

CVD Whiskerization Treatment Process for the Enhancement of Carbon Fiber Composite Flexural Strength

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ABSTRACT

Carbon fiber composite performance can be enhanced by applying an optimum level of fiber surface treatment such as whiskerization. The main objectives of this study were to conduct whiskerization through carbon nanotube (CNT)-coating of carbon fiber via chemical vapour deposition (CVD) at various conditions (temperature and hydrogen flow rate) and to investigate the enhancement in flexural strength of composites fabricated from these CNT-coated carbon fibers. The results indicated that CNTs were able to grow onto the carbon fibres with the highest amount of whiskerization occurring for samples nearest the reactant gas inlet of the CVD Rig. Various whiskerization behaviours were observed at different reaction temperatures and flow rates. From flexural tests, it was found that whiskerization treatment on carbon fibers increases the flexural strength of its composites between 44-122%.

Keywords: Carbon fibers, carbon nanotubes, composites, flexural strength

INTRODUCTION

Carbon fibers are the main reinforcing fibers used in high performance polymer matrix composites. Carbon fiber which has a very smooth surface causes the bond between fiber and matrix to be the weakest feature of the combination when laminated. Therefore, though carbon fiber possesses superior modulus as compared to glass fiber, it bonds poorly with matrix materials (Milewski *et al.*, 1971). Consequently carbon fibers were considerably inferior to boron and glass fibers that were being used in structural materials. These observations led investigators to develop various surface treatments that could improve the fiber-matrix interfacial bonding (Donnet *et al.*, 1998).

These surface treatments may be classified into oxidative treatments and non-oxidative treatments. Non-oxidative treatments that improve the fiber-resin bonding involves the deposition of more active forms of carbon on the carbon fiber surface, such as the growth of carbon whiskers (on the fiber surface) in a process called whiskerization (Donnet *et al.*, 1998). It is believed that these carbon whiskers are either carbon nanotubes (Thostenson *et al.*, 2001) or carbon nanofibers which are known for their superior strength (Downs and Baker, 1995).

Fiber bundles or fibrous textures (fabrics) can be coated using vapor-phase processes. A process of this kind which is well suited for coating fiber bundles is the method known as chemical vapor deposition, or CVD (Huber and Schmaderer, 1992). CVD of films and

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coatings involve the chemical reaction of gaseous reactants on or near the vicinity of a heated substrate surface (Choy, 2003). In this study, carbon nanotubes (CNTs) were grown on carbon fibers through a CVD process known as whiskerization treatment.

Milewski *et al.* (1971), Downs and Baker (1995) and Kowbel *et al.* (1997) found that whiskerization provided immense improvement in the surface bond by 500%, 475% and 250% respectively. Donnet *et al.* (1998) reported that whiskerization contributes immense improvement in inter-laminar shear strength (ILSS). A good measure of increment in surface bonding is by measuring the flexural strength of composites which correlates well with ILSS (Jang and Yang, 2000).

The objectives of this study were (i) to carry out whiskerization treatment by coating untreated PAN-based carbon fiber with CNTs at various reaction temperatures (800-1000°C) and hydrogen flow rates (100-500ml/min) conditions and to characterize the CNT-coated fibers at these conditions and (ii) to investigate the effect of these varying whiskerization treatment conditions on the flexural strength of carbon fiber-epoxy composite.

MATERIALS AND METHODS

Whiskerization Treatment

In this study, the whiskerization treatment was carried out using a custom-built CVD Rig. A description of the apparatus has been reported by Suraya *et al.* (2006). Whiskerization treatment was conducted on carbon fibers by bubbling hydrogen gas into benzene and then flowing this reaction gas into the quartz tube where ferrocene and carbon fiber tows were positioned. Ferrocene decomposes under high temperature and expels organic compounds whilst the Fe ions are left to diffuse into exposed pores on the carbon fibers. Benzene vapour which enters the furnace decomposes into carbon atoms. These carbon atoms are attracted to the heated Fe ions which act as catalysts, thus stimulating whisker nucleation and growth. This treatment was conducted at reaction temperatures of 800°C, 900°C and 1000°C at a heating rate of 5°C/min. At each of the reaction temperature, the hydrogen flow rate was varied at 100ml/min, 300ml/min and 500ml/min. The reactor was cooled under argon gas before collecting the treated fiber.

Fiber Characterization

The treated fiber samples from each treatment condition were then analyzed using scanning electron microscopy (SEM) (JEOL JSM-6400 model). The CNTs grown on the carbon fiber surfaces were characterized using HRTEM model Philip Tecnai 20.

Composite Processing

Composites were then fabricated from carbon fiber and epoxy resin using the hand layup method before being subjected to flexural test according to ASTM D790 using Instron Universal Testing Machine. A SEM, model JEOL JSM-6400, was then used to characterize the fracture surface of these composites.

RESULTS AND DISCUSSION

Characterization of CNT-coated Fiber

A total of nine sets of treatment conditions were experimented, and the details of the designations used for these treatment conditions are given in Table 1.

TABLE 1
Description of the treatment condition designations used

Designation	Hydrogen Flow Rate (ml/min)	Reaction Temperature (°C)
A	100	800
B	300	800
C	500	800
D	100	900
E	300	900
F	500	900
G	100	1000
H	300	1000
I	500	1000

For each treatment, CNT-coated fiber samples were taken from three main regions along the reaction tube to examine the pattern of CNT growth on the carbon fibers along the reaction tube. *Fig. 1* illustrates these three regions in the quartz tube denoted as regions 1, 2 and 3.

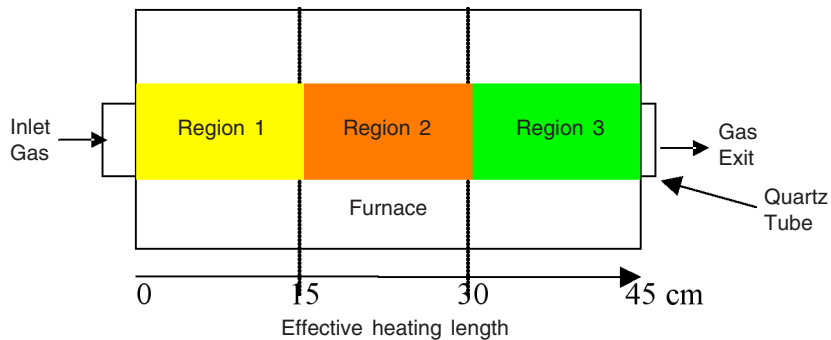


Fig. 1: Positions of the three regions in the reaction tube where CNT-coated fiber samples were taken to examine the whiskerization pattern

Fig. 2 depicts the SEM micrographs of CNT-coated carbon fibers for condition A. CNTs tend to grow from carbon fibers only at region 1. This pattern was evident for all treatment conditions. CNTs are likely to form at the inlet region of a CVD reactor where the ferrocene vapour is fed because the Fe particles (resulting from ferrocene decomposition) will increase in diameter with an increase in the axial distance and only the catalyst particles at the inlet with relatively smaller diameters are capable of performing as the growth seed for CNT growth. As the larger Fe particles form towards the reactor exit, they become too large and inactive for CNT growth (Moisala *et al.* 2006; Kuwana and Saito, 2005).

Figs. 3 to 5 depict the SEM micrographs of CNT-coated carbon fibers for conditions A to I at region 1. CNT-coated fibers consist mainly of relatively short CNT length at a

reaction temperature of 800°C whereas at higher reaction temperatures (900°C and 1000°C), longer strand-like CNT is noticeable on CNT-coated fibers. Zhao *et al.* (2005) reported similar findings where low temperature CVD processes produced short MWCNTs while high temperature CVD produces long MWCNTs. HRTEM analysis was carried out in order to examine the alignment of parallel graphitic sheets of individual CNTs (grown on carbon fibers) at 800, 900 and 1000°C, and the images are shown in Fig. 6 (a, b, c). The alignment of graphitic sheets parallel to the tube axis is evident in all the figures, with the parallel graphitic sheet of CNTs being more aligned and distinct as the temperature increases. This is because as the temperature increases, the carbon diffusion rate (from benzene decomposition) increases. Consequently, the growth rate of CNTs increases and the graphitic sheets build up with a less defect (Lee *et al.*, 2003).

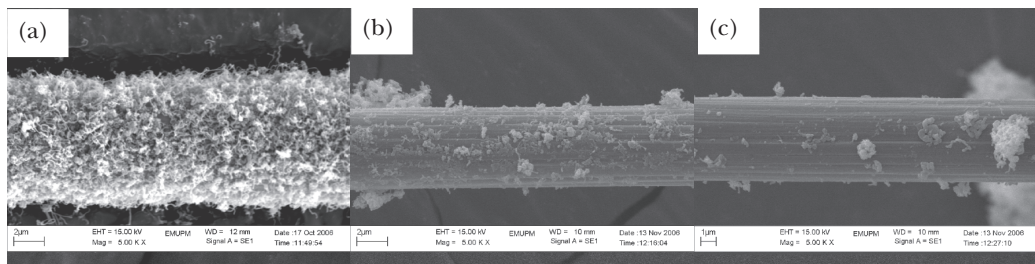


Fig. 2: SEM micrograph of CNT-coated carbon fiber at a reaction temperature of 800°C and 100ml/min of hydrogen gas flow rate, A, at (a) region 1, (b) region 2 and (c) region 3 along the reaction tube

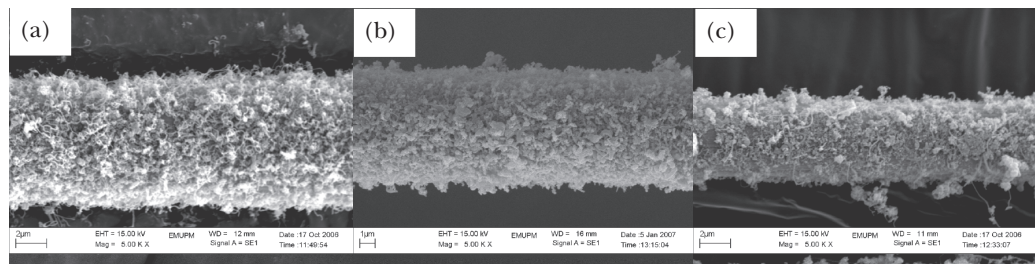


Fig. 3: SEM micrograph of CNT-coated carbon fibers at (a) 100ml/min, (b) 300ml/min and (c) 500ml/min of hydrogen gas flow rate and a reaction temperature of 800°C at region 1

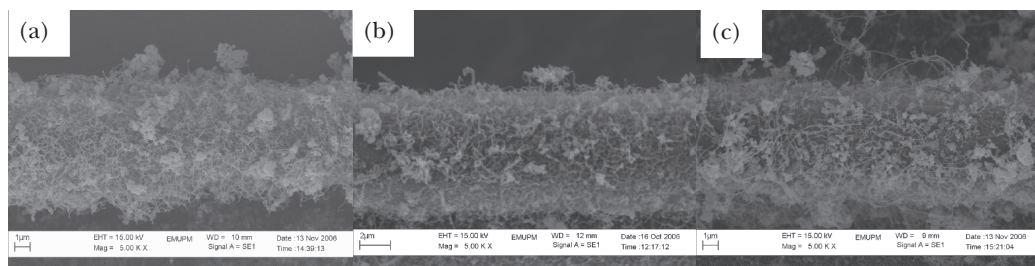


Fig. 4: SEM micrograph of CNT-coated carbon fibers at (a) 100ml/min, (b) 300ml/min and (c) 500ml/min of hydrogen gas flow rate and a reaction temperature of 900°C at region 1

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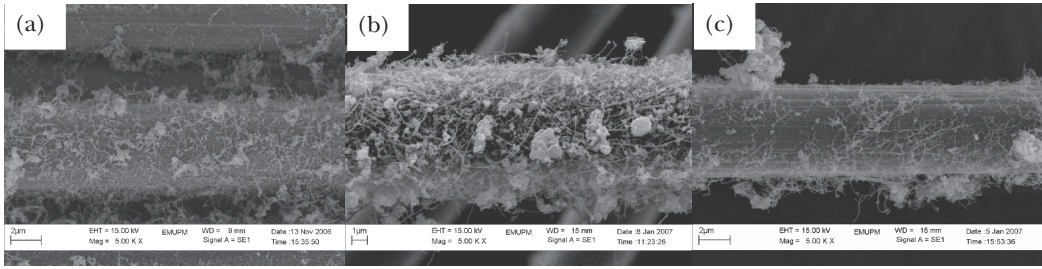


Fig. 5: SEM micrograph of CNT-coated carbon fibers at (a) 100ml/min. (b) 300ml/min and (c) 500ml/min of hydrogen gas flow rate and a reaction temperature of 1000°C at region 1

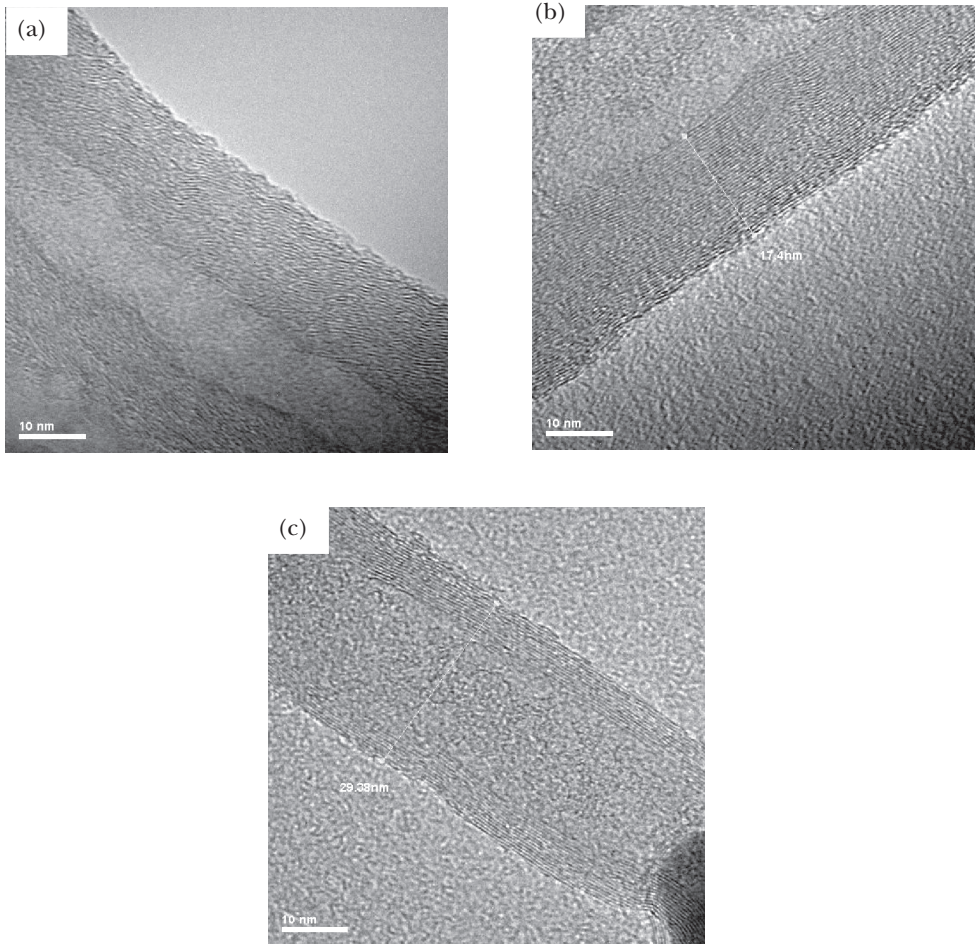


Fig. 6: HRTEM micrographs on CNT grown at (a) 800°C, (b) 900°C

Figs. 7 to 9 show the SEM micrographs of CNT-coated carbon fibers for conditions A to I at region 1 at a lower magnification. The micrographs show that most of the CNT-coated fibers at the lower hydrogen flow rate of 100ml/min comprises of fibers with amorphous carbon impurities (indicated by clumps) and relatively uneven CNT coating. At higher hydrogen flow rates of 300 and 500ml/min, the clumps on the CNT-coated fibers disappeared and the CNT coatings on the fiber were relatively more even. These observations were much more evident at lower temperatures especially at 800°C. This trend could be due to the role of hydrogen in hindering or preventing the formation of surface carbide (Fe_3C) which is the cause for low carbon deposition rates. Yang and Yang (1986) reported that surface carbide is essentially inactive for benzene decomposition.

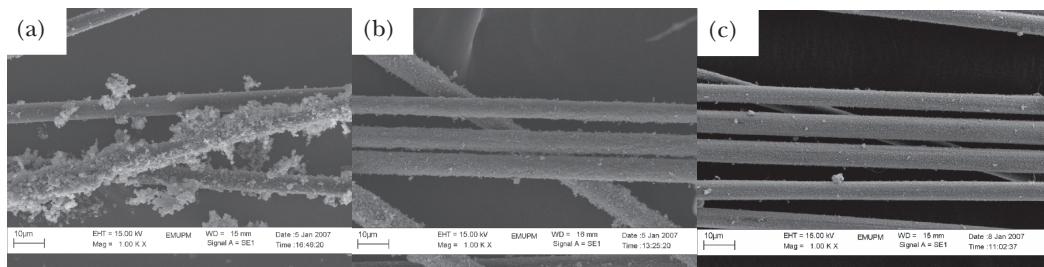


Fig. 7: SEM micrograph of CNT-coated carbon fibers at (a) 100ml/min, (c) 300ml/min and (c) 500ml/min of hydrogen gas flow rate and a reaction temperature of 800°C at region 1

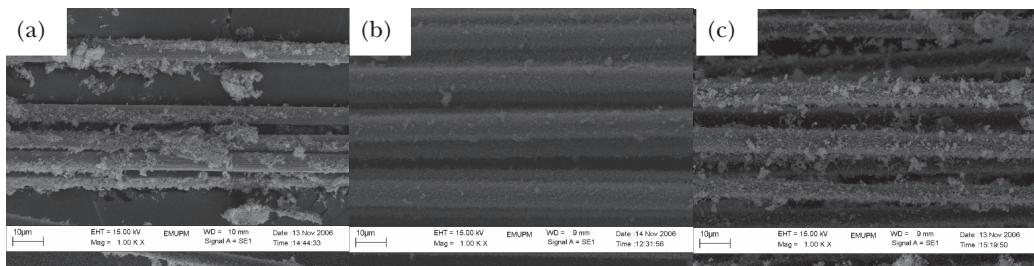


Fig. 8: SEM micrograph of CNT-coated carbon fibers at (a) 100ml/min, (c) 300ml/min and (c) 500ml/min of hydrogen gas flow rate and a reaction temperature of 900°C at region 1

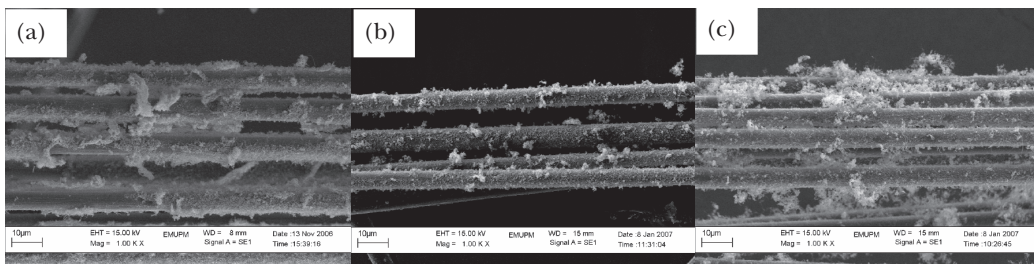


Fig. 9: SEM micrograph of CNT-coated carbon fibers at (a) 100ml/min, (c) 300ml/min and (c) 500ml/min of hydrogen gas flow rate and a reaction temperature of 1000°C at region 1

Carbide is formed, along with amorphous carbon and graphite, which deactivates the Fe activity for carbon deposition. In the presence of H₂, a high activity is obtained probably because a metallic surface is maintained, thus sustaining the activity. This explains the reduced impurities and even coating of CNT at higher hydrogen flow rate.

Whiskerization treatment on carbon fibers increases the flexural strength of composites by 44-122%. The extent of increment in flexural strength varies according to the whiskerization treatment conditions. The flexural strength of composites made from untreated and CNT-coated carbon fibers are listed in Table 2. The carbon nanotubes grown on carbon fibers improves the surface geometry of fibers by providing greater mechanical grip for matrix material which when combined with the fibers forms composites. The CNT-coated fibers have a considerable degree of cohesion even before they are impregnated with matrix filler material because the CNTs from adjacent fibrils overlap, intertwine and occupy all of the interstitial voids located between adjacent bundles of fibers (Milewski *et al.*, 1971). This type of fiber-matrix adhesion mechanism is called mechanical interlocking and results in enormous increase in flexural strength when these fibers are combined with matrix material. The resulting composite behaves in a manner resembling more nearly an isotropic material.

TABLE 2
Flexural strength of composites made from untreated and
CNT-coated carbon fibers

Whiskerization Treatment Condition	Flexural Strength (MPa)	Increment (%)
Untreated	1.45	-
800°C, 100ml/min	3.22	122
800°C, 300ml/min	3.03	109
800°C, 500ml/min	2.84	96
900°C, 100ml/min	2.62	81
900°C, 300ml/min	2.30	59
900°C, 500ml/min	2.27	57
1000°C, 100ml/min	2.25	55
1000°C, 300ml/min	2.23	54
1000°C, 500ml/min	2.09	44

Effect of Varying Reaction Temperature and Hydrogen Flow Rate

Fig. 10 compares the flexural strength of composites fabricated from CNT-coated carbon fibers at various temperatures for various hydrogen flow rates. As the whiskerization treatment reaction temperature increases from 800°C to 1000°C, at 100ml/min of hydrogen, the flexural strength of composites fabricated at these conditions decreases but is still more than composites fabricated from untreated carbon fibers. This same pattern is observed for 300 and 500 ml/min of hydrogen as the reaction temperature increases from 800°C to 1000°C. This can be attributed to the increased reaction temperature causing the surface activity of the fiber surface to decrease (Wang *et al.* 2006), resulting in lesser fiber and epoxy interaction and this in turn lowers the flexural strength of the composite. Therefore though whiskerization treatment at higher temperatures (900°C and 1000°C) enhances the flexural properties of composites by 44-

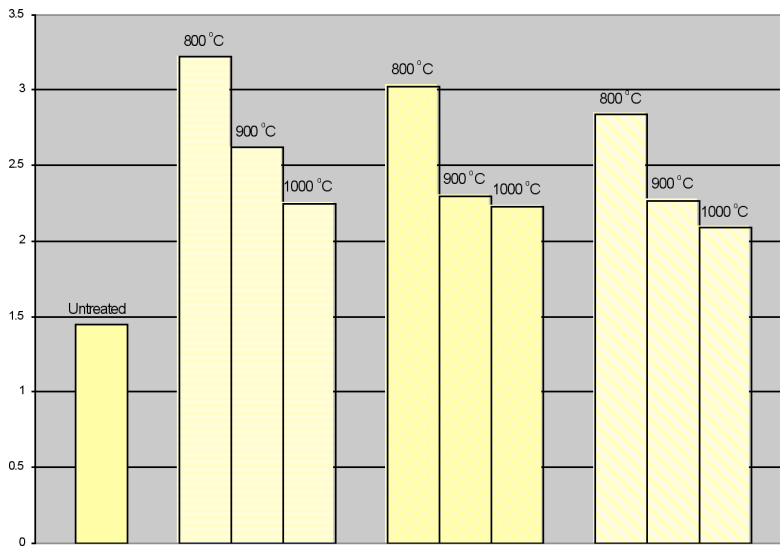


Fig. 10: Flexural strength of composites fabricated from untreated and CNT-coated carbon fibers

81%, this enhancement is less compared to flexural strength of composites fabricated from carbon fibers treated at 800°C with corresponding increment of 96-122%.

Alternatively, comparing the flexural strength of composites fabricated from CNT-coated carbon fibers at various hydrogen flow rates at the same reaction temperature indicates an overall decrease in the flexural strength of composites fabricated for all three reaction temperatures. Nevertheless the difference in flexural strength for the various hydrogen flow rates at the same temperature is not very significant with a mere 7-13% decrement. Therefore, it can be concluded that the hydrogen gas flow rate (used during whiskerization) does not play a major role in flexural strength of these CNT-coated carbon fiber composites.

CONCLUSIONS

Observation of SEM micrographs of treated carbon fiber samples taken at various points in each region showed that CNTs tend to grow from carbon fibers only at region 1 for all treatments. Observation of SEM micrographs of CNT-coated carbon fibers at reaction temperatures of 800°C, 900°C and 1000°C showed that the CNTs grown on the carbon fibers increased in length and distinctness of parallel graphitic sheets alignment as the reaction temperature increased from 800 to 1000°C. On the other hand, as the hydrogen flow rate increased from 100 to 500 ml/min, SEM micrographs depicted that the CNT coatings on the fibers were relatively more even. The amorphous carbon impurities (indicated by clumps) on the CNT-coated fibers also disappeared as the hydrogen flow rate increased from 100 to 500 ml/min but this was only observed at a reaction temperature of 800°C.

Whiskerization of carbon fibers increases the flexural strength of composites by 44-122%. Higher reaction temperature and hydrogen flow rate during carbon fiber whiskerization lowers the flexural strength of its composites with the latter condition having less impact on the strength.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support provided by the Ministry of Science, Technology and the Environment, Malaysia (MOSTE) under programme No. 03-01-01-0065-PR0072/08-05 and also acknowledge the SEM analysis service of Universiti Putra Malaysia, Bioscience Institute, Microscopy and Nanoscience Imaging Institute as well the HRTEM analysis service of Advanced Materials Research Centre (AMREC) SIRIM Berhad.

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