



PROCESSING AND CHARACTERIZATION OF NANOSTRUCTURED CARBON/CARBON COMPOSITES

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Abstract

Carbon/Carbon (C/C) composites are used in high temperature applications because they exhibit excellent high temperature properties. There are several challenges associated with the processing of C/C composites including - (a) long cycle times; (b) formation of closed porosity within fabric woven architecture; and (c) carbonization induced cracks and pores that can lead to debonding and delaminations, and therefore significant reduction of mechanical properties. This work aims at developing C/C composite material in conjunction with vapor grown carbon nanofibers (VGCNFs). The study has shown improvements to the properties of the composite at the carbonized stage, in part due to fiber bridging and some could be attributed to higher degree of process control in terms of dispersing the carbon fiber.

1.0 Introduction

Carbon/Carbon (C/C) composites are used in high temperature applications because they exhibit excellent thermo-mechanical properties [1]. There are several challenges associated with the processing of C/C composites including - (a) long cycle times; (b) formation of closed porosity within fabric woven architecture; and (c) carbonization induced cracks and pores that can lead to debonding and delaminations, and therefore significant reduction of mechanical properties. This work addresses various innovative approaches to reduce process uncertainties of C/C by using carbon nanofibers (CNFs) in conjunction with carbon fabric and precursor matrix, and investigating the resulting properties. To develop C/C composite material that benefits from CNFs addition, it is necessary to understand the phenomena of stress transfer of nanofibers relative to polymer phenolic matrix from an analytical and experimental viewpoint at all stages of the processing. By understanding the

influence of CNFs at each of these stages the properties (mechanical and functional) of the final C/C composite could be improved.

2.0 Literature

Carbon/Carbon (C/C) composites have been widely used since their development for military applications in the 70's. Their retention of mechanical properties at high temperatures in inert environments has resulted in making C/C materials primary candidates in applications like re-entry vehicles, heat shields and aircraft brakes [1]. C/C composites are generally produced from carbon fiber/high char resin preform by a series of carbonization/densification treatments [2]. Previous researchers have investigated the effect of modifying the resin and the effect of the final C/C composite. Chen-Chi et al. studied the effect of adding graphite powder on the mechanical properties of C/C composites [3]. They found an increase in the flexural strength of the composite for up to 5% powder, with higher % decreasing the properties. Kang and Jeong [4] added pitch and graphite powders to phenolic resin. They found a decrease in mechanical properties of the green composite with increased powder content. For the carbonized composite they found an increase of the mechanical properties up to 15%wt content. Yasuda et al. found similar results with furfuryl alcohol as the matrix precursor, in their studies they found the properties of the C/C composite showed a maximum at 10%wt of graphite powder addition [5]. The shape of pitch particles is angular whereas that of graphite is in general circular. In this study the material under consideration for resin modification is vapor grown carbon nanofibers (VGCNFs). These fibers have a one dimensional morphology consisting of sp^2 - bonded graphitic carbon oriented along an axis parallel to the basal plane and having a length-to-

diameter ratio of more than 100. VGCNFs are obtained by the pyrolysis of hydrocarbons such as benzene or methane at temperatures around 1100°C using ultrafine metal particles catalysts. The diameters of these fibers range from 100 nm to about 10 μm. The center consists of a hollow core proportionate to the size of the catalytic particle from which the fibers are formed. The carbon surrounding the hollow core that is deposited during the first stage is a highly crystalline filament. In the second stage the filaments thicken forming concentric, cylindrical sheaths around the initial filament developing 3-ring morphology of less order than the inner core. Dhakate et al. added VGCNFs to phenolic resin as reinforcement to develop VGCNFs based C/C composites. They found comparable mechanical properties to graphite with increased hardness and compressive strength [7].

3.0 Objectives

The major objectives of this research are to investigate the processing and performance of CNF modified C/C composites. The processing refers to as-cured, carbonized and densified stages.

4.0 Processing Considerations

Traditionally the processing of C/C composites is conducted in multiple processing steps. Woven carbon fiber is impregnated under heat and pressure with pitch from coal tar or petroleum sources. This is followed by pyrolysis (also referred to as 'carbonization') of the pitch to obtain a carbonaceous matrix. Generally, the matrix after the first carbonization is highly porous. The cycle may be repeated to obtain the desired amount of densification. The carbonization of the polymer precursor is connected with evolution of large volume of gases, also referred to as 'pyrolysis'. The loss in weight of composite during carbonization is proportional to matrix content and the linear shrinkage in fiber direction is less than 1% but the fiber reinforcement counteracts matrix shrinkage causing thermal stresses. The stresses are due to the difference in coefficients of thermal expansion in between matrix and reinforcing fiber, this consequently causes cracking of C/Cs [1].

5.0 Processing Conditions

Synthetic resins and coal tar pitch have been used as the matrix precursors for C/Cs. The matrix has a high porosity after carbonization; therefore the densification process is necessary. Impregnation

with a liquid precursor followed by curing and re-carbonization enables filling of open volume pores in C/Cs. Thus the key goal in producing C/C is to create a fully carbonized dense matrix that provides superior thermomechanical properties. The main requirements in the manufacture of high density C/C composites are high carbon yield, low volumetric expansion and low porosity upon carbonization.

For these studies, VGCNFs were mixed with phenolic resin in ratios of 1%, 3%, and 5% wt./wt. respectively. Catalyst was added to the resin-CNF mixture maintaining a resin-to-catalyst ratio of 100:8. Four layers of C-fabric were wetted with resin using a hand lay-up process followed by vacuum bagging to obtain uniform consolidation. The specimens were post cured with the following cycle, 2h at 60°C, 2h at 70 °C, 1h at 80 °C and 1h at 90 °C.

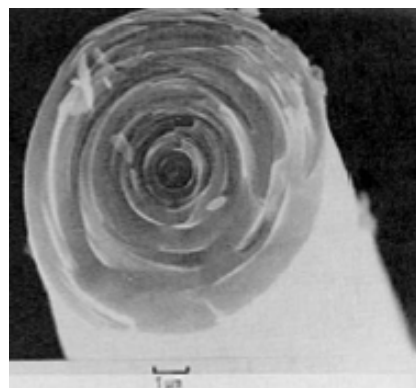


Fig. 1. Morphology of Vapor Grown Carbon Nanofiber [1]

Several methods of addition of the fibers were considered with a goal of increasing the carbon content in the material. The simplest of them was spraying the carbon fabric with the VGCNFs, and then stacking layers of carbon fabric by a hand lay-up process to produce the as-prepared laminate. The carbon fabric layers are sprayed with a solution of VGCNFs and water. Hence, in this approach incorporation of the VGCNFs is achieved on the fabric surface, as opposed to mixing VGCNFs in the phenolic resin. A set of specimens were prepared with the carbon fabric sprayed with a mixture of VGCF and deionized H₂O. The sprayed carbon fiber layers are then dried for 1 hour at 100 °C. The layers are then used in the hand lay-up process. The specimens were tested by ASTM mechanical testing procedures of flexure and interlaminar shear.

6.0 Results and Discussion

The ‘as prepared’ specimens have a steady decrease in mechanical properties as a function of increasing VGCNFs, i.e the VGCNFs did not enhance the interfacial properties as was initially expected. However, at the carbonized stage the VGCNFs dominated the properties. When comparing the neat sample to the 1%, 3% and 5% VGCNFs (Figure 2), there is an average increase in the flexural modulus from 30kPa in the neat to 70kPa in the specimens with VGCNFs addition. The improvement remained the same regardless of the amount of VGCNFs in the mixture. There are several mechanisms that could contribute to the increase of properties at the carbonized stage when compared to the neat sample. One of them was found be fiber bridging of the microcracks.

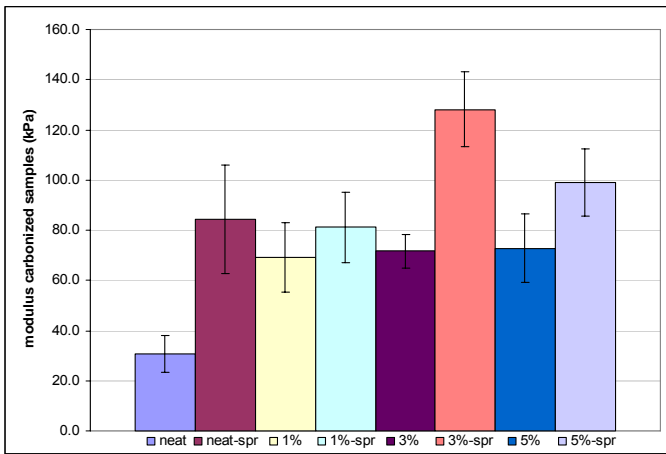


Figure 2. Comparison of carbonized C/C/VGCF composites. Note: Neat- neat resin, the 1%, 3% and 5% represent VGCNF percentages, and the –spr signifies VGCNFs were sprayed on fabric surface in addition to mixing the phenolic resin

Figure 3 shows the morphology of the C/C composite after the first carbonization. The transverse cracks in between layers of the composite are a result of the thermal stresses. These thermal stresses occur because of the difference in coefficient of thermal expansion (CTE) between the phenolic resin and the carbon fiber. The neat sample exhibited uniform spacing between the thermally induced cracks. Also voids were seen to develop in the crimp of the fabric. When comparing the neat sample versus the neat-sprayed, the addition of VGCNFs in the interlayer reduces the size and quantity of crimp voids. Also the number of transverse matrix cracks is fewer in the VGCNF incorporated samples as compared to the neat. Following from the preform the samples with

spraying of VGCNFs in the interlayer shows higher degree of consolidation. The addition of VGCNFs shows more aggressive matrix shrinkage.

The distance in between transverse thermal cracks or D for the purpose of the discussion is shown in Figure 4, sample 3.5%-s. D1 is then the average distance between transverse thermal cracks and was calculated from the microstructure. D1 increases for specimens with VGCNFs. As shown in Figure 4, D1 increases with the addition of VGCNFs (in the 1.5%-s to 3.5%-s region). The increase in D1 is speculated to occur because the VGCNFs offer more resistance to transverse matrix shrinkage. Hence this resistance results in lesser number of transverse matrix cracks when compared to the neat. However, when cracking occurs in the VGCNF specimens, this cracking has additional energy release, due to the initial increased resistance that was offered by the nanofibers. Hence, the effect of adding the nanofibers is they develop larger sized matrix cracks in the specimen, albeit lesser in number, but accompanied by inter connection between the transverse cracks (i.e. increased energy release).

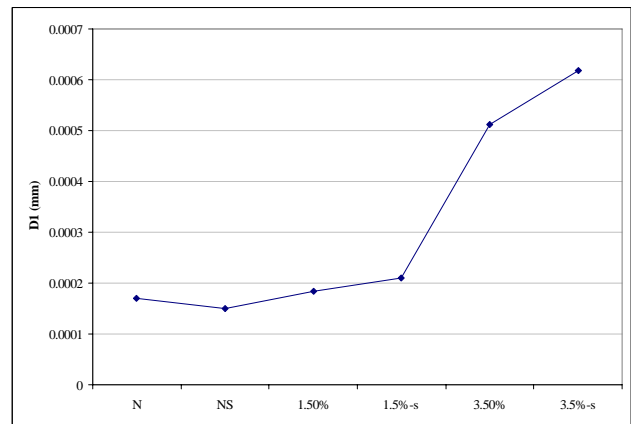


Figure 4. Effect of VGCNFs addition on D1 where D1 is the spacing in between longitudinal thermal cracks.

6.1 Mechanical Properties

As opposed to the preform stage where the properties are fiber dominated, at the carbonized stage the VGCNFs played a more distinct role. Figure 5a shows a marked increase in the flexural

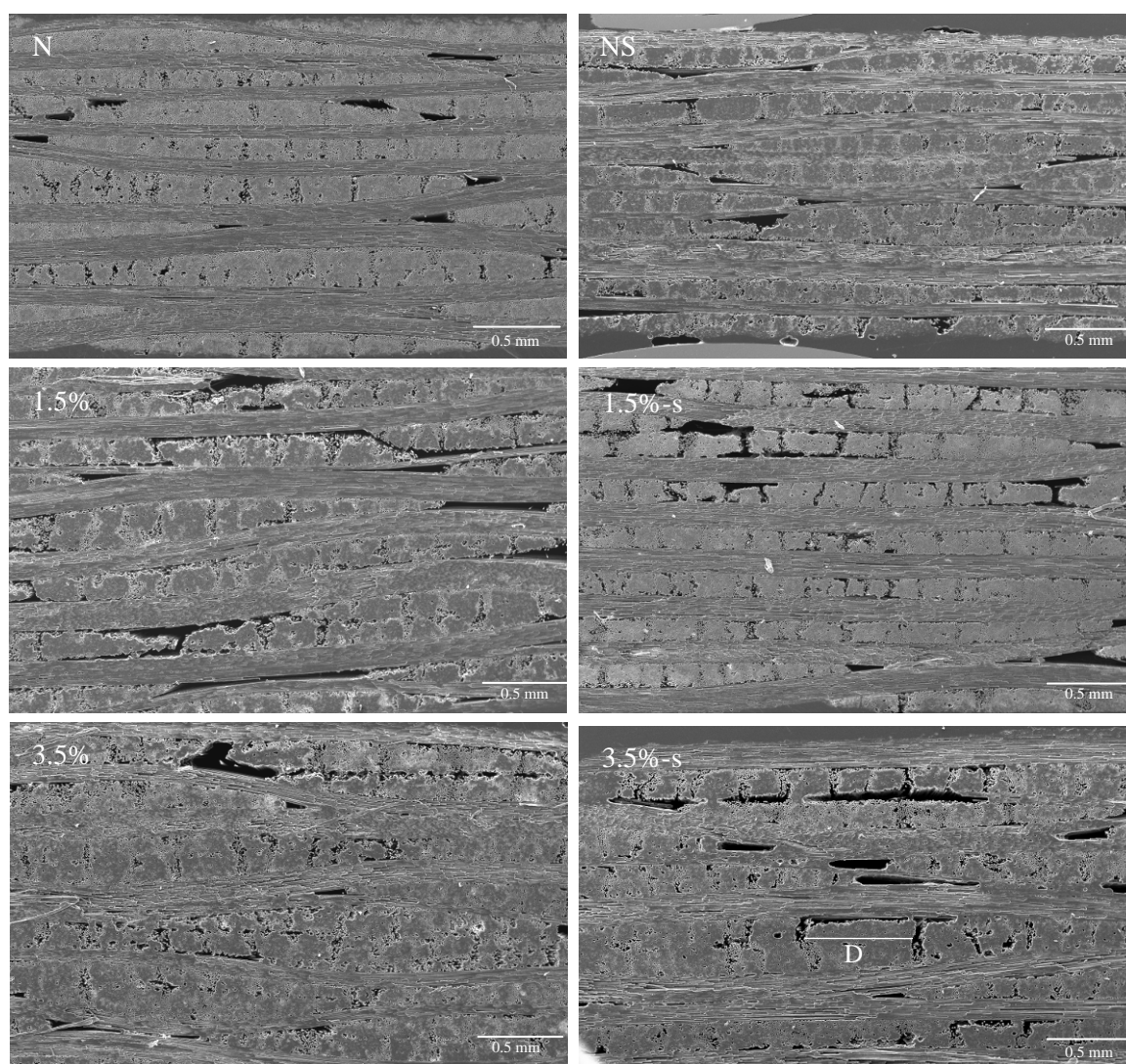


Figure 3. SEM pictures showing the morphology of the preform at different VGCNFs concentrations.

modulus with VGCNF content, regardless if it was dispersed in the matrix or sprayed. The improvement was the highest with the spraying of the VGCNFs at 3wt%-sprayed (referred to as 3%-s in Figure 5a), further addition of VGCNFs showed a decrease in the properties. When comparing the flexural strength of the neat sample to the 1% and 3% VGCNFs (Figure 5b), there is an increase from 25MPa in the neat to 60MPa at the 3%, 3%-s specimens with VGCNFs addition.

There are several mechanisms that could contribute to the increase of properties at the carbonized stage between the additions of VGCNFs when compared to the neat sample. The VGCNF fibers showed good interface with the carbonized matrix and provide restriction to the number of transverse cracks that occur.

When the matrix cracks are under tension, the fibers bridge the cracks, or there is fiber pull out. Representative fiber bridging is shown in Figure 6.

7.0 Summary

The effects of adding VGCNFs to C/C composites was investigated at the preform and 1st carbonization stages of the processing. The addition of VGCNFs at the preform stage in most cases adversely affected the mechanical properties, i.e. flexural modulus, flexural strength and interlaminar shear strength (not reported here). This was attributed to the VGCNFs acting more as inclusions than reinforcement. The VGCNFs had a notable influence on the transverse cracks that are thermally induced in that they offered higher degree of

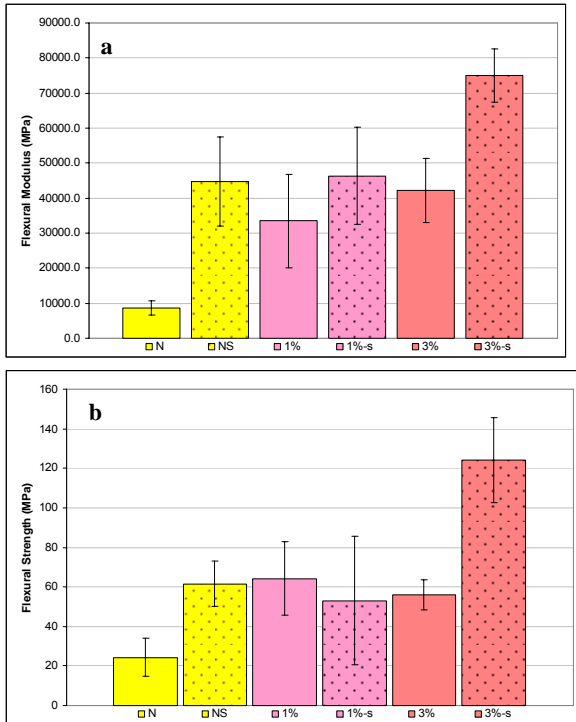


Figure 5. a) Flexural modulus b) Flexural strength for the carbon/carbon composite with different concentrations of VGCNFs after first carbonization

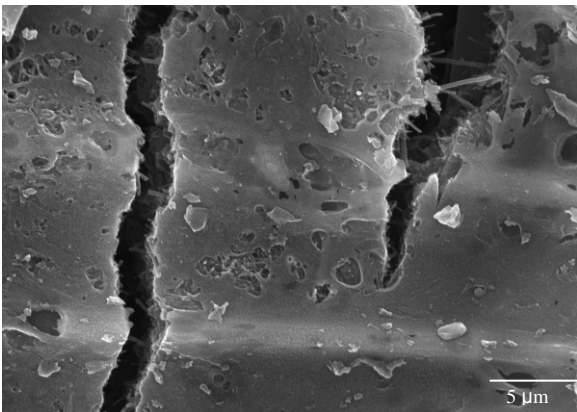


Figure 6. a) SEM of the 3.5% after 1st carbonization showing the detail of a thermal crack and surrounding carbon matrix and VGCNFs bridging the cracks caused on the tension side of the sample.

resistance to cracking. This behavior caused an increase in the crack spacing, and somewhat non-uniform cracking, yet rendered higher degree of openness of the material for the next processing cycle, namely densification. Also, the 3.5% VGCNF dispersed in resin, accompanied by fiber spraying configuration (3.5%-s) show highest improvement in mechanical properties. This improvement was attributed to increased layer wise interaction of the VGCNFs both in-plane and through the thickness.

In our study, the spraying of nanofibers offers an additional means of obtaining uniformly dispersed nanofibers throughout the microstructure. Further studies are warranted to confirm these preliminary trends.

8.0 References

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9.0 Acknowledgements

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