UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERISATION OF CARBON NANOMATERIAL ON SHORT CARBON FIBER BY FLUIDIZED BED CHEMICAL VAPOUR DEPOSITION AND FABRICATION OF CARBON NANOCOMPOSITE

MAHTA SADEGH VISHKAEI

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By

MAHTA SADEGH VISHKAEI

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October 2009

Chairman : Dr. Mohamad Amran B. Mohd Salleh

Faculty : Engineering

Although there are some researches on the whiskerization of CNPs on carbon fiber, but none has studied it in the fluidized bed. This research has carried out to study the whiskerization of carbon nanoparticles on short carbon fiber by fluidized bed reactor chemical vapour deposition (FBCVD). The CNP whiskerized CF was added by appropriate amount of Polypropylene to make a composite. Some information about catalyst, nanostructural features of nanoparticles and composite discussed. Hence, in this work, experimental studies were carried out to elucidate the influential parameters and investigate the influence of (i) synthesis temperature, (ii) catalyst type (iii) carbon source gas flow rate on CNP quality in FBCVD process. The synthesis of carbon nanoparticles (CNPs) have been done by the catalytic decomposition of acetylene over Fe/CF catalysts in a fluidized bed reactor. The general growing conditions were: 40 L/min flow rate, 450-650°C synthesis temperature, atmospheric pressure and three gas compositions: 50% , 25% and 25% $C_2H_2/H_2/N_2$. The catalyst substrate was carbon fiber with different sizes (1mm and 2mm) and metal catalyst with different content of iron (0.23%, 1.8% and 4.92%) were used to deposit on the CF surface. Characterization of the catalysts and the products was performed by X-

ray diffraction patterns (XRD), scanning electron microscope (SEM) and thermal gravimetric analysis (TGA). An apparent relationship was found to exist between the metallic iron content of the catalysts, substrate size, and the final characteristics of the carbon products. Then the composite was prepared with the best percentage of whiskerized carbon fiber and polypropylene with concentration of 2% and 98% respectively. The mixture introduced into the mixer (The rotor speed and temperature were set at 120 rpm and 180^{o}C, and mixing continued for 10 min). Finally the composite was analyzed by Dynamic Mechanical Analysis (DMA) for mechanical properties. This study indicates that the optimum condition for the growth of CNP on CF is 600 °C for 1.8% Fe on carbon fiber with 2mm length for a 30 minutes deposition time and 15L/min acetylene flow rate.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SINTESIS DAN PENCIRIAN BAHAN NANO KARBON DI ATAS KARBON FIBER PENDEK MENGGONAKAN REAKTOR LAPISAN TERBENDALIR PENGURAIAN WAP KIMIA DAN FABRIKASI NANO KOMPOSIT KARBON

Oleh

MAHTA SADEGH VISHKAEI

Oktober 2009

Pengerusi : Dr. Mohamad Amran B. Mohd Salleh

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Dalam kajian ini, satu kajian awal telah dilakukan untuk menerangkan pengaruh parameter dan mengkaji kesan (i) suhu sintesis, (ii) jenis pemangkin dan (iii) halaju gas sumber karbon ke atas kualiti CNT yang dihasilkan melalui proses FBCVD. Sintesis nano tiub karbon (CNTs) telah dijalankan melalui penguraian gas asetilena bermangkin ke atas pemangkin Fe/CF (menggunakan kaedah penyediaan impregnasi) di dalam reaktor lapisan bergerak. Keperluan pertumbuhan secara umumnya adalah seperti berikut: halaju gas 40 lit/min, suhu sintesis 450-650 °C, tekanan atmosfera dan tiga komposisi gas: 50%, 25% and 25% $C_2H_2/H_2/N_2$. Substrat pemangkin yang digunakan ialah gentian karbon pelbagai saiz (1mm dan 2mm) dan pelbagai komposisi besi (0.23%, 1.8% dan 4.92%) digunakan untuk dimendapkan di atas permukaan CF. Struktur pemangkin dan produk yang terhasil kemudiannya dicirikan dengan menggunakan pola X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) dan Thermal Gravimetric Analysis (TGA). Satu pertalian ketara dapat dilihat di antara kandungan besi metalik di dalam pemangkin, saiz substrat dan pencirian akhir produk karbon yang terhasil. Kemudian komposit nano disediakan dengan nano tiub berkualiti terbaik dan juga polipropilena dengan komposisi masing-masing

adalah 2% dan 98%. Campuran itu kemudiaannya dimasukkan ke dalam pengadun (Halaju rotor dan suhu masing-masing ditetapkan kepada 120 rpm dan 180 ^{o}C dan diadun selama 10 minit). Akhirnya, analisa komposit telah dijalankan menggunakan Dynamic Mechanical Analysis (DMA) untuk menentukan sifat mekanikalnya. Kajian ini menunjukkan kondisi optimum untuk kadar pertumbuhan CNT ialah 600 °C untuk 1.8% Fe ke atas gentian karbon dengan panjang 2mm untuk 30 minit masa pengendapan dan 15 L/min halaju gas asetilena.

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In the name of God, Most gracious, Most merciful
All gratification are referred to God

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"For all those times you stood by me
For all the truth that you made me see
For all the wrong that you made right

My husband Mr. A. Ahmadi
For all the joy you brought to my life
For every dream you made come true
For all the love I found in you

I'll be forever thankful you're the ones who held me up Never let me fall you're the one who saw me through
Through it all"

Finally, special thanks to my kind and respectful aunt, Mrs.H.Davoodi, my best friend in Malaysia and her respectful family, for their support and encouragement, and also my uncle Mr.D.Davoodi for lightening me when I found the going tough .

I certify that an Examination Committee met on October 2009 to conduct the final examination of Mahta Sadegh Vishkaei on her master of science thesis master thesis entitled " Synthesis of carbon nanoparticles on short carbon fiber by fluidized bed chemical vapour deposition (FBCVD) and fabrication carbon nanocomposite" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and universiti Pertanian Malaysia (High Degree) regulation 1981. The Committee recommends that the student be awarded the relevant degree.

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Date: 11 February 2010

DEDICATION

I hereby declare that the thesis is based on my original work expect for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

MAHTA SADEGH VISHKAEI
Date: 11 February 2010

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LIST OF ABBREVIATIONS

ARNT	Array of Carbon Nano Tube
ASTM	American Society for Testing Materials
β	Maximum of the XRD peak
CAT	Catalyst
CCVD	Catalyst Chemical Vapour Deposition
CVD	Chemical Vapour Deposition
CNT	Carbon Nano Tube
CNP	Carbon Nano Particle
CNM	Carbon Nano Material
DC	Direct Current
DMA	Dynamic Mechanical Analysis
DNA	Deoxyribo Nucleic Acid
DSC	Differential scanning Calorimetry
TDA	Thermal Differential Analysis
E'	Storage Modulus (MPa)
E"	Loss Modulus (MPa)
EDX	Energy Dispersive X-ray
EDS	Energy Dispersive Spectroscopy
EDXRF	Energy Dispersive X-Ray Fluorescence
FBCVD	Fluidized Bed Chemical Vapour Deposition
HIPCO	High Pressure Carbon Monoxide
ID	Internal Diameter

L_C	Mean Crystalline Size (along the c-axis)
λ	Wavelength of X-rays
M	Weight
MWCNT	Multi Wall Carbon Nano Tube
PECVD	Plasma Enhanced Chemical Vapour Deposition
PP	Poly Propylene
SEM	Scanning Electron Microscopy
SWCNT	Single Wall Carbon Nano Tube
TAN δ	Tangent Delta
SCF	Short Carbon Fiber
TGA	Thermal Gravimetric Analysis
T_{onset}	Degradation Temperature
T_m	Melting temperature
T_g	Glass Transition temperature
θ	Angle corresponding to the peak of XRD
U_{mf}	Minimum Velocity
U	Velocity
VPSEM	Scanning Electron Microscope Environmental
XRF	X-ray fluorescence
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Background of study

Carbon, with an electronic ground state arrangement of $1s^2$ $2s^2$ $2p^2$, has the ability to form four valence orbitals: 2s, 2px, 2py, and 2pz (Figure 1.1). The mixing of the 2s and 2p atomic orbitals is known as hybridization. Three possible hybridization states (sp^1, sp^2, and sp^3) have resulted in many important carbon structures, including carbon nano particles (CNPs). Before the discovery of fullerenes, two solid elemental carbons were believed to exist in only two crystalline phases: graphite and diamond, exhibiting sp^2 and sp^3 hybridized bonding, correspondingly. The structure of large carbon clusters with >40 carbon atoms remained unsolved until Kroto et al. synthesized fullerene C60 in 1985 and postulated its structure as that of a shortened icosahedrons (Chee et al., 2007).

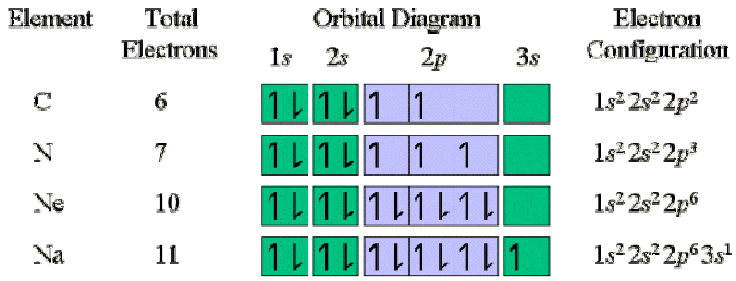

Figure 1.1. Electron configuration of carbon atom
(Source: http://intro.chem.okstate.edu/1215/Lecture/Chapter11/Fri112098.html)

There are different types of CNTs, due to the feet that the graphitic sheets can be rolled in many ways. The three types of CNTs are Zigzag, Armchair, and Chiral. It is possible to recognize zigzag, armchair, and chiral CNTs just by following the pattern across the diameter of the tubes, and analyzing their cross-sectional structure (Michael et al., 2002). Figure 1.2 explains two types of CNTs.

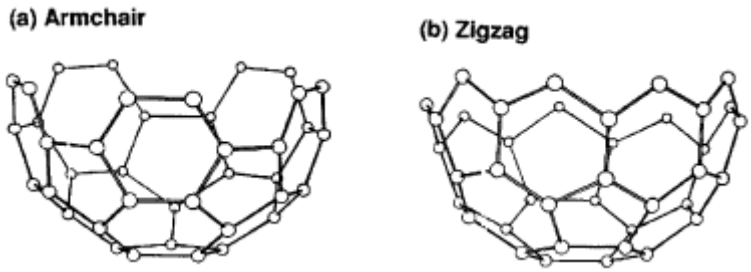

Figure 1.2: Caps to SWNT formed by cutting a fullerene C60 molecule along the equatorial plane, (a) shows the armchair cap normal to a fivefold axis while (b) shows the zigzag cap normal to a threefold axis (Source: Dresselhaus, 1992)

Carbon nanotubes (CNTs) have been investigated for a multitude of applications including energy storage, field emission devices, and composite material strengthening, because of their exclusive mechanical, optical, and electrical properties. Both multiwalled (MWCNTs) and single-walled (SWCNTs) carbon nanotubes can be used, depending on the value-added functionality required in the product. On the other hand, the use of CNTs in both research and end-user applications is currently limited by production throughput. Of the three main techniques used for CNT synthesis, that is, laser ablation, arc discharge, and chemical vapour deposition (CVD), the latter is recognized as having the most potential for large-scale, economically viable CNT production (Venegoni et al., 2002).

Carbon nanotubes (CNTs) are attractive materials with a wide range of potential applications. Various CNT based electronic devices, such as transistors (Weitz et al., 2007; Tans et al., 1998) logical circuits (Bathold et al., 2001) nano electromechanical devices (Ke and Espinosa , 2006; Rueckes et al., 2000) sensors (Brian et al., 2007; Park et al., 2006) have been established. In 1995 field emission from CNTs was reported (Rinzler et al., 1995, Deheer et al., 1995) and nanotubes becomes promising candidates as a field electron emitters. The high aspect ratio (length to diameter) of the CNTs results in a high field improvement factor, useful to field emission. These applications demand an unusual combination of material properties, such as structural rigidity, electric conductivity and small density, possessed only by CNTs. Electronic devices should also resist high temperatures caused by Joule heating and high tensile stresses to keep away from device failure (Wong et al., 2003, Pan et al., 2001).

One of the most promising uses of CNTs is in the development of nano composites, where the CNTs are used as novel fillers and binders to improve their mechanical, electrical and thermal properties. CNTs have great potential applications due to their very large aspect ratio (1000–10,000), low density, high rigidity (Young's modulus of the order of 1 TPa), and high tensile strength (up to 60 GPa). In addition, the excellent electrical conductivity (106 S/m at 300 K for single-walled CNT (SWCNT) and >105 S/m for multi-walled CNT (MWCNT)) and thermal conductivity (6600 W/mK for an individual SWCNT and >3000 W/mK for an individual MWCNT) make them suitable candidates in preparing nanocomposites with new functional properties (Kumaria et al., 2008).

It has been established in recent years that polymer based composites reinforced with a small percentage of strong fillers can significantly improve the mechanical, thermal and barrier properties of pure polymer matrix (Mahfuz et al., 2004). When these fillers are rod-shaped, the surface area per particle will lead to high mechanical strength and stiffness in axial direction and because of this they are considered the most interesting fillers for advanced applications composites. Carbon fiber reinforced composites have all the ideal properties, leading to their rapid development and successful use for many applications over the last decade (Chung, 1994). Although the carbon fiber polypropylene composite yields catastrophically, it bears a higher load than the glass fiber polypropylene composite, resulting in higher flexural strength. The effect of carbon fiber content and fiber length on mechanical and thermal properties of SCF/PP has already been studied (Fateme, 2006).

The good composite performance often depends on the degree of adhesion between the fiber and the resin binder. Adhesion is usually controlled by chemical bonding due to functional groups and by mechanical interlocking due to surface morphology and this leads researchers to develop a number of surface treatments that could improve the fiber matrix polymer interfacial bonding. Whiskerization treatment on carbon fibers was an effective way to increase the shear strength of carbon-epoxy composite materials by 400%. Whiskerization involves carbon nanoparticles growth on the surface of carbon fibers. The total surface area would increase, and enhance the mechanical interlocking between fibers and matrixes (Rebouillat, 1984).

Since nanoparticles can be grown by different methods with different parameters, the selection of a suitable type of CNP synthesis for a selective application is challenging. The CNTs can be prepared by various methods such as arc discharge, laser ablation, chemical vapour deposition (CVD) and others with CVD the most widely used method of production. Among the different techniques that have been applied for the processing of carbon nanotubes (CNTs) (Journet and Bernier, 1998) catalytic chemical vapour deposition (CCVD) appears promising in opinion due to its relatively low cost and potential high yield production. Definitely, this method, originally used to prepare carbon filaments (Rodriguez, 1993) or vapour-grown carbon fibers (De and Geus, 2000; Endo, 1998) also could be effective for the growth of nanotubes. In fact, precursors of filaments or vapour-grown carbon fibers were evidenced as having nanotubular structure (Toan et al., 1999; Serp and Figueiredo, 1996; Endo et al., 1995). The CCVD technique has been applied both in the absence and in the presence of a substrate. The earlier is a gas phase homogeneous process, the latter is a heterogeneous process. Although more scarce studies on homogeneous processes have demonstrated, that it was possible to produce selectively multiwalled carbon nanotubes (MWNTs) (Marangoni et al., 2001), single-walled carbon nanotubes (SWNTs) (Satishkumar et al., 1998, Cheng et al., 1998), or arrays of carbon nanotubes (ARNTs) (Rao et al., 1998).

Heterogeneous processes have been explored more intensively and MWNTs (Piedigosso et al., 2000; Ivanov et al., 1995), SWNTs (Colomer et al., 2000; Hafner et al., 1998) have been produced on supported or bulk catalysts. Currently, the use of bulk metal catalyst leads mainly to the production of carbon filaments, also called