EVALUATION OF CARBON VAPOUR DEPOSITION TECHNIQUE FOR WHISKERIZATION TREATMENT OF CARBON FIBERS

A.R Suraya[1], C. Vargis[1], R. Yunus[1] and S. Shamsudin[2]
[1] Department of Chemical and Environmental Engineering, Universiti Putra Malaysia, 43400 Selangor, Malaysia
[2]Advanced Material Research Centre, SIRIM Bhd, Lot 34, Jln Hi-Tech 2/3, Kulim Hi-Tech Park, 09000, Kedah
Email: suraya@eng.upm.edu.my

ABSTRACT

The main objective of this work was to evaluate the effectiveness of the chemical vapour deposition (CVD) technique for the whiskerization treatment of polyacrylonitrile (PAN) based carbon fibers. Carbon whiskers were produced by a benzene-ferrocene gas reaction inside a high temperature tube furnace. The work focuses on one pre-treatment study and two treatment studies, which were (i) the pre-treatment effect of heating rate on the carbon fibers, (ii) the morphology of treated carbon fiber samples at three different regions inside the furnace, and (iii) the effect of different hydrogen flow rates on the treatment process. The reaction temperature and duration was set at 900^{o}C and 30 minutes respectively. Treated samples were analysed using scanning electron microscopy (SEM). The pre-treatment study indicated that a heating rate of 5^{o}C/min caused the least amount of damage to the carbon fibers. The treatment studies showed that whiskers were successfully grown onto the carbon fibres with the highest amount of whiskerization occurring for samples nearest the inlet region of the furnace. Different whisker structures were also observed at different hydrogen flow rates.

Keywords: *whiskerization, carbon fibers, carbon vapour deposition (CVD), whiskers.*

INTRODUCTION

The high strength, superior stiffness, and light weight of carbon fibers have made them the dominant reinforcing fibers used in high performance polymer matrix composites. The same fibers can also reinforce brittle materials, such as ceramics and carbon, thus creating a unique class of high-temperature composite materials [1]. The expansion of the areas of application of carbon fibers is stimulated by the attractive complex properties that are not found in other materials, such as strength, electrical conductivity, stability on exposure to reactive media, low density, low-to-negative coefficient of thermal expansion, resistance to shock and heating [2].

Carbon fibers, when used without any surface treatment produce composites with low interlaminar shear strength (ILSS). This has been attributed largely to weak bonding between the fiber and the matrix. Kaelble et al. [3], Larsen et al. [4] and Daukeys [5] have shown that ILSS is directly related to the fiber matrix bonding. These observations led investigators to develop various surface treatments that could improve the fiber-matrix interfacial bonding. These surface treatments may be classified into oxidative 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* [6]. It is believed that these carbon whiskers are either carbon nanotubes or carbon nanofibers which are known for their superior strength [7]. According to Kowble et al. [8] their whiskerization process provided the highest increase in ILSS which is an improvement of 200-300%. Whiskerization will be the surface treatment method developed in this work.

Fiber bundles or fibrous textures (fabrics) can be coated using a method known as chemical vapor deposition, or CVD [9]. The CVD method involves the chemical reaction of gaseous reactants on or near the vicinity of a heated substrate surface. This atomistic deposition method can provide highly pure materials with structure control at atomic and nanometer scale level. Furthermore, CVD allows the coating of complex shape engineering components and the fabrication of nanodevices, carbon-carbon (C-C) composites and ceramic matrix composite (CMC) [10]. The main objectives of this work were to investigate the effect of three parameters on the whiskerization process, which were (i) the pre-treatment effect of heating rate on the carbon fibers, (ii) the morphology of treated carbon fiber samples at three different regions inside the furnace, and (iii) the effect of different hydrogen flow rates.

MATERIALS AND METHODS

The CVD Rig used in this work generally comprises a precursor handling system, a furnace reactor and a by-product exhaust system. A schematic drawing of the whole apparatus is shown in Figure 1. The precursor handling system mixes and meters hydrogen, benzene and ferrocene. Benzene (purchased from Merck Sdn Bhd, Malaysia) was used as the carbon source, ferrocene (purchased from Merck Sdn Bhd, Malaysia) was used as the precursor for iron (Fe) catalysts, and hydrogen (purchased from Malaysian Oxygen Berhad) as the carrier gas. The Polyacrylonitrile (PAN) based carbon fiber used in these experiments was obtained from Toho Tenax Inc. The precursor handling system was connected to a furnace reactor which comprises a quartz tube placed in a horizontal split tube furnace. The quartz tube (inner diameter: 49 mm, outer diameter: 51mm, length: 750mm) which holds strands of carbon fiber is finally connected to the by-product exhaust system which constitutes a simple cyclone separator, condenser, air filter and vacuum pump. This unit treats the effluents in the exit gas before venting it into the fume hood.

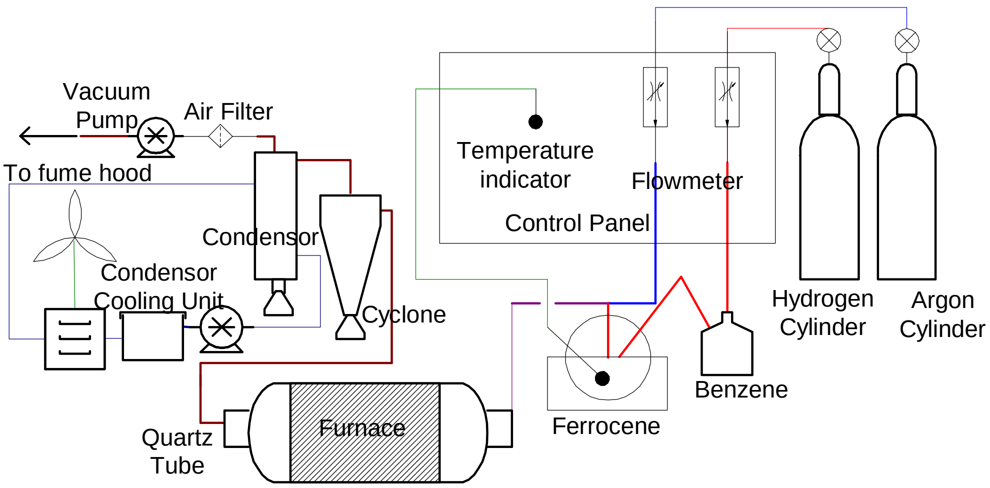

Figure 1: An illustration of the CVD Rig Set-Up

A typical experimental run follows the following procedure. Initially, strands of carbon fibers were placed inside the quartz tube furnace as shown in Figure 2. The system was then purged off with inert argon and the furnace was simultaneously heated to the reaction temperature of 900^{o}C at a certain rate. A known amount of ferrocene in the form of solid was also heated to a temperature of 120^{o}C to allow sublimation to take place. Once the reaction temperature was reached, hydrogen was allowed to bubble through the benzene and ferrocene flasks and into the furnace at the desired flow rate. After 30 minutes the hydrogen stream was stopped and all heating was switched off. The reactor was cooled under argon gas before the samples were collected.

It was important to ensure that the heating process involved in the whiskerization treatment did not damage the carbon fibers. Therefore, before carrying out the whiskerization process, a study on the effect of heating on the carbon fibers was conducted. The fibers were subjected to four different heating rates at 2^{o}C/min (low), 5^{o}C/min (medium), 10^{o}C/min (high) and 20^{o}C/min (very high). For the whiskerization treatment, two main studies, which would contribute in part to the optimization of the whiskerization process, were carried out. First was a study of the morphology of the carbon fiber samples at three different regions along the length of the furnace (as indicated in Figure 2). Regions 1, 2 and 3 were generally the inlet, middle and outlet regions of the furnace respectively. Next was a study on the hydrogen flow rate, whereby the flow rate was varied between 100-500 ml/min. Meanwhile, the reaction time for whisker growth on the carbon fibers was set for 30 minutes. It has been reported that these conditions are favourable for the growth of carbon nanotubes and nanofibers [11].

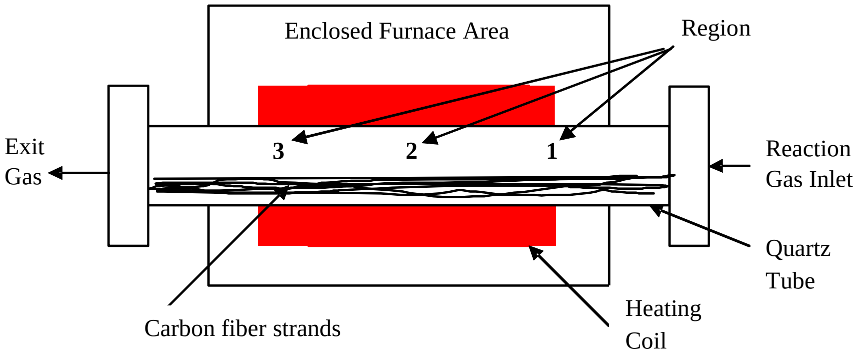

Figure 2. Schematic drawing of the cross section area of the CVD furnace reactor

The morphology of the carbon fiber samples were analyzed using a Scanning Electron Microscope (SEM) (JEOL JSM-6400 model). It should be noted that sometimes it was inevitable to capture SEM images at slightly different magnifications in order to obtain clear images. However, great care has been taken to ensure that the SEM images shown represent the actual results observed from this study.

RESULTS AND DISCUSSION

Pretreatment: *Effect of Heating Rate*

Figures 3(a), 3(b), 3(c) and 3(d) show the SEM micrographs of untreated carbon fiber samples, which were subjected to heating rates of 2^{o}C/min (low), 5^{o}C/min (medium), 10^{o}C/min (high) and 20^{o}C/min (very high) respectively. Comparing the morphology of the carbon fibers for each heating rate, it can be seen that Figure 3(b) shows relatively intact and undamaged carbon fibers. It is unclear how the carbon fibers become damaged by the other heating rates, but this observation was fairly consistent for repeated runs. Therefore the medium heating rate of 5^{o}C/min was used to reach the reaction temperature of 900^{o}C.

Whiskerization Treatment

Effect of Sample Location inside Furnace

Figures 4(a), 4(b) and 4(c) respectively show SEM micrographs of whiskerized carbon fibers obtained from Regions 1, 2 and 3 of the furnace. The hydrogen flow rate was 100 ml/min. Two main points come to light from these results. Firstly, the stark contrast between the untreated and treated carbon fibers is evident. It can be seen that the treatment process produces carbon whiskers on the surface of the smooth fibers. These images are very much similar to the images of whiskerized carbon fibers found from other previous research [12]. Further inspection of these nanostructures using Transmission Electron Microscopy (TEM) will be carried out to identify whether they are indeed carbon nanotubes or nanofibers. These promising results indicate that the custom-built CVD rig can be successfully used for the whiskerization treatment of carbon fibers.

The mechanism of whiskerization is believed to involve several steps. Vaporized ferrocene is transported into the high temperature furnace containing samples of carbon fibers via a hydrogen stream. Under the high temperature, the ferrocene decomposes and expels the organic compounds whilst the Fe ions are left to diffuse into exposed pores on the carbon fibers. Benzene vapour which enters the furnace simultaneously decomposes as well, leaving carbon atoms attracted to the heated Fe ions which act as catalysts, thus stimulating whisker nucleation and growth.

Secondly, it can be seen that Figures 4(a) and 4(b) show whiskerized carbon fibers, with relatively denser whiskers in the former, whereas Figure 4(c) shows a carbon fiber with virtually no whiskers present. These observations were consistently seen in repeated experimental runs. From the apparent amount of whiskers growing on the carbon fibers it appears that the whiskerization treatment was most effective in Region 1 and least effective in Region 3. This implies that the conditions affecting the whiskerization process is non-uniform along the tube. A likely possibility for the most whiskerization to occur in Region 1 could be due to it being closest to the inlet region of the furnace, which is rich with benzene and ferrocene.

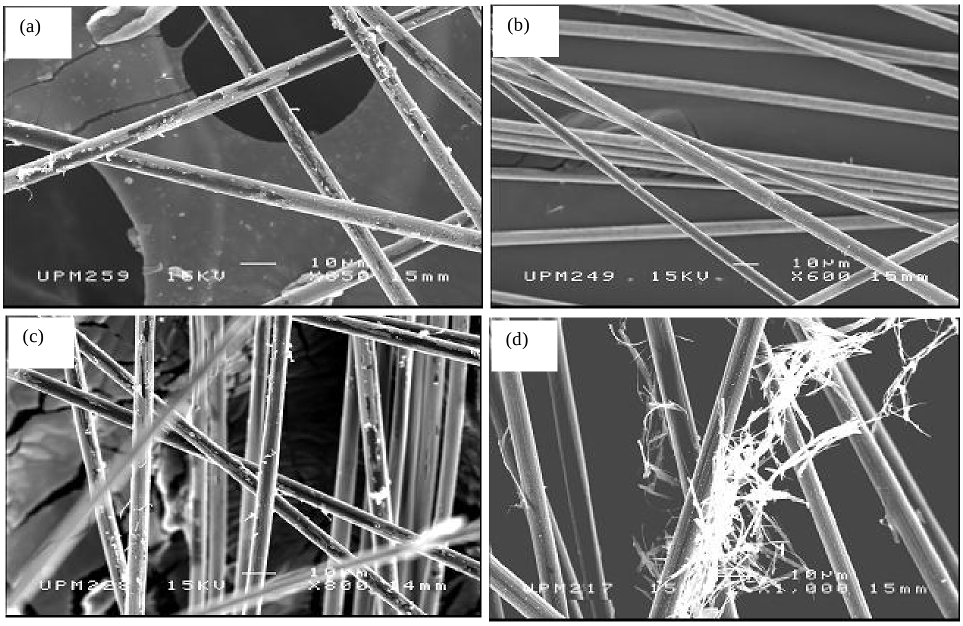

Figure 3: SEM micrograph of carbon fibers subjected to different heating rates: (a) at 2^{o}C/min (low), (b) 5^{o}C/min (medium), (c) 10^{o}C/min (high) and (d) 20^{o}C/min (very high).(Magnification of 10000X)

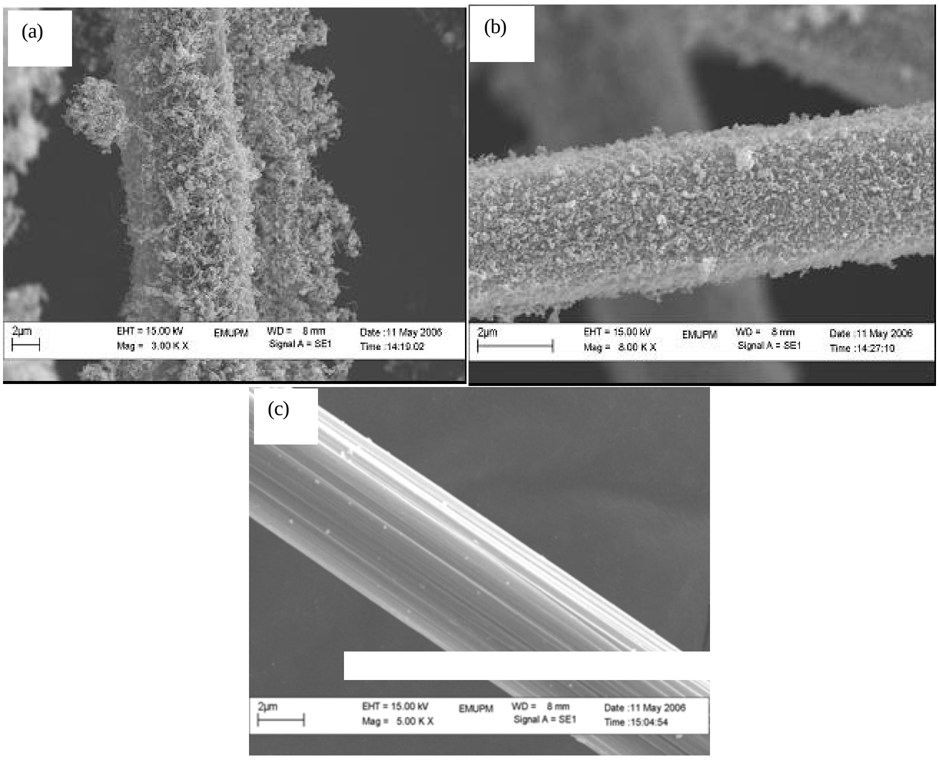

Figure 4: SEM micrographs of whiskerized carbon fibers obtained from (a) region 1, (b) region 2 and (c) region 3 of the tube furnace at a temperature of 900^{o}C and a hydrogen flow rate of 100 ml/min.

The carbon fibers in this region would be exposed most to these gases, resulting in the high amount of whiskers on the fibers. If the concentration of these gases decreases along the tube, this could explain the relatively lower amount of whiskers on the fibers in Region 2 and finally the least amount of whiskers on the fibers in Region 3. Further investigation would be needed to optimize the whiskerization treatment in terms of furnace efficiency. However, it appears that the length of the furnace renders Region 3 redundant for the process under the current operating conditions.

Effect of Hydrogen Flow Rate

Figures 5(a) and 5(b) show the SEM micrographs of whiskerized carbon fibers obtained with hydrogen flow rates of 100 ml/min and 500 ml/min respectively. Both samples were taken from Region 1 of the furnace. It can be seen that both figures display totally different whisker structure. The nanostructures in Figure 5(a) appear short and chunky, whereas the ones in Figure 5(b) appear relatively long and strand-like. Further inspection of these nanostructures using Transmission Electron Microscopy (TEM) will be carried out to identify the characteristics of these structures in more detail. At this stage the role of hydrogen in producing different nanostructures is not yet fully understood. It is anticipated that different structures would increase the ILSS of the composites at different magnitudes.

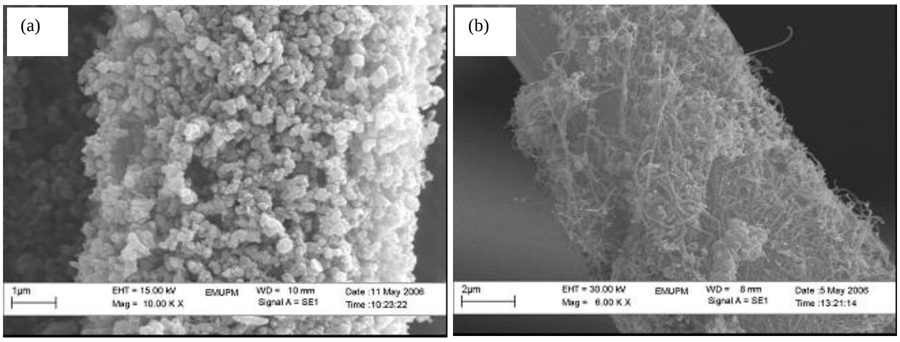

Figure 5. SEM micrographs of whiskerized carbon fibers from region 1 at: (a) 100 ml/min and (b) 500 ml/min. The treatment temperature was 800^{o}C.

Yoon and Baik [13] reported that carbon nanofiber growth increases with increasing hydrogen flow rate. This was attributed to the crucial role played by hydrogen in the growth of carbon nanofiber, as it dilutes the hydrocarbon and cleans the surface of catalyst. However, early investigation showed that the effects of hydrogen could also be both accelerating and suppressing [14]. Nevertheless it is evident that the hydrogen flow rate is a critical parameter that needs to be further studied especially for optimization purposes.

CONCLUSION

Under the current experimental set-up and operating conditions, carbon whiskers were successfully grown on the polyacrylonitrile (PAN) carbon fibers. A heating rate of 5^{o}C/min was chosen for the treatment process since it was found that this heating rate does not damage the carbon fibers. It was found that the whiskerization treatment was most effective in Region 1 of the tube furnace and least effective in Region 3. This was attributed to Region 1 being closest to the inlet region of the furnace, which is rich in benzene and ferrocene. It was also found that different whisker structures were obtained at different hydrogen flowrates, whereby short and chunky, and long and strand-like structures were grown at 100 ml/min and 500 ml/min respectively. These promising results indicate that the carbon vapor deposition technique used in this work can be successfully used for the whiskerization treatment of carbon fibers.

ACKNOWLEDGEMENT

The authors would like to acknowledge the financial support provided by the Ministry of Science, Technology and Innovation (MOSTI) under Programme No. 03-01-01-0065-PR0072/08-05 and also acknowledge the SEM analysis service from the Bioscience Institute, Universiti Putra Malaysia.

REFERENCES

[1] Buckly, J. D. and Edie D. D. (1993) Carbon-carbon Materials and Composites, Noyes Publications: USA. pp 20-37.

[2] Ermolenko, I. N. , Lyubliner, I. P. and Gulko, N. V. (1990) Chemically Modified Carbon Fibers. Edited by Dyllick-Brenzinger, C. and Ebel. H. F., VCH: Weinhem, pp 207-208.

[3] Kaelble, D. H., Dynes, P. J., Crane, L. W., Maus, L. (1975). Interfacial mechanisms of moisture degradation in graphite-epoxy composites. Journal of Adhesion **7**(1): 25-54

[4] Larsen, J. V., Smith, T. G., Erickson, P. W. (1971) Carbon fiber surface treatment. NOLTR **71**:165-170

[5] Daukeys, R. J. (1973) The influence of stretching ratio in stabilization on the microstructure and mechanical properties of carbon fibers. Journal of Adhesion **5**: 1-99

[6] Donnet, J. B., Wang, T. K., Peng, J. C. M. and Rebouillat, S. (1998). Carbon Fibers (3rd Ed.), Marcel Dekker Inc.: New York, pp 162.

[7] Thostenson, E. T., Ren, Z., Chou, T. (2001). Advances in the science and technology of carbon nanotubes and their composites. Composites Science and Technology **61**: 1899-1912

[8] Kowbel, W., Bruce, C., Withers, J. C. (1997) Effect of carbon fabric whiskerization on mechanical properties of C-C composites. Composites Part A **28A**: 993-1000.

[9] Huber, R. and Schmaderer, F. (1992) Application of CVD-coated multifilament fibers. Materials & Design **13**(2): 77-82

[10] Choy, K. L. (2003). Chemical vapour deposition of coatings. Progress in Material Science **48**: 57-100.

[11] Iyuke, S. E., Danna, A. (2005) Morphological study of carbon nanotubes synthesized by FCCVD. Microporous and Mesoporous Materials **84**: 338-342.

[12] Thostenson, E. T., Li, W. Z., Wang, D. Z., Ren Z. F. (2002) Carbon nanotubes/carbon fiber hybrid multiscale composites. Journal of Applied Physics **91**(9): 6034-6037

[13] Yoon, Y. J. and Baik, H. K. (2001) Catalytic growth mechanism of carbon nanofibers through chemical vapor deposition. Diamond and Related Material **10**: 1214-1217.

[14] Yang, K. L. and Yang, R.T. (1986) The accelerating and retarding effects of hydrogen on carbon deposition on metal surfaces. Carbon **24**(6): 687-693.

ISSN 1823-1039 ©2006 FEIIC