Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 1939–1944

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Mechanical properties of SiC/SiC composites fabricated by PIP process with a new precursor polymer

Zheng Luo*, Xingui Zhou, Jinshan Yu, Ke Sun, Fei Wang

Science and Technology on Advanced Ceramic Fibers and Composites Laboratory, National University of Defense Technology, Changsha 410073, China

Received 20 May 2013; received in revised form 18 July 2013; accepted 22 July 2013
Available online 27 July 2013

Abstract

Three dimensional four-directional (3D4d) silicon carbide (SiC) fiber reinforced SiC matrix composites (SiC/SiC) were fabricated by the precursor impregnation and pyrolysis (PIP) process with a new precursor polymer, liquid polycarbosilane with active Si–H and 3CHåCH$_2$ groups (LPVCS). The densification, mechanical properties and microstructure of the SiC/SiC composites were studied. The composite processed with LPVCS exhibited excellent physical and mechanical properties. The density and the porosity of the composites were 2.16 g/cm^3 and 6.7%, respectively. The flexural strength of the composites was 619.4 MPa and fracture toughness was 29.1 MPa m$^{1/2}$. The results indicated that LPVCS was a kind of potential precursor polymer for the preparation of SiC/SiC composites.

Keywords: C. Mechanical properties; New precursor polymers; PIP; SiC/SiC composites

1. Introduction

SiC/SiC composites are excellent thermal structural materials owing to their outstanding high-temperature strength, fracture toughness, chemical inertness, and low density [1–4]. Currently, the SiC/SiC composites are the leading candidates for aircraft engine hot-section components [5–8]. The precursor impregnation and pyrolysis (PIP) process is one of the main preparation processes of the SiC/SiC composites and has been widely employed because of its advantages in microstructure control, low costs and large-scale components fabrication with complicated shapes [9–10].

Polycarbosilane (PCS) is a conventional precursor polymer for SiC matrix, and it could be solved in Xylene for infiltrating into SiC fiber performs. Pores and cracks are formed due to gas evolution and volumetric shrinkage of the precursor polymer during pyrolysis which leads to the performance degradation of the composites [11–14]. Many efforts have been done to search the new precursor polymers to improve the mechanical properties of the SiC/SiC composites due to the shortcomings of poor efficiency of impregnation, low ceramic yield and small pores existing in the matrix. Kotani et al. [15–16] prepared SiC/SiC composites by the PIP process with the matrix precursor, liquid polycarbosilane with a lot of functional Si–H bonds (PVS). The PVS was applied because of its advantages of sufficient stability at ambient temperature, low viscosity, and continuous thermosetting behavior. It showed that the density and process efficiency of the SiC/SiC composites were increased and the flexure strength was 602 MPa. Kohyama et al. [17] developed a near-stoichiometric SiC matrix by mixture of PCS and polymethylsilane (PMS). It demonstrated remarkable improvements in tensile properties and fatigue limits (at 1300 °C) of the SiC/SiC composites were attained. Nannetti et al. [18] prepared SiC/SiC composites with the matrix precursor, allylhydridopolycarbosilane (AHPCS), contributing to great increase of composites' thermal diffusivity under high-temperature pyrolysis treatment at 1700 °C, which promoted polymer derived SiC matrix crystallization.

A new precursor polymer called LPVCS which is prepared by taking 2,4,6,8-tetravinyl-2,4,6,8-tetramethylcyclotetrasiloxane (V4) as curing agent and liquid polycarbosilane as starting materials is used for the preparation of high performance SiC/SiC composites.

---

*Corresponding author. Tel.: +86 731 84576397; fax: +86 731 84573165.
E-mail address: lzzw2003@sina.com (Z. Luo).

0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2013.07.102

LPVCS exhibits a low viscosity and good stability at room temperature, as well as a high ceramic yield and low cost. 3D4d braiding performs are composed of four directional yarns which are braided with the same braid angles in the interior of the material (Fig. 1). The 3D4d braided performs as reinforcements had the advantages of through-thickness reinforcement, low delamination tendency, high damage tolerance and near-net-shape manufacturing [19]. In this work, the 3D4d SiC/SiC composites were fabricated with two different precursor polymers, LPVCS and PCS, for comparison. The density, mechanical properties and microstructure of the SiC/SiC composites were studied.

2. Materials and experimental procedure

LPVCS and PCS were provided by National University of Defense Technology, China. Polymer-derived KD-I SiC fiber bundles provided by National University of Defense Technology were used as reinforcements. The PyC coating was prepared on the SiC fiber fabric with a thickness of about 500 nm (Fig. 2) by chemical vapor deposition method at 900 °C in an acetylene atmosphere. The fiber volume fraction of the 3D4d SiC fiber performs was about 46.5%. The SiC fiber performs were impregnated with LPVCS or PCS solution by a vacuum infiltration method and pyrolyzed at 1100 °C in an inert Argon atmosphere. The impregnation and pyrolysis process were repeated until weight increase was less than 1%. Four sets of specimens with different precursors and interfaces were prepared (Table 1).

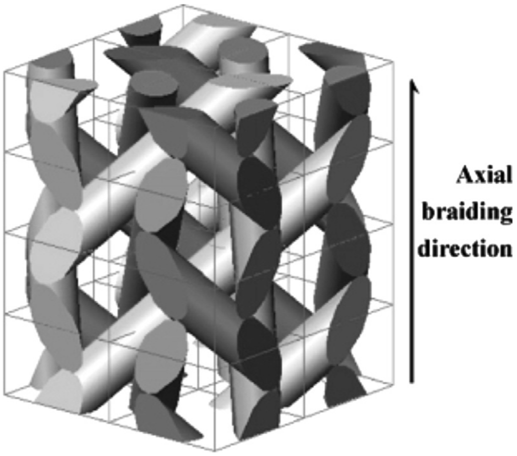

Fig. 1. Schematic of 3D4d preform.

The densities and open porosities of the SiC_f/SiC composites were measured by Archimede's method. The flexural strength was measured by three-point-bending test on a GTM91100 apparatus. The dimension of the samples for the test was 4.0 mm (B) × 3.0 mm (H) × 60.0 mm (L). The span length was 30 mm, and the crosshead speed was 0.5 mm/min. The fracture toughness of the SiC/SiC composites was determined with the single edged-notched beam method (SENB). Cross section morphology was observed by X-ray tomographic techniques, samples were scanned using a Metris X-tek 320 kV source at the Henry Moseley X-ray Imaging Facility in the University of Manchester. The microstructure of the fracture surfaces was characterized by a JSM-5600LV scanning electron microscope (SEM) and a JE-200 transmission electron microscopy (TEM).

Table 1
List of specimens with different precursors and interfaces.

Specimen	Interface coating	Precursor	Preparation cycle
1#	–	LPVCS	10
2#	–	PCS	14
3#	PyC	LPVCS	10
4#	PyC	PCS	14

Table 2
Basic characteristics of LPVCS and PCS.

	LPVCS	PCS
State at RT	Liquid	Solid
Density (g/cm^3)		
As-received	1.04	1.15
After pyrolysis	2.42	2.34
Impregnation	Without solvent	Solved in Xylene
Viscosity (mPa s)	20	25
Volume change	Shrinkage	Expansion
Ceramic yield (%)	59.5	31.5

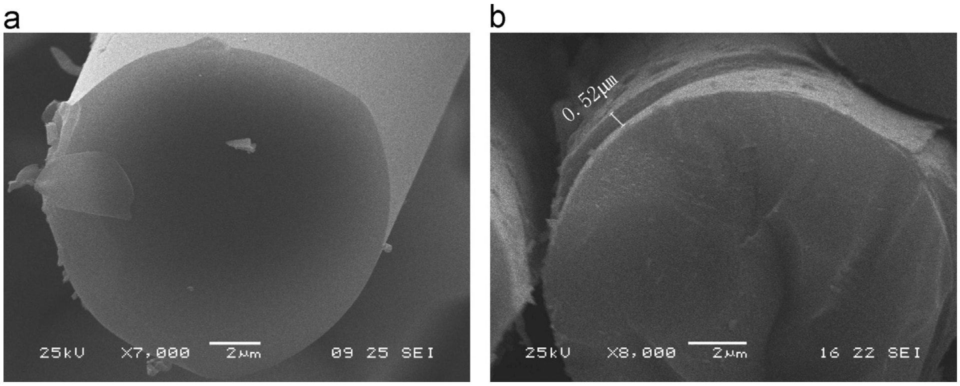

Fig. 2. Microstructure of the SiC fibers: (a) before the CVD method; (b) after the CVD method.

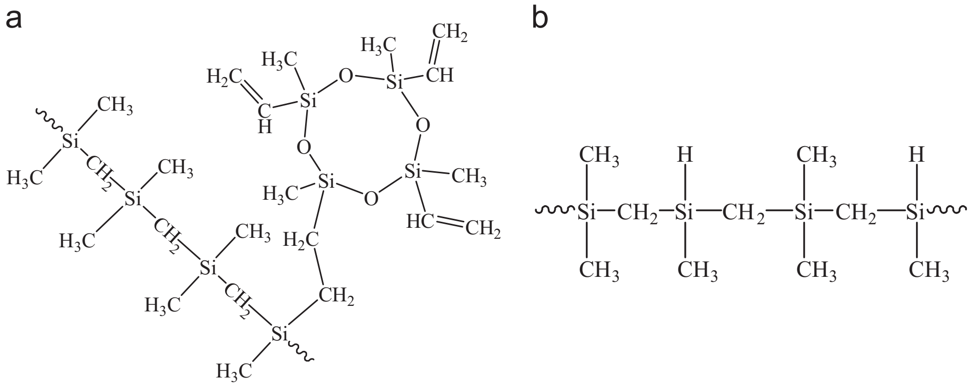

Fig. 3. The molecular structure of the precursor: (a) LPVCS; (b) PCS.

3. Results and discussion

3.1. Basic characteristics of LPVCS

The basic characteristics of LPVCS and PCS are listed in Table 2. The molecular structure of LPVCS and PCS are shown in Fig. 3. LPVCS demonstrates a superior rheological characteristics and ceramic yield to PCS. LPVCS is a liquid precursor with excellent wettability with SiC fiber and low viscosity at RT. The optimum curing temperature of LPVCS is 300 °C [20]. When heated to 1100 °C, the cured products transform to compact SiC ceramics with the shrinkage of the volume [21]. So the thermosetting and pyrolysis properties of LPVCS are advantages for reducing pores in the PIP process.

3.2. Preparation cycles and density

The weight increase–cycle curves of SiC/SiC composites (1# and 2#) were shown in Fig. 4. The composites were densified for 10 and 14 cycles PIP processes. The preparation cycles of 1# were shorter than those of 2# obviously. This indicated that LPVCS exhibited higher densification efficiency than PCS. At the first 4 cycles, LPVCS showed much higher efficiency than PCS. After 5 cycles of the PIP process, the weight increase of 1# was gradually declined. The efficiency enhancement was not only for the superior rheological characteristics and ceramic yield from LPVCS, but also volume shrinkage during the pyrolysis process of LPVCS. However, the pyrolysis of PCS caused serious volume expansion and formed abundant closed pores.

The densities and the porosities of 1# and 2# were listed in Table 3. In each cycle, 1# exhibited higher density and lower porosity. The density and porosity of 1# after 10 cycles PIP process were 2.11 g/cm^3 and 5.1%, respectively. While the density and porosity of 2# after 14 cycles PIP process were 1.97 g/cm^3 and 8.8%, respectively.

3.3. Mechanical properties and microstructure

The properties of SiC/SiC composites were listed in Table 4. Fracture surface morphology of the composites was shown in Fig. 5. The flexural strength and fracture toughness of 1# were only 249 MPa and 9.4 MPa m$^{1/2}$. The composites showed no fiber pullout in Fig. 5(a), which indicated strong fiber/matrix interfaces. This was attributed to the volume shrinkage of LPVCS during curing and the pyrolysis process which produced strong interface bonding. However, both flexural strength and fracture toughness of 3# increased significantly to 619.4 MPa and 29.1 MPa m$^{1/2}$, respectively. Large quantities of long pulled-out fibers could be seen on the fracture surfaces of 3# in Fig. 5(c). This was typical of crack arresting, deflecting and branching behavior which leaded to the pseudo-ductile fracture mode of the composites. This indicated that the PyC coatings provided weak interfacial bonding and played an important role for the excellent mechanical properties of the composites. The flexural strength and fracture toughness of 4# were only 390MPa and 18.7 MPa m$^{1/2}$, respectively, not much higher than the properties of 2#. And long pulled-out fibers could be seen both on the fracture surfaces of 2# and 4# in Fig. 5(b) and (d). The expansion of PCS during paralysis produced weak interfacial bonding between fiber and matrix, so the PyC coatings played a limited role for the mechanical properties of the composites.

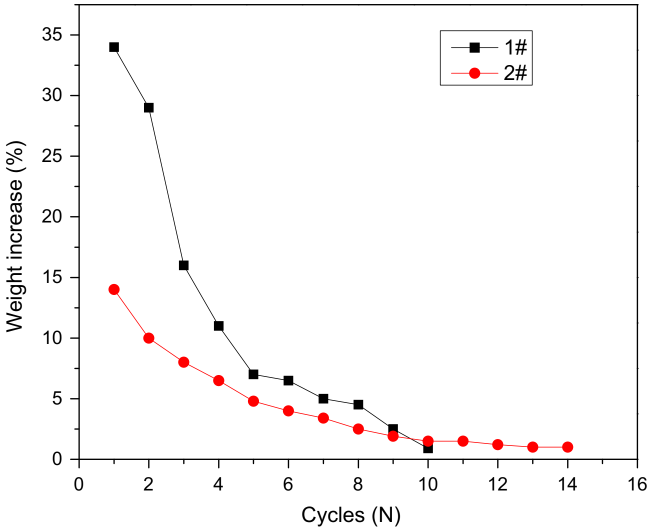

Fig. 4. weight increase–cycle curve of 1# and 2#.

Table 3
Density and porosity of 1# and 2#.

Property	Cycle													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Density of 1# (g/cm^3)	1.25	1.51	1.69	1.84	1.93	2.02	2.04	2.07	2.09	2.11	–	–	–	–
Density of 2# (g/cm^3)	1.14	1.37	1.52	1.63	1.71	1.76	1.81	1.85	1.89	1.91	1.93	1.95	1.96	1.97
Porosity of 1# (%)	48.3	38.0	28.1	21.0	16.8	12.3	10.8	8.2	6.3	5.1	–	–	–	–
Porosity of 2# (%)	50.5	40.2	29.2	24.8	21.2	18.7	16.5	15.1	13.6	12.3	11.1	10.3	9.6	8.8

Table 4
Properties of the SiC$_f$/SiC composites.

Specimen	Density (g/cm^3)	Open porosity (%)	Flexure strength (MPa)	Elastic modulus (GPa)	Fracture toughness (MPa m$^{1/2}$)
1#	2.11	5.1	249.0	49.1	9.4
2#	1.97	8.8	323.1	87.0	11.2
3#	2.16	6.7	619.4	79.7	29.1
4#	2.04	11.0	390.0	46.9	18.7

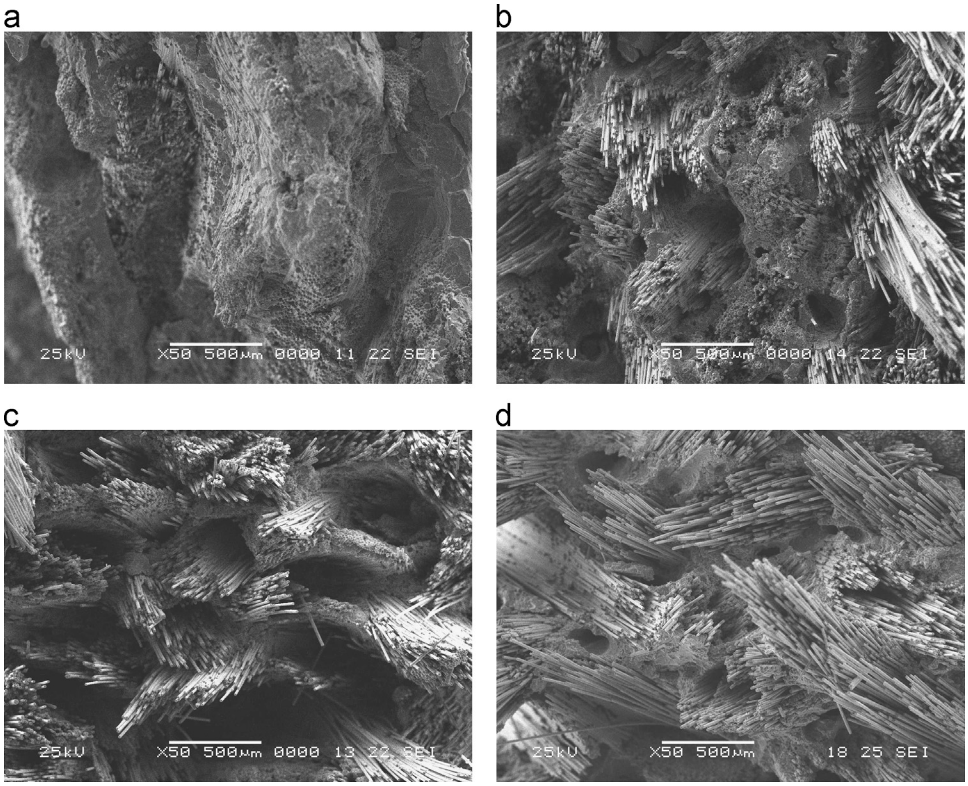

Fig. 5. Fracture surface of the SiC$_f$/SiC composites: (a) 1#; (b) 2#; (c) 3#; and (d) 4#.

The microstructure of 3# at a higher magnification was shown in Fig. 6. The PyC coatings were frequently found attached to the pull-out fiber surfaces, as seen in Fig. 6(c) and (d). Fig. 6(c) and (d) illustrated the matrix crack deflection and branching in the interface area of the SiC/SiC composites. Cross section morphologies were shown in Figs. 7 and 8. There were much more pores and defects between and within the SiC fiber bundles in 4# than in 3#. The pores and defects leaded to crack initiation and significantly affected the mechanical properties of 4#. This might be the main reason why 4# showed lower mechanical properties than 3#.

TEM observation of 3# was shown in Fig. 9. Based on the evidence from the selected area diffraction (SAD) pattern, the PyC interface was completely amorphous. The role of interfaces in the composites was extremely important for structure applications. The interfaces arrest, deflect and branch the cracks that had initiated at the outer or pore surfaces of matrix. The deflection of the cracks along interface enabled energy

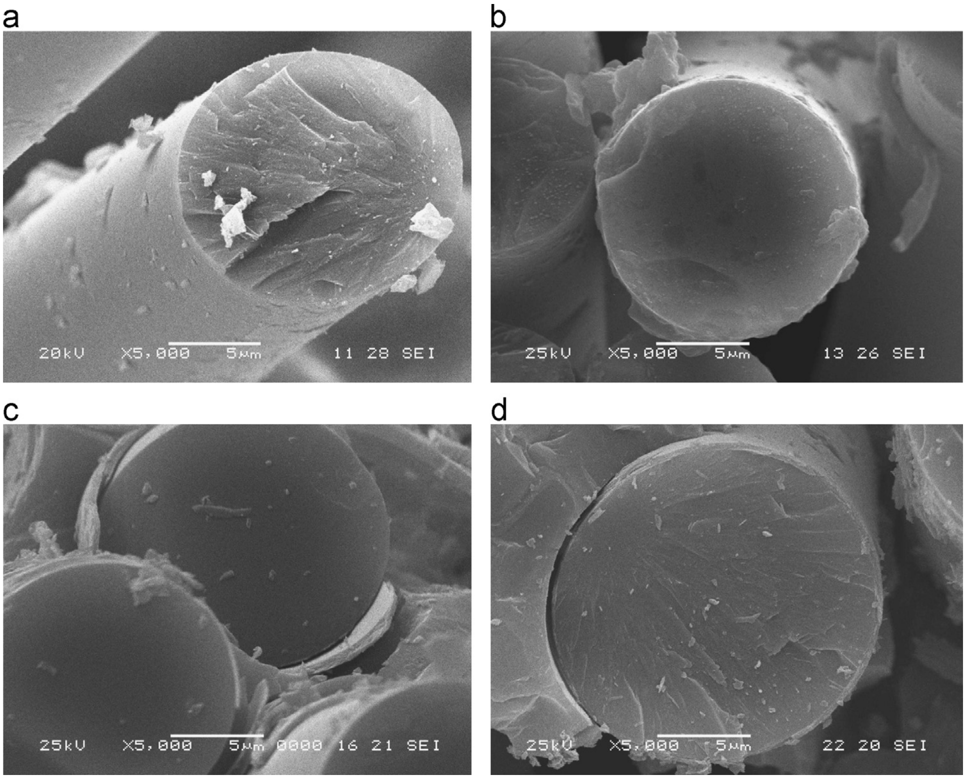

Fig. 6. Fracture surface of 3# (high magnification): (a) 1#; (b) 2#; (c) 3#; and (d) 4#.

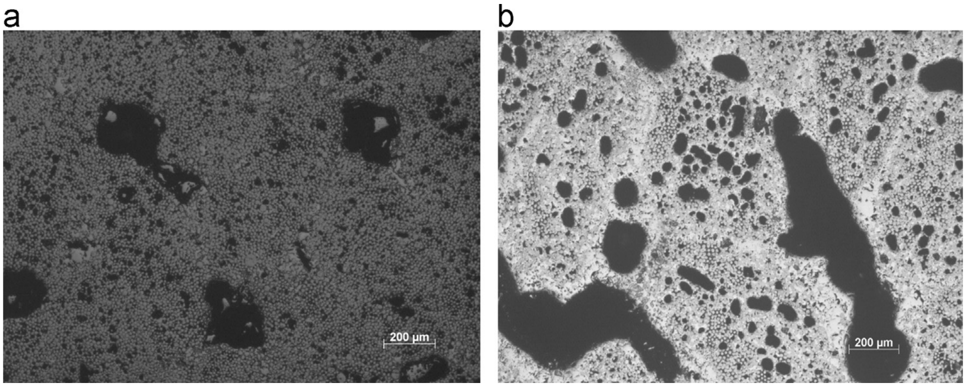

Fig. 7. Cross section perpendicular to the braiding direction: (a) 3#; (b) 4#.

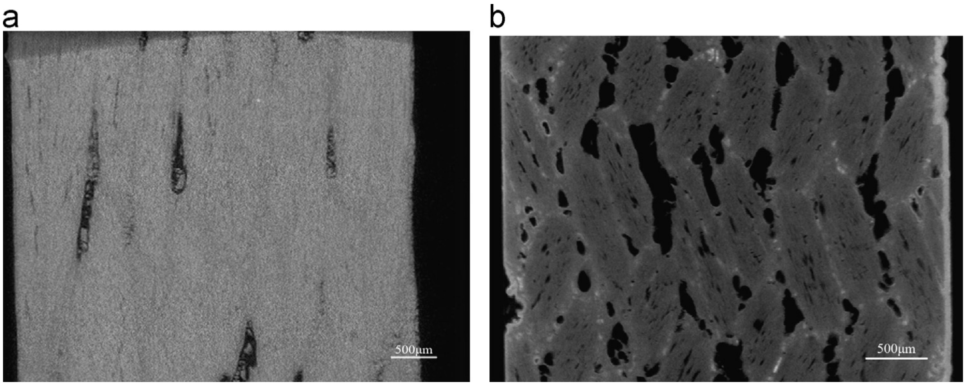

Fig. 8. Cross section parallel to the braiding direction: (a) 3#; (b) 4#.

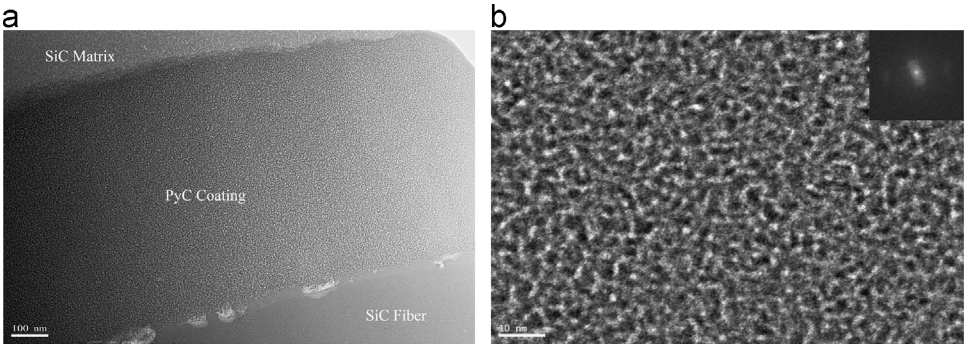

Fig. 9. TEM image and SAD-pattern of PyC interface: (a) TEM image of 3#; (b) PyC interface.

dissipation through friction, and consequently allowed a pseudo-ductile fracture behavior in SiC/SiC composites. Hence, the PyC interface leaded to significant improvement of the mechanical properties of the SiC/SiC composites.

4. Conclusions

A new precursor polymer, LPVCS, was adopted as the ceramic precursor substituting for PCS. The preparation cycles of the PIP process could be reduced. After 10 PIP cycles, the density and porosity of the SiC/SiC composites were 2.16 g/cm^3 and 6.7%, respectively. The PyC coating was prepared between fiber and matrix by the CVD process to weaken the strong interface bonding of SiC/SiC composite. The SiC/SiC composites exhibited significant improvements in mechanical properties: flexural strength and fracture toughness were 619.4 MPa and 29.1 MPa m$^{1/2}$, respectively. LPVCS is a candidate precursor polymer for SiC matrix composites preparation.

Acknowledgments

The authors acknowledge the support of the National Natural Science Foundation of China (Grant no.50172228), the Research Fund of State key Laboratory of CFC (Grant no. 9140C820301110C8201) and the aid program for Science and Technology Innovative Research Team in Higher Educational Institutions of Hunan Province.

References

[1] H.J. Yu, X.G. Zhou, et al., Mechanical properties of 3D KD-1 SiC$_f$/SiC composites with engineered fibre-matrix interfaces, Composites Science and Technology 71 (5) (2011) 699–704.

[2] H.L. Wang, X.G. Zhou, et al., Microstructure, mechanical properties and reaction mechanism of KD-1 SiC$_f$/SiC composites fabricated by chemical vapor infiltration and vapor silicon infiltration, Materials Science and Engineering A—Structural Materials 528 (6) (2011) 2441–2445.

[3] K. Yoshida, Development of silicon carbide fiber-reinforced silicon carbide matrix composites with high performance based on interfacial and microstructure control, Ceramic Society of Japan 118 (2010) 82–90.

[4] R. Naslain, Design, preparation and properties of non-oxide CMCs for application in engines and nuclear reactors: an overview, Composites Science and Technology 64 (2004) 155–170.

[5] D. Brewer, HSR/EPM combustor materials development program, Materials Science and Engineering A A261 (1999) 284–291.

[6] D. Brewer, G. Ojard, M. Gibler, Ceramic Matrix Composite Combustor Liner Rig Test. ASME Turbo Expo 2000, Munich, Germany, May 8–11, 2000, AMSE Paper 2000-GT-0670.

[7] G.S. Corman, K. Luthra, Silicon melt infiltrated ceramic composites (HiperComp), in: N. Bansal (Ed.), Hand book of ceramic composites, Kliwer Academic, NY, 2005, pp. 99–115.

[8] G.N. Morscher, G. Ojard, R. Miller, Y. Gowayerd, U. Santhosh, J. Ahmad, et al., Tensile creep and fatigue of Sylramic-iBN melt-infiltrated SiC matrix composites: retained properties, damage development, and failure mechanisms, Composites Science and Technology 68 (2008) 3305–3313.

[9] F. Sirieix, P. Goursat, A. Lecomte, A. Dauger, Composites Science and Technology 37 (1990) 7–19.

[10] D. Suttor, T. Erny, P. Grail, H. Goedeke, T. Hung, Ceramic transactions, in: H. Hausner, S. Hirano, G.L. Messing (Eds.), Ceramic Science and Processing Technology, vol. 51, American Ceramic Society, Westerville, OH, 1995, pp. 211–215.

[11] B.E. Walker Jr., R.W. Rice, P.F. Becher, B.A. Bender, W.S. Coblenz, Preparation and properties of monolithic and composite ceramics produced by polymer pyrolysis, American Ceramic Bulletin 62 (8) (1983) 916–923.

[12] H. Yoshida, N. Miyata, M. Sagawa, S. Ishikawa, K. Naito, N. Enomoto, C. Yamagishi, Preparation of unidirectionally reinforced carbon-SiC composite by repeated infiltration of polycarbosilane, Journal of the Ceramic Society of Japan 100 (4) (1992) 454–458.

[13] D.W. Shin, H. Tanaka., Low-temperature processing of ceramic woven fabric/ceramic matrix composites, Journal of the American Ceramic Society 77 (1) (1994) 97–104.

[14] T. Tanaka, N. Tamari, I. Kondoh, M. Iwasa, Fabrication and mechanical properties of 3-dimensional Tyranno fiber reinforced SiC composites by repeated infiltration of polycarbosilane, Journal of the Ceramic Society of Japan 104 (5) (1996) 545–547.

[15] M. Kotani, T. Inoue, et al., Effect of SiC particle dispersion on microstructure and mechanical properties of polymer-derived SiC/SiC composite, Materials Science and Engineering A 357 (1–2) (2003) 376–385.

[16] M. Kotani, T. Inoue, et al., Consolidation of polymer-derived SiC matrix composites: processing and microstructure, Composites Science and Technology 62 (16) (2002) 2179–2188.

[17] A. Kohyama, M. Kotani, et al., High-performance SiC/SiC composites by improved PIP processing with new precursor polymers, Journal of Nuclear Materials 283–287 (2000) 565–569.

[18] C.A. Nannetti, A. Ortona, et al., Manufacturing SiC-fiber-reinforced SiC matrix composites by improved CVI/slurry infiltration/polymer impregnation and pyrolysis, Journal of the American Ceramic Society 87 (7) (2004) 1205–1209.

[19] L. Chen, X.M. Tao, C.L. Choy, On the microstructure of three-dimensional braided performs, Composites Science and Technology 59 (3) (1999) 391–404.

[20] Y.Q. Wang, S.Y. Cai, Synthesis and properies of a liquid polycarbosilane containing allyl groups, Silicon Materials 24 (2) (2010) 85–88.

[21] Y.Q. Wang, Study on Liquid SiC Ceramic Precursor with Si–H and 3CHåCH$_2$ Active Group, National University of Defense Technology, Changsha, China, 2010.