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‘I admit that had read this thesis and in my opinion this thesis was satisfied from the aspect of scope and quality for the purpose to be awarded Bachelor of Mechanical Engineering (Thermal Fluid)’

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TEXTURAL INVESTIGATION OF CARBON NANOTUBE USING NITROGEN
ADSORPTION ANALYSIS

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DECLARATION

“I hereby declare that the works in this report is my own except for my summaries and quotations which have been duly acknowledge”

Signature :

Name of Author :

Date :

To my beloved Mum and Dad

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Thanks to Allah for the blessings and love that was given to me. In this great opportunity, I'm acknowledging all the people who were involved and became an important role in the completion of this project.

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ABSTRACT

Carbon Nanotubes (CNT's) are carbon that come in a different molecular structures (allotropes). They are cylindrical in shape and their structural size are so small, they are considered to be nano particles. Prior to their discoveries in 1991, diamond is considered to be the element with the toughest and has the highest thermal conductivity in the world. But, CNT's managed to top diamond in terms of strength, thermal and electrical conductivity. In this research, we are focusing on the analysis and evaluation of CNT's textural properties using Nitrogen adsorption analysis. A test was carried out at University of Malaya's lab facility using Nitrogen (N_2) as the adsorption gas in Brunauer, Emmett and Teller (BET) testing machine. BET method was used because it can give the total surface area of a specimen including within the particles. Three specimens of CNT's were tested which are MER, Nanoamor and Pyrograf. The investigation went through several details such as pore types and pore diameter of CNT's to ensure that the objective is achieved. The testing data shows that Pyrograf tops the other two specimens in terms of surface area, total pore volume and micropore volume. Pyrograf has the BET surface area of $1.718E+03 \text{ m}^2/\text{g}$, total pore volume of 1.078 cc/g and micropore volume of $6.845E-01 \text{ cc/g}$. It is clear that the textural properties play an important role in surface area measurement, which later becomes the medium of interactions between CNT's and their surroundings. The findings of this research will improve CNT's applicability in Nanotechnology as well as gaining the interest from other scientific body to further the studies in carbon nanotube's textural investigations.

ABSTRAK

Tiub Nanokarbon adalah karbon yang terhasil di dalam struktur molekul yang berbeza. Ia berbentuk silinder dengan saiz yang amat kecil, sehingga ia dikategorikan sebagai partikel nano. Sebelum penemuannya pada tahun 1991, berlian dianggap sebagai elemen yang memiliki kekuatan dan konduktiviti termal yang paling tinggi. Namun, tiub nanokarbon berjaya mengatasi kemampuan berlian dari segi konduktiviti termal, kekuatan dan juga konduktiviti elektrik. Di dalam kajian ini, fokus terarah kepada analisis and penilaian sifat-sifat tekstur menggunakan analisis penyerapan Nitrogen. Kajian telah dijalankan di kemudahan makmal Universiti Malaya dengan menggunakan Nitrogen (N_2) sebagai gas peresap di dalam mesin ujian Brunauer, Emmet dan Teller (BET). Kaedah BET digunapakai kerana ia mampu mengira nilai keseluruhan luas permukaan sesuatu spesimen termasuk luas di dalam partikel. Tiga sampel tiub nanokarbon digunakan di dalam kajian iaitu MER, Nanoamor dan Pyrograf. Siasatan mengambil kira beberapa perincian penting seperti jenis liang dan diameter liang tiub nanokarbon demi memastikan objektif tercapai. Data ujikaji menunjukkan Pyrograf mempunyai luas permukaan tertinggi, isipadu keseluruhan liang terbesar dan isipadu liang mikro terbesar. Luas permukaan BET Pyrograf adalah $1.718E+03 \text{ m}^2/\text{g}$, isipadu keseluruhan liang pula adalah 1.078 cc/g manakala isipadu liang mikro adalah $6.845E-01 \text{ cc/g}$. Sifat-sifat tekstur tiub nanokarbon didapati memainkan peranan yang penting didalam bacaan luas permukaan, yang merupakan perantara bagi tiub nanokarbon dan persekitarannya. Penemuan dari kajian ini diharap dapat membantu kita dalam menambahbaik pengaplikasian dan kajian terhadap tiub nanokarbon di masa hadapan.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

This research will be carried out to study the surface texture of Carbon Nanotube.

Using Nitrogen Adsorption analysis method with nitrogen as the adsorption gas, we will examine the properties of Carbon Nanotube's (CNT's) surface feature. Important data such as pore size, types of pores and their porosity will be collected for analysis purposes.

Investigation of the data will be carried out to determine if they play an important role in giving Carbon Nanotube their fantastic properties and abilities.

The findings of the research will allow a better understanding on the relationship between CNT's surface texture with their mechanical, electrical and chemical properties.

1.2 Objective

To analyze and evaluate the texture properties of Carbon Nanotube (CNT) using nitrogen adsorption analysis.

1.3 Scope

The research will focus on the investigation of carbon nanotube's texture using Nitrogen Adsorption Analysis (B.E.T method) to find:

- i. Surface area
- ii. Porosity
- iii. Types of pores
- iv. Diameter of pores

1.4 Problem statement

Carbon nanotubes have many attractive properties, and their structure and areas of application can be compared with those of graphene. Manufacturing them in large scale is a challenging task as it is one of the hardest materials to be manipulated.

Apart from the manufacturing obstacles, applying them in modern nanotechnology requires a lot of time, energy and cost for studies and development. One of the most promising industry related to carbon nanotube is the electronic industry. Carbon nanotube's thermal conductivity is said to be better than all but the purest diamond and electrical conductivity similar to copper. (Holister,2003)

One of the key factors in determining materials conductivity is the area of their surface. Generally, higher surface area means better abilities in certain fields of technology.

In this research, investigations on the textural build of carbon nanotubes were carried out to identify the factors that contributed to their high surface area. They will be tested using Nitrogen (N_2) adsorption in Brunauer, Emmett and Teller (BET) testing machine. We will look into several areas such as BET Surface area, pore size distribution, size of pores, pore volume, etc.

The findings of this research may unveil some of the secrets behind carbon nanotube's excellent mechanical, chemical and electrical properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Carbon nanotube

Since its discoveries 20 years ago by Sumio Iijima, carbon nanotube has been a novelty item in the scientific world. Numerous research were carried out to shed light on the mysterious yet special material. Previous findings revealed that (Hollister et al. 2003), with one hundred times the tensile strength of steel, thermal conductivity better than all but the purest diamond, and electrical conductivity similar to copper, but with the ability to carry much higher currents, they seem to be a wonder material. However, when we hear of some companies planning to produce hundreds of tons per year, while others seem to have extreme difficulty in producing grams, there is clearly more to this material than meets the eye. There are two most common types of carbon nanotube which is Single-Wall Carbon Nanotubes (SWNTs) and Multi-Wall Carbon Nanotubes (MWNTs). According to the research (Baughman et al. 2002), Single-walled Nanotubes (SWNTs) consist of a single graphite sheet seamlessly wrapped into a cylindrical tube and Multiwalled Nanotubes (MWNTs) comprise an array of such nanotubes that are concentrically nested like rings of a tree trunk.

Although their basic building block is carbon, but Carbon Nanotube (CNT) is complex to produce. Currently, SWNTs are synthesized by one of three different techniques: pulsed laser vaporization, arc discharge growth, or chemical vapor deposition (CVD) on supported or gas phase catalysts (Weisman and Subramoney 2006) and purified using oxidation method either in gas-phase (by heating pristine or brominated deposit in air or flowing oxygen at ~ 700 °C), or in liquid-phase (Bonard et al. 1997).

SWNTs is typically smaller than MWNTs with diameters range from 0.4 to 3 nm for SWNTs and from 1.4 to at least 100 nm for MWNTs (Baughman et al. 2002). In the research by Nathan and Ba (2004), nanotubes can be either conducting or semiconducting making them an attractive candidate for micro and nanoelectronic research. The nature of the structures in nanotubes makes them inherently strong and stiff, giving them possible use as a new type of carbon fiber reinforcing material.

2.2 Growth and physical appearance

Carbon clusters called fullerenes are formed with predominantly sp_2 bonding between the atoms when a high temperature carbon vapor cools down and condenses in an inert atmosphere (Lucas et al. 1997).

The formation and growth of carbon nanotubes are stimulated by the transition metal catalysts, such as iron and/or nickel nanoparticles (Zhou 2005). Porous carbons produced by thermal decomposition of organic materials may have pore diameters, down to 0.3 nm, or mesopores of several nanometres, but they typically have a broad pore-size distribution, which limits their ability to separate molecules of different sizes (Gogotsi et al. 2003).

Due to their nano size, their pore size are commonly categorized into two different group which is micropore and mesopore. Mesopore is basically larger than micropore. The mechanical properties are strongly dependent on the structure of the nanotubes. This is due to the high anisotropy of graphite (Salvetat et al. 2009). The

pore diameter (i.e. the inner diameter) of the nanotubes can be controlled by variation of the synthesis conditions used to produce the CNTs. Increasing the size of the pore diameters often leads to a decrease in the specific surface area of the substance (Sigurdson 2009) and the concentration of micropores decrease with the increase of radius (Staszczuk et al. 2003). Their tiny tubes with diameters down to 0.4 nm, while their lengths can grow up to a million times their diameter has allowed the creations of simple logic circuit. These structures are promising for the semiconductor industry which is leading the search for miniaturization (Prabhu and Vinayagam 2010). The unique electronic properties also meant that CNT based sensor have more sensitivity and wider detection range (Jia et al. 2008).

2.3 Textural investigations

The textural investigation usually focus on the surface properties of CNT's such as surface area, pore types, pore size and porosity. It is believe that we can understand a lot about CNT capabilities through textural investigation.

According to Iijima (2007), many unique properties of CNTs depend on their structures and morphologies. When come to detailed comparisons between experiment and theory, well-controlled and characterized specimens (diameter, length, quantity, chirality, structural perfection, impurity, homogeneity) will be eventually needed. When the diameter of a certain CNT's are above 200 nm, it is considered to be hollow (tubes). When the obtain diameter is around 100 nm and below, it is form as wires (Curiale et al. 2004).

An example of their surface properties were shown in the research carried out by Rakhi (2009) in which he stated that CNTs possess excellent electron transfer rate, which is larger than conventional carbon electrodes and also allows surface chemistry for tethering foreign biomaterials such as enzymes and nucleic acids.

Although it is said to be stronger than diamond, improvement in tensile, compressive and flexural properties can still be done and the physical and mechanical properties of the identified nanomaterial reinforced polymer composite were characterised by experimentation in order to ascertain them (Frederick ,2008).

CNT is also not readily dispersible in fluid. According to Grulke (2009), dispersion is improve by chemical etching, coupling agents, surfactants, dispersant, polymer wrapping, etc. These modification often change the transport properties of the nanotube.

In the absence of a suspending agent, nanocarbons do not disperse in solution, much less in a polymer matrix. The reason is simple enough. The extended pi-electron system leads to strong attractive van der Waals forces that are aggravated by the fact that tubes can interact over extended distances when aligned side by side (Zhao, 2003).

An example of successful dispersion of CNT and fluid is activated carbon. Activated carbon (AC) has been proven to be an effective adsorbent for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media, or from gaseous environment. It is a widely used adsorbent in the treatment of wastewaters due to its exceptionally high surface areas which range from 500 to 1500m² g⁻¹, well-developed internal microporosity structure as well as the presence of a wide spectrum of surface functional groups (Yin et al. 2006).

Apart from the interaction of CNT along a polymer chain, Yoke et al. (2005), found out that vertically aligned-multi walled carbon nanotubes(VA-MWNTs) are not as resistant as diamond against ion erosion. Erosion rate can be higher than 2.5 µm/hour under the irradiation of 250 eV Xe ions. The melting of the catalyst particles (Fe and Ni) at the tips of MWNTs is one of the reasons for such a high erosion rate.

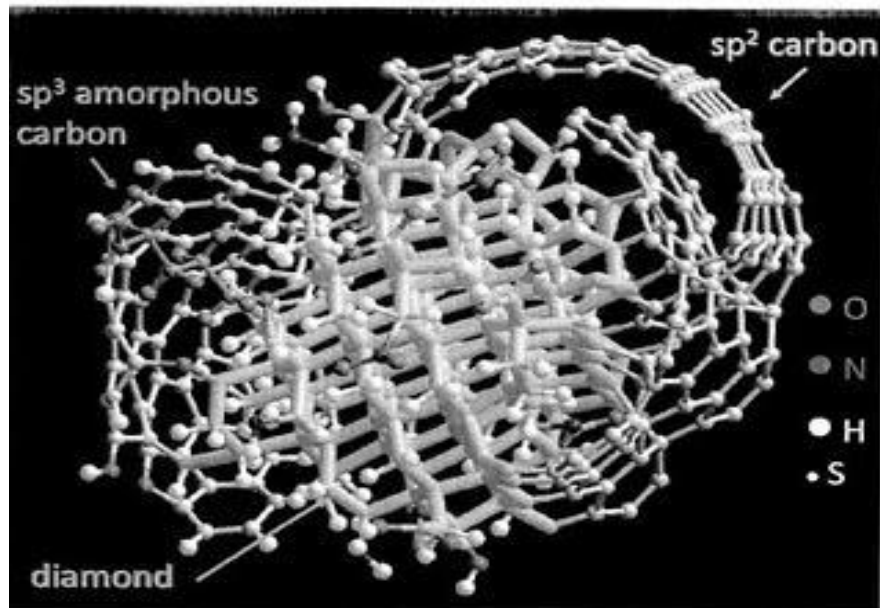


Figure 2.1: Detonation of Nanodiamond (source: nanopatentsandinnovations.blogspot.com)

In the case of carbon based materials emission, the factors influencing the field assisted emission are, nature of bonding of the carbon material namely if it is diamond like σ bonds (sp^3 type bonding) or graphite like π bonds (sp^2 type bonding) and the nano dimension of the self aligned carbon based nanomaterials (Satyanayarana, 2006).

2.4 Adsorption properties

The unique microporous structure of carbon nanotubes is speculated to have remarkable adsorption properties. Theoretical studies have shown that N₂ adsorption surface area of arrays of single-walled nanotubes (SWNTs) could be as high as 3000 m²/g (Sandeep et al. 2004).

According to Quantachrome Corporation (2010), pore size and pore volume measurements have been almost exclusively limited to the adsorption of nitrogen and argon. But some pores (or parts of pores) accessible to H₂ may not be accessible to other molecules because of size restrictions or due to very slow diffusion.

Hydrogen (H₂), is suitable for the analysis of pore size distribution or PSD. The pore size distribution (PSD) is one of the essential factors in characterizing mesoporous materials. The nitrogen adsorption isotherms at 77 K have been utilized to calculate the PSD of many porous adsorbents. In the past, nitrogen adsorption isotherms were studied using fractal theory (Ferreiro, 2010). Fractal theory demonstrate a limit in a complex physical process by searching for simpler process underneath.

Nitrogen (N₂) adsorption in the other hand, emphasizes the changes in the intraparticle structure of the particles during compression (Westermarck, 2000). A generic problem that always arise is impurities, which can readily coat the surface of SWNT bundles, thus influencing adsorption on the external surface of the outermost nanotubes of the bundle (Sandeep et al. 2006).

Because of their cylindrical and hollow geometry, and nanometre-scale diameters, it has been predicted that carbon nanotubes can store a liquid or a gas in the inner cores through a capillary effect (Daenen et al. 2003). It is reported that SWNTs were able to perform this criteria by using gas phase adsorption (physisorption) (Daenen et al. 2003).

In the terms of hydrogen storage within nanotubes, it will depend on a variety of parameters, including storage capacity and nanotube purity (Kalenczuk, 2005).

2.5 BET testing

In this research, Brunauer, Emmett and Teller (BET) testing with nitrogen as the adsorption gas will be used. The BET theory is the most popular model used to determine the surface area.

BET theory is based on estimating the monolayer capacity from multilayer adsorption data at relative pressures generally ranging from 0.05 Pa to around 0.3 Pa. However, micropores (<2 nm) are filled below the relative pressure of 0.05, and with microporous samples, there is more N₂ uptake than would be the case with multilayer physical adsorption. This often leads to the calculated BET area being an overestimate of the actual surface area (Fanxing et al. 2004).

CHAPTER 3

METHODOLOGY

3.1 Methodology chart

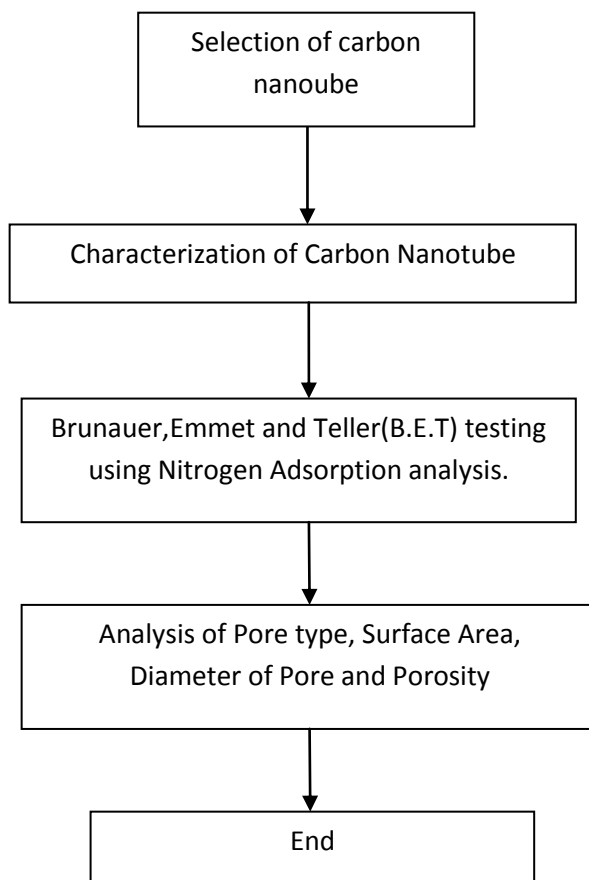


Figure 3.1: Methodology Chart

3.2 Selection of carbon nanotube

First is the selection of carbon nanotube's to be use. There are a lot of carbon nanotubes available in the global market nowadays coming in various sizes and price. We are looking for the one that has an affordable price and also available in the needed quantity.

Table 3.1: Properties Of carbon nanotube available in the market

SWNT		Characterization method
Production method	CCVD	
Available form	Black powder	
Diameter	0.8-1.4 nm	TEM, Raman
Length	$\geq 5\mu\text{m}$	SEM, TEM
Bundles	15-30	SEM, TEM
Nanotubes purity	60% $<x<$ 65% (raw: NTX8) \geq 85% (purified: NTX9)	TGA, SEM
Metal particles	40% $>x>$ 35% (NTX8) \leq 15% (NTX9)	TGA
Amorphous carbon	$<$ 1%	TGA, Raman
Surface area	500-600 m^2/g (NTX8) \sim 900 m^2/g (NTX9)	BET