

Property enhancements via matrix microstructure modification of carbon–carbon composites prepared by CVI processing

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Carbon-carbon (CC) composites have received considerable interest for aerospace applications due to their superior strength retention at high temperatures and high heats of ablation etc. [1]. In the manufacturing of CC composites, carbon fiber preforms can be categorized dependent upon their final applications, e.g. UD, 2-D, 3-D and *n*-D etc. [2, 3]. Among them, even though they are high labor-dependent, carbon fiber rod-network *n*-D preforms have been used for thick (larger than 100 mm thickness) and high performance CC composites, especially for aerospace applications. In general, rod-network *n*-D CC composites are employing three routes for densification (1) chemical vapor infiltration (CVI) of hydrocarbon gases (2) liquid process with impregnation and pyrolysis of high carbon yield polymers or pitches (liquid process) (3) combination of CVI and liquid process [4].

In CVI process, under suitable conditions, pyrolytic carbon (PC) matrix has a preferred crystalline orientation which results in considerable anisotropy. In pyrolytic graphite (PG) which is more anisotropic than PC, for instance, the thermal expansion in the thickness direction (*c* direction in graphite structure) is approximately 20 times that in the plane of deposition (*ab* plane) [5]. Similarly, mechanical properties measured parallel to the *ab* plane are considerably higher than those measured perpendicular to it. Even though the degree of anisotropy is lower than that of PG, PC anisotropy creates considerable thermal stresses during CC processing, which lead to delaminations between PC matrix and the carbon fiber rods and micro-cracks in PC matrix itself. These delamination defects may be eliminated or at least greatly reduced by the modification of PC microstructure resulting in increase of CC composites performance [6, 7].

High-strength PAN-based carbon fiber (ACELAN TZ-307, Korea) with 12 K manufactured by Taekwang Industries Co., (Korea) was used in the present study. The fiber has tensile strength of 3800 MPa, tensile modulus 260 GPa, elongation 1.3%, and density of 1800 kg/m³ [8]. Polyvinyl alcohol (PVA 110, Kuraray, Japan) was used as a binder for carbon fiber rods preparation. Carbon fiber rods with 1.0 mm diameter were prepared using a typical pultrusion process. Three-D orthogonal rod-network preforms (*W*150 × *D*150 × *H*200 mm) having 59% fiber volume percent

were manufactured using the pultruded rods. In order to evolve thermal gradient from center to surface of a preform, a preform was drilled at the center of a preform in order to install a graphite heater. Prior to drilling a hole, a preform rigidization with PVA solution (10 wt%) having fillers was impregnated and dried at 90 °C in an oven to prevent preform distortion. For the purpose of the modification of microstructure of PC, fillers materials (1 volume percent of total pore volume in the preform) were supplied as PC nucleation sites during the preform rigidization stage. Three types of filler materials which are milled carbon fiber with an average length of 150 μm, 175 μm (PANEX FM150 and FC175, Zoltek, USA), and SiC (Aldrich 35739-1) powder with size less than 20 μm were used. Densification of preforms was accomplished by thermal-gradient chemical vapor infiltration (TGCVI) processing at 1100 °C in pressure of 760 torr using methane without carrier gas for 120 hr. High temperature heat treatment was carried out for 2 hr holding at 2000 °C in argon atmosphere. Bulk density at each of processing step was obtained from weight and dimensional measurements on the flexural specimens prior to testing. Microstructural observation was accomplished by using an optical microscope (Optiphot 150, Nikon, Japan). Thermal expansion property was determined by thermo-mechanical analyzer (TMA 2940, TA Instrument, USA). The specimen size was in 10 mm (*D*) × 10 mm (*H*). Flexural strength was determined by means of 3-point bending in accordance with ASTM C1341. The specimen size for the mechanical testing was 120 mm (*L*) × 15 mm (*W*) × 10 mm (*t*). Five samples from each processing condition were tested with the span-to-depth ratio of 10:1 at 2.8 mm/min crosshead speed at room temperature.

Fig. 1 shows bulk density variations at the each step of composites processing. Starting with preforms of density 1.06 g/cm³, CC composites underwent densification to around 1.52–1.55 g/cm³ by CVI processing, slight density variations depending on the preform positions in CVI furnace. In considering the effect of the fillers, it seems that the addition of fillers did not contribute for density increment. A high temperature heat treatment at 2000 °C rendered composites slightly lower in density as shown in Fig. 1. This is known due to the evaporation of non-carbon elements

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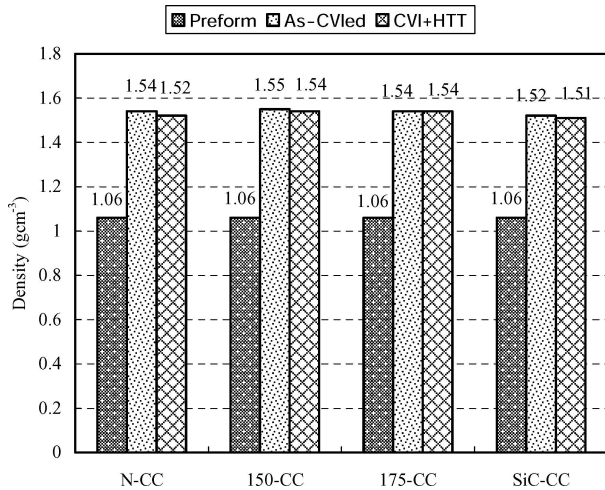
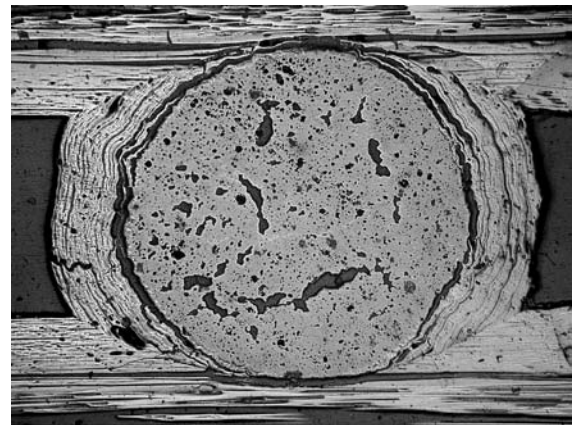


Figure 1 Density increments of C-C composites.

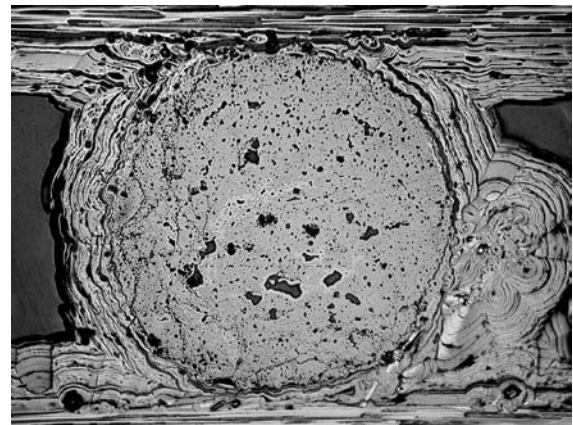
such as nitrogen, hydrogen, and oxygen, etc., and carbon oxidation [9].

After densification by CVI, microstructures of CC were observed as shown in Fig. 2. In the figure, there are carbon fiber rods in circular and straight shapes and well-developed PC matrix around the rods with about $180\ \mu\text{m}$ in thickness. In CC composites without filler (N-CC), there are continuous circumferential delamination cracks between the rod and PC layer, as shown in the figure. And many micro-delaminations in PC matrix are also observed in PC matrix itself. From N-CC microstructure observation, it is anticipated that mechanical strength is low because of not being high mechanical and frictional interlocking adhesion between the components, which are known as main adhesion mechanisms of CC composites. Differently from N-CC, even though there are circumferential delaminations, filler added CC (SiC-CC, 150-CC, and 175-CC) have discontinuous and relatively tortured cracks between PC matrix and carbon rods. This is ascribed to CVI PC nucleation effects by fillers. Among the filler composites, 150-CC and 175-CC demonstrate lower delamination cracks than SiC-CC. Regardless of filler types, all filler tend to concentrate to crossing areas of carbon fiber rods, as shown in figures. This seems to play a role like glue between the rods which leads to improved adhesion.

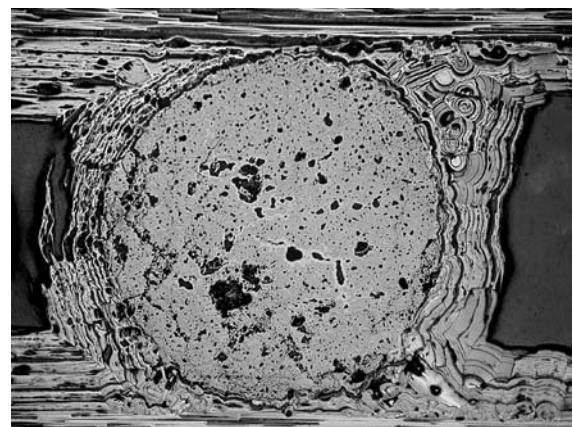
The flexural strength of CC composites is given in Fig. 3. As shown, after CVI densification, the strength of 150-CC and SiC-CC was increased by more than 100% as compared to that of N-CC. However, in the case of 175-CC 50% strength increase was obtained. This lower enhancement may come from non-uniform impregnation of PVA and filler mixture due to relatively larger filler length. After high temperature heat treatment at $2000\ ^\circ\text{C}$, all C-C demonstrated decrease in strengths, but lower strength decrease in filler added CC composites (31%, 8%, and 41%) compared to that of N-CC (53%). From this result, matrix modification by fillers to less anisotropic is more effective when CC composites undergo HTT, which gives rise to crack growth by a larger thermal expansion. The strength decrease of 175-CC was only 8% after HTT, as shown in the figure. This can be attributed to non-homogeneous



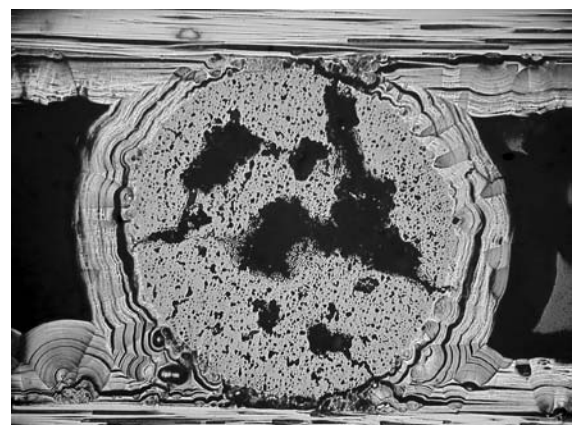
(a) N-CC



(b) 150-CC



(c) 175-CC



(d) SiC-CC

Figure 2 Optical microstructures of CC composites with fillers densified by TGCVI and heat treated at $2000\ ^\circ\text{C}$.

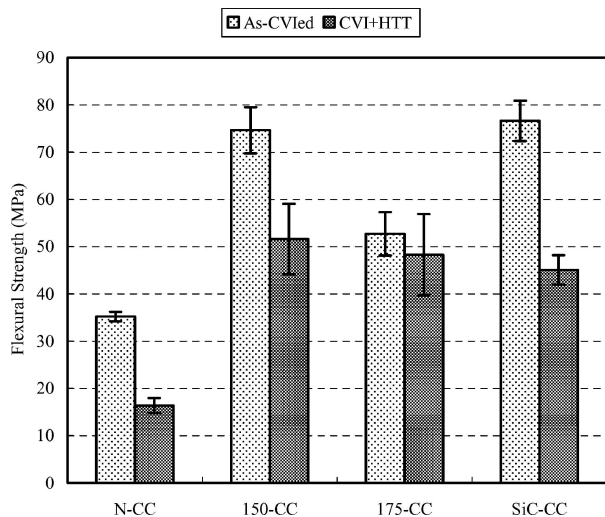


Figure 3 Flexural strengths of CC composites with fillers densified by TGCVI and heat treated at 2000 °C.

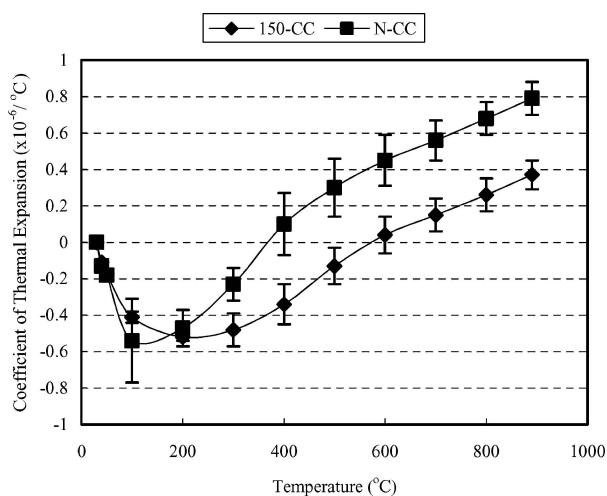


Figure 4 Coefficients of thermal expansion of CC composites densified by TGCVI and heat treated at 2000 °C measured by TMA.

property of the composites by poor impregnation of PVA and filler mixture as discussed earlier. In comparing flexural strength after HTT, 150-CC (214%), 175-CC (195%), and SiC-CC (175%) showed significant improvement in flexural strength as compared to that of N-CC. In summary, CVI carbon matrix modification by filler materials in CC is found to have significant enhancement of the strength by providing adhesion increase, more exactly mechanical interlocking and higher frictional interaction between fiber rods and matrix, with suppressing matrix delamination cracks, which are caused by thermal stresses during CVI densification and HTT.

Fig. 4 shows the coefficients of thermal expansion of N-CC and 150-CC measured up to 900 °C in inert atmosphere. The data are average value of three samples

from each CC. In all CC composites, CTE values tend to be negative from just higher than RT, and then the values show more decrease with temperature increase to around $-0.55 \times 10^{-6} / ^\circ\text{C}$, as shown in the figure. In comparing two samples, N-CC shows slightly higher maximum negative CTE at 100 °C, but recovers faster to positive expansion at about 380 °C than 150-CC. On the other hand, 150-CC revealed its maximum negative CTE at around 200 °C and this is continued until 590 °C. A maximum CTE was $0.78 \times 10^{-6} / ^\circ\text{C}$ for N-CC and $0.38 \times 10^{-6} / ^\circ\text{C}$ for 150-CC, respectively. From CTE observation, a plausible explanation for higher CTE in N-CC than 150-CC is as follows. It can be assumed that the rod has lower CTE than that of PC matrix because the rod is composed of carbon fibers with very low CTE, usually about $-0.1 \times 10^{-6} / ^\circ\text{C}$ [8]. On the other hand, PC matrix is known to have positive CTE [10]. It means that CTE of CC is dominated by matrix thermal expansion property. If the adhesion between the rod and PC matrix is higher in CC, expansion of PC matrix will be more constrained by the carbon fiber rod, so global expansion of CC can be reduced.

Microstructural modification of PC matrix in 3D CC composites manufactured by TGCVI was tried via addition of filler materials. As discussed earlier, it can be concluded that PC matrix microstructure variations from highly anisotropic to less-anisotropic by providing PC nucleation sites is very effective for enhancing thermal and mechanical strength. More researches on improving not only processibility but also property homogeneity are needed.

References

1. R. TAYLOR, in "Comprehensive Composite Materials" (Elsevier, Oxford, 2000) p. 387.
2. C. R. THOMAS, in "Essentials of Carbon-Carbon Composite" (The Royal Society of Chemistry, Cambridge, 1993) p. 118.
3. J. D. BUCKLEY and D. D. EDIE in "Carbon-Carbon Materials and Composites" (Noyes, 1993) p. 71.
4. S. M. LEE, in "International Encyclopedia of Composites Vol. 1" (VCH, Inc. 1990) p. 171.
5. T. R. GUESS and W. R. HOOVER, DoE Technical Report, SC-DR-720450, Sandia Laboratories, Albuquerque, New Mexico (1972).
6. B. GRANOFF, H. O. PIERSON, D. M. SCHUSTER and J. F. SMATANNA, DoE Technical Report, SC-DR-720337, Sandia Laboratories, Albuquerque, New Mexico (1972).
7. B. GRANOFF, H. O. PIERSON and D. M. SCHUSTER, *J. Compos. Mater.* **7** (1973) 36.
8. ACELAN Carbon Fiber Data Sheet, Taekwang Ind. Co., Ltd. (1994).
9. G. SAVAGE, in "Carbon-Carbon Composites" (Chapman & Hall, London, 1992) p. 43.
10. D. L. SCHMIDT, AFML Technical Report, ADA-325314, University of Dayton, Dayton, Ohio (1996) p. 9.

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