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Influence of heating rate on the microstructure and mechanical properties of Carbon fiber/Si—C—N composites via polysilazane pyrolysis

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Continuous fiber reinforced ceramic matrix composites (CFCMCs), which exhibit non-brittle mechanical behavior, high strength, low density, and high thermal stability, are desirable candidates for high temperature structural materials. The precursor-infiltration-pyrolysis (PIP) route to processing of CFCMCs has attracted increasing interest in recent years for its advantages such as low processing temperature, controllable ceramic compositions, availability of complex reinforcements (three-dimensional textiles) and near-net-shape technologies. Many different preceramic polymers have been discovered since their original development by Yajima *et al.* [1]. Polysiloxane (PSO), polycarbosilane (PCS), and polysilazane (PSZ), which give Si—O—C, Si—C, and Si—C—N ceramics upon pyrolysis, respectively, are the most often used preceramic polymers at present.

In our previous study [2], a novel PSZ with Si—H and Si—CH=CH_2 groups, which crosslinks readily in the presence of a catalyst (H_2PtCl_6) or an initiator (dicumyl peroxide), was synthesized. This PSZ has low viscosity of 14.5 mPa · s at room temperature and high ceramic yield of 80 wt%, which makes it suitable for the fabrication of three-dimensional braided carbon fiber reinforced Si—C—N composites (3D-B C_f/Si—C—N) [3]. This work focuses on the effects of heating rate on the microstructure and mechanical properties of 3D-B C_f/Si—C—N composites.

Carbon fibers with tensile strength of 3000 MPa and elastic modulus of 210 GPa were selected for this study. Three-dimensional braided carbon fiber preform has a fiber volume fraction of about 50% and a volume ratio of 8:1:1 in the x, y, z directions. Three 3D-B C_f/Si—C—N composites, which were denoted as samples P1, P5, and P10, were fabricated by repeating eight cycles of vacuum infiltration, curing at 120 °C for 6 h, and pyrolysis at 1000 °C for 1 h with the protection of high purity flowing N_2. Each pyrolysis of samples P1, P5, and P10 was performed with a heating rate of 1 °C/min, 5 °C/min, and 10 °C/min, respectively. The flexural strength was tested by a three-point bending method with the span/height ratio of 15 and a cross-head speed of 0.5 mm/min. Each data point was an average over five values. After the flexure tests, scanning electron microscopy (SEM) was employed to observe the fracture surfaces of the composites.

TABLE I The flexural strengths of samples P1, P5, and P10

Sample	Flexural strength (MPa)
P1	170.0
P5	361.0
P10	604.0

The flexural strengths of samples P1, P5, and P10 fabricated via infiltration and pyrolysis of PSZ are summarized in Table I. It can be noted from Table I that the flexural strength increased remarkably with increasing the heating rate of each pyrolysis, demonstrating that the flexural strength of 3D-B C_f/Si—C—N composites can be improved if the pyrolysis heating rate is increased.

Figs 1 and 2 show the fracture surfaces and load-displacement curves of samples P1 and P10, respectively. It is clear from Fig. 1a that sample P1 shows a flat fracture surface without fiber pull-out, indicating very strong fiber/matrix bonding. A strong interfacial bonding tends to allow a crack to propagate straight through the fibers. Consequently, sample P1 exhibited typical brittle fracture behavior with a displacement of only about 0.3 mm (Fig. 2a). In Fig. 1b, many pulled-out fibers and a long pull-out length are observed, indicating that the interfacial bonding of sample P10 is much weaker than that of sample P1. Weak fiber/matrix bonding facilitates toughening by matrix cracking, interfacial debonding, fiber pull-out and fracture. Accordingly, sample P10 showed tough fracture behavior with a displacement of about 1.5 mm (Fig. 2b).

The mechanical properties of CFCMCs are determined by their microstructures. It has been documented that the fiber/matrix interfacial characteristics play a critical role in determining the mechanical properties of CFCMCs. In previous studies [4–6], it has been well documented that the atoms in the matrix can diffuse into or react with carbon fibers during pyrolysis to create fiber/matrix bonding and a reduction in fiber strength. In our previous studies [7], the diffusion of Si atoms into carbon fibers was observed during the fabrication of C_f/Si—O—C composites via polysiloxane pyrolysis.

During the fabrication of sample P1, there was quite a lot of time due to the low heating rate for Si atoms in matrix to diffuse into carbon fibers, resulting in very strong fiber/matrix bonding and a great reduction in

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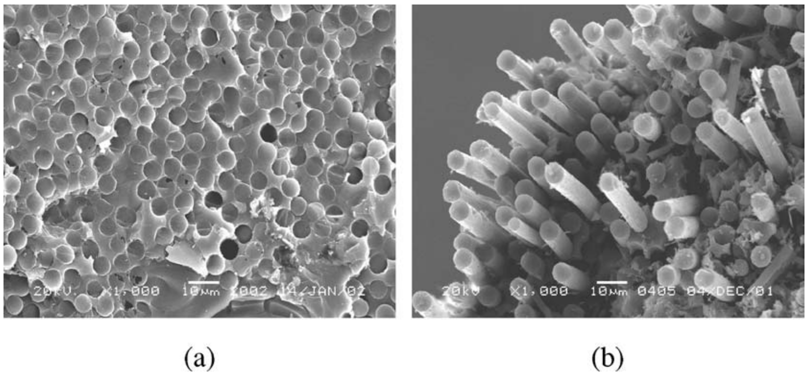

Figure 1 SEM photos of fracture surfaces of samples: (a) P1 and (b) P10.

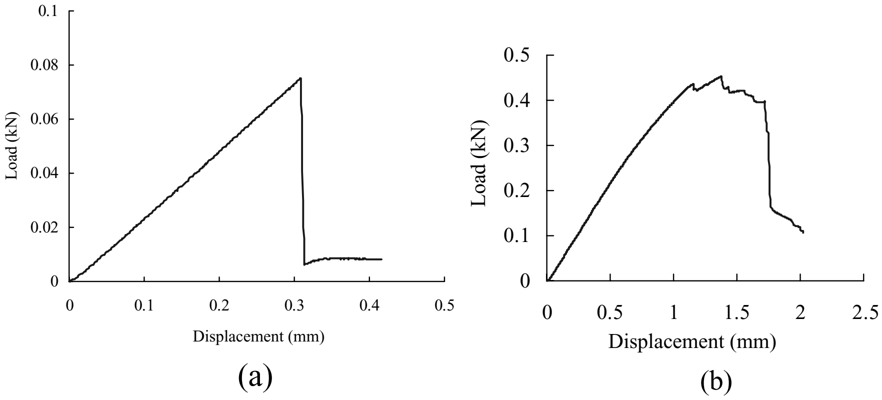

Figure 2 Load-displacement curves of samples: (a) P1 and (b) P10.

fiber strength. Therefore, sample P1 showed low flexural strength and brittle fracture behavior. When the heating rate was increased, the Si atoms in matrix had much less time to diffuse into carbon fibers, leading to weak fiber/matrix bonding and little reduction in fiber strength. Therefore, sample P10 exhibited much higher flexural strength than that of sample P1, and tough fracture behavior.

In summary, 3D-B C_f/Si—C—N composites were fabricated through PIP route. The flexural strength of 3D-B C_f/Si—C—N composites can be enhanced remarkably as a result of weakened interfacial bonding if the pyrolysis heating rate was increased. The composite, each pyrolysis of which was conducted with a heating rate of 10 °C/min, shows 604 MPa in flexural strength.

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