

SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

**PREPARATION AND CHARACTERIZATION OF
CNT/EPOXY NANOCOMPOSITES
USING COLLOIDAL POLYMERIZATION METHOD**

By

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DECLARATION

I hereby declare that the work embodied in this thesis entitled “PREPARATION AN CHRACTERIZATION CNT/EPOXY NANOCOMPOSITES VIA COLLOIDAL POLYMERIZATION METHOD” has been carried out by me in Department of Materials Engineering of Universiti Sains Malaysia during the period of 2018 and has not been submitted earlier for the award of any degree or diploma to this or any other university.

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LIST OF ABBREVIATIONS

| | |
|---------------|---|
| CNTs | Carbon Nanotubes |
| MWCNTs | Multiwalled Carbon Nanotubes |
| OMWCNTs | Oxidized multiwalled carbon nanotubes |
| MWCNTs/Epoxy | Multiwalled carbon nanotubes epoxy nanocomposites |
| OMWCNTs/Epoxy | Oxidized multiwalled carbon nanotubes reinforced epoxy nanocomposites |
| FTIR | Fourier Transformed Infrared Spectroscopy |
| FESEM | Field Emission Electron Microscope |
| HRTEM | High Resolution Transmission Electron Microscope |
| TMD | Tetra Methylhexaethylene diamine |
| XRD | X-Ray Diffraction |
| DGEBA | Diglycidyl ether of bisphenol-A |
| SWCNTs | Single walled carbon nanotubes |
| F-MWCNTs | Functionalized multiwalled carbon nanotubes |
| F-oMWCNTs | Oxidative functionalized multiwalled carbon nanotubes |
| TEM | Transmission Electron Microscope |
| TGA | Thermogravimetric analysis |
| DSC | Differential scanning calorimetry |
| P-MWCNTs | Pristine Multiwalled carbon nanotubes |
| IR | Infrared |
| oCNTs | Oxidized carbon nanotubes |
| DWCNTs | Doubled walled carbon nanotubes |
| CSCNTs | Cup stacked carbon nanotubes |
| UTM | Universal Testin machine |
| CNTs/Epoxy | Carbon nanotubes reinforced epoxy |
| CVD | Chemical Vapor Deposition |
| FWHM | Full Width Half Maximum |
| RBM | Radial Breathing Mode |

| | |
|-----|----------------------|
| DI | Deionized Water |
| RPM | Rotation Per Minutes |
| 2D | 2 Dimensional |

LIST OF SYMBOLS

| | |
|--------------------------------|--|
| D | Defect band |
| G | Graphitic band |
| I _D | Defect intensity |
| I _G | Graphitic intensity |
| I _D /I _G | Ratio intensity of defect to graphitic |
| GPa | Giga Pascal |
| MPa | Mega Pascal |
| θ | Theta |
| °C | Degree Celcius |
| ϵ_r | Dielectric Constant |
| T _{onset} | Maximum temperature level before decomposition initiated |
| T _{endset} | Temperature where decomposition finished |
| m _i | Weight percent where the decomposition is initiated |
| m _e | Weight percent where the decomposition is finished |
| K | Kelvin |
| T _g | Glass Transition Temperature |
| T | Temperature |
| nm | nanometer |
| μm | micrometer |
| ml | mililiter |
| h | hour |
| g | graam |
| Å | Angstrom |
| °/min | Degree per minutes |
| Kv | Kilovolt |
| ° | Degree |
| Hz | Hertz |
| GHz | Gigahertz |

| | |
|------|----------------|
| a.u. | Arbitrary unit |
| (c) | Colloid method |
| (n) | Normal method |

PENYEDIAAN DAN PENCIRIAN
KOMPOSIT NANO CNT/EPOKSI
MELALUI KAEDAH PEMPOLIMERAN KOLOID

ABSTRAK

Multilapis Karbon Tiub Nano (MWCNTs) mempunyai ciri-ciri yang sangat baik untuk dijadikan sebagai bahan pengukuhan. Walaubagaimanapun, disebabkan oleh sifatnya yang semulajadi, ia akan menggumpal di dalam epoksi dan akan mengurangkan sifat komposit nano. Pengoksidaan dengan menggunakan kaedah Hummers adalah untuk mengatasi masalah penggumpalan, akan tetapi MWCNTs yang telah dioksida akan menggumpal semula di dalam epoksi. Komposit nano MWCNTs/epoksi telah dihasilkan melalui kaedah pempolimeran koloid bertujuan untuk mengatasi masalah penggumpalan semula. OMWCNTs telah dicampurkan terlebih dahulu dengan cecair pengeras TMD yang mempunyai tahap kelikatan yang rendah. Mikroskop elektron pengimbas pancaran medan (FESEM) membuktikan proses pengoksidaan mengurangkan ikatan antara MWCNTs untuk menghasilkan penyebaran yang lebih berkualiti. HRTEM menunjukkan terdapat kerosakan pada permukaan MWCNTs selepas pengoksidaan. Penurunan darjah penghabluran disebabkan oleh pengoksidaan dibuktikan melalui XRD. Sementara itu, spektroskopi Raman telah menunjukkan peningkatan kerosakan melalui D-band selepas pengoksidaan. Kehadiran kumpulan karboksil pada permukaan MWCNTs selepas pengoksidaan dibuktikan melalui FTIR. Komposit nano oMWCNTs/epoksi yang telah dihasilkan melalui kaedah pempolimeran koloid direkodkan tertinggi untuk kekuatan tegangan. Selain itu, ia juga mempunyai nilai tertinggi untuk kekonduksian terma dan juga untuk pemalar dielektrik.

**PREPARATION AND CHARACTERIZATION
OF CNT/EPOXY NANOCOMPOSITES
USING COLLOIDAL POLYMERIZATION METHOD**

ABSTRACT

Multiwalled Carbon Nanotube (MWCNTs) have an excellent properties to be used as a reinforcement material. However, due to its own nature behaviour, it tend to agglomerate in epoxy and this reduces the properties of nanocomposites. Oxidation by Hummers method is to overcome the agglomeration, but oxidized MWCNTs tend to re-agglomerate in epoxy. MWCNTs/epoxy nanocomposite sample have been prepared using colloidal polymerization method to overcome the re-agglomeration problem. The oMWCNTs have been mixed first with the low viscosity of TMD hardener. Field emission electron microscope (FESEM) proved that the oxidation reduce the entanglement of MWCNTs in order to produce better dispersion. HRTEM shows presence of damage at the surface of MWCNTs after oxidation. The reduction of crystallinity due to oxidation proved through XRD. Meanwhile, Raman spectroscopy shows the increase of defect through the D-band after oxidation. The presence of carboxyl functional group on the surface of MWCNTs after oxidation have been proved by FTIR. The oMWCNTs/epoxy nanocomposites prepared by colloidal polymerization method recorded the highest value for tensile strength. Apart from that, it also have the highest value for the thermal conductivity and also for dielectric constant.

CHAPTER ONE

INTRODUCTION

1.1 RESEARCH BACKGROUND

CNTs were first discovered by M. Endo and his co-workers in the late 1970s (Oberlin et al., 1976) and caused tremendous interest when S. Iijima published his paper in Nature in 1991 (Iijima, 1991). CNTs have own many unique properties such as CNTs is the most stiffest fibres that have recorded over tensile strength of 50-100GPa and modulus of 1.4TPa which recorded as the highest in the meantime (Zhu et al., 2003). Apart from that, it has superior thermal and electrical conducting properties. Therefore, CNTs have attracted great interest as a reinforcement materials. Recently level of interest has increase regarding CNT filled epoxy nanocomposites.

In spite of the fact that the CNT creation cost is higher than that of conventional fillers, its low loading to matrix is beneficial since it is expected to produce high properties for the matrix at low proportions. This is due to high aspect ratio and high surface area to volume ratio of the nanosized particles (Zhou et al., 2008; Hu et al., 2008; Santos et al., 2008). Apart from that thanks to the versatility of epoxy which are good chemical resistance, high modulus and satisfactory of thermal stability (Saeb et al., 2013; Jin et al., 2015). Epoxy surface coatings are among the most broadly used industrial finishes and provide superior adhesion, flexibility and corrosion resistance when applied to metallic substrates (Jones et al., 1996).

Other than widespread use of CNT as reinforcement in epoxy nanocomposites, scientists are still unable to discover the full potential of CNT in epoxy nanocomposites. This is because due to strong van der Waals force, the CNT tend to agglomerate in epoxy matrix that lead to poor dispersion. Apart from that, their large surface area per unit volume create weak interfacial interaction with the polymer. Many attempts have been made to minimise the related issues for example via functionalization (Hameed et al., 2014). The result of this studies show that properties of functionalized CNTs epoxy composite increased and performed much better than pure CNTs epoxy nanocomposites.

However, according to the Santos et al., (2006) the functionalized CNTs did not only fully prevent the agglomeration but delayed the re-agglomeration from occurred. This is attribute from the nature of CNTs itself that is tend to re-agglomerate easier and also from the epoxy that have high viscosity level. Even the level of re-agglomeration is not high as the agglomeration of pure CNT but some effort should be done to optimise performance of CNT reinforcement in order to produce excellent CNT/epoxy nanocomposites that is needed for advance future technology.

In this experiment, conventional mixing method to fabricate the CNT/epoxy nanocomposites have been modified so called colloidal polymerization method. The nanocomposites fabricated by using this method with the assist of oxidized CNT that have been attached of COOH or carboxylic functional group to its surface. Apart from that, different % of oCNTs have been incorporated to the epoxy matrix. Through this newly method, the oxidized CNT have been added first with lower viscosity of TMD curing agent or hardener instead of adding first with higher viscosity of epoxy resin. The strong and stable cross-linking formed between the carboxylic functional group of CNT with amines functional group of TMD hardener form stable colloid that able to prevent re-agglomeration. Apart from that, higher density of cross-linking between the amines group

TMD with epoxide group of epoxy further enhanced the properties and performance of the CNT epoxy nanocomposites produced.

A large number of research have dealt with CNT-reinforced epoxy. This is because, CNT based epoxy nanocomposites is a one kind of material that have high chance opportunity to produce high technology advanced product. This is mainly due to its better features such as very good in mechanical, thermal and also electrical properties.

1.2 Problem Statement

Nowadays, the Epoxy/CNT nanocomposites is among important polymer nanocomposites. Reinforcing the epoxy with CNT have proven to substantially increase the properties of epoxy in terms of mechanical, thermal and also electrical properties. However, further improvement is limited due to natural behaviour of CNT that tend to agglomerate to form poor dispersion in epoxy matrix. Even though oxidation of CNT have been proposed to improve the level of dispersion, the CNT tend to re-agglomerate in epoxy that will produce undesirable properties of nanocomposites. Limited work has previously been undertaken towards optimising epoxy composites via fabrication methods. The sequence of mixing for epoxy composite preparation is rarely studied. Most of the researchers only depend on ‘assistant’ to the mixing process such as mechanical mixing and sonication to ease the dispersion of CNT in epoxy matrix. However, the re-agglomeration factors were always being ignored. In this study, a different mixing sequence so called colloidal polymerization method is identified to achieve well-dispersed CNT to produce better CNT/epoxy nanocomposites.

1.3 Research objectives

The main objectives for this project are:

- 1) To study the effect of oxidation to the morphological and properties of pure multiwalled carbon nanotubes.
- 2) To prepare oxidized multiwalled carbon nanotubes (oMWCNTs) reinforced epoxy nanocomposites via colloidal polymerization method.
- 3) To characterize the oxidized multiwalled carbon nanotubes (oMWCNTs) reinforced epoxy nanocomposites that have been prepared by colloidal polymerization method using tensile testing, thermal conductivity testing and dielectric constant testing.
- 4) To study the effect of 0.1 %, 0.2% of CNTs loadings to the properties of epoxy nanocomposites produced.

1.5 Scope of Research

Re-agglomeration problem face by the oxidized CNTs has led to the focuses on modification of conventional mixing method to introduce new fabrication method called colloidal polymerization method. Through colloidal polymerization method, reaction between TMD and CNTs form stable colloid that prolonged quality dispersion which prevent re-agglomeration to occur after sonication process or before curing process. The effectiveness of the method will be confirmed through correlation between quality dispersion with tensile test thermal conductivity test and also dielectric test. Apart from that, this work not only focuses mainly on the fabrication method of the nanocomposites but the method will also be correlated with oxidized CNTs with different weight % loadings of the CNTs (0.1%,0.5% and 2%).

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

In this chapter, the progress of CNTs/epoxy nanocomposites are reviewed regarding on functionalization of the pure CNTs, fabrication of CNTs/epoxy nanocomposites via colloidal polymerization method and also the enhancement of the nanocomposites properties. CNTs tend to agglomerate in epoxy make it necessary to be functionalized. In this experiment, the CNTs have been oxidized by simplified Hummers method. The re-agglomeration of oxidized CNTs, cause the colloidal polymerization method have been introduced. The formation cross-linking between group of CNTs and TMD form stable colloid that prevent agglomeration re occurred. The increase in cross-linking also enhance nanocomposites properties.

2.2 Carbon Nanotubes

2.2.1 History of Carbon Nanotubes

The first CNTs were set up by M. Endo in 1978, as a major aspect of his PhD learns at the University of Orleans in France. In spite of the fact that he delivered very small diameter filament (around 7 nm) utilizing a vapor-growth technique, these strands were not perceived as nanotubes and were not contemplated deliberately. It was simply after the revelation of fullerenes, C₆₀, in 1985 that researchers began to investigate carbon structures further. In 1991, when the Japanese electron microscopist Sumio Iijima observed CNTs, the field truly began to progress. He was considering the material deposited on the cathode during the arc-evaporation synthesis of fullerenes and came across CNTs. A brief timeframe later, Thomas Ebbesen and Pulickel Ajayan, from

Iijima's lab, demonstrated how nanotubes could be created in bulk quantity by varying the arc-evaporation conditions. Nonetheless, the standard arc evaporation method just for only production of multiwall nanotubes .After some examination, it was discovered that the presence of metals, for example, cobalt to the graphite electrode brought about to a great degree fine single wall nanotubes. The synthesis in 1993 of single walled carbon nanotubes (SWNTs) was a noteworthy occasion in the improvement of CNTs. In spite of the fact that the disclosure of CNTs was an unplanned occasion, it opened the route for a thriving examination into the properties of CNTs in labs everywhere throughout the world, with numerous researchers exhibiting promising physical, chemical, structural, and optical properties of CNTs (Tarawneh et al., 2013)

2.2.2 Structure of Carbon Nanotubes

The carbon nanotubes (CNTs) are carbon allotropes comprising of C sp² hybridizations, as graphene (Stobinski et al., 2010). Carbon nanotube (CNT) is one type of carbon, with nanometer-sized diameter and micrometer-sized length (where the length to diameter ratio surpasses 1000 (Bethune et al., 1993). The atoms are orchestrated in hexagons, same arrangement as in graphite. The structure of CNT comprises of enrolled cylindrical and hollow graphitic sheet (called graphene) rolled up into a seamless cylinder with diameter of the order of a nanometer. It is comprehended that CNTs is the material lying in the middle of fullerenes and graphite as a very new individual from carbon allotropes (Aqel et al., 2012).

2.2.3 Type of Carbon Nanotubes

CNTs can be separated into three classifications based on the quantity of tubes exhibit in the CNTs, They exist in a wide assortment of structures, i.e. single wall (SWCNTs), double wall (DWCNTs) and multi wall (MWCNTs) carbon nanotubes, where the round and hollow concentric planes associate with each other because of the van der Waals force (Stobinski et al., 2010). A single walled carbon nanotubes (SWCNTs) shaped by the rolling of a single layer of graphite (called a graphene layer) into a seamless cylinder (long wrapped graphene sheets). As expressed previously, CNTs have a length to diameter proportion of around 1000 and all the more so they can be considered as almost one-dimensional structure.

Most SWCNTs have a diameter of near 1 nm. More definite, a SWCNTs comprises of two separate region with different physical and chemical properties. The first is the sidewall of the tube and the second is the end top of the tube. SWCNTs are very important variety of a CNTs in light of the fact that they display important electric properties that are not shared by the MWCNTs variations. The most essential building piece of these frameworks is the electric wire, and SWCNTs can be superb conductors. SWCNTs are still exceptionally costly to deliver, and the discovery of new synthesis technology is important for carbon nanotube future developement. If less expensive methods of synthesis cannot be found, it would make it financially difficult to apply this innovation to business scale applications (Aqel et al., 2012). Double walled CNTs (DWCNTs) are made of two concentric carbon nanotubes in which the external tube encases the inward tube (Saeed and Khan et al., 2013).

Multiwalled carbon nanotubes (MWCNTs) can be considered as a gathering of concentric SWCNTs (consist of multiple layers of graphite rolled in on themselves to frame a tube shape) with various diameter. The length and diameter across of these

structures contrast a lot from those of SWCNTs and, obviously, their properties are additionally altogether different. The interlayer distance in MWCNTs is near to the distance between graphene layers in graphite, around 3.3 Å. The extraordinary case of MWCNTs (double walled carbon nanotubes DWCNTs) must be underlined here in light of the fact that they join fundamentally the same as morphology and properties when compare with SWCNT. DWCNT synthesis on the gram scale was first proposed in 2003 by the chemical vapor deposition (CVD) procedure, from the selective reduction of oxides solid solutions in methane and hydrogen (Aqel et al., 2012). MWCNTs are promising material for many future applications considering their unique structure and properties. Because of their large particular surface area and conductivity, MWCNTs can be progressively connected as a help for metallic catalyst in electrooxidation reaction in fuel cells other variety of reactions and gas storage (Stobinski et al., 2010).

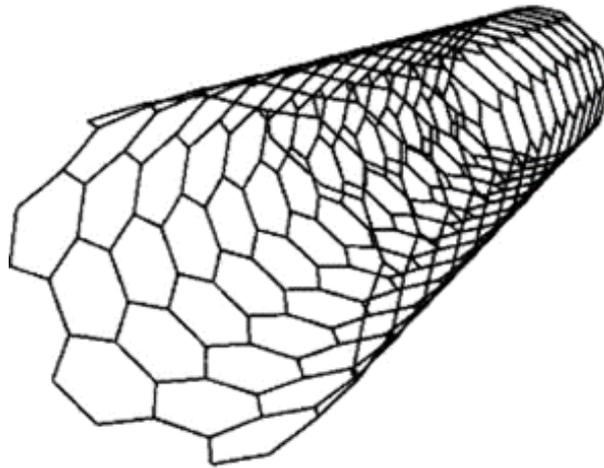


Figure 2.1 : Structure of Single Walled Carbons Nanotubes (SWCNTs) (Saeed and Khan et al, 2013).

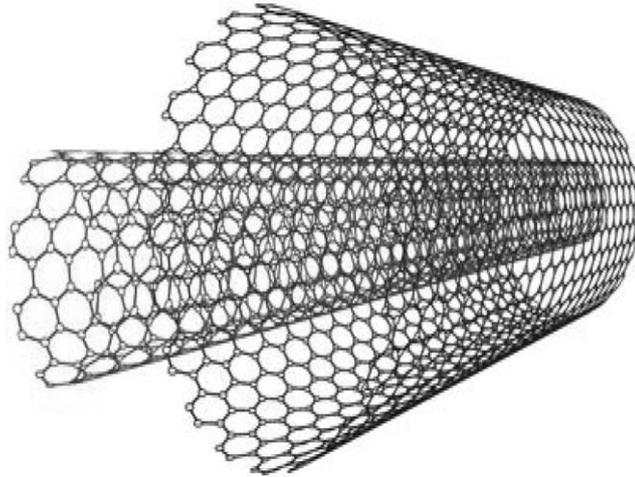


Figure 2.2 : Structure of Doubled Walled Carbons Nanotubes (DWCNTs) (Saeed and Khan et al, 2013).

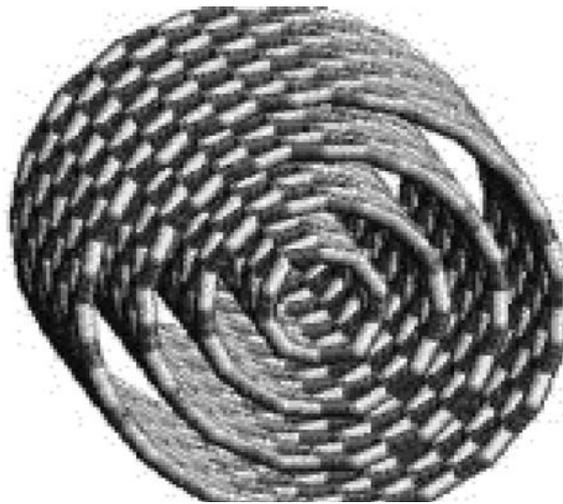


Figure 2.3 : Structure of Multiwalled Carbons Nanotubes (MWCNTs) (Saeed and Khan et al, 2013).

2.3 Epoxy

Epoxy resins are one of the most important polymeric or semi polymeric materials, part of the thermosetting family which play an important role in composite materials. Petroleum-based epoxy monomers are known for superior properties such as tensile strength, high stiffness and excellent electrical strength. These are broadly connected in various applications, development, automotive and aviation enterprises

because of a few attractive properties, for example, good mechanical strength, dimensional stability, great wetting, fire retardance, resistance to chemical and low cure shrinkage (Paluvai et al., 2014).

Epoxy resin is produced by mixing epoxide group with bisphenol. The amine group reacts with the epoxide group to form a covalent bond reinforced with dense cross-linking arising from reaction of the NH group and epoxide group subsequently producing high rigidity and strength of thermoset polymer (Jin et al., 2010).

Chemical structure of epoxy called oxirane or glycidyl group as shown in figure 2.4. The oxirane group of an epoxy reacts with different curing agents such as aliphatic amines, aromatic amines, phenols, thiols, polyamides, amidoamines, anhydrides, thiols, acids and other suitable ring opening compounds forming rigid thermosetting products. Due to high degree of cross-linking cause epoxy have brittle characteristics thus decrease the impact strength and other properties. Hence, some modification needed to improve their flexibility and toughness as well as thermal properties. By incorporation of flexible polymer, inorganic solid particle (nanosize) and elastomer, the degree of brittleness of epoxy resin will be reduced and also increase its thermomechanical property (Paluvai et al., 2014).

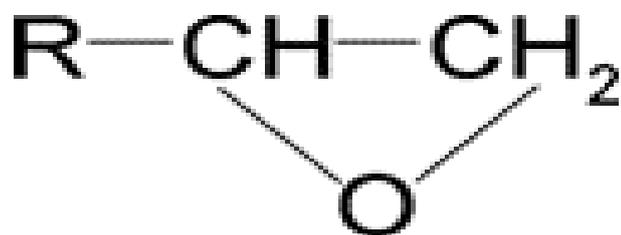


Figure 2.4 : Epoxide Ring Chemical Structure (Acebo et al., 2017).

2.4 Carbon Nanotubes Reinforced Epoxy Nanocomposites

Epoxy resin material have characteristics combination of good thermal and dimensional stability, excellent chemical and corrosion resistance, high tensile strength and modulus, ease of handling and processability and low degree of shrinkage ensuring their uses in wide range of application such as aviation and electronics industries in the form of structural adhesives, advanced composite matrices, and packaging materials (Ahmetli et al., 2012). But due to high degree of cross-linking lead to brittleness characteristics. Apart from that, it also have high tendency to delaminate, and low fracture toughness that limit their use (Hameed et al., 2014). Hence, modification of epoxy monomer is compulsory to improve their flexibility, toughness as well as thermal properties. Many method have been introduced to reduce the brittleness of the epoxy, but one of the most effective method is by incorporation of inorganic solid nanoparticles to the epoxy. The solid nanoparticle is carbon nanotube that will reinforce into epoxy matrix to become carbon nanotube reinforced epoxy nanocomposites.

But there are several obstacle or problem encountered while exploring CNTs as filler materials that are (i) poor dispersion (in solvents / matrix) and tendency of forming agglomerates and bundles, (ii) low solubility in organic/ inorganic solvents, (iii) low chemical reactivity with most species with a tendency to make weak bond (s) , resulting poor interfacial strength, and (iv) the presence of impurities such as carbon soot / catalyst nanoparticles that undermine the properties of the final composites. Poor dispersion of CNTs reinforcement in epoxy matrix and poor interfacial strength or interfacial adhesion between carbon nanotubes with epoxy matrix will extremely effect the mechanical property of the CNTs epoxy nanocomposites, thus this will restrict its uses in a variety of applications (Hameed et al., 2014).

In order to overcome this related problem, several methods can be used that are by physical treatment such as ultrasonication, calendaring, ball milling, stirring, and extrusion or through chemical modification process including oxidation, amidation, thiolation, silylation, halogenation, hydrogenation, and reaction with polymer. There are many results on the effect of ultrasonic treatment, magnetic stirring, use of surfactants, and nanotube functionalization on the dispersion behavior of CNTs in the epoxy matrix. The chemical functionalization is one of the most effective ways of improving CNTs dispersion and/or CNTs–matrix bonding, which subsequently enhance the mechanical properties (Tensile Strength, Young's modulus) and/or thermomechanical properties (glass transition temperature, storage, and loss moduli) of matrix (Hameed et al., 2014).

2.5 Functionalization of Carbon Nanotubes

2.5.1 Type of Functionalization

There are two types of functionalization that are non-covalent and covalent functionalization. The non-covalent functionalization of CNTs involves non-covalent coating with surfactants, surface wrapping with long polymer chains such as polystyrene sulfonate and noncovalent adsorption of non-charged polymer chains such as polyvinyl pyrrolidone. The advantage of non-covalent functionalization is that the surface properties of CNTs for example dispersion property can be changed without alteration of the intrinsic structure of CNTs after modifying. However, the surfactants, polymer chains and electric acceptor which can be used for this method are very limited, their dispersion is not very stable compared to covalent functionalization and most importantly, it is difficult to further modify CNTs with different functionalities (Van Thu et al., 2013).

Covalent functionalization involves the incorporation of new elements (e.g., oxygen, fluorine, nitrogen) or organic functionalities (e.g., biomolecules) into the CNTs surface (Wepasnick et al., 2011). The main advantage of covalent functionalization is that it can greatly improve the solubility and compatibility of CNTs compare with non-covalent functionalization. The disadvantages of covalent functionalization of CNTs are that the structure and the original properties of CNTs are changed after modification. Generally, the more modification on the surface, the more the outstanding properties of CNTs will be altered (Van Thu et al., 2013). There are two different types on how the chemical functional group been attached to the surface of CNTs. Direct covalent functionalization that involve covalently attached of the functional group to the sidewalls surface of the CNTs. While indirect covalent functionalization involve the attachment of functional group to the defect region on the CNTs surface. Defects at the sidewalls of CNTs originally present before functionalization occur. After functionalization, there are also defect produced at the sidewalls and also at the end cap of CNTs. The attachment of functional group from functionalization will stabilize the defect present.

2.5.2 Covalent Functionalization

Covalent functionalization is a method that is based on the covalent linkage of functional entities onto carbon scaffold of CNTs. CNTs tend to agglomerate in epoxy due to presence of strong van der Waals force and also due to its tiny size of nanostructures. Thus this will lead to poor dispersion of CNTs in epoxy matrix that will reduce the stress transfer from matrix to epoxy. This will automatically reduce the mechanical properties of the epoxy and also other property such as thermal property. Functionalization of CNTs introduce defect at the end cap and also at the sidewalls of the CNTs structure and this defect will be stabilized by the introduction of chemical functional group on the surface

of the CNTs such as amino, carboxyl or glycidyl which is also cause from functionalization process. This chemical functional group lead to the reduction of van der Waals force between the CNTs, thus separate the CNTs bundles to individual tube form . This will increase dispersion CNTs in epoxy to allow more stress to be transferred from matrix to CNTs reinforcement thus increase mechanical properties of the matrix or the nanocomposites.

Another challenges of the CNTs is that, CNTs is chemically inert in characteristics due to the strong covalent sp² bonds of the carbon atoms on the nanotube surface (Chiang et al., 2009) and its hydrophobic in nature and also it has large surface area per unit volume. This will lead to poor interfacial adhesion between the CNTs and epoxy matrix thus will also reduce the stress transfer from matrix to epoxy and also will reduce the mechanical properties of epoxy and also others properties. The defect and chemical functional group produced on the surface of CNTs from functionalization process enable covalent bonding and this will cause the hydrophobic nature of CNTs change to hydrophilic nature of CNTs. Thus will increase interfacial adhesion between matrix and CNTs and allow more stress transfer to CNTs and and increase the mechanical property of matrix or nanocomposites.

2.5.3 Covalent Functionalization of CNT by Oxidation

Activation and Functionalization of CNTs by oxidation will produce chemical functional group with oxygen. It can be performed using oxidizing agents such as nitric acid, sulphuric acid, a mixture of sulfuric acid and nitric acid, potassium permanganate, sulfuric acid in presence of potassium permanganate, hydrogen peroxide in presence of nitric acid, hydrogen peroxide, ozone, an oxygen-based atmosphere by an inductively coupled plasma or microwave energy and water. Treatment with different oxidizing

agents will introduce different functional groups on the CNTs surface including alcoholic, carboxylic, aldehydic, ketonic, and esteric oxygenated functional groups.

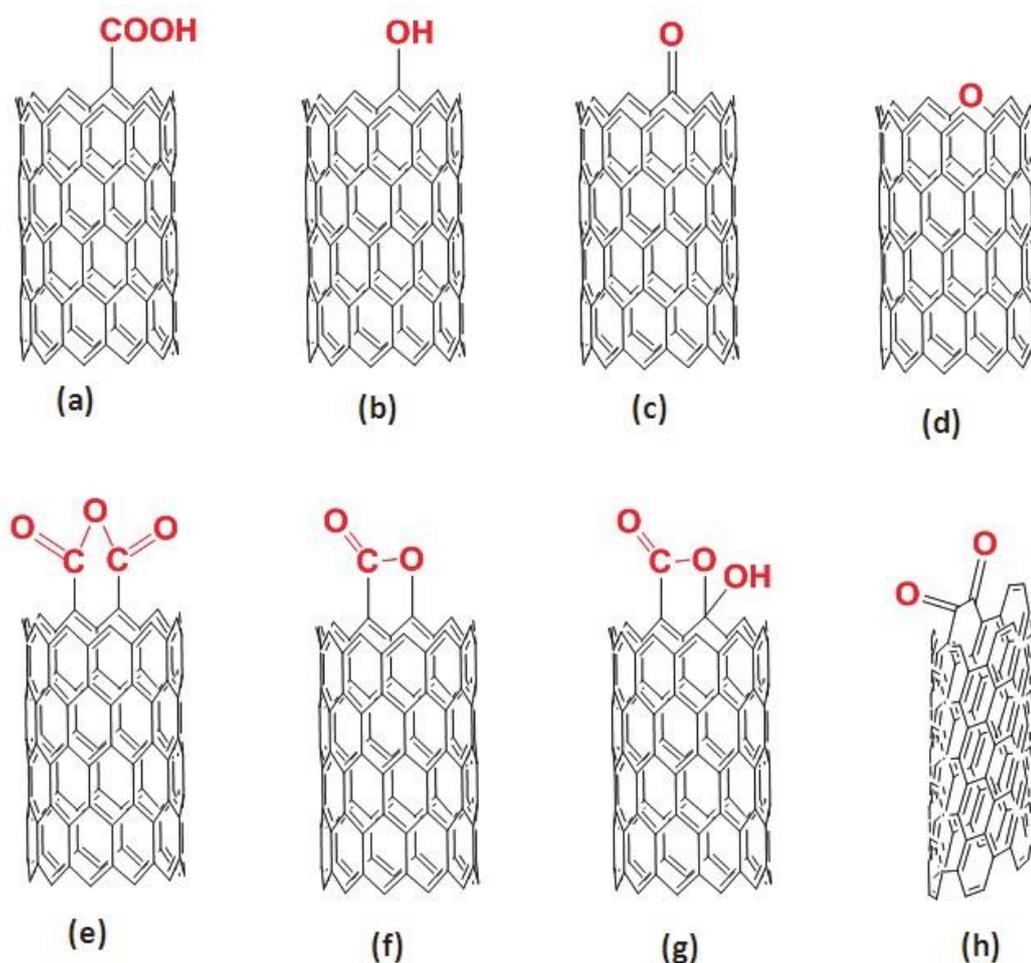


Figure 2.5 : Possible structures of oxygen-containing groups on the carbon nanotube surface (Gupta et al., 2011).

Hydroxyl groups (b) on the edge of nanotube could be of phenolic character. Oxygen could be substituted for edge carbon atoms in xanthene- or ether-type (d). Carboxyl groups (a) might give carboxylic anhydrides (e) if they are close together. Also, carbonyl groups might condense to lactone groups (f) or form lactols (g) if they are in close to hydroxyl groups or carboxyl groups. The existence of carbonyl groups could be isolated (c) or arranged in quinone-like structure (h) (Gupta et al., 2011).

2.6 Characterization of Functionalized MWCNTs

2.6.1 Field Emission Electron Microscope (FESEM)

From the FESEM images as shown in figure 2.6, before process of oxidation functionalization occur the CNTs structure entangle each other. This is due to presence of strong van der Waals force of the CNTs structure. This will make more difficult for the CNTs to well disperse in any form of matrix. After oxidation functionalization occur, the CNTs disentangle. The attachment of functional group on the CNTs surface will weaken the van der Waals force of the CNTs. This will make the functionalized CNTs to be well disperse in the matrix. After oxidation also we can see that the functionalized CNTs become more smaller and narrower in size. Apart from that, from the FESEM images of functionalized CNTs, shows that there is no structural damaged of CNTs. This proved that CNTs is strong enough to stand oxidative functionalization with concentrated acid solutions (Sankal et al., 2012).

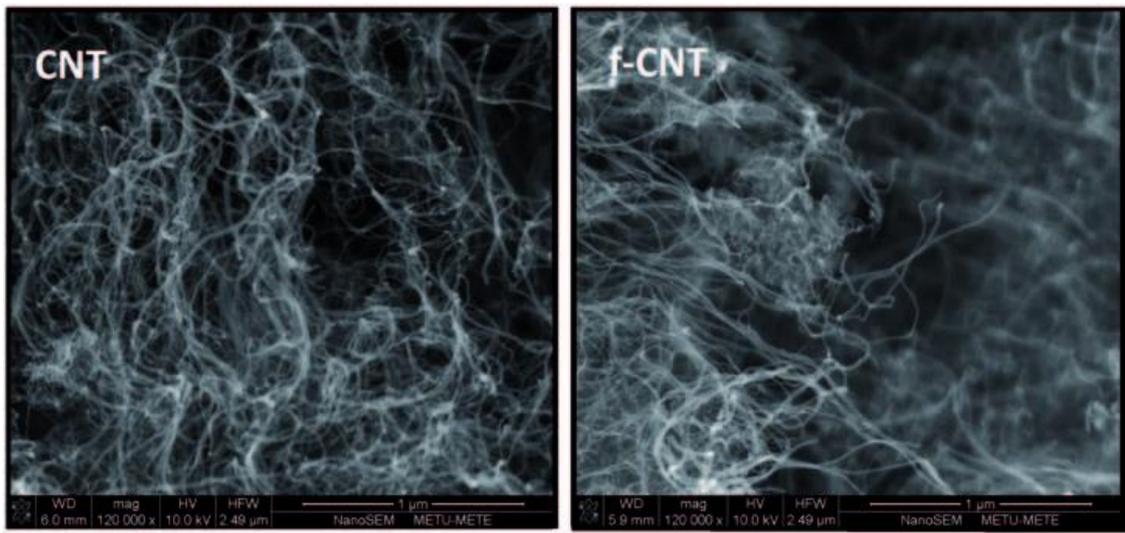


Figure 2.6 : Images of field emission scanning electron microscope of pure MWCNT and O-MWCNT (Sankal et al., 2012).

2.6.2 High Resolution Transmission Electron Microscope (HRTEM)

HRTEM or high resolution transmission electron microscope at low magnification it can assess length and dispersion of CNTs. At high magnification it able to count number of walls in MWCNTs, measure diameter, assess structural integrity and identify structural changes (sidewall damage) caused by functionalization of CNTs as well as presence of adsorbed amorphous carbon (Wepasnick et al., 2010).

From the figure 2.7, high resolution TEM image of a pristine MWCNTs show the presence of amorphous carbon wrapped around the MWCNTs. The outermost walls of the MWCNTs were long and straight, proved for a uniform and largely defect-free sidewall structure of MWCNTs. Figure 2.8 shows high resolution TEM image of oxidized MWCNTs. The overall level of amorphous carbon was reduced and a few defects were generated at the sidewall surface of MWCNTs. Breaks at the outermost graphene sheets of MWCNTs proved that the sidewall had been damaged after oxidation (Wepasnick et al., 2010).

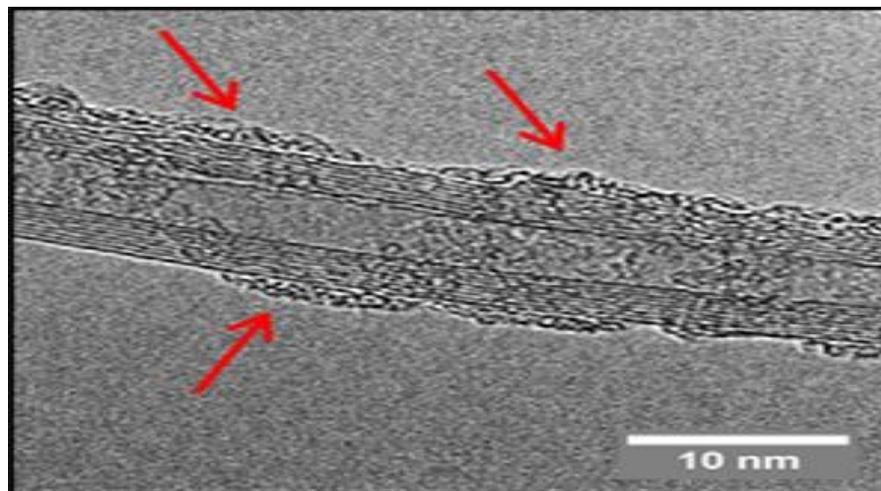


Figure 2.7 : HRTEM image of pristine MWCNTs (red arrows show presence of amorphous carbon) (Wepasnick et al., 2010).

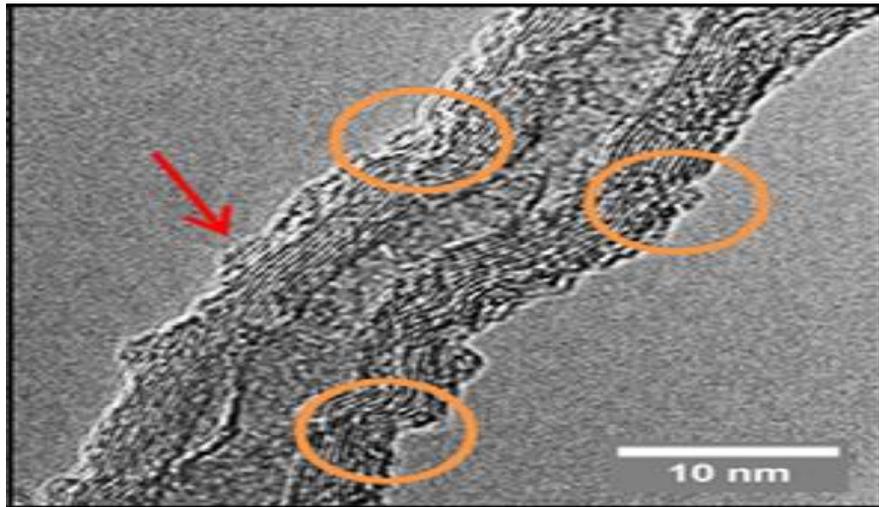


Figure 2.8 : HRTEM image of oxidized MWCNTs (Circle shows presence of damages) (Wepasnick et al., 2010).

Pristine MWCNTs have a diameter from 8 to 18.2 nm as shown in figure 2.9. After acid oxidation of the MWCNTs, the diameter of the oxidized MWCNTs increase in the range of approximately up to 22.2 nm as shown in figure 2.10. This shows that the oxidation functionalization treatment will increase the diameter of MWCNTs, thus proved presence of attachment of the COOH functional group on the surface of the MWCNTs (Van Thu et al., 2013).

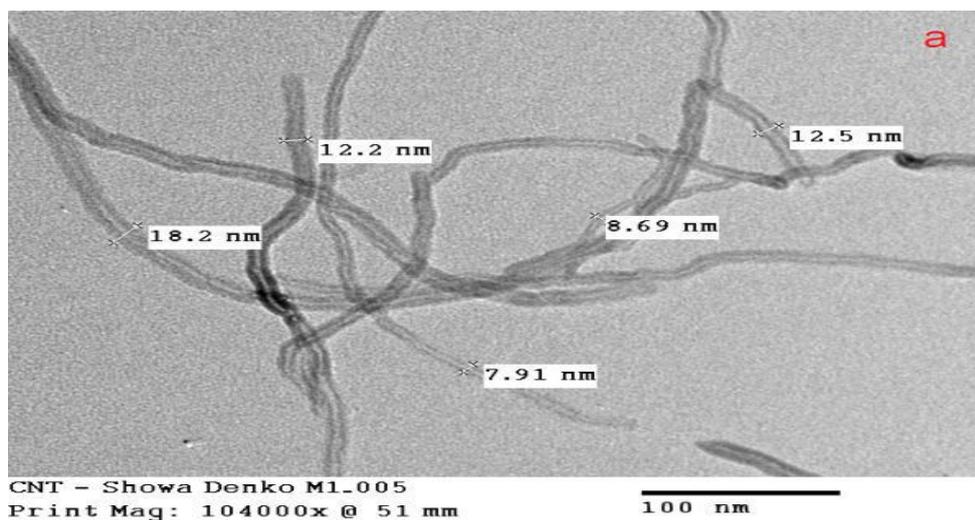


Figure 2.9 : The TEM images of pristine MWCNTs (Van Thu et al., 2013).

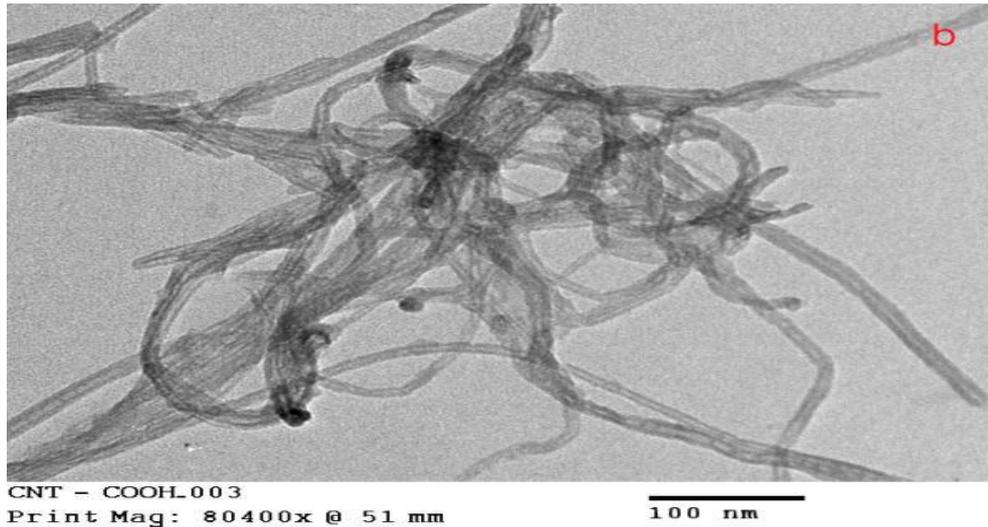


Figure 2.10 : The TEM images of COOH MWCNTs (Van Thu et al., 2013).

2.6.3 X – Ray Diffraction (XRD)

X Ray diffraction method is one of a method to characterize sample regarding of its crystal structure. In this experiment, XRD used to reveal the detailed information about crystallographic structure of MWCNTs before and after oxidation functionalization process take place. Crystal structure is an ordered arrangement of atoms, ions or molecules in a crystalline materials. When x-rays radiation strike the surface of crystal, they are partially scattered by the atoms while there is a part of the x-ray that is not scattered will pass through to the next layer of atom. This will causes an overall diffraction pattern. If beams diffracted by two different layers of atom are in phase, constructive interference of a monochromatic beam of x-rays scattered at specific angles from each set of lattice planes in a sample produces x-ray diffraction peaks.

Figure 2.11 shows XRD patterns of pure and oxidized MWCNTs. X-ray diffraction method is to reveal the detailed information about crystallographic structure of functionalized MWCNTs. An increase in the peak width and reduced intensities of the diffraction peak as shown in figure 2.11 shows that oxidation of MWCNTs with acid treatment ($\text{HNO}_3+\text{H}_2\text{SO}_4$) cause decreased the degree of crystallinity of MWCNTs (Javed

et al., 2015). A decrease in the order crystallinity in carbon materials will make the XRD peaks broader. Accordingly, COOH functionalized MWCNTs have either smaller d_{002} or a wider Full Width Half Maximum (FWHM) which implies that the COOH functionalization had actually deteriorated the degree of crystallinity of the MWCNTs. Moreover, the process seemed to start with widening the FWHM, followed by shifting the C (0 0 2) diffraction towards lower angles (Khani et al., 2013).

The inter-planar spacing of the crystal structure corresponding to a specific diffraction angle was analyzed by Bragg's law, and the proportions were determined by the relative intensity of the XRD pattern (Zhang et al., 2005). The significant XRD patterns of the pristine MWCNTs observed at 2θ of 25.4° and 42.4° were corresponded to (002) and (100) planes of the carbon atoms, respectively. While the XRD pattern of the COOH functionalized MWCNTs also shows similar (002) reflection peak (Cheng et al., 2013). The strongest and sharpest diffraction peak at around $2\theta = 26^\circ$ could be indexed as the (002) reflection of graphite, corresponding to the inter-planar spacing of approximately 0.34nm. This spacing was less than that of graphite (0.376nm) (Suzuki et al. 1990), which for some reason could be due to the curvature of MWNTs. The introduction of COOH functional group into the open end of MWCNTs or the defect sites of MWNTs through functionalization with acid treatment appeared to slightly expand the inter-planar spacing (Rao et al., 1996). The XRD pattern shows intense peak at $2\theta = 25.9^\circ$ corresponding to the (002) reflection. This peak is less compared to the normal graphite, $2\theta = 26.5^\circ$, this peak shows a downward shift, which is attributed to an increase in the sp^2 , C=C layers spacing (Zhang et al., 2002). The main features of XRD pattern of CNTs is similar to those of graphite due to their intrinsic nature (Aqel et al., 2012).

The XRD pattern of both pristine and COOH functionalized CNTs are quite similar. This is because it prove that COOH functionalization with acid treatment

(H₂SO₄+HNO₃) does not damage the cylindrical wall structure of MWCNTs (Cheng et al., 2013).

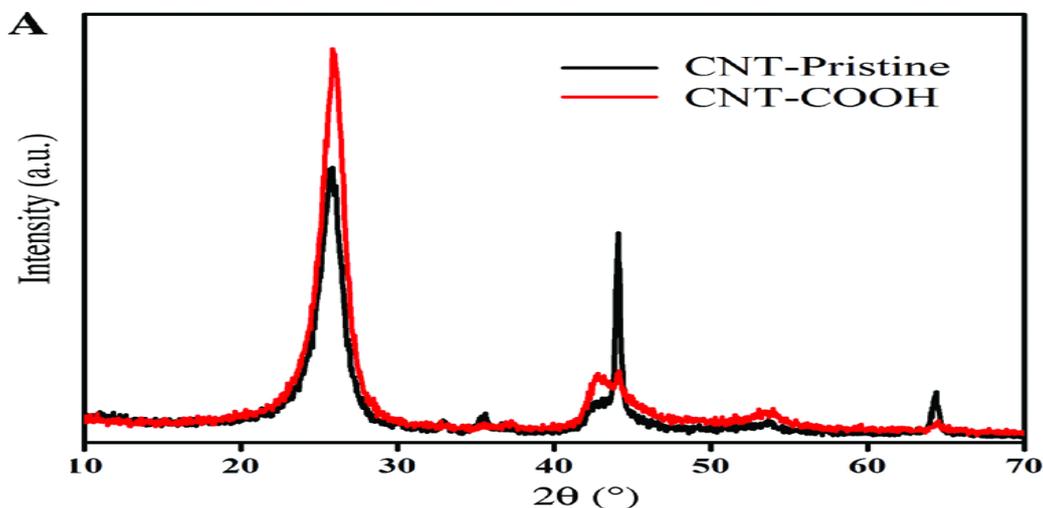


Figure 2.11 : XRD pattern of pure MWCNTs and COOH-MWCNTs (Javed et al., 2015).

2.6.4 Fourier Transformed Infrared Spectroscopy (FTIR)

Figure 2.12 shows IR spectrum of oMWCNTs after being oxidized with mixture of H₂SO₄ and HNO₃. The broad peaks at 1180 cm⁻¹ could be assigned to C–O stretch from phenol or lactone groups and also to C–C bonds. The band at 2910cm⁻¹ and 2850cm⁻¹ corresponds to CH stretching. Absorption peak at approximately 1715cm⁻¹ of wavenumber shows that it is corresponding to the stretching vibration of C=O or carbonyl group from the carboxylic group (COOH). Carbonyl characteristics peak also observed at about 1636cm⁻¹ and can be appointed to the carbonyl group from the quinone or the ring structure. The peak at 3400cm⁻¹ assigned to the vibration group or hydroxylic group. This peak can be assigned to the hydroxylic group of moisture, alcohol, or carboxylic groups (COOH). This result clearly indicates that the COOH group is successfully attached onto the surface of MWCNTs (Gupta et al., 2011).

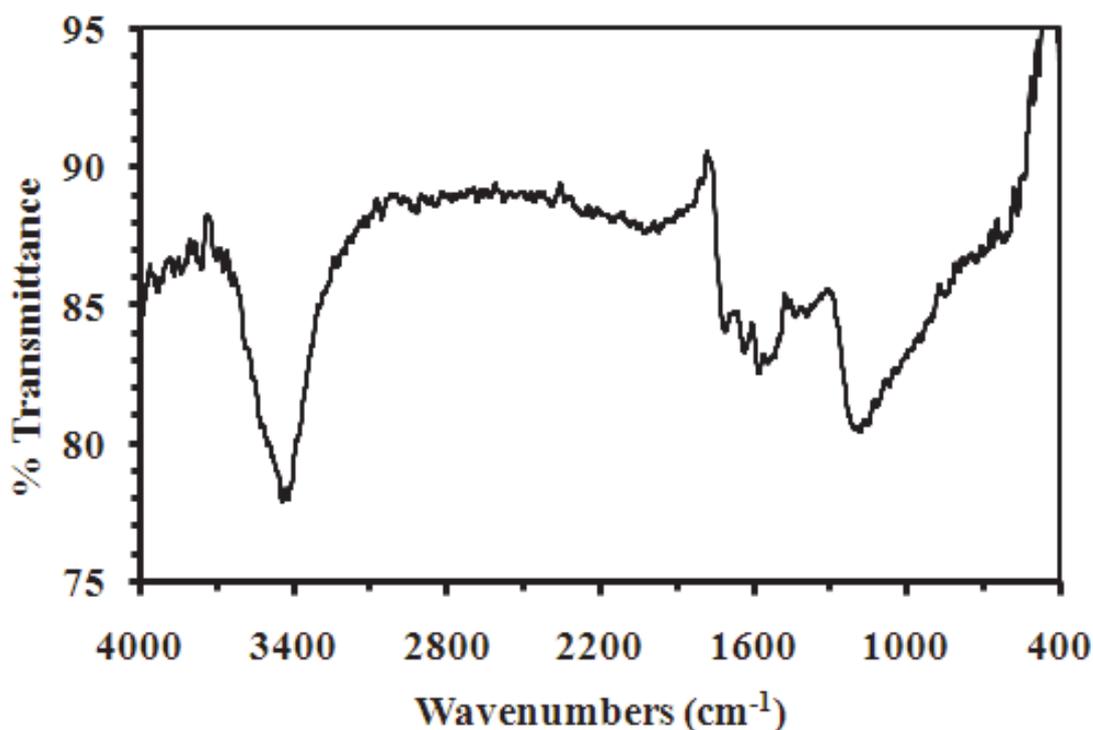


Figure 2.12: IR spectrum of O-MWCNTs (Gupta et al., 2011).

From the figure 2.13, Absorption band at 3436cm^{-1} assigned to the presence of hydroxyl groups (OH) on the surface of unmodified MWCNTs. The presence of hydroxyl group on pure MWCNTs surface is believed to be resulted from either ambient atmospheric moisture or oxidation during purification of CNTs (Ramanathan et al., 2005). Since the moisture in the KBr powder could not be totally disposed of, it could be assumed that most of the O-H functional group could be originate from moisture in KBr powder rather than from the functional groups attached to the surface of the CNTs during purification. Peak at 2942cm^{-1} and 2894cm^{-1} wavenumber are related to asymmetric and symmetric methylene stretching bands, respectively. The presence of these functional groups explained that unmodified MWCNTs already have several functional groups possibly produce during synthesis or purification process (Sankal et al, 2012).