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وزارة التعليم العالي والبحث العلمي
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Department of Physics

Study of multi walled carbon nanotube production properties and applications

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بِسْمِ اللَّـهِ الرَّحْمَـٰنِ الرَّحِيم

(يا أَيُّهَا الَّذِينَ آمَنُوا إِذَا قِيلَ لَكُمْ
تَفَسَّحُوا فِي الْمَجَالِسِ فَافْسَحُوا يَفْسَحِ
اللَّهُ لَكُمْ ۖ وَإِذَا قِيلَ انْشُزُوا فَانْشُزُوا يَرْفَعِ
اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ وَالَّذِينَ أُوتُوَا الْعِلْمَ
دَرَجَاتٍ ۚ وَاللَّهُ بِمَا تَعْمَلُونَ خَبِيرٌ)

صدق الله العلي العظيم

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اقرار المشرف

اشهد ان اعداد البحث المرسوم بعنوان (انتاج الانابيب النانوية الكربونية وخصائصها وتطبيقاتها) من قبل الطالب (محمد سامي حاتم محمود) قد اجرت تحت اشرافي في قسم الفيزياء- كلية العلوم- جامعة بابل كجزء من متطلبات نيل شهادة البكالوريوس في علوم الفيزياء

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الإهداء

أمتن لكل من كان له الفضل في مسيرتي وساعدني ولو باليسير

الأبوين، الاهل، الأصدقاء، الأساتذة المبجلين

أهدي لكم بحث تخرجي

شكر وتقدير

نحمد الله عزوجل الذي وفقنا في اتمام هذا البحث العلمي والذي وهبنا الصحة والعافية والعزيمة فالحمد لله حمدا كثيرا

نتقدم بجزيل الشكر والتقدير الى الاستاذ الدكتور المشرف على كل ما قدمه لنا من توجيهات ومعلومات قيمة ساهمت في اثراء موضوع دراستنا في جوانبها المختلفة

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Chapter One

Introduction

1.1-Introduction

Polymers are materials which consist of large number of structural units by link of the same type. Over the past few decades, as the polymers and plastics industry has very quickly . By the end of 2000, near 200 million tons per year of plastic resources were formed universal (about 2% of the wood used, and nearly 5% of the oil harvested) to complete the ever-growing requirements of the plastic era; in the manufacturing world plastic equipment are used at a rate of nearly 100 kg per person per year. Plastic materials with over 250 billion dollars per year supply about 4% to the disgusting marital generate in the United States. Plastics have no complement in other equipment in conditions of weight, simplicity of manufacture, capable use, and finances. Polymers have been entered in all parts of our lives. It is difficult to find affordable life with all services of services without the polymer industry [1].

Polymers of unique composition have the properties of semiconductors, while mainly commercial polymers are insulator. Known that polymers are simply shaped chemists and physicists happening median the twentieth irregular double century to conduct studies designed to expand conductor polymers characterized by the bonds, polymeric materials can be synthesized and processed into different shapes according to the required application such as thin films [2]. Polymers divided into natural and artificial, the natural included proteins, starches, cellulose and rubber, either the industrial. They have a lot of properties and uses. The molecules in the polymer are a large compared with molecules hydrocarbon (where it is the

foundation of the organic material) because of their size they are often referred to as macromolecules. Polymers possess many characteristics such as low cost, easy configuration, high resistance, flexibility, in addition to the mechanical properties of things, so it is used in electronic devices industry[3].

1.2- Classification of Polymers

Polymers are frequently separated according to whether they can be melted and reshaped throughout purpose of heat and pressure, called thermoplastics, or whether they decompose previous to they can be melted or reshaped, called thermosets. While.together thermoset polymers and thermoplastics can be recycled, because thermoplastics can be reshaped simply throughout the submission of heat and pressure, recycling of thermoplastics is easier Therefore, polymers classify into diverse types of dissimilar sources.

1- Classification Based on Source.

2- Classification Based on Structure of Polymers such as linear, branched, or network polymers as shown in figure (1.1). It can be seen from the figure that the real structures are in three-dimensional (3D), which is particularly necessary for the network.

4-Classification Based on Molecular Forces

There is also conductive polymers, such as (polyaniline) and other non-conductive.

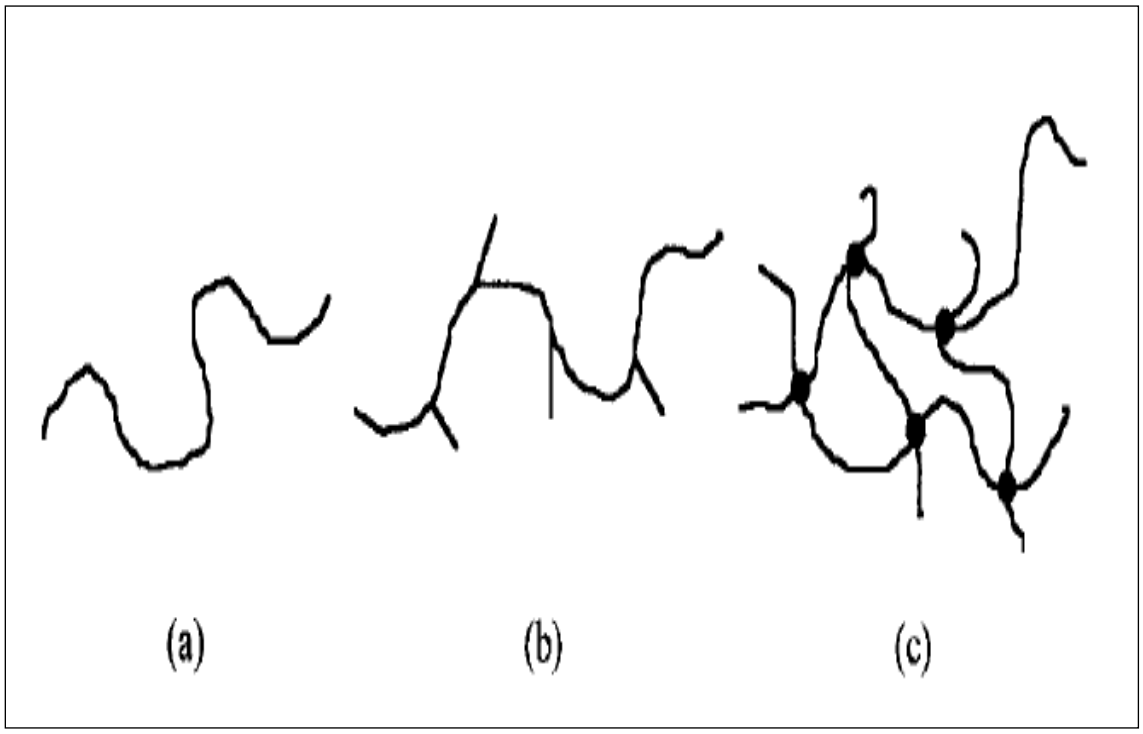


Fig . (1.1): Schematic diagram of (a) a linear polymer, (b) a branched polymer and (c) a network polymer [4].

1.3-Conductive polymers

It is known that polymers are insulating materials electric , but this image has changed after the discovery made by each of the (Heeger), (MacDiarmid) and (Shirakawa) who reached the possibility of modification of polymeric materials to become good conducts electricity like metal material.

The most important characteristic is the use of polymers manufacturing cost few. And found the following applications, which entered into commercial application, the effects introduced by the work done by both the heeger and McDiarmid and Shirakawa on contemporary technology:a Restaurant:

uses an electric conductor and shielding electronic circuit of electromagnetic radiation, as manufactured as an anti-corrosive[5].

1.4-Carbon Nanotubes

In which the atoms are connected in a three-way curved foils a vicious form cylinder is obtained carbon arc with the change of energy in order to become a continuous stream rather than AC, and thus can be obtained the tubular structures in a sediment on the pole. These pipes consisting entirely of carbon, and has named nanotubes, due to the diameter of a few nanometers. There are many ways to produce nanotubes composed of carbon molecules, which are:

a- Action electrical analysis using electrodes of graphite in molten salts, b- Thermal catalyst for hydrocarbon analysis and c- Evaporation of graphite using a laser [32, 33]. In addition, depending on the working methods of the nanotubes, have different electronic properties, some are expected to be a metal while others are semiconductors. It turns out that these nanotubes are incredibly strong it Hundreds of times stronger than steel, and partly due to the geometric hexagon shape, which can distribute forces and deformations due to the strength of the commonwealth of carbon - carbon, as well as, consequently has the properties of electronic unusual [6].

Carbon nanotubes have been used in many areas such as automotive fuel tanks industry, Tennis rackets, golf, skiing and sticks on the snow, and the coating of military materials that are not detected by radar. One of the new applications of nanotechnology, nano-carbon component of the ink tube is a ink was developed by Dr. Lee Jin Wong of the Korea Institute of Electrical Technology Research. The technique is highly developed it

includes coating plastic surfaces so the ink to make a thin surface able to conduct electricity. It can be applied this technique on a variety of areas, including touch screens and displays foldable [7]. CNTs can be classified into two types: One is multi-walled CNTs (MWCNTs) and the other is the single-walled CNTs (SWCNTs), as in figure (1.4)

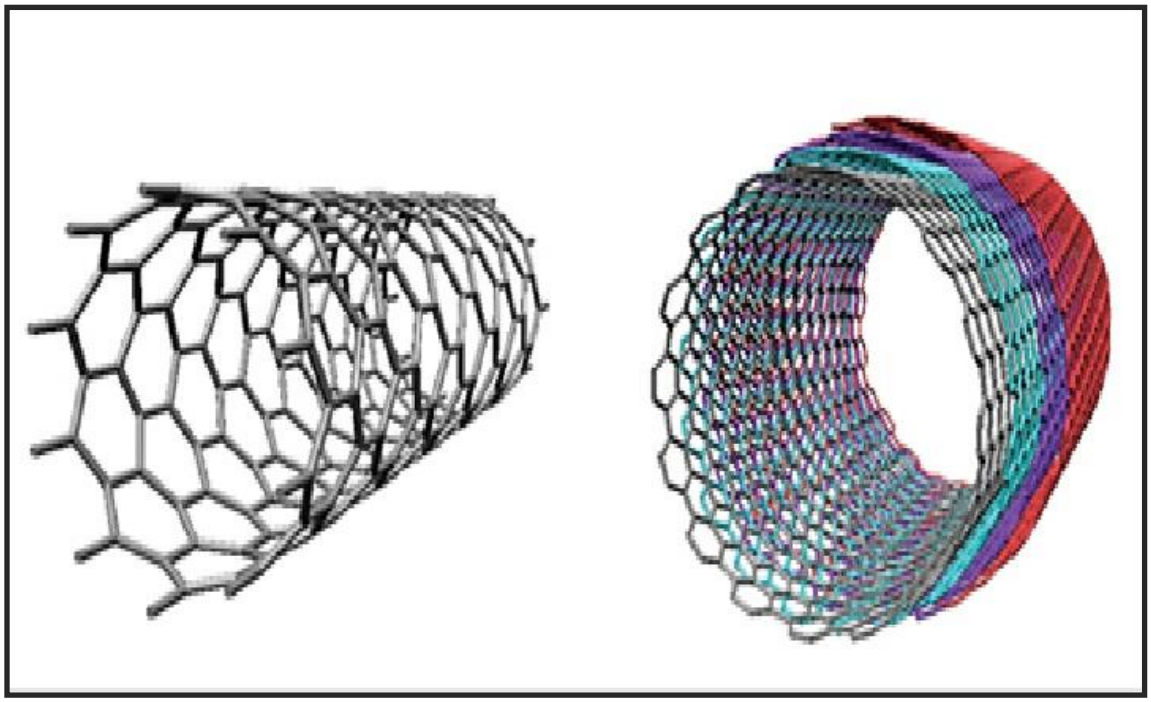


Fig . (1.4): Schematic representation of (a) SWCNTs and (b) MWCNTs[21]

1.5.1 Classification Based on the Origin of the Polymers

Polymers are classified as dependence to their sources into three categories:

1.5.1.1 Natural Polymers

They are natural plant or animal products such as cellulose, rubber and others. Expensive and difficult to obtain, there are three main types of natural polymers [8], polysaccharides, proteins and polyclonidat.

1.5.1.2 Modified Natural Polymers

They are natural polymers that undergo some modifications as a change in their chemical composition by introducing new polymer groups or changing the composition of some active groups in it or by injecting a natural polymer with another synthetic. Examples include cotton with acrylic fibers, cellulose acetate and Cellulose Esters.

1.5.1.3 Sunthetic Polymers

Represent the vast majority of industrially important polymers. They are made up of simple chemical compounds, including plastics, synthetic fibers, glues and others.

1.5.2 Classification based on the chemical nature of the Polymer

1- Organic polymers: Polymers produced from organic or prepared sources of organic compounds such as polycarbonate and polypropylene.
2- Inorganic polymers: They consist of inorganic compounds such as sulfur oxides.
3- Semi-organic polymers: They contain synthetic units composed of some mineral elements as well as some organic groups such as poly-silphon

1.5.3 Classification Based on The Mechanism of Chain Growth

1- polymers with chain growth (relatively fast polymers) such as polystyrene.

2- polymers with a growth (step by step) such as poly terephthalate ethylene[9].

1.5.4 Classification Based on Thermal Stability

1.5.4.1 Thermoplastics

Polymers whose properties change as temperature changes.They become flexible when their temperature approaches the temperature of their glass transition (Tg) (The thermal degree at which the polymer transforms from a solid to a flexible rubber material), the polymer is above the glass transition rate of soft and flexible, and it increases its elasticity at high temperature. These polymers have great industrial importance such as polyethylene Poly Styrene.

1.5.4.2 Thermosetting Polymers

Polymers that undergo chemical changes at high temperature, their chains become intertwined and become insoluble after thermal treatment, non-fusion and poor thermal and electrical conductivity such as phenol formaldehyde [10].

1.6 Physical Properties of Polymers

The important applied properties of polymers such as melting point, degree of glass transition and their ability to crystallize, melt, absorb and resist dyes for various environmental conditions such as cracking, rupture, mechanical and thermal properties and others are responsible for the physical (crystalline) composition of those polymers Polymers are characterized by these characteristics, which can be added to many developments on polymers, such as increasing the degree of fusion, increase thermal resistance and others On the other hand, undesirable properties in polymers can be eliminated by controlling several factors [11].

1.7 Aim of the Research

The aim of this research is to prepare conductive polymer materia (Study of multi walled carbon nanotube production) and study of properties

Chapter Two

Introduction

2.1 Introduction

In this chapter, was addressed to the mathematical relationships that[12].

2.2 Solution casting method

The most common method for preparing CNT/polymer nanocomposites involves mixing of CNT and polymer in a suitable solvent. The benefit of solution blending is rigorous mixing of CNTs with polymer in a solvent which facilitates nanotube de-aggregation and dispersion. This method consists of three steps: dispersion of nanotubes in a suitable solvent, mixing with the polymer (at room temperature or elevated temperature) and recovery of the nanocomposite by precipitating or casting a film. Both organic and aqueous medium have been used to produce CNT/polymer nanocomposites [48, 49]. In this method dispersion of nanotube can be achieved by magnetic stirring, shear mixing, reflux or most commonly, ltrasonication. Sonication can be provided in two forms, mild sonication in a bath or high-power sonication. The use of high-power ultrasonication for a long period of time can shorten the nanotube length, i.e. reduces the aspect ratio, which is detrimental to the composite properties[13].

2.3 Structural Properties

2.3.1 Fourier Transform Infrared (FTIR)

(FT-IR) is a technique that is used to obtain an infrared spectrum of absorption , emission , photoconductivity or Raman scattering of a solid , liquid or gas. (FT-IR) spectrometer simultaneously collects spectral data in

wide range of spectral range. Spectra were recorded as a sample dispersion in (potassium bromide) through (IR) disk as (sample 1 mg to 200 mg KBr) with a scanning range of (500-4000) cm^{-1} and resolve (1 cm^{-1}) [14]

2.3.2The X-ray diffraction (XRD)

X-ray diffraction is one of the experimental techniques used on a large scale to determine the lattice parameters, the preferred orientation of the crystal. X-ray diffraction simple mechanism. When the X-ray beam is monochromatic incident on the crystal sample, and constructive diffraction (or interference) of parallel planes of atoms with a spacing (d) between the planar Bragg happen if the law is satisfied.

$$2d \sin\theta = n \lambda \quad \cdots\cdots\cdots\cdots\cdots\cdots (2.1)$$

Where :

d: the distance between the two surfaces in a row.

λ : Wavelength of the beam falling, (1.54 Å)

n: integer (represents order diffraction).

θ : Angle of incidence and reflection of the package X-rays falling on a particular surface [15].

Chapter Three

Introduction

3.1 Introduction

This chapter includes the preparation of multi-walled carbon nanotubes as well as the preparation of their solutions and the required specifications and optimal conditions of preparation which are used in this work. It also includes the description of deposition system used , and the diagram (3.1) explain the main step for procedure [16].

3.2- Preparation of Polymers

Polymers prepared in accordance with the following steps:

1- Thawing (2.5g) of aniline hydrochloride in (50 ml) distilled water.
2- Thawing (5.71gm) of the initiator (ammonium persulfate) in (50 ml) distilled water.
3- Both solutions are saved each separately for one hour at a temperature (18 - 24) C°.
4- The two solutions are mixed in a beaker , are agitated briefly and leave to polymerize.
5- Combines polymer deposited on the filter paper, washed three times with (0.2 M HCL l) by (100 ML) and the washing process repeat with acetone.
6- Polymer leaves for a full day (24 hours) to dry and then combines[17].

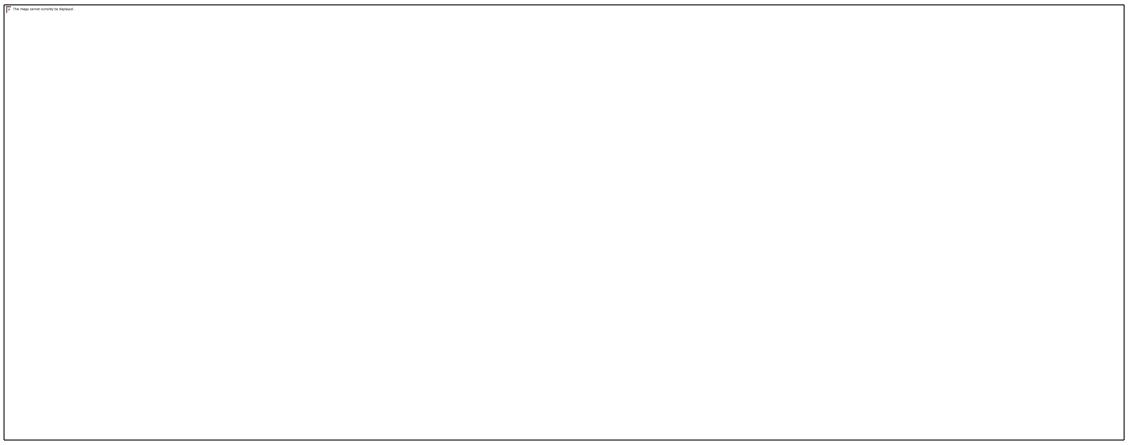
3.3 - Solutions Preparation

To prepare the solution dissolve (0.16gm) of the polymers in 50 ml of (DMF), then the solution is placed on the magnetic mixer and stir well to dissolve the material. It is then added carbon nanotubes to a solution for the purpose of doping different proportions(1%,3%,5%).

After that ,the films were prepared by spin coating [18].

3.4 Spin Coating

Spin coating is a versatile and effective technique to polymers films. It is an attractive method to prepare a wide variety of powders and thin film materials for various industrial applications. Polymers films have been deposited using this technique. Spin coating opens up the possibility to control the film morphology. The quality and properties of the films depend heavily on the process parameters. A spin coating system, (model V T C-100) , this system is present in the laboratory of the Department of General Science, College of Basic Education, University of Babylon, employed to prepare thin films. The system consists of several parts which have been arranged so as to make use of them in the preparation of various films on various substrates. In this system the thickness of the prepared films can be controlled by increasing or decreasing the rotation speed of the system, where the increasing of the speed rotation of the system the thickness of the films are decreasing and vice versa. Also the homogeneity of the prepared films depends on the speed of rotation and on the balance and stability of the system, Fig.(3.2) shows the spin coating system [19].



3.5 Substrates Cleaning

3.5.1- Glass Substrate

It can be summarized cleaning the glass substrate as follows:

a- Has been cleaned using detergent with water to remove any oil or dust that can be attached to the substrate surface and then placed under tap water and rub gently.

b- Put in a clean beaker containing distilled water and then rinsed in a unit of ultrasound for 15 minutes.

c- After this the step 2 is repeated by replacing the distilled water with pure alcohol , which reacts with contamination such as grease and some oxides .

d- Eventually, the slides are dried with blowing air, then wiped with soft paper [20].

3.5.2 FTIR Measurement

Tested the samples of (PANI) nano films are by Fourier Transfer Infrared Spectroscopy (FTIR), by using Vertex 70 from broker company, figure (3.6) shows that (FT-IR) instrument that found in Babylon University / College Basic Education, Department of General Science. The spectrums have recorded as a dispersion of the sample in (potassium bromide) by (IR) disk as (1 mg sample in 200 mg KBr) with the scanning range from (500-4000) cm^{-1} and the resolution of ($1cm^{-1}$)

3.5.3 X-ray Diffraction (XRD)

Has been examining all the crystal structures of the polymer which prepared using X-ray diffraction (6000) diffraction apparatus supplied by a Japanese company (SHIMADZU) at Babylon University / College Basic Education, Department of General Science, as in figure (3.5). It has the following specifications:[22]

Target : Cu

Wavelength : 1.5406 Å

Current : 30 (mA)

Voltage : 40 (kV)

Fig(3.5): X-ray diffraction system.

Chapter Four

Introduction

4-1 Introduction

This chapter presents the results and discussion of the experimental measurements , structural with (MWCNTs), where deposited on substrates by spin coating technique.

4-2 Diagnosing Tests

4-2-1 FTIR Test

in Figure (4-3), the emergence of value at 2927.94 cm^{-1} returning to stretch group CH_2 in carbon nanotubes and also the emergence of value at(2779.42 cm^{-1}) returning stretchable (CH) in carbon nanotubes, the emergence of values between (11635.64- 1486 cm^{-1}) evidence of a C = C aromatic attributable to polymers.

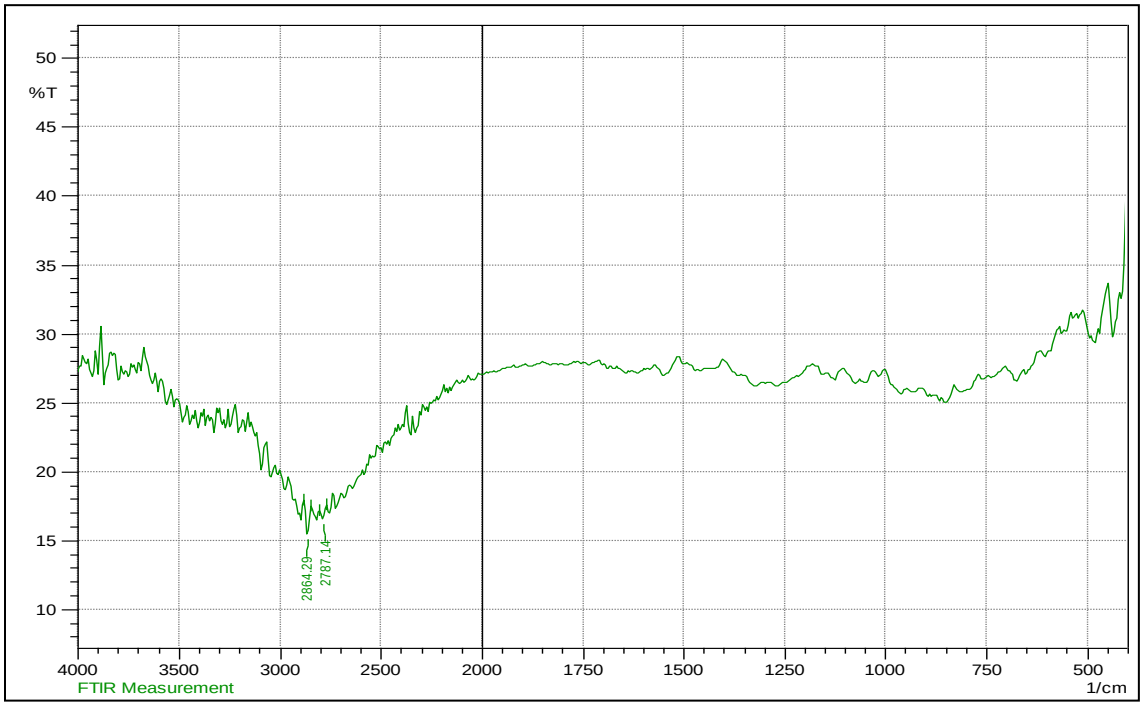


Fig. (4-1) FTIR for carbon nanotubes (MWCNTs)

4-2-2- X– Ray Diffraction Test (XRD)

Figure (4-7)which represents the X-ray diffraction of pure polyamers , appears broad summit at (25^{o}) which shows that the polyaniline is (Amorphous) while figure (4.8)represents X-ray diffraction of the polymer doped by carbon nanotubes with ratio 1%, we notice the appearance of two peaks at (5^{0}-30^{o}) . An angle (5^{o}) shows the diffraction for the parallel levels in the polymeric chain, an angle (30^{o}) shows the diffraction of the levels orthogonal.

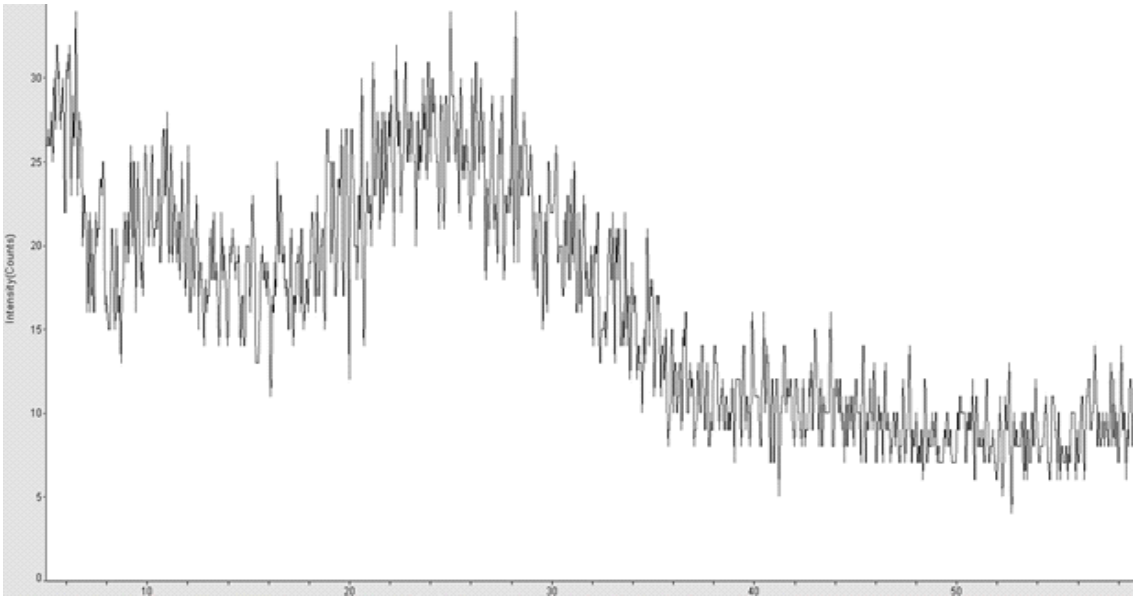


Fig. (4.8) X-ray for polyaniline / MWCNTs(1%)

And the figures (4.9,4.10) appear tested for the films with the ratio (3%,5%), Where all films are show to have a random structure. These results are identical to the results of the researchers

4-3- Conclusions

From preparing pure and MWCNTs- thin by spin coating technique it can be concluded:

1- The method of polymer preparation by polymerization was successful

2- spin coating technique is a good technique in the preparation of thin films

3-It is found through a study that these polymers possess random installation

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