# DENSIFICATION OF CARBON/CARBON COMPOSITES USING CNT-CONTAINING PHENOLIC RESIN

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## ABSTRACT

In the fabrication of polymer resin-based carbon/carbon (C/C) composites, it is inevitable for a porous C/C composite to be formed after carbonization. As a result, densification, either by chemical vapor infiltration or by liquid phase impregnation followed by recarbonization, is required to obtain a densified composite. Although liquid phase impregnation, with polymer resins or pitches used as impregnant, is a simple technique, several cycles of impregnation/recarbonization are necessary in order to achieve the desired density and hence the required mechanical properties. Consequently, densification efficiency is an important factor in reducing the number of densification cycles and hence the processing cost. One common approach to increasing the densification efficiency is to open up the closed pores resulting from the previous densification cycles by an intermediate graphitization heat treatment. In the present study, liquid phase impregnation/recarbonization densification process using carbon nanotube (CNT) dispersed phenolic resin is proposed for the first time. The density and open porosity of composites were followed and the densification efficiency was analyzed to show the effects of densification with and without CNT addition on the mechanical and electrical properties. Decrease of resistance of 6.3% was measured in the thickness direction of C/C composites after four densification cycles as compared with composites densified without CNT addition. Increase of flexural strength of 11.3% was also obtained after final graphitization with CNT addition.

## 1 INTRODUCTION

Carbon fiber reinforced carbon matrix (C/C) composites are primarily developed and designed for high temperature structural applications due to the maintenance of their strength and modulus at high temperature. In fact, C/C composites retain their strength and modulus in an inert atmosphere or in vacuum to temperatures higher than those tolerated by other materials, such as superalloys and ceramics [1-2]. In addition, C/C composites have low thermal expansion, good wear resistance, and excellent biocompatibility. As a result, applications were also found as refractory materials, brake lining for high speed vehicles, and biomedical materials, etc. [2-3].

In the fabrication of polymer resin-based carbon/carbon (C/C) composites, it is inevitable for a porous C/C composite to be formed after carbonization. As a result, densification, either by chemical vapor infiltration or by liquid phase impregnation followed by recarbonization, is required to obtain a densified composite. Although liquid phase impregnation, with polymer resins or pitches used as impregnant, is a simple technique, several cycles of impregnation/ recarbonization are necessary in order to achieve the desired density and hence the required mechanical properties. Consequently, densification efficiency is an important factor in reducing the number of densification cycles and hence the processing cost. However, related studies are rarely found in the open literature [4-10]. One common approach to increasing the densification efficiency is to open up the closed pores resulting from the previous densification cycles by an intermediate graphitization heat treatment [10]. In the present study, liquid phase impregnation/recarbonization densification process using carbon nanotube (CNT) dispersed phenolic resin is proposed for the first time. The density and open porosity of

composites were followed and the densification efficiency was analyzed to show the effects of densification with and without CNT addition on the mechanical and electrical properties.

## 2 EXPERIMENTAL

The reinforcements used for C/C composites in this study were two-dimensional plain woven carbon fiber (CF) fabrics, which were woven using 3k PAN-based CF tows. For both the matrix materials and the impregnant of the densification, the resol-type phenol-formaldehyde resin (Chang Chun Co., Taiwan) was used. For the fabrication of CF/phenolic resin composites, the CF fabrics were impregnated with the phenolic resin using hand lay-up and then the vacuum bag hot pressing technique was used to fabricate the composites. For the fabrication of C/C composites, the phenolic resin based composites were cut, weighed and then carbonized to convert into C-C composites in a horizontal tube furnace at a heating rate of 2℃/min to 1000℃ in an argon atmosphere. The carbonized composites were then graphitized in an Astro 1000-3060-FP20 graphite furnace to 2300℃ under a helium atmosphere. The heating rate for graphitization is 5℃/min and the hold time is 30 minutes.

Densification of the graphitized composites was carried out by phenolic resin impregnation/ recarbonization cycles. Before the impregnation, CNTs were dispersed in the phenolic resin (0.3 wt.%). Impregnation was carried out under vacuum for 6 hr in a mold with the composites inside the phenolic resin solution, which had been preheated at 60℃. Then the temperature was raised to 80℃ for a suitable time at atmospheric pressure to form the B-stage. The composites impregnated with B-staged phenolic resin were then cured and then recarbonized using the same processing conditions as those of carbonization for as-fabricated composites. It needs to be mentioned that for the four impregnation/recarbonization densification cycles, addition of CNTs was only adopted in the first densification cycle as indicated in the experimental flowchart (Fig. 1).

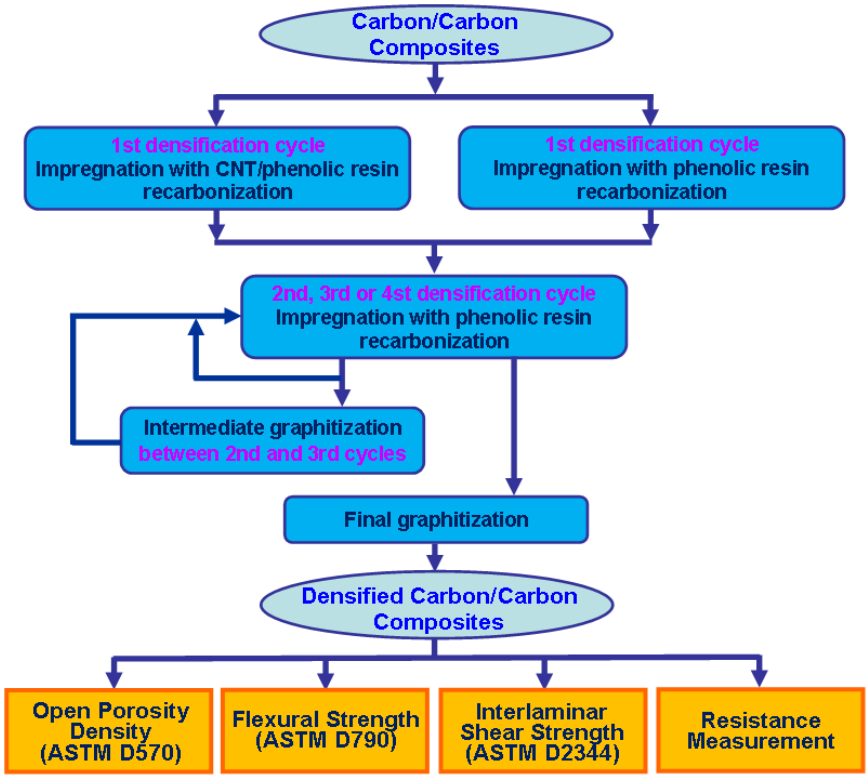


Figure 1: Flowchart of experimental procedures.

The open porosity, apparent density and bulk density of the C/C composites before and after each densification cycle were measured according to ASTM-D570. The mechanical properties and fracture behavior were studied using the three-point bending test according to ASTM D-790. The fracture

surfaces of the composites after bending tests were observed using SEM. The interlaminar shear strength of the composites was measured using the short-beam shear test according to ASTM D-2344. The resistance of the composites was measured using the two-point method [11]. Fig. 2 shows the experimental setup for the resistance measurement of C/C composites. For the comparison purpose, the thickness of the composites remained unchanged in the measurement.

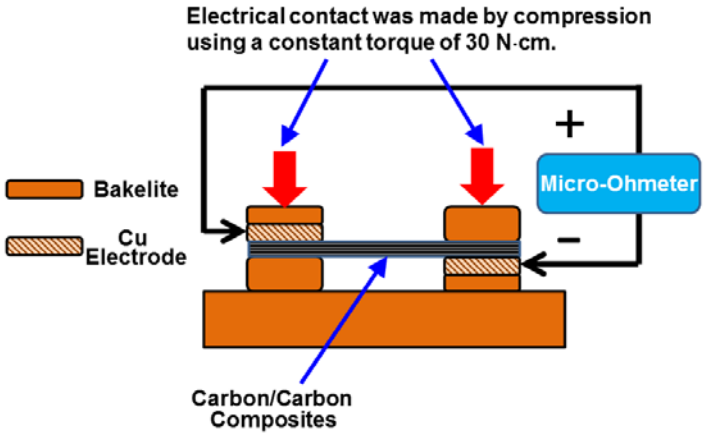


Figure 2: Experimental setup for the resistance measurement of C/C composites.

## 3 RESULTS AND DISCUSSION

### 3.1 SEM structure observation

Fig. 3 shows the microstructure of C/C composites densified using phenolic resin (Fig. 3(a) and 3(b)) and densified using CNT-containing phenolic resin (Fig. 3(c) and 3(d)). It can be seen that both the phenolic resin and CNT-containing phenolic resin can enter into the co-planar cracks (symbol *C*) and transverse cracks (symbol *T*) and densify the composites.

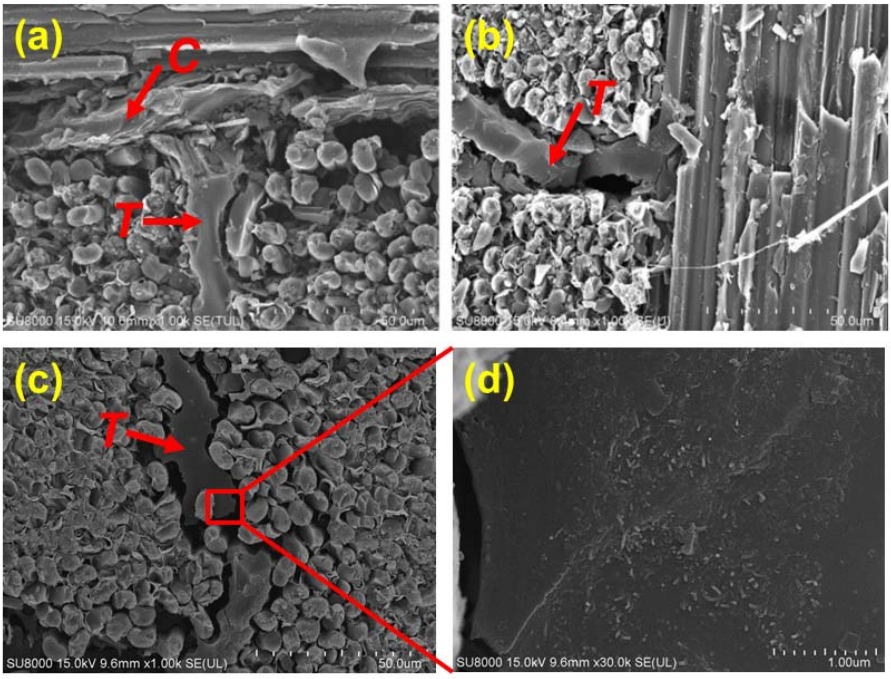


Figure 3: SEM images of C/C composites showing the densification of C/C composites in the co-planar (symbol *C*) and transverse (symbol *T*) cracks: (a)(b) densified using phenolic resin; (c)(d) densified using CNT-containing phenolic resin.

### 3.2 Flexural strength

#### 3.2.1 Effect of CNT loading

Fig. 4 shows the effect of CNT loading on the flexural strength and modulus of C/C composites densified using CNT-containing phenolic resin. As shown, although the average strength was slightly higher for the 0.3 wt% CNT loading, no significant difference can be found considering the data variation. On the other hand, the flexural modulus increased with the increase of the CNT loading. In the following experiments, a CNT loading of 0.3 wt% was adopted.

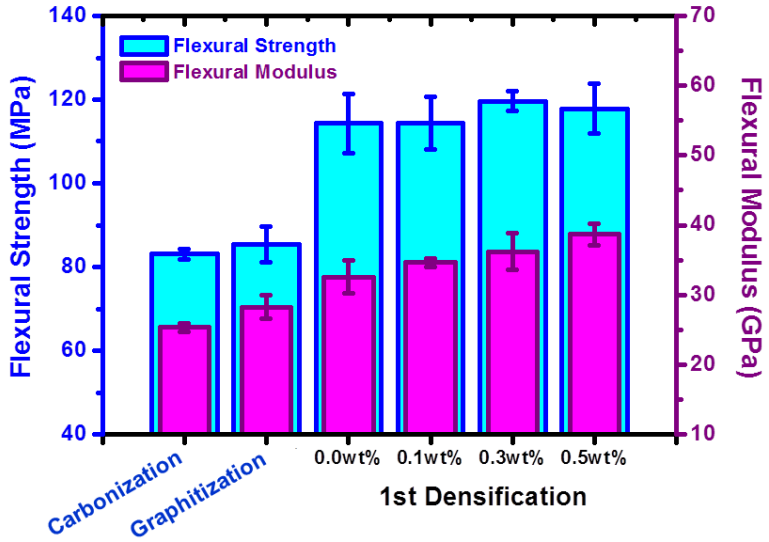


Figure 4: Effect of CNT loading on the flexural strength and modulus of C/C composites densified using CNT-containing phenolic resin.

#### 3.2.2 Effect of densification using CNT

Fig. 5(a) shows the variation of open porosity after different heat treatment and densification processes for the densification with and without CNT addition. The carbonized composite has an open porosity of 16.6 % and a slight increase to 17.2 % was measured after graphitization. For the four densification cycles, obvious decrease of open porosity can be found except the fourth cycle presumably due to the blockage of the open pores.

The efficiency of densification process could be evaluated by the volumetric densification efficiency, $Y_v$, which was defined by Rellick [4] as the ratio of the volume of the carbon matrix generated in a densification cycle, to the volume of porosity available for densification:

$$Y_v = \Delta V / \theta \, . \tag{1}$$

Equation (1) could be rearranged as [4]

$$Y_v = y_w y_\lambda \rho_p / \rho_c \, , \tag{2}$$

where $y_\lambda$ is the impregnation efficiency of phenolic resin, $y_w$ is the carbon yield of the phenolic resin impregnant after recarbonization, $\rho_p$ is the density of the phenolic resin impregnant, and $\rho_c$ is the density of the recarbonized phenolic resin. According to equation (2), the maximum densification efficiency could be estimated as follows. By assuming perfect impregnation efficiency ($y_\lambda = 1$) and taking $\rho_p = 1.284$ g/cm$^3$, $\rho_c = 1.543$ g/cm$^3$, and $y_w = 0.507$, the maximum densification efficiency is calculated to be $Y_v \approx 0.422$. In the above calculation, $\rho_c$ and $y_w$ were obtained by carbonizing the phenolic resin in an open crucible. The volumetric densification efficiency, $Y_v$, as defined in equation (1), was calculated in this study using the data of open porosity and bulk density as follows:

$$Y_v\,(n) = [\rho_b(n) - \rho_b(n\text{-}1)] \,/\, \theta(n\text{-}1)\, \rho_c \, , \tag{3}$$

where $Y_v\,(n)$ is the volumetric densification efficiency of the $n^{th}$ densification cycle, $\rho_b(n)$ is the bulk

density after the $n^{th}$ densification cycle, $\theta(n)$ is the open porosity after the $n^{th}$ densification cycle, and $\rho_c$ is the density of the recarbonized phenolic resin. The evolution of calculated densification efficiency with the densification cycles is presented in Fig. 5(b). A slight increase of efficiency at the third densification cycle was obtained because of the intermediate graphitization after the second cycle, which opens up the closed pores. For the effect of CNT addition, although the open porosity was lower after the fourth cycle and final graphitization for the addition of CNTs, the effect was not significant.

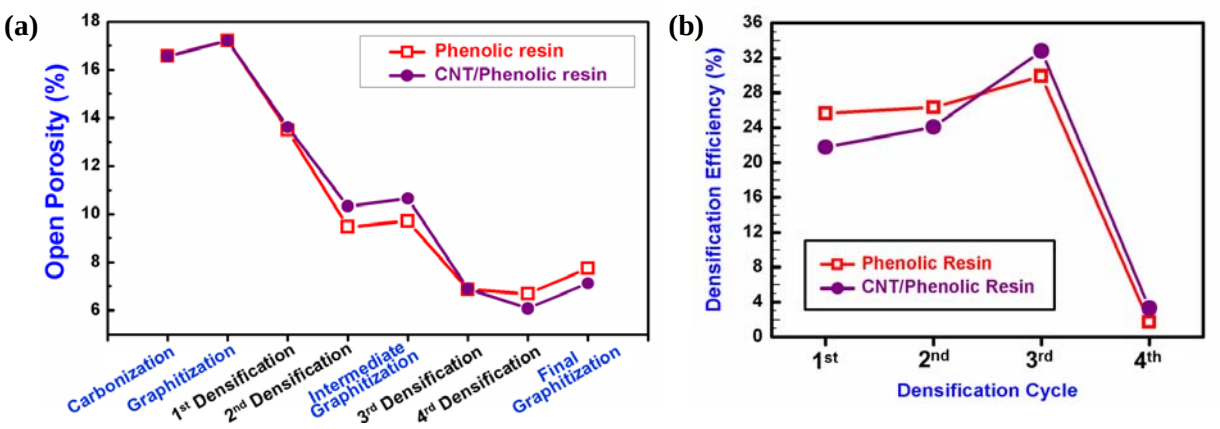


Figure 5: Variations of (a) open porosity and (b) densification efficiency after different densification cycles for the densification with and without CNT addition.

Variation of flexural strength after different heat treatment and densification processes for the densification with and without CNT addition was presented in Fig. 6. The flexural strength of carbonized composites was 83.1 MPa. The average strength slightly increased to 85.4 MPa after graphitization. Obvious enhancement in the strength was found after the first and second densification cycles. An increase percentage of 95% was measured after the second cycle. However, the strength remained relatively constant after the fourth cycle. Decrease of the strength after final graphitization was expected due to the increase of cracks resulting from the high temperature heat treatment. For the effect of CNT addition, although the average strength was raised slightly, no significant improvement could be found after the first and the fourth cycles. Larger scatter of the strength was observed for the fourth densification cycle with the addition of CNTs. It is also interesting to note the improvement of strength after the final graphitization with the addition of CNTs.

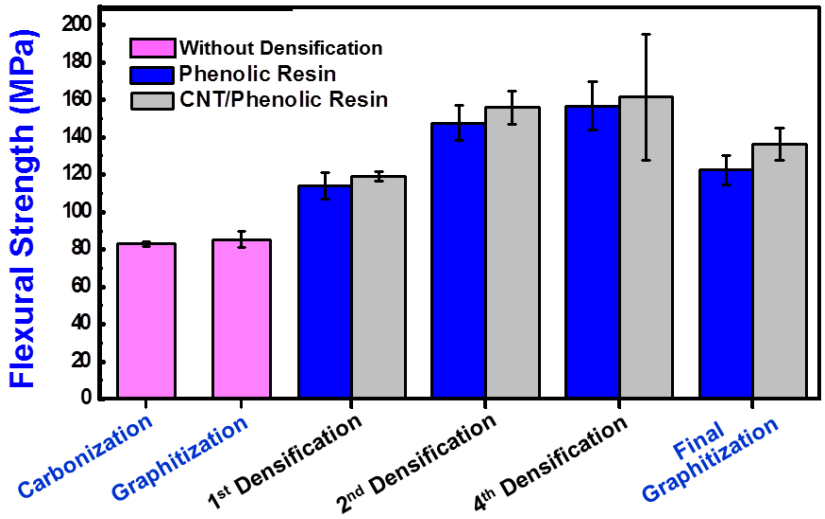


Figure 6: Variation of flexural strength after different heat treatment and densification processes for the densification with and without CNT addition.

### 3.3 Interlaminar shear strength

Short-beam shear tests were performed to measure the interlaminar shear strength of the C/C composites after different heat treatment and densification processes for the densification with and without CNT addition, and the results were presented in Fig. 7. As shown, significant increase of the interlaminar shear strength was measured after 2nd densification for both composites densified with and without CNT addition. For the effect of CNT addition, an increase of the interlaminar shear strength of 18.6% was measured after final graphitization.

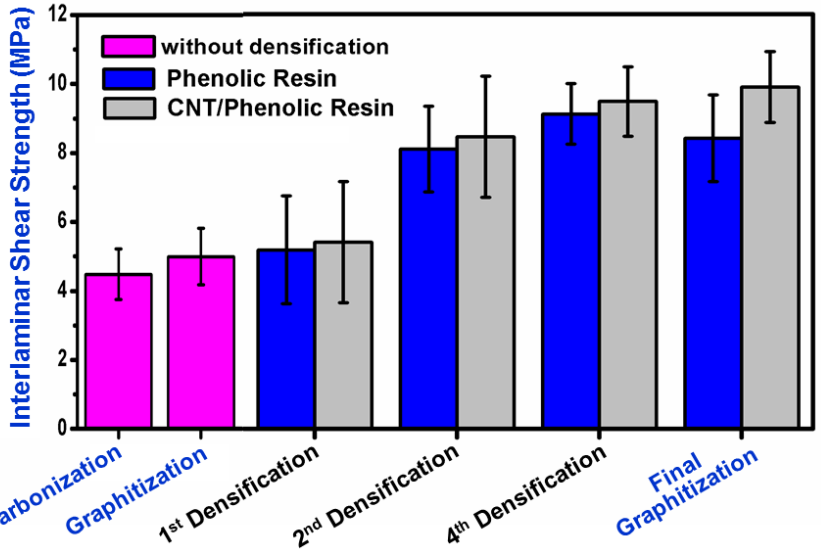


Figure 7: Variation of interlaminar shear strength after different heat treatment and densification processes for the densification with and without CNT addition.

### 3.4 Resistance measurement

The electrical resistance of the C/C composites in the thickness direction was measured and presented in Fig. 8. A significant drop of the resistance was measured after graphitization obviously due to the improvement of crystallinity. Gradual decrease was also found following the densification cycles and also final graphitization. Larger decrease of resistance was also obtained with the addition of CNTs. Observation of microstructure, as shown in Fig.3, indicated that the CNT-containing phenolic resin can enter into both the co-planar and transverse cracks, which resulting in the larger decrease of resistance in the thickness direction with the addition of CNTs.

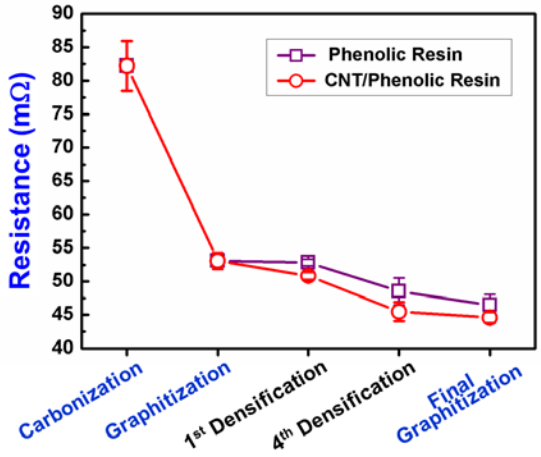


Figure 8: Variation of electrical resistance of the C/C composites in the thickness direction after different densification cycles for the densification with and without CNT addition.

## 4 CONCLUSIONS

Densification of two-dimensional C/C composites was investigated using CNT-containing phenolic resin as the impregnant. Microstructure observation indicated that CNT-containing phenolic resin can enter into the co-planar cracks and transverse cracks of the C/C composites in the densification process. Decrease of resistance of 6.3% was measured in the thickness direction of C/C composites after four densification cycles as compared with composites densified without CNT addition. Increase of flexural strength of 11.3% was also obtained after final graphitization with CNT addition.

## ACKNOWLEDGEMENTS

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