Mechanical Properties of Cf/SiC Composites with Ameliorated Interface Employing a New Precursor

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Abstract. Three dimensional and four directional carbon fiber reinforced SiC matrix (Cf/SiC) composites were fabricated by precursor infiltration and pyrolysis process with ameliorated interface employing a new precursor, liquid polyvinylcarbosilane (LPVCS). LPVCS is a novel precursor with active Si-H and –CH=CH2 groups with relatively high oxygen content (~7.3wt. %). The mechanical properties improvement led by ameliorated interface was researched. Samples with ameliorated interface employing LPVCS showed better mechanical properties than those employing polyacarblosilane (PCS). The flexural strength and fracture toughness of the Cf/SiC composites fabricated with PCS were 301 MPa and 11.2 MPa•m$^{1/2}$, respectively, whereas the equivalent values of the samples fabricated with ameliorated interface were 421 MPa and 25.6 MPa•m$^{1/2}$, respectively. Employing LPVCS for the first infiltration and pyrolysis cycle formed suitable interface, then employing PCS as precursor for the left cycles formed relatively low oxygen content matrix, this the main reason of mechanical properties improvement.

1. Introduction
Thermal structural materials used in the advanced aero and space applications, such as turbine engine components, hypersonic flight vehicles, and space-craft reentry protection systems, are required to possess extraordinary mechanical properties under high temperature [1-4]. Continuous carbon fiber reinforced SiC matrix composites (Cf/SiC) are considered as one of the most promising thermal structural materials owing to their outstanding high temperature mechanical properties, fracture toughness, and low density [5-7].

There are three common ways to fabricate the Cf/SiC composites: chemical vapor infiltration (CVI), liquid silicon infiltration (LSI), and precursor infiltration and pyrolysis (PIP) [8]. The materials’ shape as well as the fabrication time and cost vary for the different fabrication approaches. The CVI process has the longest fabrication period with a porosity of 10-15%. The LSI process requires a shorter fabrication period of 20-30 hours, and the composites have smaller porosity, however the high process temperature will be harmful to the carbon fiber. The PIP process have been widely employed for fabrication of composites because of its advantages in drastic reduction in costs, large-scale production, fabrication with complicated shapes and controllable microstructure.

The coating is important in order to improve the mechanical properties of composites. The mechanical properties of Cf/SiC composites with coating, such as PyC, EBC, carbon nanotube, showed more than twice the flexural strength and fracture toughness [9-11]. The coating was usually prepared by chemical vapor deposition (CVD) method, however CVD process always cost much time.

In the author’s preliminary work we found that the precursor LPVCS pyrolyzed products formed suitable interface with T300 carbon fiber, however, the high oxygen content of LPVCS pyrolyzed
products reduced the high temperature performance of matrix. Employing LPVCS in the first infiltration and pyrolysis cycle to form suitable interface and then employing PCS in the left cycles to form low oxygen content matrix is a method to improve the mechanical properties of Cf/SiC composites. In this work, the mechanical properties of Cf/SiC composites at room and elevated temperature was studied in detail. In addition, the microstructure were also analyzed.

2. Materials and experimental procedure

2.1. Materials
In the fabrication of composites, T300 carbon fiber was employed as the reinforcement. The general characteristics of the T300 carbon fiber are listed in Table 1. All samples were braided into 3D performs by three dimension and four steps braiding technique. The fiber volume fraction and the braiding angle of the composites were 36.3% and 24.8°, respectively. PCS and LPVCS were provided by NUDT, China. The continuous carbon fiber performs were infiltrated with LPVCS in the first cycle and then PCS to the end. Pyrolysis was carried out at 1200 °C in Ar. LPVCS required crosslinking at 300 °C before pyrolysis. The infiltration and pyrolysis process was repeated until the weight increase was less than 1%.

2.2. Experimental procedure
The densities and open porosities of the Cf/SiC composites were measured by Archimedes’ method using kerosene oil as the immersion medium. The bending strength of the composites was characterized by three point bending test following the general guidelines of the Chinese Standard GBT6569-2006. The dimensions of a test samples were 4 mm × 4mm × 65mm, the span length and the cross head speed were 50 mm and 0.5 mm/min, respectively. The fracture toughness of the Cf/SiC composites was determined with the single edged-notched beam method (GBT 23806-2009). The dimensions of the samples for the test were 3.5 mm (B) × 7.0 mm (H) × 40.0 mm (L). The span length was 30.0 mm and the crosshead speed was 0.1 mm/min. Analysis of the pyrolysates was performed by X-ray diffraction (XRD, D8 Advance, Bruker, Germany). The fracture surfaces was observed by scanning electron microscopy (SEM, S-4800, Hitachi, Japan). The oxygen content was measured using an N/O analyzer (EMGA-820, Horiba, Japan) and the carbon content was measured using a C/S analyzer (EMIA-320V2, Horiba, Japan).

| Diameter (μm) | Density (g·cm⁻³) | Tensile strength (GPa) | Young Modulus (GPa) |
|---------------|-------------------|-----------------------|---------------------|
| T300          | 5.1±0.2           | 1.76                  | 6.2±1.9             | 391                |

3. Results and discussion

3.1. General Characteristics of PCS and LPVCS
The molecular structures of PCS and LPVCS are shown in Fig. 1. PCS has a main chain of Si-C, with SiC₄ and SiC₃H building blocks. LPVCS is the product of LPCS and V₄ preliminary reaction. LPCS is Low-molecular polycarbosilane and has a familiar structure with PCS but with low Si-H content. V₄ refers to 2, 4, 6, 8-tetravinyl-2, 4, 6, 8-tetramethylcyclotetrasiloxane and has -CH=CH₂ and Si-O. When heated to 300 °C, LPCS and V₄ form a net structure. LPVCS is a liquid precursor with excellent wettability at room temperature that demonstrates a similar ceramic yield to PCS, with a pyrolysis temperature was 1200 °C. There is more oxygen in the SiCxOy phase when using more LPVCS. The SiCxOy phase reduces the mechanical properties of Cf/SiC composites at elevated temperature.
3.2. XRD diffraction patterns

XRD diffraction patterns of the pyrolysis products of PCS and LPVCS at 1200 °C are shown in Fig. 2. The pyrolysis products of PCS and LPVCS were almost the amorphous SiC. However, weak peaks appeared at 36.5°, 60.1° and 71.9° associated with the (111), (220) and (311) planes of β-SiC crystals, respectively. A weak peak was observed at 26.5°, which indicated the existence of free carbon.

3.3. Properties of Cf/SiC Composites at Room and Elevated Temperature

The weight changes and density increment of the prepared Cf/SiC composites during the PIP process are shown in Fig. 3. The density of Cf/SiC composites increased and weight increase reduced with the infiltration and pyrolysis cycle increase. After 12 cycles of infiltration and pyrolysis, the density and porosity prepared samples were 1.79g/cm³ and 12.1%, respectively.

The mechanical properties of Cf/SiC composites at room and elevated temperature (1400 °C, 1600 °C) are showed in Table II. With ameliorated interface by employing LPVCS for the first cycle of infiltration and pyrolysis, the flexural strength and fracture toughness of the Cf/SiC composites were 421 MPa and 25.6 MPa•m¹/², respectively, which were 40% and 128% higher than those (301MPa, 11.2 MPa•m¹/²) fabricated with PCS. After heat-treatment (1400 °C) for one hour in Ar, the flexural strength and fracture toughness of the Cf/SiC composites were 395 MPa and 22.9 MPa•m¹/², respectively, with high retention rate approximately 90%. After heat-treatment (1600 °C) for one hour in Ar, the flexural strength and fracture toughness of the Cf/SiC composites were 297 MPa and 18.2 MPa•m¹/², respectively, with retention rate approximately 70%.

In summary, employing LPVCS for the first infiltration and pyrolysis cycle is a method to form suitable interface improving mechanical properties, in addition the samples get high mechanical properties retention rate at elevated temperature because of low oxygen content.
Figure 3. Weight changes and density increment of the prepared Cf/SiC composites during the PIP process

Table 2. Mechanical Properties of /SiC Composites

| Temperature/°C | Flexural strength/MPa | Fracture toughness/MPa·m$^{1/2}$ |
|---------------|----------------------|-------------------------------|
| 1200          | 421                  | 25.6                          |
| 1400          | 395                  | 22.9                          |
| 1600          | 297                  | 18.2                          |

3.4. Microstructural characterization and damage mechanisms

Typical fractured surfaces of the specimens for bending tests are shown in Fig 4. Toughness fracture formed after ameliorated interface, showing significant amounts of unstick, fracture and pulling out of carbon fiber. T300 carbon fiber and PCS pyrolysis products always formed strong interface force because of groove on the carbon fiber surface. However, LPVCS pyrolysis products formed weak interface with T300 carbon fiber because the oxygen in matrix reacted with the carbon fiber.

In Ar, three reasons led to the damage in mechanical properties. First, oxidation of the carbon fiber led to strength reduce (Eqs. (1)), damage to the surface of the carbon fiber was observed in Fig 5. Second, decomposition of the SiCxOy phase led to porosity and non-densification of the matrix (Eqs. (2)), which was observed in Fig 5. Third, growth of the β-SiC grain size reduced the matrix strength, which was observed in Fig 6.

\[
C (s) + O_2 (g) = CO_2 (g) \tag{1}
\]

\[
SiC_{x}O_{y} \rightarrow SiC (s) + C (s) + SiO (g) + CO (g) \tag{2}
\]
4. Conclusions
Employing LPVCS for the first infiltration and pyrolysis cycle is a method to form suitable interface to improve the mechanical properties of Cf/SiC composites, in addition the samples get high mechanical properties retention rate at elevated temperature because of low oxygen content. In Ar, three reasons led to the damage in mechanical properties. First, oxidation of the carbon fiber led to strength reduce. Second, decomposition of the SiCxOy phase led to porosity and non-densification of the matrix. Third, growth of the β-SiC grain size reduced the matrix strength. The further work will focus on reducing the porosity of Cf/SiC composites.

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