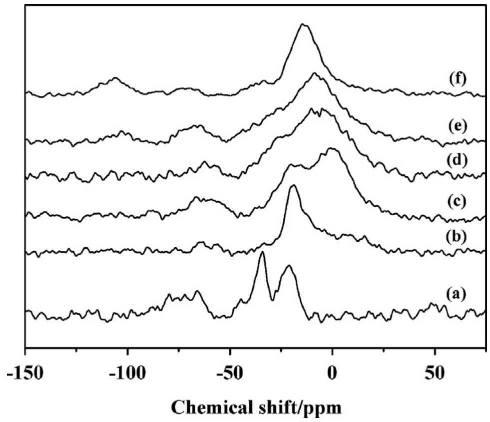


Fig. 6. ^{29}Si-MAS-NMR spectra of V-PMS-3 heat-treated at different temperatures ((a) 150, (b) 400, (c) 600, (d) 800, (e) 1000, and (f) 1200 °C).

SiC_2O_2 to $SiCO_3$. The peaks at -16 ppm (SiC_3H) and 0 ppm (SiC_4) [23], enhanced dramatically with the temperature rise to 600 °C, indicating the complete transition of Si–Si to Si–C by Kumada rearrangement and dehydrogenation. The peaks at -108, -74, -34 and -16 ppm of V-PMS-3 treated at 1200 °C for 2 h were assigned as SiO_4, $SiCO_3$, SiC_2O_2 and SiC_4, respectively [26–28]. Therefore, we can also speculate that the as-pyrolyzed product of V-PMS-3 consists mainly of $SiC_x(O)_{4-x}$(x=0–4) coordination units in the ceramic network, and the main coordination unit is SiC_4.

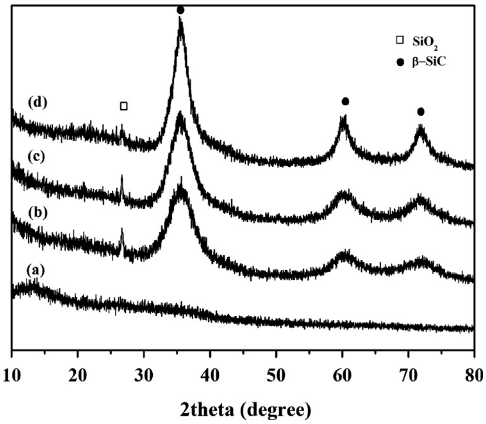


Fig. 7. XRD patterns of V-PMS-3 derived ceramic at different temperature ((a) 1000, (b) 1200, (c) 1400, and (d) 1600 °C).

Table 2
Ceramic composition at different temperatures.

No.	Si (wt%)	C (wt%)	O (wt%)	C/Si	Ceremic composition
V-PMS-3-1000	57.16	26.70	16.14	1.09	$SiC_{1.09}O_{0.49}$
V-PMS-3-1200	57.27	26.14	16.59	1.07	$SiC_{1.07}O_{0.51}$
V-PMS-3-1400	60.44	27.84	11.72	1.07	$SiC_{1.07}O_{0.34}$
V-PMS-3-1600	65.71	32.00	2.30	1.14	$SiC_{1.14}O_{0.06}$

3.3. *Crystallization behavior and composition of the pyrolyzed products*

Fig. 7 shows the XRD patterns of the pyrolytic residues of V-PMS-3 obtained at different temperatures. The product obtained at 1000 °C was amorphous and highly disordered. Further heating to 1200 °C lead to partially crystallization, three broad major peaks were observed at $2\theta=36°$ (111), 60° (220), and 72° (311), which are characteristic of locally ordered SiC_4 unit [29]. The intensity of broad peaks at $2\theta=36°$, 60° and 72° increases with the temperature rise, indicating more ordered SiC_4 structures and the increase of crystallinity. In the samples treated above 1200 °C, the small peak appeared at $2\theta=26°$ can be assigned as quartz phase, which come from the cyclosiloxane introduced by D4Vi. When the temperature increased to 1600 °C, the peak of quartz phase at $2\theta=26°$ almost disappeared, which should attribute to the carbothermal reductions occurring between SiO_2 and free carbon [30]. The crystallization behavior of the obtained ceramic produced from V-PMS is similar to PCS-derived SiC ceramic, but is different from typically SiOC ceramics produced from silicone, which should attribute to the difference of the composition and structure between V-PMS and silicone [31,32].

Table 2 shows the ceramic composition of final pyrolyzed products at different temperatures. The ceramics obtained by pyrolyzation at 1000 °C, 1200 °C, 1400 °C, and 1600 °C are presented as V-PMS-3-1000, V-PMS-3-1200, V-PMS-3-1400, and V-PMS-3-1600, respectively. The results indicate that the Si(O)C ceramics pyrolyzed at different temperatures have the stoichiometric C:Si ratio of 1.09–1.17. It is generally accepted that evolution of gases in oxygen-containing species (i.e., SiO and CO) takes place above 1400 °C [30,33]. Thus, the oxygen content was dramatically decreased and the C:Si ratio was increased to 1.17 when the temperature increased to 1600 °C. This result is in good accordance with the XRD analysis.

3.4. *The microstructure of the ceramics*

Compared with powder sintering processes, pressureless pyrolysis at lower temperatures is the most attractive advantage for PDCs. The final residues of V-PMS-3 were black dense monolithic solids without visible pores. The microstructures of the product pyrolyzed under different temperatures were investigated by SEM and typical micrographs were shown in Fig. 8. It was evident that the surfaces of the ceramics were smooth and

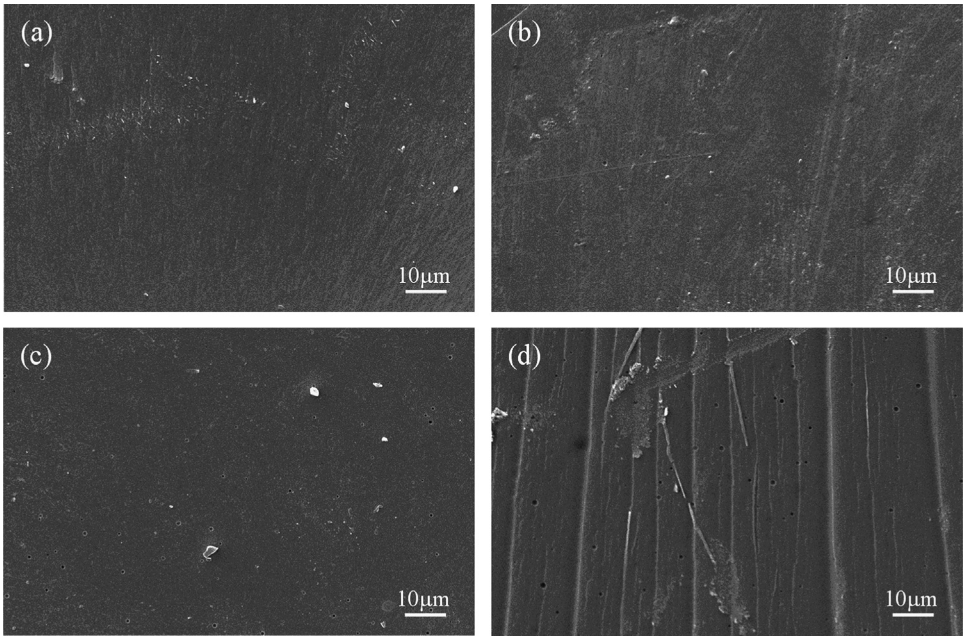


Fig. 8. SEM pictures of V-PMS-3 derived ceramic at different temperature ((a) 1000, (b) 1200, (c) 1400, and (d) 1600 °C).

dense under 1400 °C. This indicated that V-PMS-derived ceramics should possess good mechanical property, as well as outstanding high temperature stability. When the temperature was 1600, obviously pores were observed in Fig. 8 (d), which confirmed the volatilization of oxygen-containing species. It should be noted that, for the traditional PCS which is widely used as SiC precursor, only foam-like or porous solid ceramics were obtained upon pyrolysis [34–39]. In this work, owing to its ideal rheology, excellent thermal curability and high ceramic yield, V-PMS can easily be converted into nonporous ceramic materials for high-temperature application.

4. Conclusion

A novel liquid precursor (V-PMS) rich in vinyl groups was synthesized by modifying PMS with D4Vi. The obtained V-PMS is well soluble in common solvents and the viscosity is controllable by easily changing the mass ratio of PMS to D4Vi. V-PMS can easily be cured to a hard and dense monolithic solid by heating at 150 °C for 2 h, and it gives a high ceramic yield of 81% when treated up to 1200 °C. The polymer to ceramic conversion is complete at 800 °C and an amorphous Si(O)C phase was obtained when treated at 1000 °C. The obtained ceramics derived from V-PMS are basically dense without obvious cracks and pores when heated under 1400 °C. The desirable combination of properties, such as the controllable viscosity, outstanding thermal curability and high ceramic yield, suggest V-PMS exhibits great potential for preparing high performance Si(O)C ceramic materials for high-temperature application.

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