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Processing and Properties of Multifunctional Two-Dimensional Nanocomposite Based on Single Wall Carbon Nanotubes

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Processing and Properties of Multifunctional Two-Dimensional Nanocomposite

Based on Single Wall Carbon Nanotubes

A dissertation submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

By

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Abstract


Truly single layer (monolayer) films of unmodified zigzag single-walled carbon nanotubes by using the Langmuir-Blodgett (LB) technique have been processed successfully. Measurements of their mechanical and optoelectric properties were achieved. Different theoretical equations were used based on the results obtained from the experimental part to study the properties and structures of the produced material and their composite. The produced films were highly oriented as determined by polarized Raman spectroscopy and as shown by scanning tunneling microscopy (STM). The films have a significant amount of flexibility which makes their behavior similar to rubbery materials. They can also be deposited on different types of substrates with different shapes depending on the required applications. Nanocomposites utilizing Poly (methyl methacrylate)-(PMMA) matrix were also prepared and characterized. Both direct mixing and in-situ polymerization techniques were employed to investigate the effect of mixing method on the produced composite properties. In addition to that, a comparison process between the theoretical models which were used to estimate the composite modulus with the experimental results for direct mixing method of composite is applied with emphasizing the effect of the interphase factor on the empirical calculated composite modulus values.
# Table of contents

**CHAPTER 1: Introduction** ................................................................. 1

1.1 Introduction ............................................................................ 1

1.2 Transparent Conducting Electrode ......................................... 1

   1.2.1 Transparent Conductive Polymer Electrode .................... 2

   1.2.2 Transparent Conducting Electrode Based on Metallic Nanowires ... 2

   1.2.3 Transparent Conducting Electrode Based on Metallic Nanoparticles 3

   1.2.4 Transparent Conducting Electrode Based on CNTs ........... 3

1.3 Carbon Nanotubes Films ..................................................... 4

   1.3.1 Direct Growth Method for Processing SWCNTs Thin Films .... 4

   1.3.2 Solution-Based Method for processing SWCNTs Thin Films .... 6

1.4 Methods to Align Carbon Nanotubes in Solution-Based Films .......... 7

   1.4.1 SWCNTs Aligned by Magnetic Field Induction ............... 7

   1.4.2 SWCNTs Aligned by Langmuir-Blodgett Technique .......... 9

1.5 SWCNTs Nanocomposite Material ....................................... 16

1.6 Motivation and Objectives ................................................. 19

   1.6.1 Motivation .................................................................. 19

   1.6.2 Objectives .................................................................. 19

**CHAPTER 2: Experimental Details** ............................................ 22

2.1 Materials Used ...................................................................... 22

   2.1.1 SWCNTs: Properties and structure ............................ 22

   2.1.2 Poly (Methyl Methacrylate) PMMA Polymer Properties and Structure ......................................................... 33

2.2 Measuring Techniques ....................................................... 35

   2.2.1-1 Langmuir-Blodgett Technique ............................... 35

   2.2.1-2 Langmuir-Blodgett Device .................................... 37

   2.2.1-3 Langmuir-Blodgett Film’s Deposition ...................... 44

   2.2.2 Films Characterizations Techniques ......................... 50

   2.2.2-1 Scanning Tunneling Microscopy (STM) .................. 50

   2.2.2-2 Raman Spectroscopy ............................................ 56

   2.2.2-2.1 Raman Characteristics of SWCNTs ................... 61

   2.2.2-3 High-Resolution Transmission Electron Microscopy HRTEM 64

   2.2.2-4 Keithley Instrument ................................................ 66

   2.2.2-5 Ultraviolet-Visible Spectrophotometer ..................... 68

   2.2.2-6 Other Films Processing Instruments ........................ 70

**CHAPTER 3: Results and Discussions** ....................................... 74
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Characterizations of SWCNTs</td>
<td>74</td>
</tr>
<tr>
<td>3.2 Production of a SWCNTs Monolayer</td>
<td>79</td>
</tr>
<tr>
<td>3.3 Characterizations of SWCNTs Monolayer Films</td>
<td>84</td>
</tr>
<tr>
<td>3.3-1 Calculations of a Monolayer Film Processing for SWCNTs</td>
<td>84</td>
</tr>
<tr>
<td>3.3-2 Structural Characterizations for the produce Monolayer Films of</td>
<td>87</td>
</tr>
<tr>
<td>SWCNTs</td>
<td></td>
</tr>
<tr>
<td>3.3-3 Mechanical Properties of Well-Aligned Monolayer Films of SWCNTs</td>
<td>89</td>
</tr>
<tr>
<td>3.3-4 Electrical Properties of Aligned SWCNTs Films</td>
<td>94</td>
</tr>
<tr>
<td>3.3-5 Optical Properties of Well-Aligned SWCNTs Films</td>
<td>102</td>
</tr>
<tr>
<td>3.4 Production and Characterization of SWCNTs/PMMA Nanocomposite Films</td>
<td>104</td>
</tr>
<tr>
<td>3.4.1 Nanocomposite by Direct Mixing Process</td>
<td>106</td>
</tr>
<tr>
<td>3.4.1-1 Mechanical Properties</td>
<td>106</td>
</tr>
<tr>
<td>3.4.1-1-1 Comparing Composite Films Stiffnesses with a Define</td>
<td>112</td>
</tr>
<tr>
<td>Composite Theory</td>
<td></td>
</tr>
<tr>
<td>3.4.1-2 Electrical Properties</td>
<td>122</td>
</tr>
<tr>
<td>3.4.2 Nanocomposite by the In-Situ Polymerization Technique</td>
<td>126</td>
</tr>
<tr>
<td>3.4.2-1 Mechanical Properties</td>
<td>126</td>
</tr>
<tr>
<td>3.4.2-2 Electrical Properties</td>
<td>128</td>
</tr>
<tr>
<td>3.4.3 Comparing Results for Direct Mixing and In-Situ Polymerization</td>
<td>134</td>
</tr>
<tr>
<td>3.4.3-1 Comparing Mechanical Properties for Two Composites Production</td>
<td>134</td>
</tr>
<tr>
<td>Methods</td>
<td></td>
</tr>
<tr>
<td>3.4.3-2 Comparing Electrical Properties</td>
<td>136</td>
</tr>
<tr>
<td>3.4.4 Comparing Results for Chemically and Physically linked SWCNTs in</td>
<td>140</td>
</tr>
<tr>
<td>the Produced Monolayer film</td>
<td></td>
</tr>
<tr>
<td>3.4.4-1 Comparing Mechanical Properties</td>
<td>140</td>
</tr>
<tr>
<td>3.4.4-2 Comparing Electrical Properties</td>
<td>142</td>
</tr>
</tbody>
</table>

**CHAPTER 4: Conclusions and Recommendations for Future works** .......... 144

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 conclusion</td>
<td>144</td>
</tr>
<tr>
<td>4.2 Recommendations Future work</td>
<td>146</td>
</tr>
</tbody>
</table>

**References**........................................................................................................... 147
List of Figures

Figure (1-1) SEM images for grown SWCNTs on a Si-wafer by using direct growth method ................................................................. 5
Figure (1-2) TEM images at a lower and high magnification of Iron-coated CNTs ........ 8
Figure (2-1) High resolution images of SWCNTs of diameter 37 nm ......................... 23
Figure (2-2) A schematic of how the graphene sheet can be rolled to form different shapes of nanotubes ......................................................... 25
Figure (2-3) A comparison between the structure of (single and multi) wall carbon nanotubes ........................................................................ 26
Figure (2-4) The typical hexagonal sheet which made from hybridization of the carbon atoms ................................................................. 28
Figure (2-5) Schematic for different types of SWCNTs ................................................. 30
Figure (2-6) Structure of PMMA ................................................................. 34
Figure (2-7) Langmuir-Blodget equipment ................................................................. 38
Figure (2-8) Film phases form as the compressing process continues with time ............ 40
Figure (2-9) Wilhelmy plate details a cross-section ..................................................... 41
Figure (2-10) An isotherm for pure water before starting the separation process ........... 43
Figure (2-11) Nima Technology UK model 1222D2 ....................................................... 45
Figure (2-12) Schematic of the LB trough with all the other main parts ....................... 46
Figure (2-13) Deposition process by using Langmuir-Blodgett technique for a monolayer and multi-layers production process ....................... 48
Figure (2-14) Different types of produced molecular films formed by the deposition process ........................................................................ 49
Figure (2-15) Nano Surf easy Scan, E-Line (STM) ....................................................... 51
Figure (2-16) Two-modes operation of the STM device ................................................ 53
Figure (2-17) Energy levels for different scattering ...................................................... 58
Figure (2-18) Renishaw in Via Raman microscope ...................................................... 60
Figure (2-19) Raman spectrum of SWCNTs and peaks assignment ............................... 65
Figure (2-20) Keithley 2401 device ............................................................................ 67
Figure (2-21) Cary 50 Scan UV Visible Spectrophotometer device .............................. 69
Figure (2-22) Fisher Scientific, Model FS20 ................................................................ 71
Figure (2-23) Beckman Coulter, Allegra™ X22R ......................................................... 72
Figure (2-24) Glass and steel types of substrates ....................................................... 73
Figure (3-1) Radial breathing modes regions of the Raman spectrum with the characteristics of Raman modes measures ........................................ 75
Figure (3-2) HRTEM image is showing a single wall carbon nanotube at the nano level ........................................................................ 76
Figure (3-3) Scanning Tunneling Microscopy image showing the structure of the SWCNTs ........................................................................ 78
Figure (3-4)  A diagram for the main factors used in the experimental work and how they relate to each other................................................. 80
Figure (3-5)  The effect of solution volume added to the trough on the produced number of layers ................................................................. 82
Figure (3-6)  Effect of solution sonication times on the number of films layers produced for (1000 μl) solution, the line is provided to guide the eye ........ 83
Figure ((3-7)-A)  Langmuir-Blodgett isotherm for a monolayer film of SWCNTs ........ 86
Figure ((3-7)-B)  Stress/Strain curve for a monolayer SWCNTs film in compression based on the LB isotherm shown in figure ((3-7)-A)......................... 93
Figure (3-8)  HH Polarized Raman spectra at different orientation angles between the SWCNTs alignment angle and polarization angle. Spectra are showing first and second order SWCNTs surface modes ........................................ 88
Figure (3-9)  HR-STM shows a monolayer film structure of aligned SWCNTs .......... 90
Figure (3-10)  Histogram comparison for the conductivity (S/cm) in both directions for a monolayer film ................................................................. 91
Figure (3-11)  Comparison between conductivity (S/cm) of SWCNTs films as function of number of layers with cooper, silver, and Indium Tin Oxide (ITO) films in log scale ................................................................. 95
Figure (3-12)  Conductivity (S/cm) as a function of rotation angles in polar coordinates for the produced monolayer of SWCNTs ...................................... 96
Figure (3-13)  Conductivity (S/cm) as a function of rotation angles in polar coordinates for the three layers produced films ........................................ 98
Figure (3-14)  Conductivity (S/cm) as a function of rotation angles in polar coordinates for the five layers produced films ........................................ 99
Figure (3-15)  Conductivity (S/cm) as a function of rotation angles in polar coordinates for the seven layers produced films ..................................... 100
Figure (3-16)  Conductivity (S/cm) as a function of rotation angles in polar coordinates for the eleven layers produced films ...................................... 101
Figure (3-17)  UV visible analysis for the produced films ...................................... 103
Figure (3-18)  Schematic for the direct mixing process ....................................... 107
Figure (3-19)  Isotherm shows surface pressure as a function of the area for (0.037 Vt) SWCNTs nanocomposite films produced by the direct mixing process .. 109
Figure (3-20)  STM image for strips of SWCNTs mixed with (0.1 Vt) SWCNTs ......... 110
Figure (3-21)  Average film stiffness as a function of SWCNTs volume fraction for nanocomposite produced by the direct mixing method ................. 111
Figure (3-22)  Comparison between defined composite theory and lab results for the produced composite films ..................................................... 113
Figure (3-23)  Fitting interphase factor to the experiment data of direct mixing composite films ................................................................. 116
Figure (3-24)  Fitting Ishai-Cohen model to the experiment data of direct mixing composite films ................................................................. 118
Figure (3-25) Fitting Verbeek model to the experimental data of direct mixing composite films ................................................................. 119
Figure (3-26) Comparing three models to the experiment data of the direct mixing composite films ................................................................. 121
Figure (3-27) Conductivity (S/cm) in both direction as a function of SWCNTs Vf by direct mixing method ................................................................. 123
Figure (3-28) Histogram comparison for the conductivity (S/cm) in both direction as a function of SWCNTs Vf ................................................................. 124
Figure (3-29) Ratios between conductivities in the transverse and longitudinal directions for the direct mixing method ................................................................. 125
Figure (3-30) Average film stiffness as a function of SWCNTs Vf by in-situ polymerization .................................................................................................... 127
Figure (3-31) Conductivity (S/cm) in both direction as function of SWCNTs Vf (in-situ) polymerization .................................................................................................... 129
Figure (3-32) Histogram comparison for the conductivity (S/cm) in both direction as a function of SWCNTs Vf (in-situ) ................................................................. 130
Figure (3-33) Ratios between conductivities in the transverse and longitudinal directions for the (in-situ) polymerization method ................................................................. 131
Figure (3-34) Schematic for the effect of the free radicals on the structure of SWCNTs in the (in-situ) polymerization process ................................................................. 133
Figure (3-35) Average film stiffness as a function of SWCNTs Vf by both direct mixing and (in-situ) polymerization methods ................................................................. 135
Figure (3-36) Conductivity in the longitudinal direction as a function of SWCNTs Vf by both direct mixing and in-situ polymerization methods ................................................................. 137
Figure (3-37) Conductivity in the transverse direction as a function of SWCNTs Vf by both direct mixing and in-situ polymerization methods ................................................................. 139
Figure (3-38) Comparing between film stiffness (MPa) of the produced SWCNTs monolayer of physically linking VS chemically linking processes .......... 141
Figure (3-39) Comparing between conductivity values (S/cm) for the produced SWCNTs monolayer of physically linking VS chemically linking processes .......... 143
List of Tables

Table (1-1) Electrical properties for SWCNTs films ............................................ 15
Table (1-2) Electrical properties for SWCNTs nanocomposite films ....................... 18
List of Equations

Equation 1: SWCNTs (circumference (Ch)) ......................................................... 27
Equation 2: Action force acting on Wilhelmy plate ............................................. 39
Equation 3: Relation between nanotubes diameter and frequency ....................... 62
Equation 4: Frequency for individual nanotubes .................................................. 62
Equation 5: Nanotubes diameter mathematical equation .................................... 84
Equation 6: Number of carbon atoms per unit cell ............................................. 84
Equation 7: SWCNTs unit cell length .................................................................... 84
Equation 8: Transverse modulus for the bulk composite ...................................... 112
Equation 9: Transverse modulus for the bulk composite with the interphase effect..... 114
Equation 10: Ishai-Cohen model to estimate the composite modulus.................... 117
Equation 11: Verbeek model to estimate the composite modulus......................... 117
Equation 12: Einstein model to estimate the composite modulus......................... 117
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Ali M. Al Mafarage

2019 April 19
Dedication

This dissertation work is dedicated to my family especially, my lovely wife for the inspiration, support, strength and endless love
CHAPTER 1: Introduction

1.1 Introduction

The superior mechanical, chemical, and optoelectrical properties of single-walled carbon nanotubes (SWCNTs) makes them a candidate for enormous applications in different fields such as sensors and transistors, smart materials, multifunctional composites, and transparent conductors [1-3]. These superior properties for SWCNTs do not result only from the outstanding unusual characteristic of individual CNTs, but also due to the collective behavior of individual tubes with each other [4-7]. Hence, to recognize the superior properties of SWCNTs in engineering products and devices a process capable of producing films on a scale large enough for engineering applications and with a capability to control the product structure [8].

1.2 Transparent Conducting Electrode.

The development in the field of optoelectronic devices such as touch screen liquid crystal displays and solar cells increases the demand for the production of transparent conducting electrodes [9-13]. Those electrodes consist of a layer (or layers) of electrically conductive and optically transparent material [14, 15]. Transparent conducting films (TCFs) usually perform as electrodes when a circumstance calls for a low resistance electrical contact without blocking the light such as in photovoltaics [16, 17]. The main feature for the transparent material is possessing broadband gaps which had energy
values larger than those for visible light. Two types of TCFs, inorganic and organic have been developed [16-20]. Transparent conducting oxides such as Indium Titanium Oxide (ITO) are a good example of the inorganic films. The organic films are usually developed by either transparent conducting polymers or polymers filled with conducting nano-particles, wires, or CNTs [15, 18, 20]. Different types of transparent electrodes are discussed below.

**1.2.1 Transparent Conductive Polymer Electrode.**

Polyacetylene, polypyrrole, and polyaniline represent main types of polymers with conjugated double bonds that are the main precursors from which conductive polymer is derived [21, 22]. Some types of the polymer allow the conductivity to reach 1000 S/cm [21-26].

**1.2.2 Transparent Conductive Electrodes Based on Metallic Nanowires.**

A network of wires which are randomly conducting or meshing represent a new generation of transparent conductive electrodes [27-29]. The voids between nanowire mesh are transparent to light while the charge is collected by the nanowires or meshes themselves [30, 31]. Those electrodes can be obtained from the process of depositing silver or copper or any other types of conducting nanomaterials [11]. Silver nanowires have the best electrical conductivity with high optical transmittance and low resistance [32, 33].
For silver nanowire networks (TCFs), the sheet resistance is 20 Ω/sq, and transmittance is 95% [33, 34]. It represents one-dimensional nanostructure with a normal size between 5 to 100 nm [30, 35, 36]. The process of producing flexible transparent electrodes can be achieved by depositing silver nanowire on a flexible structure [37].

1.2.3 Transparent Conductive Electrodes Based on Metallic Nanoparticles.

Nanoparticles can be defined as particles which have one or more dimension in the range of 100 nm or less [38, 39]. They can be used to produce a transparent conductive electrode [38, 39]. Nanoparticles usually have unique chemical and electronic properties [40-42]. The interaction process between nanoparticles and the polymer matrix can be very complex, so they can remain dispersed in the matrix or agglomerate together [40-42]. Silver nanoparticles are widely used nanoparticles in the process of producing transparent conductive electrodes, due to their high electric conductivity and low agglomeration behavior leading to high optoelectric properties of the composite (the transparent electrodes) [32, 43-47].

1.2.4 Transparent Conductive Electrodes Based on CNTs.

Carbon nanotubes (CNTs) can be used to produce conductive transparent electrodes due to their superior and unique electric conductivity as well [48, 49]. CNTs films are more favorable over other types of transparent conductive films because they have excellent electrical stability and can provide a more mechanically robust material
system [4, 50]. Utilizing CNTs in transparent conductive electrodes was shown to provide the following advantages [51, 52]:

- Better light transmission.
- Better thickness control.
- Better electron transport and mobility.
- More thermal stability for high-temperature applications.
- More economic due to the very low load of CNTs required for similar electro-optic performance.

1.3 Carbon Nanotubes Films

Processing SWCNTs in large thin films has been in the focus of scientific and engineering investigations for the past two decades [53]. So far, two methods were successfully utilized to process such films: direct growth method [54] and solution-based method [55-57].

1.3.1 Direct Growth Method for Processing SWCNTs Thin Films.

In the direct growth method, the catalyst metal nano-particles used for nanotubes growth are first spread on a substrate then the growth process of carbon nanotubes takes place leading to the growth of nanotube carpets in which the CNTs are normal to the substrates as shown in figure (1-1) [58]. The direct growth method, however, suffers
Figure (1-1) SEM images for grown SWCNTs on a Si-wafer by using direct growth method adopted from [58].
several limitations and challenges. The major challenge is related to the possibility of preparing identical nanoparticles of the catalyst with the same size, shape, and composition to produce the same type of nanotubes [5, 49, 59].

The major limitation is that imposed on the substrate material which must be able to withstand the high-temperature environment of the tubes growth process. Also, it’s more challenging to control the stability of these nano-sized particles at a high temperature of the growth rate processes [57, 60-62].

**1.3.2 Solution-Based Method for Processing SWCNTs Thin Films.**

The solution-based method is more favorable to provide the advantages of being done at room temperature, at normal atmospheric pressure with the ability to deposit CNTs on a variety of substrates such as polymer or ceramics [63-65]. Two favorable processes are used for the alignment of SWCNTs based on the solution-based methods which are magnetic field induction and the Langmuir-Blodgett technique [66]. Other processes such as dip-coating, spin-coating, and spray-coating have been investigated to produce transparent conducting electrodes. However, such processes were found less favorable due to the following reasons [67-71]:

- It’s almost impossible to control SWCNTs agglomeration during the process.
- It’s difficult to get consistent uniform thickness for the produced films.
- Limitations on the produced films size.
1.4 Methods to Align Carbon Nanotubes in Solution-Based Films.

1.4.1 SWCNTs Alignment by Magnetic Field Induction.

In the magnetic field induction method, an external magnetic field is applied on SWCNTs which can be dispersed or embedded in the polymer matrix. Due to the anisotropy in the magnetic susceptibility of SWCNTs, a driving force is produced as a result from the difference between the external and the tubes magnetic fields which will force the SWCNTs to align along the direction of the externally applied field with regular patterns [72].

The major challenges for using this process is representing the purity of SWCNTs since some of them are conductors, and others are semiconductors which make them have different responses to the externally applied fields [66, 72-75].

The limitations for the magnetic field induction method can be represented by the process of functionalization of SWCNTs with conductive particles such as iron particles to improve the alignment process [76]. In addition to that, the process of maintaining the orientation of SWCNTs after removing the external applied magnetic field is critical because some of the tubes tend to return to their original position [77]. Finally, a large amount of energy can be consumed due to the orientation processes, sometimes can even affect the properties of the SWCNTs applied [78-81]. Figure (1-2) shows an image for the functionalized CNTs with iron particles.
Figure (1-2) TEM images at a lower and high magnification of Iron-coated CNTs adopted from [82].
1.4.2 SWCNTs Alignment by Langmuir-Blodgett Technique.

Langmuir-Blodgett (LB) represents one of the reliable techniques used to deposit a homogeneous film with very precise control over the thickness and molecular organization [83]. From the (pressure-area) isotherm for LB films, the deposition process can be handled at specified pressure values with different types of substrates [72, 84-87].

Many research groups have utilized the LB techniques to orient SWCNTs [88]. However, the challenge was in producing a true monolayer of well-aligned SWCNTs and deposit them on different types of substrates [88-95].

Kim et al., 2002 published research about the procedure of producing optically homogeneous thin film formed from single-wall carbon SWCNTs by using the LB techniques. The produced film consists of 25 layers produced by layer-by-layer deposition with controllable thickness. To achieve such films, chemical treatments and functionalization of SWCNTs must be considered [96].

Kim et al., in 2003 also published another research on building 100 or more layers either with horizontal lifting or vertical dipping, which allow to radially control the film thickness by using the LB technique. They mentioned that the tubes are oriented in the direction of the trough barrier (horizontal lifting) and form a homogenous film [97].
Luccio et al., 2004 reported the using of the LB technique to deposit a mono-layer of SWCNTs on the surface of silicon (Si 100) to study the properties of the produced films. They mentioned that their results are promising for the fabrication of high degree of ordered CNTs films which has a particular structure, mechanical, and physical properties [98]. Their reported results, however, did not show any experimental proof for the film structure nor the film thickness.

Liu et al., 2005 reported that monolayers of carbon nanotubes at the level of the air-water interface had been stabilized. The electrochemical behaviors of the produced LB films had also been studied. The produced films were ultrathin with an enhancement in their electrical properties due to better stability produced monolayers at the air-water interface [99].

Antolini et al., 2006 reported that functionalization of SWCNTs with arachidic acid would enhance the deposition of SWCNTs by using the LB technique [100].

Li et al., 2007 used the LB techniques to produce functionalized SWCNTs films and measured their current conductivity. They used synthesis (chemical treatments) to prepare their samples, and they announced that the SWCNTs used are oriented in the produced samples. No details about the produced film’s thicknesses or structures were mentioned in this work [101].

Zhang et al., 2008 adopt a chemical functionalized SWCNTs by using LB technology. Different factors affecting the structure of the produced films were studied.
They produced multilayer films of SWCNTs up to 18 layers. A model was used in their research to explore the ordering behavior of the produced films [102].

Tao et al., 2008 used the LB technique for massively paralleled and controlled organization of nanostructures in the produced films. Specific factors were studied and optimized to monitor the effect of spacing and arrangement of particles on the structure of the produced films. This study discussed the challenges for new production tools that enable devices’ flexibility and functionality of using the LB technique as compared with other used assembling methods [103].

Venet et al., 2009 prepared thin films containing SWCNTs by using the LB technique. The morphology for the produced films had been invested by using AFM device. Electrical characterizations for the in-plane network produced films were also investigated [104].

Giancane et al., 2010 suspend functionalized SWCNTs in an organic solvent. They use the LB to transfer the produced suspension on a substrate. Covalent chemistry is used to perform the functionalization and dispersion process [105].

Giancane et al., 2010 used polymer to improve the dispersion of SWCNTs and study the stability of those tubes in the produced solution at the air-water interface by using the LB techniques and deposit them on solid substrates. They also examine the effect of changing the deposition pressure on the structure of the produced films [106].

Choi et al., 2010 using the LB technique and soft lithography combined in a patterning method for hierarchically aligned assembly of SWCNTs. The LB technique
successfully transfers films of unidirectional alignment of SWCNTs pattern by applying the deposition process of certain pressure on a silicon substrate. They announced that the produced films could fit different types of substrates [107].

In 2011 Massey et al., fabricated films of a network form from SWCNTs by using the LB method. A 99 layer film is produced by using a layer-by-layer deposition which shows a high degree of anisotropicity in properties [108].

Ma et al., 2011 provide an overview of the development in the process of aligned SWCNTs. They mentioned the two most famous methods used in this process. They discussed the process of using the LB technique to align and orient CNTs with focusing on the main challenges as compared with other procedures to align nanoparticles [109].

Di et al., 2012 prepare flexible and robust carbon-based films of CNTs; LB techniques are used in this research. The produced films fabricated from spinnable nanotubes array and then continuously deposited layer by layer to produce seamless rolled films. The authors mentioned that good mechanical properties are achieved for the produced films [110].

Myhra and Rivier 2013, summarized the techniques and methods which can be applied to characterize CNTs (including the LB technique). They provide an overview of old and new techniques and procedures used. They focus on the main factors that can affect quality control and fabrication properties of the produced product [111].
Kuriyama et al., 2013 used the LB technique to create films of synthesizing aligned carbon nanotubes. They study the factors that can improve the growth of the CNTs and measure the properties of these nanotubes in the produced films [92].

Vishalli et al., 2015 reported that a thin film of functionalized SWCNTs had been processed by using the LB technique. They used quartz substrate to deposit the required homogeneous films. The Atomic Force Microscopy (AFM), UV-visible NIR and FTIR technique are used to characterize the produced films which had reasonable stability. The researchers announced that the LB technique had the ability to produce films and deposited on different types of substrates with maintaining the purity of the pristine SWCNTs used. The produced films have a uniform network of SWCNTs with good transparency to the UV visible [83].

Sato et al., 2016 used the LB technique to produce films of synthesized vertically aligned carbon nanotubes. They used the LB technique to deposit catalyst of specific nanoparticles with filler molecules which will adjust the distance between the anticipated nanoparticles. Due to this controlling process, the density of the vertical CNTs will adapt in the produced films [112].

Yahya et al., 2017 used the LB technique to produce conductive transparent films of SWCNTs. The transparency for the produced films by using the LB technique was the best as compared with the values gotten from other deposition methods. In addition to that, the variation in electrical parameters for the films produced by the LB technique is lower as compared with other deposition techniques [113].
Beigmoradi et al., 2018 reported the latest methods that have been used for the alignment and arrangement of CNTs in the structure of the produced films. They compared the mechanical, electrical and chemical properties for the produced films by using different deposition techniques and mentioned that the LB technique had more flexibility and used for the fabrication of electromagnetic devices on a large scale as compared with other deposition techniques. The limitations and challenges of each deposition method are discussed with mentioning the treatments that should be taken into consideration to improve the alignment process [114].

Another group of researchers focuses on studying the electrical properties of SWCNTs and how they contribute to improve the conductivity of the produced films. The synthetization effect on the conductivity value for SWCNTs also was observed by many researchers. Table (1-1) below summarized most of the measured electrical properties for SWCNTs films.
Table (1-1) Electrical properties for SWCNTs films.

<table>
<thead>
<tr>
<th>No.</th>
<th>Nanotubes materials used</th>
<th>Film Thickness and typed</th>
<th>Measured Conductivity</th>
<th>Year</th>
<th>Notes</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SWCNTs individual rope</td>
<td>w/o functionalization</td>
<td>(4.4 ± 1.6) × 10^5 S/cm</td>
<td>2009</td>
<td>1- Acidic treatments. 2- Annealing effect on resistance.</td>
<td>[115]</td>
</tr>
<tr>
<td></td>
<td>SWCNTs network bundles.</td>
<td>w functionalization</td>
<td>(5.6 ± 1.2) × 10^5 S/cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>w/o functionalization</td>
<td>∼3 × 10^4 S/cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>w/o functionalization</td>
<td>∼1 × 10^4 S/cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bundle diameter 2.3 nm.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>SWCNTs network bundles</td>
<td>Functionalized</td>
<td>2000 S/cm</td>
<td>2007</td>
<td>Solution based filtration process.</td>
<td>[116]</td>
</tr>
<tr>
<td>3</td>
<td>SWNT bucky-paper</td>
<td>No information</td>
<td>550 – 3000 S/cm</td>
<td>2005</td>
<td>1- Electrical conductivity is measured using the four-probe method with silver paint contact. 2- SWNTs undergo chemical treatments involving exposure to different types of molecules will influence its properties.</td>
<td>[117]</td>
</tr>
<tr>
<td></td>
<td>Treatment increase conductivity.</td>
<td></td>
<td>550 – 70 S/cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Treatment decrease conductivity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Ap-SWCNTs (swcnt purity 49 %)</td>
<td>Up to 50 nm Network</td>
<td>250 S/cm</td>
<td>2004</td>
<td>1- Chemical functionalization of SWNTs decrease conductivity. 2- SWNTs prepared by the electric arc discharge method. 3- Solution concentration of 0.02 mg/mL, which ultrasonication for 1h in a bath sonicator. 4- Keithley 236 source-measure unit controlled by custom LabVIEW software use to generate the I-V curve. 5- As more SWNTs are deposited, the conductivity continues to increase rapidly until conductivity is relatively invariant to further increases of a film thickness of ∼ 50 nm is reached. 6- The films of SWNT-ODA show conductivities that are about 2 orders of magnitude lower than those of the nonfunctionalized SWNTs. 7- Conductivity is temperature dependent.</td>
<td>[118]</td>
</tr>
<tr>
<td></td>
<td>P2-SWCNTs (swcnt purity 89 %)</td>
<td>non- functionalize</td>
<td>230 S/cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>P3-SWCNTs (swcnt purity 94 %)</td>
<td>up to 100 nm Network</td>
<td>400 S/cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SWCNTs-ODA (swcnt purity 90 %)</td>
<td>functionalize</td>
<td>3 S/cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SWCNTs-PABS (swcnt purity 90 %)</td>
<td></td>
<td>0.3 S/cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>HiPCO SWCNT in-plane.</td>
<td>isotropic SWNT</td>
<td>1.3e3 S/cm</td>
<td>2003</td>
<td>Electrical conductivity was measured using the four-probe method.</td>
<td>[119]</td>
</tr>
<tr>
<td></td>
<td>HiPCO SWCNT heat-treated.</td>
<td>solution Network</td>
<td>9.0 e2 S/cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>film functionalize</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Individual nanotubes</td>
<td>individual</td>
<td>0.17 to 196 S/cm</td>
<td>1997</td>
<td>Smalley</td>
<td>[1]</td>
</tr>
<tr>
<td>7</td>
<td>SWCNTs rope-like (70-90 %).</td>
<td>50-200 Å diameter</td>
<td>1e4 to 2.9e4 S/cm</td>
<td>1996</td>
<td>1-Measuring the electrical resistivity of single rope by four probe point. 2- Rope length ten to hundred micrometers.</td>
<td>[120]</td>
</tr>
</tbody>
</table>
To this end, SWCNTs represent a promising material which can be preferred for a variety of applications. Most of the work done in this area cannot be held without changing the structure of SWCNTs which will undermine their superior properties. Most of the researchers mentioned before do not provide strong evidence for the process of producing well-aligned monolayer films of SWCNTs, which means the SWCNTs in the produced films were randomly oriented. That led to the need of using a percolation process before reaching a significant electrical conductivity for the produced films, which will influence the properties of SWCNTs used.

In this study we will show a new methodology to produce well-aligned SWCNTs inside a transparent PMMA matrix is a big advantage in the field of transparent conductor films and their composites.

1.5 SWCNTs Nanocomposite Material.

Nanocomposite material, in general, is made from two or more significantly different materials in their physical properties. It’s the material at which one constituent has a dimension less than 100 nm [121]. The produced material will have different properties and characteristics than the individual compound. The main feature is that the nanoscale constituent can dramatically modify and improve the properties on the microscopic material [3]. SWCNTs with their superior mechanical and electrical properties are one of the best candidates for this new class of multi-functional composites [3]. For the polymer matrix, the PMMA (Polymethylmethacrylate) is used due to their
unique optical properties are also the most promising candidate for multi-functional
composites and especially for transparent conducting electrodes applications.

Many factors can influence the properties for the nanocomposite materials. One of
the most important factors is the alignment of tubes in the matrix and interaction between
CNTs and polymer chains [122]. The structure of the nanocomposite is more complex
than that of micro-composite [123]. Generally, SWCNTs add to the matrix to enhance
their mechanical properties, increase stiffness and increase electrical conductivity as
shown later in the experimental section. Therefore, the uniform dispersion of CNTs in the
matrix without damaging the tubes will affect the process of transferring loads between
CNTs and the matrix which will result in the strengthening of the nanocomposite [124].
This point is still a major challenge in the field of a multi-functional nanocomposites.

Table (1-2) below summarizes most of the measured electrical properties for
SWCNTs nanocomposite films [3, 122, 124-127].

Our goals for this research are to producing large uniform monolayer films of
well-aligned SWCNTs; studying the characteristics (mechanical and optoelectrical) of
such films and their composite; and investigating the effect of direct mixing vs. in-situ
polymerization on the properties of the produced films and their nanocomposites.
### Table (1-2) Electrical properties for SWCNTs nanocomposite films.

<table>
<thead>
<tr>
<th>No.</th>
<th>Nanotubes composite materials used</th>
<th>Film Thickness and typed</th>
<th>Measured Conductivity</th>
<th>Year</th>
<th>Notes</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pure (PANI) polymer 1wt% SWCNTs 8wt% SWCNTs</td>
<td>Synthesis Synthesis Synthesis</td>
<td>1.60 $\times 10^{-2}$ S/cm 1.00 $\times 10^{-1}$ S/cm 3.57 $\times 10^{-1}$ S/cm</td>
<td>2017</td>
<td>1- Four probe method used. 2- Pellet of SWCNT. 3- The conductivity of all samples decreases with increasing the temperature. 4- Polyaniline (PANI) is the most conductive polymer used because it’s easy synthesis and good electrical properties so that it can use as an electronic material.</td>
<td>[128]</td>
</tr>
<tr>
<td>2</td>
<td>SWCNTs mixed with polycarbonate.</td>
<td>Nanocomposite from mixing SWCNTs with the matrix at different wt.%</td>
<td>10 $\times 10^{-3}$ S/cm</td>
<td>2017</td>
<td>1- Flexible and conductive nanocomposite based on using SWCNTs. 2- Conductivity increase as the wt.% of SWCNTs increase.</td>
<td>[129]</td>
</tr>
<tr>
<td>3</td>
<td>Pristine SWCNTs</td>
<td>Ceramic matrix composite</td>
<td>2 S/cm</td>
<td>2017</td>
<td>1- Developing ceramic matrix composite containing (1-6) vol. % SWCNTs. 2- Hot process method is used.</td>
<td>[130]</td>
</tr>
<tr>
<td>4</td>
<td>SWCNTs mix with polyurethane nanocomposite</td>
<td>SWCNT oriented in the matrix.</td>
<td>3.7 $\times 10^{-1}$ S/cm</td>
<td>2017</td>
<td>1- Conductivity increase as wt.% of SWCNTs increase. 2- A graph shows the relation between the wt.% of SWCNTs and the conductivity values.</td>
<td>[131]</td>
</tr>
<tr>
<td>5</td>
<td>Swcnts with PMMA 0.5wt% swcnt 1wt% swcnt</td>
<td>Network Functionalization</td>
<td>1e-11 S/cm 1e-6 S/cm</td>
<td>2004</td>
<td>Draw as a curve</td>
<td>[132]</td>
</tr>
</tbody>
</table>
1.6 Motivation and Objectives.

1.6.1 Motivation.

To this end, it’s clear that:

- Successful processing of highly aligned monolayer films of SWCNTs is still needed.
- Investigation of the mechanical and optoelectric properties of such films is crucial.
- Ability to process a monolayer of SWCNTs/PMMA composite films with well-aligned SWCNTs has not been developed yet; hence, their mechanical and optoelectrical properties have not been yet investigated.

In this work, we will address every point of such challenges as shown later.

1.6.2 Objectives.

The primary purpose of this study is to utilize the LB techniques to produce a monolayer of zigzag single-wall carbon nanotubes with a high degree of alignment to study their properties without the need of any chemical modification process. Due to the assembly and alignment process of SWCNTs, we aim to improve the mechanical and electrical properties of the produced films and their transparent nanocomposites without causing any additional defects or adding additional impurities in the fabrication process.
The sheet conductivity of the produced films will be observed in both directions to show the effect of the tubes’ orientation on the conductivity measured. The in-situ polymerization process (bulk polymerization) will also be included in this study to explain the difference in mechanical properties for the produced composite films between the regular mixing of tubes with the polymer (as a dry powder mix with a solvent in a particular concentration) and the in-situ polymerization process as the weight fraction of the nanotubes changes.

To fully characterize the nanofilms and transparent nanocomposite we will utilize Scanning Tunneling Microscopy (STM), Raman spectroscopy and High-Resolution Transmission Electron Microscopy (HRTEM) [133-135]. In addition to using Keithley device to measure electrical properties of the produced films [136-138].

Many factors have been optimized to produce the supposed layer including sonication, and evaporation time. The structure of tubes in the produced films is altered as will be shown later because in this work none of the surfactant (surface treatments) or any synthetization (chemical treatments) methods are used.

The deposition process by using LB is applied for different substrates. Glass and silicon substrates are used in Raman spectroscopy device. Steel substrates are used for the scanning tunneling microscopy analysis device, as shown later.

The films’ stiffness is calculated for a monolayer of SWCNTs and multilayers in addition to the relation between the produced films’ stiffnesses, and the SWCNTs volume
fraction \( V_f \) is also observed. Since the structures and orientations of SWCNTs in the produced films are related to their electrical properties, the effect of measuring electrical properties with rotation angles for monolayer are considered. The electrical properties of the produced nanocomposite are observed.

The work in this dissertation is divided into the following sections. Chapter two describes experimental details which include materials and devices used with overview types and properties, in addition to the main equipment required for the thin films fabrication process. Chapter three describes the process of producing a thin film monolayer processing method with the characterizations of the produced monolayer in addition to studying the stiffnesses and optoelectrical properties. Finally, Chapter four includes the conclusions and recommendations for this work and future development.
CHAPTER 2: Experimental Details.

2.1 Materials Used:

2.1.1 SWCNTs: Properties and Structure.

In 1993 Iijima and his co-worker Ichihashi announced the observation of the most exciting carbon nano species named Single-Walled Carbon Nanotubes (SWCNTs) [139]. The found SWCNTs was in carbon soot observed in the carbon arc chamber in a similar way to that used for fullerene production [140]. A new field of carbon nanoscience was established by the discovery of fullerene molecules and carbon nanotubes [53]. A fullerene can represent as a molecule of carbon in the form of spheres, tubes, and many other shapes [8, 55]. The cylindrical shape fullerenes are named carbon nanotubes. The structure of the fullerenes is similar to graphite, which is formed from stacking graphene sheets in which the hexagonal rings are linked together [8]. One dimensional structure usually in the form of tubes or cylinders the diameter ranges usually lie between fractions of nanometers to several nanometers. If they form single tubes, they are named single-wall carbon nanotubes [8]. In the case of several tubes concentrated inside each other, they are called Multiwall carbon nanotubes [141]. Figure (2-1) shows high resolution (HRTEM) images of SWCNTs of diameter (37 nm) [142].
Figure (2-1) High resolution images of SWCNTs of diameter 37 nm adopted from [142].
The easiest method to imagine the structure of carbon nanotubes merely is rolling a sheet of graphene to form single, double or multi-wall carbon nanotubes [143]. Carbon nanotubes are representing one of the most reliable materials that are known to humans [142, 144, 145]. They possess a unique structure with special electrical properties which nominates them to be perfect for a variety of applications. A SWCNTs usual size is of the order of nanometer with a high aspect ratio (length to diameter ratio), end of the tubes could be open or closed [146]. Length of SWCNTs can be several micrometers while the diameter is a couple of nanometers; as an example the diameter of human hair is 50,000 times larger than the diameter of the nanotubes [146]. Figure (2-2) shows how the graphene sheet can warp to form the structure of single wall carbon nanotubes.

As mentioned before SWCNTs are formed by rolling a single sheet of graphite, the hexagonal typical (honeycomb) which represents the lattice structure of the graphene sheet which is made from covalent SP² hybridization bond connecting the carbon atoms [8]. Figure (2-3) shows structure of SWCNTs and MWCNT with the hexagonal shapes.
Figure (2-2) A schematic of how the graphene sheet can be rolled to form different shapes of nanotubes adopted from [147].
Figure (2-3) A comparison between the structure of (single and multi) wall carbon nanotubes adopted from [148].
Here, $a_1$ and $a_2$ represent the two principal axes directions of the unit vector of the primary hexagonal unit cell as shown in figure (2-4). If any two carbon atoms on flat sheet geometry are connected by a straight line and then the sheet is rolled around that axes of the selected line, this becomes the circumference of the tube [149]. In this case, the two atoms anticipated at the start and end of the line chosen must coincide and become the same point on the tube surface as shown in figure (2-4) [55]. If a random spot on the surface selected to be the origin (0,0) in the two-dimensional flat sheet, the coordination of any other flat sheet can be easily described in term of ($a_1$ and $a_2$) unit vector [8].

The line connecting any two-carbon atoms on the flat sheet geometry can usually be expressed as a vector ($C_h$) which can be represented at the multiplication of the unit vectors ($a_1$ and $a_2$) by the assigned position for the vector point of the original coordinate (0,0). It can be represented by the mathematical relation shown:

$$\overrightarrow{C_{h_1}} = n\overrightarrow{a_1} + m\overrightarrow{a_2} \equiv (n,m) \quad \text{........ (1)}$$

The vector that is representing the circumference of a tube is the chiral vector ($C_h$). The angle that is measured between the chiral vector and $a_1$ is defined as the chiral angle ($\Theta$) as shown in figure (2-4).
Figure (2-4) The typical hexagonal of a graphene sheet which made from hybridization of the carbon atoms adopted from [8, 74].
The chiral vector can be used to identify the SWCNTs. Two multiple integers \((n, m)\) are used to define the chiral vector. Depending on the tubes’ chiral angle architectural configuration, the C-C bond can be classified into three distinct categories: armchair, zigzag and chiral tubes. Armchair tubes are formed when the chiral tube angle is equal to \(30^\circ (\theta = 30^\circ)\) in this case the multiplication of the tubes’ vectors is similar which mean \((n=m)\). Zigzag tubes all have a chiral angle equal to zero \((\theta=0)\) and their \((m)\) multiplication is always equal to zero [66]. All the remaining other tubes with \((0 < \theta < 30^\circ)\) are classified as chiral tubes. Figure (2-5) shows the schematic of three types of tubes.

The chirality angle is not only determining the geometry of the SWCNTs, but also many of their characteristic properties such as thermal, optical and electronic properties of the tubes [148]. Depending on their chirality, electronic band structure of the nanotubes can be classified as either metallic or semiconducting behavior materials [145]. The armchair single-wall carbon nanotubes, in general, behave as metallic \((m=n)\) meanwhile one-third of the chiral and zigzag are expected to be metallic [144, 150]. The remaining part of the SWCNTs are supposed to be semiconducting; figure (2-5) shows also the metallic and semiconducting nanotubes and how they are identical in some points [139]. Several diameters of SWCNTs have been observed as max as 5 nm and lower to 0.4 nm [136].
Figure (2-5) Schematic for different types of SWCNTs adopted from [8, 74, 151].
In general, most of products of the SWCNTs contain a mixture of both types of the tubes, metallic and semiconductor. Sometimes they need to be separated for some specific electronic applications. Depending on the growth process and/or conditions used for the exact ratio of metallic to semiconducting can be varied [152]. Several methods are reported to separate metallic from semiconductor SWCNTs, and some of them have an efficiency close to 95% [108]. Those separation methods can be done during growth, during solution preparation, as post-process step, or during deposition. An example of using nanotubes in the bulk material will enhance the strength without needing a high degree of purity [66, 144, 148]. On the other hand, for electronic applications the purity becomes crucial [74, 87].

The main purpose of the SWCNTs which work as a filler in the composite matrix is to increase the conductivity of the insulator matrix and to enhance mechanical properties of the composite matrix [153]. The mechanical properties such as Young's modulus and tensile strength (in this case it can be considered as the stress required to break the sample) of the produced composite will mainly depend on the orientation and the percentage of content of SWCNTs in the nanocomposite [144]. Many results are obtained from mixing CNTs with different matrices and then testing at the macro level [154]. Many different models are used to estimate the mechanical properties of SWCNTs and how it affects the properties of the produced composite [155]. The electrical properties of the produced films are mainly influenced by the structure of the SWCNTs [156]. Therefore, the electrical properties will be examined in this research to observe the
effect of alignment process of SWCNTs on the improvement in the electrical properties as a comparison with other studies made.

There are three techniques used to produce SWCNTs: arc discharge, laser ablation and chemical vapor deposition (CVD) [157, 158]. Arc discharge represents one of the simplest methods which depends on high temperature to produce SWCNTs [159]. The produced SWCNTs by this process can have structural defects due to high temperature used in the processing process [160]. Also, this method can produce a small amount of SWCNTs which is needed for more purification steps [158].

Laser ablation is a more expensive method than arch discharge and CVD methods to produce SWCNTs [150, 161]. Laser ablation process can provide a control over the diameter of the produced SWCNTs with a good quality product [2, 87, 150, 161]. However, it’s not suitable for mass production of SWCNTs [161].

Chemical vapor deposition (CVD) represents one of the most usable processes to produce SWCNTs [162, 163]. The size of the metal particles used in this method will control the diameter of the produced nanotubes [164]. CVD process can produce SWCNTs with good quality and high performance suitable for different applications [165]).

To this end, some information about the structure, production and properties of SWCNTs are mentioned. SWCNTs from “LUNA®” brand is used in our research as shown in the result section.
2.1.2 Poly (Methyl Methacrylate) PMMA Polymer Properties and Structure

PMMA is a polymer consisting of esters of methacrylic acids with a chemical formula \((C_5 H_8 O_2)_n\). It’s bright and colorless polymer available in the market in the form of pellets or sheets under the name Plexiglas or acrylic glass. It’s produced by free-radical polymerization of methyl methacrylate (MMA) in bulk. PMMA is a linear thermoplastic polymer with high mechanical strength and Young’s modulus, with a low elongation at breaking and it doesn’t shatter or rupture [166]. PMMA is considered as one of the hardest thermoplastics with high resistance to scratch and with high impact resistance [167-169]. PMMA has an excellent dimensional stability with low moisture and water absorption capacity. Also, it exhibits excellent optical properties, so that it can transmit more light. The density of PMMA is between 1.17 to 1.2 g/cm\(^3\) which can consider it as lightweight material, also it has high glass transition temperature and mold shrinkage [170]. Figure (2-6) shows the structure of PMMA.

PMMA can dissolve in most of the organic solvents due to their structural properties and it is also more acceptable to modify in their performance than any other types of polymers [167]. The concentration of the used PMMA with solvent is controlled and then sonicated after mixing it with nanotubes to promote the distribution of the nanotubes over the surface of the PMMA spherical particles and to prevent particle clustering [171].
Figure (2-6) structure of PMMA.
In current work Poly (methyl methacrylate) (PMMA), methyl methacrylate (MMA) monomer and UV initiator (2-HYDROXY-2-METHYLPROPIOPHENONE) are purchased and certified from Sigma-Aldrich Science in the USA.

2.2 Measuring Techniques

Several measuring and characterization techniques were utilized in this study to produce and characterize the produced films. The following is a detailed description of each.

2.2.1-1 Langmuir-Blodgett Technique.

Langmuir-Blodgett (LB) films are created by the process of successive deposition of a series of monolayers related to one or more types of amphiphilic molecules which mainly spread at the interface between water and air [172]. Those films usually form from a regular planar array of molecular layers which have a well-known and predetermined thickness. The term ‘Langmuir-Blodgett films’ refers to the monolayers deposited from the liquid-gas interface on a selected solid substrate [13]. Both the liquid and gas typically used are water and air. The interesting issue about the LB technique is their ability to produce a sequence of ordered multilayers of organic molecules which can be controlled precisely. The constructed structure by using LB can show a high degree of order in the direction normal to the plane, which can be relied on and confirmed by using
the x-ray diffraction. The degree of order can vary widely within the plain depending on
the material and details of deposition. A historical development for the Langmuir-
Blodgett can be discussed as shown: the first historical reference to this technique is
made long time ago by Aristotle who studies the process of spreading oil on the surface
of troubled water. After that, many translations made by other researchers such as Hett
(1837), mentioned that “the process of pouring oil on the surface of water make it more
transparent” [13]. Pliny in 1864 mentioned how the sea water becomes smooth by oil “so
divers sprinkle oil from their mouth because it calms the rough element and carries light
down with them.” [13]. Till the end of the nineteenth century Agnes Pockels (1894),
successfully produced significant improvements by spreading a monolayer in her private
home using common stuff. In 1913 Davaux and Hardy found that a good monolayer can
be formed from spreading material with a polar head group. In 1917 Langmuir adopted a
study of monolayers of amphiphilic compounds at the level of the air-water interface and
how the films can transfer from a specific liquid surface to a solid substrate, which later
gave his name to that subject. In 1935 Katherine (a colleague of Blodgett) successfully
gave a systematic account of multilayers of “carboxylic acids deposited on a solid surface
from the air-water interface” [13]. After this year of publishing their work, many research
papers appear on this topic. It took about three decades till Kuhn and his colleague
Gaines (1966) adopted the interest of using the LB techniques in the field of electronics.
Their research was widely accepted in Europe, Japan, and the USA, so they opened a new
era for using the LB techniques in many practical industrial applications that require ultra-thin, large scale, and well-structured films deposition.

2.2.1-2 Langmuir-Blodgett Device.

The first part that can be discussed is the trough and the barrier which are used in the compressing system. Trough represents the first part of the system that can act as a container for the subphase, which is named the Langmuir-Blodgett trough. The trough always is in contact with the subphase; therefore, the material used should be inert, not able to act with the organic solution used in the cleaning and spreading process [173]. The barriers are connected to motors with a particular gearing system combined with certain belts and controlled by a computer program to assess its speed and direction. Figure (2-7) shows schematic drawing for the trough; a well may also be presented in the middle of the trough (in common cases, sometimes it could be close to one of the edges) [93, 133]. The well used in the deposition process is made from a noble material providing the base for the substrate holder. The direction of the deposition process is also controlled by motors with a specific gearing system held together by belts. The number of the produced layers can be monitored by a computer screen. After spreading the solution (solvent and nanomaterial) on the surface of the trough and given a suitable time for the solvent to evaporate, then an order can be provided to the barrier to move and start the compressing process. A phase diagram will begin to show up on
Figure (2-7) Langmuir-Blodget equipment.
the attached computer monitor as shown in figure (2-8) which measures the variation of the pressure in mN/m units and the compressed area in cm$^2$ or Å$^2$. A sudden modification in the slope of the pressure curve can indicate the formation of the solid phase. After the spreading process starts, in the beginning, the molecules are assumed to be in the gaseous state with no interaction between them and the pressure will be zero [174]. As the barrier moves with time the slope of the curve starts to change which indicates the transferring from the gaseous to the liquid state [175]. After that, a sudden change in the slope happens as the barrier compresses further, which indicates the formation of solid state as shown in figure (2-8).

The second part is the Wilhelmy plate and the pressure sensor. The two common processes used in monitoring the surface pressure is the Wilhelmy plate and Langmuir balance. Figure (2-9) shows the dimension of the Wilhelmy plate. This plate is connected to the pressure sensor, the forces acting on this plate are gravity and the tension which are directed downward while the buoyancy acts upward because of the displaced water. The acting force can be expressed by the mathematical equation [176]:

$$F = (\rho_w)gLwt + 2\gamma(t + w)cos\Theta - gtw\hbar(\rho_l) \quad \ldots \ldots \quad (2)$$

$l$, $w$, and $t$ are the dimensions of the rectangular plate. $\rho_w$ is material density, $\rho_l$ is liquid density, $h$ represents the immersed part of the plate in the liquid, $g$ represents the gravitation constant, $\Theta$ is the contact angle.
Figure (2-8) film phases form as the compressing process continues with time adopted from [172].
Figure (2-9) Wilhelmy plate details a cross-section adopted from [177]
The Wilhelmy plate is formed from a filter paper or a small plate from a nonreactive material which is usually platinum. It is thin with a rectangular shape of a few centimeters in length and height. Wilhelmy plate should be in contact with the surface of the subphase after connecting to the pressure sensor and then it should be left for a period to get settled [133]. The water used for the subphase should be of higher purity distilled and deionized then microfiltered immediately before using [178]. The chosen material for the manufacture of the Wilhelmy plate should have good wetting when contacting the liquid surface [22]. A picture for the isotherm produced by Langmuir-Blodgett techniques of using distilled water is shown in figure (2-10). Deionized water is used in our work to compare the results for the produced isotherms; there was no significant difference from the same isotherm produced by using distilled water.

The Nima® device used for our experimental work has a rectangular shape trough. It consists of two side troughs which have two compressing barriers and two pressure sensors. The entire compressing and deposing processes are controlled automatically by computer. After opening the software page series of command windows will show up, which include barrier menu, dipping menu, graph menu and calibration menu. The variety in the software options menu gives the user more degree of freedom to monitor and control the deposition and compressing processes. The instrument with their controller is kept in a clean environment with a steel frame bench covered by transparent plastic walls to reduce the external vibration and air currents.
Figure (2-10) An isotherm for pure water before starting the separation process.
The area of the trough when it’s completely opened is 500 cm\(^2\) and after
compressing it can reach about 50 cm\(^2\). The width of the trough is constant and equal to
20 cm. Those numbers will be used later in the calculations processes. For the produced
films the compressing speed for the moving barrier is constant, and it was set to 100
cm\(^2\)/min. The deposition speed is considered as 5mm/min. Figure (2-11) shows an image
for the Nima® device.

2.2.1-3 Langmuir-Blodgett Film’s Deposition.

For Langmuir film to be formed, it’s necessary for the selected substance to be
insoluble in water and for each molecule to have a hydrophilic region which will help it
to reside on the surface of the subphase (usually distilled water). Langmuir film can be
defined as a two-dimensional crystal arrangement of molecules at the level of the air-
water interface [133] as shown in Figure (2-12). The usual process used for formation of
the Langmuir-Blodget films is by lowering and raising a solid substrate through the film
while the surface pressure should be maintained constantly. A hydrophobic (water-
hating) and hydrophilic (water-loving) interaction can be illustrated as if considered a
mixture of a polar liquid, for example, water and carboxylic acid [106]. Two distinct
scenarios can be applied in this situation. Entropy consideration required the added
carboxylic acid to be dispersed into the water, while the internal energy tries to reduce
configuration
Figure (2-11) Nima Technology UK model 1222D2.
Figure (2-12) Schematic of the LB trough with all the other main parts adopted from [175].
interaction of the polarity between water molecules and with polar head groups. Due to that effect, the polar and non-polar interaction will be reduced.

A monolayer of the amphiphilic molecules can be existing at the level of the liquid-gas interface. After observing the produced molecules, it becomes easy to recognize that the polar part of the molecular group will be in contact with the polar liquid [176].

The common forms of Langmuir-Blodget film deposition can be shown in figure (2-13). The first case when the substrate is a hydrophilic, the monolayer can be transferred as a carpet as the substrate is raised through the water in the air-water interface level [179]. To get a proper film deposition, the substrate must be placed inside the subphase before the monolayer spread, to avoid agglomeration. The second case when the substrate used is hydrophobic, the deposition process can take place on the up selected path, which can be achieved by lowering the substrate to the water subphase [13]. Three common types of depositions that can be produced depending on the stacking pattern, which are Y, X and Z modes. The most common deposition which can produce on the down and up path head-to-head and tail-to-tail which is called Y-type and it’s the most common one. The X-type deposition is when the downstroke maintains for the monolayer only, while the Z-type is when the transfer happens to the upstroke as shown in figure (2-14). A mix deposition mode sometimes is encountered for some materials
Figure (2-13) Deposition process by using Langmuir-Blodgett technique for a monolayer and multi-layers produced process adopted from [180].
Figure (2-14) Different types of produced molecular films formed by the deposition process adopted from [179].
depending on the deposition type as the LB film is built up. The nature of the materials involved represents an essential aspect in selecting the speed in which the substrate can move without disturbing the air-water level [175]. For deposition process to be successful, the common barrier speed used is 4 mm/min with a temperature in the range of 4 to 30 °C for a variety of materials [176]. If the temperature is raised above 30 °C, the evaporation takes place which will affect directly on the subphase. In addition to pressure, many other factors can affect the quality of the produced films such as physical structure and the chemical composition of the substrate surface [133, 180].

2.2.2 Films Characterizations techniques:

2.2.2-1 Scanning Tunneling Microscopy (STM).

Scanning Tunneling Microscope (STM) represents the main instrument prepared to do straightforward acquisition of three-dimensional (3D) pictures of solid surfaces with atomic determination [181]. Figure (2-15) shows an image for the STM device used in the current research. STMs must be utilized to examine surfaces that are electrically conductive to some degree [182]. Very high vertical determination resolution is acquired because the tunneling current changes exponentially with the separation between the metal tip and the examined surface going about as two electrodes. Regularly, tunneling current minimized by a factor of 2 as the partition is expanded by 0.2 nm. High sidelong resolution depends upon the sharp tips [183].
Figure (2-15) Nano Surf easy Scan, E-line (STM).
The rule of STM is clear. A sharp metal tip (one anode of the tunnel intersection) is brought sufficiently close (0.3–1 nm) to the surface to be examined (second cathode) that, at an advantageous working voltage (10 mV–1 V), the burrowing current differs from 0.2 to 10 nA, which is quantifiable. The tip is scanned over a surface at a separation of 0.3–1 nm, while the tunneling current amongst it, then the surface is detected [184].

The STM can be worked in either the consistent current mode or the steady height mode, as shown in figure (2-16). Depending on the received feedback, the height of the tip z is changed to keep the current constant. The removal of the tip given by the voltage connected to the piezoelectric drives at that point yields a topographic map of the surface. Then, in the steady height mode, a metal tip can be checked over a surface at about steady height and constant voltage while the current is observed. The feedback network reacts quickly enough to keep the average current steady. The steady current mode is used typically in the case of atomic-scale images [183]. This mode isn't handy and workable with the nonuniform surfaces. A three-dimensional picture [z (x, y)] of a surface comprises different scans [z(x)] showed along the side with each other in the y-direction [185]. It ought to be noticed that if different atomic species are available in the observed sample, the different atomic species within the sample may deliver distinctive tunneling current for a given bias voltage.
Figure (2-16) two-modes operation of the STM device adopted from [183].
In this case, the stature information may not be a direct portrayal of the topography of the surface of the sample [186]. Since the STM device is more concerned about the surface of the sample, so it becomes essential to prepare the surface and clean it very well before starting the deposition process to produce the required film to test. The assembly of the particles on surfaces is mainly dependent on the interaction between the atom-atom and the atom particle substrate interactions [183, 186]. The epitaxial growth is controlled due to that interaction between the molecules (adhesion) in addition to the growth process [187]. Another typical property can be controlled due to the atomic interaction which is the surface absorption and mobility. This turns out to be imperative amid the structure arrangement since the dispersion decides the probability of meeting different adsorbates. The most important feature for the surface science is the diffusion of the molecules and the atoms across the surface and their aggregation into the complex structure [188, 189].

The STM device can determine interactions between the molecules themselves and the molecules with other atoms in addition to following a single particle [190]. STM device represents one of the most usable devices used in observing the structure of different materials at the nano-level [191].

Specimens to be scanned with STM must be sufficiently conductive to permit a couple of nanoamperes of current to flow from the inclination voltage source to the zone to be examined [191]. In different situations, nonconductive samples can be covered with a thin layer of a conductive material to enhance imaging. The tunneling current and the
bias voltage depends on the prepared sample [183]. Generally, they are set at some
standard values for commitment and fine-tuned to improve the nature of the image. The
features of the scanned sample represent an essential aspect for the scan measure use. A
most extreme output rate of 122 Hz can be utilized which is typically identified with the
scan size [189]. Output rate over 10 Hz is utilized for small scan areas (ordinarily 60 Hz
for nuclear scale imaging scanner) [190]. The scan rate should be brought down for
substantial outputs, particularly if the example surfaces are rough or contain huge
advances [182]. Moving the tip rapidly along the examined surface at high output rates
with high sweep sizes will prompt a tip crash. Basically, the output rate should be
conversely relative to the sweep estimate (ordinarily 2–4 Hz for 1 lm, 0.5–1 Hz for 12
lm, and 0.2 Hz for 125 lm scan size) [182]. Output rate long/time is equivalent to filter
length partitioned by the scan rate in Hz. For instance, for 10 µm × 10 µm filter estimate
checked at 0.5 Hz, the output rate is 10 µm/s. Ordinarily, 256 × 256 information designs
are most regularly utilized. The sidelong determination at larger scan area is around
equivalent to examined length divided by 256.

In this study Scanning Tunneling Microscopy (STM) is used to provide
measurements in the nano levels, which can show the surface of the tubes and can
contribute in the determination of the tubes diameters and qualities [186].
2.2.2-2 Raman Spectroscopy.

Raman spectroscopy is spectroscopy named after Indian physics researcher Sir Chandrasekhara Venkata Raman in 1922, by using only a simple instrument he discovered and called it Raman spectroscopy [8]. He used his own eyes, sunlight and a telescope to recognize this remarkable phenomenon. Over time, a fast improvement in this field has taken place especially after using sophisticated equipment which includes computers, better excitation sources, improved detectors and holographic light gratings [192]. Raman spectroscopy represents one of the non-contact methods useful for measuring vibrational, rotational and other low-frequency modes in the system [193]. Raman spectroscopy represents one of the common aspects used in the chemistry field because it can provide a fingerprint for the structure by which molecules with their chemical bonding can be identified [194]. The inelastic scattering of light by matter can be defined as the Raman effect or Raman phenomenon. When matter scatters monochromatic light, two types of interaction can take place and result in two distinguishable scattering processes: Rayleigh scattering and Raman scattering [195].

Rayleigh scattering, in this type of interaction there is no energy transfer or change between the incident light molecules or atoms of tested matter. Therefore, the scattered photon should have the same energy or frequency as the applied incident light [195]. On the other hand, due to the interaction which involves energy exchange between the material molecules and the incident photon a new frequency or energy for the scattered photon will be produced. In this case, the difference between the frequencies of
the natural frequency and the incident photon will be called Raman scattering which is the elastic scattering in nature for the Raman effect due to the scattering effect of crystal lattices or molecules which either gain or lose photon energy [192]. Figure (2-17), shows the scattering in frequency due to the Raman effect; as illustrated in the previous paragraph the elastic scattering or Rayleigh scattering does not gain any change in the energy which means that there is no loss or gain due to interaction with the material. Inelastic scattering has two components which are experiencing a loss or gain of energy. The light that scatters with low energy is known as stokes line with a frequency equal to \( \nu_0 - \nu_r \), while the one high energy \( \nu_0 + \nu_r \) is known as anti-stokes lines as shown in figure (2-17). As a general measure, the intensity of the “Rayleigh” scattering is six orders of magnitude larger than the Raman scattering [192].

Since the Raman scattering process is weak in nature, the applied laser should be properly focused on the selected sample to ensure that the scattered light is efficiently connected. A coherent beam of monochromatic light placed by the laser can be used to excite Raman spectra [193]. Due to the laser property, the intensity is sufficient to produce a useful amount of Raman scatter and allow clean spectra, free from extraneous bands. Good wavelength stability and low backward emission represent the main features for using the laser in Raman spectroscopy [196].
Figure (2-17) Energy levels for different scattering adopted from [192].
Most commercially available Raman spectrometers use a continuous laser wave such as argon-ion (514.5 nm), helium-neon (633 nm) or diode lasers (830 nm). Since the laser can provide a coherent beam of monochromatic light, it’s used to excite the Raman spectra. The intensity of the applied laser will be sufficient to produce a useful amount of Raman scatter and allow for clean spectra free of extraneous bands [196]. Figure (2-18) shows an image for the Raman spectrometer instrument used in the current study.

The photons from light are focused on a sample surface, and they are absorbed by the material molecules and scattered. The photons of Raman scattering can occur due to change in rotational, vibrational or electronic energy of the material molecules [196]. The molecules can be identified by plotting the energy of those transitions as a spectrum. The difference between the energy of the applied photon and the Raman scattered photon is equal to the energy of the vibration of the scattering molecule.

Rayleigh scatters can be specified when the scattered photons have the same wavelength as the incident photons source [197]. When the scattered photons are shifted to different wavelengths the Raman scattering effect will appear clearly. If the Raman scattered photons are shifted to a shorter wavelength, it is called Stokes shift [198]. In that case, if the scattered photons are shifted to a longer wavelength, the anti-Stokes shift will be produced. In the Rayleigh scattering, the excited electron is retained back to the same level that it starts with.
Figure (2-18) Renishaw inVia Raman microscope device.
Anti-stokes Raman scattering happens when the final energy level is higher than the initial level, while Stokes Raman scattering occurs when the final level of energy is lower than the initial level. In general, stokes scattering is much more likely to happen than anti-stokes scattering. The reason for that is the Boltzmann distribution for the electron is most likely to be in lower energy state [198].

2.2.2-2.I Raman Characteristics of SWCNTs

High aspect ratio represents one of the major characteristics of the SWCNTs, which have well-defined atomic structure. One of the methods used to determine the orientation of the SWCNTs is by applying polarized light parallel or perpendicular to the SWCNTs axis. After analyzing the reflected light, a lot of information can be collected about the dimension of the tubes [192].

Raman spectroscopy is one of the most popular techniques used for characterization of SWCNTs. Raman spectroscopy can scan the energy of excitation light and produce Raman maps. Those maps can have a unique identification (n,m) for nanotubes. Raman mapping can detect not only the semiconducting but also metallic tubes.

Radial breathing mode (RBM) is related to the radial expansion-contraction of the nanotube. The mathematical relation between the nanotube diameter and frequency \(v_{RBM}\) can be represented as [194]:
\[ \nu_{RBM} = \frac{A}{d+B} \] \hspace{1cm} (3)

Where (A and B) are constant depending on the structure of the nanotubes.

For individual nanotubes in nanometers (nm):

\[ \nu_{RBM} = \frac{234}{d+10} \] \hspace{1cm} (4-A)

For double wall nanotubes

\[ \nu_{RBM} = \frac{248}{d} \] \hspace{1cm} (4-B)

Those mathematical relations are beneficial in deducing the CNTs diameter from the RBM position. Typical RBM range is between 100-350 cm\(^{-1}\) as shown in figure (14).

Bundling mode, which is a particular form of RBM is named due to the collective vibration in a bundle of SWCNTs [195].

G- mode, represents the fundamental mode (G from graphite). It is represented to planar vibrations of carbon atoms and also presented to the planar vibration of carbon atoms in most graphite [196]. From figure (19) it is clear that “G-band” of SWCNTs is shifted to the lower frequencies relative to graphite (1580 cm\(^{-1}\) ) and then it spreads to several peaks. Both of the splitting patterns and intensity depend on the tubes structure and excitation energy [196]. The G-mode can be used with lower accuracy that RBM to estimate the diameter of the tubes and whether they are semiconducting or metallic tubes.
D-mode, this type of frequency is presented in many graphite-like carbons and also originated from structural defects. One of the essential features to qualify the structure quality of carbon nanotubes is the ratio of the G/D modes. This ratio can give an idea of the functionalization of the nanotubes. As this ratio increases significantly to more than 100, which provides an indication of high-quality nanotubes. For lower functionalization of nanotubes, the G/D almost remains unchanged [200].

G’-mode represents the second strongest after the G-mode in graphite. The intensity of the G’-mode is usually stronger than the that of the D-mode due to the possibility of transitions of the system from one quantum state to another [201]. D-mode usually indicates the defect in the structure, so it is forbidden in the ideal nanotubes. The range of the G’-mode is between 2500-to-2900 cm$^{-1}$. This mode represents the intersite feature of the SP$^2$ carbon, which is always observed in the Raman spectra even when the D-band is not recognized. Both of the semiconductor and metallic SWCNTs can be observed the G’-band. The spectral position of the G’-mode depends on the diameter, which can be used roughly to estimate the diameter of the SWCNTs [201].

Anti-stokes scattering, since the Raman scattering from CNTs is resonant in nature, can be observed as both stokes and anti-stokes scattering. The excitation process can occur to the tubes whose band gap energy is similar to the laser energy. The intensity ratio of the stokes/anti-stokes lines can be used to estimate the band gap of individual tubes. A focused laser beam is used in the measurement process, which can produce local
heat in the nanotubes without changing the overall temperature of the observed samples [198]. Schematic illustration for this mode is shown in a figure (2-19).

In this study, Raman spectroscopy is used to observe the alignment of the tubes in the produced films and to observe the type of SWCNTs used by analyzing the peaks of the waves measured as shown in the resulting section [195].

2.2.2-3 High-Resolution Transmission Electron Microscopy (HRTEM).

High-resolution transmission electron microscopy (HRTEM) is one of the devices which can transfer information from specimen to image [202]. Using both scattered and transmitted beams, HRTEM can provide an interference image [203]. The produced image is a phase contrast image and it can be as small as a unit cell of the crystal. HRTEM can provide information from observing samples on a very fine scale, finer than 0.2 nm [202]. In the point of an image plane, all the electron merging from the specimen are combined. HRTEM has been successfully and widely used to analyze crystal structure and the imperfection in the lattice for various types of material on an atomic resolution scale [202, 204, 205]. The principles of working of HRTEM are similar to that of TEM, but the provided image has higher resolution at the atomic scale level [203, 206, 207]. HRTEM can be used to observe the structure and diameter of SWCNTs. It also has the ability to show point defects and impurities at very precise levels [208-210].
Figure (2-19) Raman spectrum of SWCNTs and peaks assignment adopted from [199].
2.2.2-4 Keithley Instrument.

Keithley 2401 model represents the latest model in the 2400 series of the Keithley instruments family. This model can perfectly fit low voltage applications. It’s one of the analyzers for the semiconductor parametric with the ability to measure pA and μV. The precise measurements provided by this device for volt, current or resistance make it preferred for a variety of applications, especially thin films due to low resistance sensitive required. Keithley 2401 model can connect to a computer by using the IV- software. The device has two modes of sensing which are four and two points sensing. In addition to that, it can be programmed by using the sweep option which can accelerate the test automatically with the ability of continuous operation or single measurement with characterization of I/V, V/I, I/R, or V/R [118]. Figure (2-20) shows an image for the Keithley device used in this research.

Since the structure of SWCNTs mainly affects the electrical properties as mentioned in the previous sections; Keithley 2401 model is used to observe the electrical properties of the thin films of SWCNTs and their composite with the four-points probe because it can provide very sensitive measuring at a low levels (1μV−20V and 10 pA−1A) for both of volt and ampere, which makes it a perfect fit for thin films measurement applications [108, 211, 212]. The four-points sensing is used widely in measuring the resistance for thin films. It depends on using a separate pair for voltage (which will
Figure (2-20) Keithley 2401 device.
usually be inside) and current (which will usually be outside) with more accuracy than the two-point sensing [119, 129, 212].

2.2.2-5 Ultraviolet-Visible Spectrophotometer.

Ultraviolet-visible spectroscopy (UV-Vis) is an instrument used to quantitively analyze the amount of absorption and reflection of light from the tested sample. UV-Vis is usually used for thin films applications to measure the optical properties and thickness [213, 214].

Basic rule for UV-Vis is by measuring the intensity of light reflected from the surface of the observed sample and then compare it with the intensity from the source meter. Ratio between those two intensities is known as transmittance which is usually written as % T. In additional to that UV-Vis can measure the percentage of reflected light by comparing the intensity of light reflected from the surface of the sample with the original value from the source meter. Ratio between reflected intensity and source intensity is known as % R reflectance [215, 216].

The diversity in the absorption range of SWCNTs to the applied beam of light with low spectra bandwidth in addition to the best possible signal to noise ratio all those together can be better observed by using Cary® 50 Scans UV Visible Spectrophotometer [217-219]. This device can show the best performance for the UV analysis of thin films applications. Figure (2-21) shows an image for Cary 50 Scan UV Visible Spectrophotometer.
Figure (2-21) Cary 50 Scan UV Visible Spectrophotometer device.
2.2.2-6 Other Films Processing Instruments.

In addition to the devices mentioned in previous sections, others were used to observe the factors of the produced-monolayer films of SWCNTs; our work starts by using sonicator in a 60 MHz ultrasonic bath (Fisher Scientific, Model FS20) of constant frequency for a specified period of time. Figure (2-22) shows an image for the bath sonication device used in the current study. The main purpose for using this device is to achieve a homogeneity for the produced solution and to prevent agglomeration and aggregation of the used SWCNTs [220, 221].

After that the sonication process of solution is completed then the solution is centrifuged by using Beckman Coulter, Allegra™ X22R at 12000 RPM for anticipated period of time. The principal rule for the centrifuging process is separating the solid and the agglomerate part from the solution depending on the differences between the density of solutions and agglomerate particles. Due to high rotating speed and the effect of centrifuging forces the solid particles will collect on the sidewall and bottom of the centrifuged tubes. Figure (2-23) shows an image for the centrifuging device used in the current study. Only the pure part of the solution is considered after the centrifuging process is completed [222-224]. Film deposition was done on both glass and metal substrates simultaneously. Figure (2-24) shows images for most of the substrates used in our work.
Figure (2-22) Fisher Scientific, Model FS20.
Figure (2-23) Beckman Coulter, Allegra™ X22R.
Figure (2-24) Glass and steel types of substrates.
CHAPTER 3: Results and Discussions

3.1 Characterizations of SWCNTs.

In our work, highly purified Luna® single-walled carbon nanotube powder with less than 1 wt. % of metal catalyst remaining in them is used. Several tests are applied to characterize the SWCNTs and obtain precise details regarding their structure, namely, Raman spectroscopy, high resolution transmission electron microscopy, and scanning tunneling microscopy.

Figure (3-1) shows the radial breathing modes (RBM) region of the Raman spectrum for the Luna® SWCNTs used in this study after sonication and centrifuging. The RBM region of the spectrum shows three modes, at 106.85 cm\(^{-1}\), 156.3 cm\(^{-1}\), and 171.24 cm\(^{-1}\), with integrated peak intensity (area under the peak) of 500, 9978, and 27300, respectively. Hence, based on the Raman integrated intensity of the peaks, our sample mainly consists of two types of nanotubes at a ratio of 27% and 73% respectively. Since the majority (73%) of the nanotubes used in this investigation are metallic zigzag (18,0), we will consider only the presence of such tubes in our sample to simplify the Langmuir-Blodgett isotherm calculations.

In addition to the Raman analysis measurements, we conduct a High-Resolution Transmission Electron Microscopy (HRTEM) tests to observe the structure of SWCNTs used in our work. Figure (3-2) shows an image produced by HRTEM which provides
Figure (3-1) Radial breathing modes regions of the Raman spectrum with the characteristics of Raman modes measures.
Figure (3-2) HRTEM image is showing a single wall carbon nanotube at the nano level.
information about the SWCNTs diameter. From figure (3-2) it’s clear that the diameter of our used SWCNTs is 1.49 nm; this value will be used later to compare with the theoretically calculated value of SWCNTs diameter based on their chirality vectors.

Figure (3-3) shows a high-resolution Scanning Tunneling Microscopy (STM) image. The sample investigated was deposited on a steel substrate by using the LB techniques. The zigzag nature of the tubes which can be observed from the hexagons orientations and arrangements appeared clearly and can be recognized.

To this end, the information observed in the characterizations section of SWCNTs will be used in the next sections in the process of producing a monolayer of SWCNTs.
Figure (3-3) Scanning Tunneling Microscopy image showing the structure of SWCNTs.
3.2 Production of SWCNTs Monolayer Films.

Figure (3-4) summarized the experimental work related to the preparation of the solution and the process of sonication with considering the evaporation time. After mixing SWCNTs powder with dimethylformamide (DMF) solvent to improve the dispersion process, we start with sonicating our solution for 20 minutes then 1 hour with an increment of 30 minutes in each time as shown in the diagram of figure (3-4). The solution prepares from mixing purified zigzag SWCNTs powder with DMF solvent in clear and clean containers. For each anticipated sample we centrifuge it for 30 minutes and then dilute in the ratio of 1 to 10. The concentration of SWCNTs in pure centrifuged saturated solutions was measured using the gravimetric method and was found to be 0.046 mg/ml based on ten measurements using a balance with 0.1mN sensitivity [225].

After optimizing all the factors mentioned in figure (3-4), a monolayer of SWCNTs can be produced by using 1000 µl of solution (DMF and SWCNTs) sonicated for 3 hours then centrifuged for 30 minutes, finally left to evaporate the solvent for 30 minutes after spreading the solution on the subphase surface in the trough.
Figure (3-4) A diagram for the primary factors used in the experimental work and how they relate to each other.
In order to reach the optimum conditions of producing a monolayer film, the impact of each factor affecting the number of produced layers is studied separately. For example, during the separation process, the impact of evaporation time is considered, so three different evaporation times are selected (30 minutes, one and two hours), to study the effect of evaporation time on the number of the produced film layers. The same process is also applied for the quantity of the solution added to the trough as shown in the diagram of figure (3-4), (500 µl, 1000 µl, 2000 µl) with concentration of 0.046 mg/ml. Figure (3-5) shows the surface pressure with the compressed area isotherm for different quantities of SWCNTs solutions added to the trough for anticipated 6.5 hours sonication time which will mainly influence the number of the produced layers. Figure (3-6) shows examples for calculating the number of layers for different sonication times. For each one of those sonication times the surface pressure-area isotherm produced, and the slope of the solid phase is accounted then the number of produced layers is specified as shown.
Figure (3-5) The effect of solution volume added to the trough on the produced number of layers.
Figure (3-6) Effect of solution sonication times on the number of films layers produced for (1000 µl) solution, the line is provided to guide the eye.
3.3 Characterizations of SWCNTs Monolayer Films.

3.3-1 Calculations of a Monolayer Film Processing for SWCNTs.

Nanotubes diameters \( d \) can be calculated from their chirality vector multiples \((n,m)\) by using the equation [226]:

\[
d = \frac{a}{\pi} \sqrt{n^2 + nm + m^2} \quad \text{......... (5)}
\]

Where \( a = |a_1| = 1.421\sqrt{3} = 2.461 \text{ Å} \). Based on results presented in previous section (3.1), our SWCNTs are mainly metallic zigzag \((18,0)\) type. The number of carbon atoms per unit cell was shown to be equal to \(2N\), and \(N\) for the \(18,0\) nanotubes can be calculated according to the equation [226]:

\[
N = \frac{2(n^2 + nm + m^2)}{3d_H} \text{ since } n-m=3qd_H \quad \text{......... (6)}
\]

Where, \(d_H\) is the highest common divisor of the coordinate multiples \(n\), and \(m\), that equals 6 in our case leading to 72 carbon atoms per unit cell of the \(18,0\) SWCNTs. Hence the molecular weight of a unit cell of \(18,0\) SWCNTs equals 864 g/mole. This value will enable us to calculate the number of unit cells added to the Langmuir-Blodgett trough which will be used to calculate the area per unit cell of the formed SWCNTs film as explained below.

The SWCNTs unit cell length \((T)\) can be determined from the equation [226];
\[ T = \frac{a\sqrt{n^2+nm+m^2}}{\sqrt[3]{d_H}} \] since \( n-m = 3qd_H \) \ldots (7)

For the 18,0 nanotube, \( T \) equals 4.26 Å. Noting that the diameter of the tube should be increased by 3.37 Å to accommodate for the width of the electronic shell around the carbon skeleton area of a unit cell on the surface of the subphase surface should be \( T^*(d+3.37) = 74.45 \text{ Å}^2 \) \[8\]. Since the total numbers of unit cells are specified for a monolayer film area, it can also be used to calculate the number of the produced layers in the film as shown in figure (3-(7-A)). Using the value of the produced monolayer area will help in calculating the film thickness which is 1.42 nm and it’s in agreement with the value measured from HRTEM analysis before. The thickness value will be considered in calculating the produced films stiffness.

Figure (3-(7-A)) shows a typical LB isotherm with the solid phase region fitted to a linear equation to determine the solid phase film area at zero-applied surface pressure \[176, 227, 228\]. Once the solid phase film area is determined at zero-applied surface pressure, the nondeformed dimensions of the solid phase film can be determined.
Sonication time (3 hours) (1000 µl)

$y = 29.005 - 0.38578x \quad R^2 = 0.99715$

At zero pressure average area/unit cell $= 75 \, \text{Å}^2$, which indicating 1 layer

Figure (3-(7-A)) Langmuir-Blodgett isotherm for a monolayer film of SWCNTs.
3.3-2 Structural Characterizations of the Produce Monolayer Films of SWCNTs.

Figure (3-8) shows an HH polarized Raman spectra for the aligned nanotubes at different orientations with the tube axial directions in the produced monolayer film. The spectral range covers the wavenumbers between 1125 cm$^{-1}$ and 3200 cm$^{-1}$ emphasizing the nanotubes Raman active surface modes (D, G, and G’ bands) [8]. The spectra was recorded at different angles between the polarization direction and the nanotubes orientation achieved in the LB trough. It is well known (from spectra analysis) that in the HH backscattered Raman measurement arrangement, the intensity of the surface Raman modes depends on the orientation angle between the polarization and orientation directions [192, 196, 199, 229, 230]. It is very clear from the polarized Raman results that our films are highly oriented as indicated by the total disappearance of all Raman surface active modes as the laser polarization direction is perpendicular to the nanotubes orientation [8, 200].
Figure (3-8) HH Polarized Raman spectra at different orientation angles between the SWCNTs alignment angle and polarization angle. Spectra are showing first and second order SWCNTs surface modes.
Figure (3-9) shows a high-resolution Scanning Tunneling Microscopy (STM) image. The sample investigated was deposited on steel substrate by using LB techniques with the same conditions for the produced monolayer to emphasize that alignment of the tubes bundles is parallel to the compressing direction. Tubes alignment is again very clear in the image.

Figure (3-10) shows the measured electric conductivity of the film lengthwise, as well as normal to that of the transverse conductivity of the film ($4.8 \times 10^4$ vs. $1 \times 10^4$ S/cm) which provides another evidence for the alignment of the tubes in the produced monolayer film. It is important to note that our measured electric conductivity of the film in the tube axial direction is higher than the value $2.9 \times 10^4$ S/cm reported previously for crystalline ropes of metallic SWCNTs that are 20 nm in diameter [231], and that our film conductivity measured in the transverse direction is slightly lower than the $1 \times 10^4$ to $3 \times 10^4$ S/cm reported for SWCNT networks [115]. Since the exact type of metallic tubes were identified in the aforementioned work, it is clear that our current results are within the range of the reported electric conductivity of metallic nanotubes reported before. After the successful production, for the first time of a real monolayer SWCNTs film, we next discuss it’s mechanical and electrical properties.
Figure (3-9) HR-STM shows a monolayer film structure of aligned SWCNTs.
Figure (3-10) Histogram comparison for the conductivity (S/cm) in both directions for a monolayer film.
3.3-3 Mechanical Properties of Well-Aligned Monolayer Films of SWCNTs.

Realizing that the width of the LB trough is constant (0.2 m, in our study), the length of the film can also be determined. Hence, by considering a unit length along the film width, the measured surface pressure can be transformed into a load \( F \), and the measured film area can be deduced to film length \( L \). Knowing the film thickness, then it is straightforward to convert the load length curve into a stress-strain curve for the nano-films. The stress-strain curve for a monolayer film is shown in figure (3-(7-B)). From this figure, the stiffness of the film in transverse direction under compression is determined to be 10.215 ±1 MPa. Such a low value of film stiffness compared to the well-known extremely high radial stiffness of SWCNTs is not surprising because none of the chemical or functionalization process were used in our study, which definitely will influence the structure of SWCNTs [232-234]. The modulus of elasticity of individual CNTs is reported to be in the range of 1-2 TPa [66, 142, 145, 235, 236]. Figure (3-(7-B)) also showed that the monolayer SWCNTS film is very compliant with linear elastic behavior up to 30% strain; the film is basically behaving as a liquid crystal (LC) film of very stiff rods [237, 238]. Such a similarity in compressive mechanical behavior between aligned nanotube films and liquid crystal (LC) films was reported and discussed previously in the literature [225, 239, 240]. Besides, it is important to note the deviation from the linear behavior for the produced film under compression into a non-linear responds with a clear stiffness increase (figure 3-(7-B)). Such action further supports the LC-like behavior of nano-films consisting of carbon nanotubes.
Fig (3-(7-B)) Stress/Strain curve for a monolayer SWCNTs film in compression based on the LB isotherm shown in figure (3-(7-A)).
3.3-4 Electrical Properties of Aligned SWCNTs Films.

As illustrated in the previous sections, the structure and alignment of the SWCNTs mainly influence their properties [241]. The electrical properties of the bundles of SWCNTs monolayer will be examined in this section [211]. Figure (3-11) shows log scale for the conductivity of the produced films as a function of numbers of produced SWCNTs layers as compared with the log conductivity of silver copper (bulks) and Indium Tin Oxide (ITO) films. The conductivity of SWCNTs monolayer is close to the values of copper and silver and it is higher than the values of Indium Tin Oxide (ITO) films with the thickness in the range of (50-100) nm [242-247]. Conductivity values start decreasing as the numbers of layers increases. This reduction in the film conductivity could be due to either orientation loss or layer interference effect on the film energy gap and electronic structure.

The impact of the orientation process for the produced SWCNTs monolayer film is tested which shows that the conductivity of the longitudinal direction is about five times higher in magnitude than it’s value of the transverse direction, which can provide an evidence for the effect of orientation and alignment in the produced monolayer films on the measured conductivity values. As shown in figure (3-12), Polar coordinates are used to illustrate the variations in the values of the measured conductivities as a function of rotation angles.
Figure (3-11) Comparison between conductivity (S/cm) of SWCNTs films as function of number of layers with cooper, silver, and Indium Tin Oxide (ITO) films, in log scale.
Figure (3-12) Conductivity (S/cm) as a function of rotation angles in polar coordinates for the produced monolayer of SWCNTs.
For the produced monolayer the conductivity in the longitudinal direction is close to \((5 \times 10^4 \text{ S/cm})\) and started to decrease till it measured \((1 \times 10^4 \text{ S/cm})\) in the transverse direction with symmetry as the rotating angles change between 0° and 360°. From the polar coordinates conductivity figure, it’s clear that the orientations of the tubes in the produced monolayer had a significant effect on the values of the measured conductivities.

This variations in the values of the measured conductivities confirm our previous results by using different tests that our produced a monolayer of SWCNTs is well-aligned.

Our current study produced films with higher conductivity as compared with the values mentioned in the table (1-1) at section (1-2) in the current study, we did not include any chemical or surfactant treatments which mainly influence the structure of SWCNTs in the produced films [136].

The same measurement processes were applied for 3, 5, 7 and 11 layers of pristine SWCNTs (i.e. the electric conductivity was measured as a function of rotation angle from tube axial direction). Figure (3-13) shows the values of conductivities as the rotation angles changed for three layers of deposited thin films. By comparing the measured values, it’s clear that the film does have high orientation.

Figures (3-14) and (3-15) illustrate the effect of the rotation angles on the values
Figure (3-13) Conductivity (S/cm) as a function of rotation angles in polar coordinates for the three layers produced films.
Figure (3-14) Conductivity (S/cm) as a function of rotation angles in polar coordinates for the five layers produced films.
Figure (3-15) Conductivity (S/cm) as a function of rotation angles in polar coordinates for the seven layers produced films.
Figure (3-16) Conductivity (S/cm) as a function of rotation angles in polar coordinates for the eleven layers produced films.
of the measured conductivities for 5 and 7 layer produced films. From the figures it’s obvious that the effect of orientation processes is still significant. It is important to note the significant drop, however, in the measured conductivity values. Such results indicate that the measured drop in the electric conductivity of films with up to 7 layers is mainly due to layer/layer interaction and their impact on the film’s electronic structure.

For films with 11 deposited layers as shown in figure (3-16) the effect of orientation becomes insignificant indicating that the film with 11 layers is mainly isotropic materials considering the electronic structure. Further investigation should be done by using density functional theory (DFT) calculations to better understand the effect of increasing the number of the deposited layers of SWCNTs on the value of energy gap and electronic structure of the nano-films.

3.3-5 Optical Properties of Well-Aligned SWCNTs Films.

The produced films have high optical transparency, as shown in the measurements applied for the UV-visible absorption in figure (3-17). Our results show clearly that the films of different thicknesses have a maximum absorption of less than 0.3% within the wave length range between 300 nm and 1000 nm.

The produced films were transparent to visible and near infrared radiation even for the 7-layer films. Our current results emphasize the importance of such aligned SWCNTs films in transparent conductive electrodes much needed for advancing the photovoltaic efficiency limit.
UV Visible of SWCNTs for the produced layers

Figure (3-17) UV visible analysis for the SWCNTs produced films.
3.4 Production and Characterization of SWCNTs/PMMA Nanocomposite Films.

SWCNTs were added to the matrix to enhance their mechanical and physical properties [84]. The process of dispersion of SWCNTs tubes in the polymer matrix (PMMA) without damaging the structure of those tubes is crucial [126]. The concentration of SWCNTs in the PMMA matrix should be well designed to avoid clustering and agglomeration of the tubes which will produced a poor dispersion process [248]. The poor dispersion process will produce non-desirable nanocomposite products. Two common methods used to produce nanocomposites of SWCNTs with PMMA matrix are direct mixing and in-situ polymerization techniques [3, 248-251].

Direct mixing method represents one of the processes used to produce nanocomposites. This process involves mixing polymer which can be dry or liquid with solvent (DMF) till achieving the required concentration. After preparing the polymer solution, a mixing process is running with a SWCNTs solution by using a sonication device. The sonication process will enhance the process of dispersion of SWCNTs on the surface of the PMMA matrix [3]. The major challenge for the direct mixing method is to anticipate the best concentration and sonication time which will enhance the process of dispersion of SWCNTs in the PMMA matrix. In addition to that the high viscosity of the anticipated polymer matrix may directly influence the dispersion and properties of the produced nanocomposite [125].
In-situ polymerization is also used to process nanocomposite material. In this process, the liquid monomer is mixed with SWCNTs solution after satisfying the required concentration percentage. After that, the initiator is added to the solution. In our work, we used UV initiator because none of the chemical or thermal initiators satisfied our requirements and concerns. For UV initiator the mixing process is handled in a dark place after adding to the monomer, and SWCNTs solutions then sonicate all together to ensure well dispersion of SWCNTs in the monomer solution. After anticipating the required quantities and starting the separation processes on the trough of the LB device we used to produce the nanocomposite required films, a UV light with specific wavelength is applied to the surface of the trough for certain period of time to start the polymerization process while the solvent evaporation process is in progress. The low viscosity of the monomer will enhance the dispersion of SWCNTs. The main challenge for the in-situ polymerization process is represented by the effect of the initiator used which may influence the structure of the SWCNTs and the produced nanocomposite as a result [121, 252-254].

Both of the direct mixing and in-situ polymerization techniques used in this study are discussed in detail in the next sections.
3.4.1 Nanocomposite by Direct Mixing process.

3.4.1-1 Mechanical Properties.

In this section, the stiffnesses of the produced films are measured as a function of SWCNTs volume fraction ($V_f$) by using the Nima device which depends on the Langmuir-Blodgett technique. A specific volume fractions of the SWCNTs is mixed with the PMMA matrix. The produced solutions are sonicated for 30 minutes to enhance the dispersion of SWCNTs and achieve a homogenous solution without agglomeration of the tubes [170]. After finishing the preparation process a specific amount of solution is taken and spread on the surface of the distilled water subphase on the trough of the Nima device. The same conditions used before with the process of producing a monolayer of SWCNTs are applied in this section also. The solution spreads on the trough subphase for 30 minutes to allow for the solvent to evaporate, after that the compression process is set up. Figure (3-18) shows a schematic for the direct mixing with a deposition process. The isotherm for each percent of SWCNTs is processed separately and repeated three times. After that, the analysis processes are applied to account for the stiffnesses of the produced films.

By analyzing pressure-area isotherm, the values of pressure in mN/m with areas in cm$^2$ for the solid phase are selected. Then the pressure is transformed into stress by dividing it with the thickness of the deposited layer which will change with each percent
Figure (3-18) schematic for the direct mixing process.
of SWCNTs added. The area also transfers to \( m^2 \) and length of the produced film is specified and considered as \( L_0 \) for that percentage of solution added to the trough. Then the amount of strain is accounted by calculating the change in length for the produced films divided by its original length. Later, the number of stresses and strains for the specified films are drawn, and the slope of the curve which represents the stiffness in MPa is calculated. Figure (3-19) shows an example for the isotherm which had 0.037 volume fraction \( (V_f) \) of SWCNTs. A high-resolution STM image for 0.01 \( V_f \) of SWCNTs is shown in figure (3-20) which illustrate the arrangements of deposited strips of SWCNTs as mixed with PMMA matrix.

After finishing the calculation processes for the produced average films stiffnesses as the percentage of SWCNTs volume fraction was modified, the results are drawn in figure (3-21). The graphed values represent the bulk modulus in the lateral direction for the produced composite films as mixed with a different volume fractions \( V_f \) of SWCNTs [155]. Zero percent of the matrix (PMMA) which indicate pristine SWCNTs in bundles with a lateral modulus of 10 MPa approximately. The modulus of pure PMMA is less than that of pristine SWCNTs and its significant increase as the volume fraction of SWCNTs increase.
Figure (3-19) Isotherm shows surface pressure as a function of the area for (0.037 Vf) SWCNTs nanocomposite films produced by the direct mixing process.
Figure (3-20) STM image for strips of SWCNTs nanocomposite which had (0.01 Vf) SWCNTs.
Figure (3-21) Average film stiffness as a function of SWCNTs volume fraction for nanocomposite produced by the direct mixing method.
Comparing Composite Films Stiffnesses with a Defined Composite Theory.

The Rule of mixture is used in this section to compare transverse modulus of a defined composite theory with the values of stiffnesses calculated based on our experiment’s runs for the direct mixing process of SWCNTs with PMMA. When the material is loaded in the direction perpendicular to the reinforcement direction, the overall transverse modulus of the bulk composite in the macro level can be calculated using the following mathematical equation:

\[ E_2 = \frac{E_m \times E_f}{(E_m \times V_f) + (E_f \times V_m)} \quad \ldots \ldots \quad (8) \]

Where;

- \( E_2 \) = transverse modulus of a composite.
- \( E_m \) = represents material property for the PMMA matrix.
- \( E_f \) = represents material property for SWCNTs reinforces.
- \( V_f \) = SWCNTs volume fraction.
- \( V_m \) = PMMA volume fraction which is equal to \( V_m = 1 - V_f \).

The value of \( E_f \) can be taken as 1 TPa which is accepted in the literature [153, 235, 236, 255]. For polymer matrix (PMMA) \( E_m \) can be taken as 2.5 GPa [256-258].

Figure (3-22) shows the values for transverse modulus in a log scale for both defined composite theory and experimental lab results (direct mixing method) as a function of SWCNTs volume fractions.
Figure (3-22) Comparison between defined composite theory and lab results for the produced composite films.
The behavior of the two curves illustrates that film stiffnesses increase as the SWCNTs volume fraction increases, which confirms the assumptions of using SWCNTs as a reinforcement in the produced nanocomposite films [122, 124, 125, 250]. The differences between the values of the transverse modulus for the produced composite from the defined composite and the lab results for direct mixing method are significant. One of the causes for these differences is, for the defined composite theory single tube properties in the bulk level are anticipated and considered; therefore, they are expected to be high as compared with the properties of bundles of the same tubes considered [248]. This is especially significant when the properties are examined in the nano level where many assumptions at the bulk and macro level cannot be applied [8]. Another reason is the effect of load/stress transmissivity between fiber-matrix can have significant influence on the properties of the produced composite which is not included in the mathematical relation used for calculating the transverse modulus in the bulk level [259-261]. By using the same equation (8) used to theoretically calculate ($E_2$) and add the interphase effect it will be:

$$\frac{1}{E_2} = \frac{V_f}{E_f} + \frac{V_m}{E_m} + \frac{V_f V_m}{K} \ldots \ldots (9)$$

Where K represents the interphase factor. If an arbitrary value for the calculated $E_2$ is anticipated from figure (3-22) and inserted in equation (9) with considering the others constant parameter ($E_m$, $E_f$, $V_m$, $V_f$), then the value of k parameter will be significant [262-264]. The theoretical results of the calculated transverse modulus for the produced
composite can be modified significantly by contributing the effect of the interphase factor [260]. Interphase basically can be defined as the volume of the material affected by the interaction at the interface of polymer matrix with filler [265]. It also can be represented as three-dimensional zone, which will be distinct from the two-dimensional interface and can give an indication for the presence of mechanically and chemically altered zone between the existing adjacent phases [265]. The interphase helps in the gradation from one phase to another, which will prevent the abrupt change due to the huge differences in the properties of the composite material [266, 267].

Figure (3-23) shows the fitting of interphase to our experimental data which provide a good agreement apparent from the curve behavior. The value of interphase parameter (k) is calculated and it was 20.4 MPa which should be considered in the theoretical equation to improve the process of predicting more precise values for the determined composite modulus [265]. The existence of the interface is improving the strength of the produce composite because it will restrict the mobility and deformation of the matrix by introducing mechanical restraint which will reflect directly on the measured properties [265, 268]. The degree of restriction mainly depends on the distinct properties of the carbon nanotubes and the used matrix [269-271].

Many models include empirical and semi-empirical mathematical equations were proposed to predict the modulus of filler-polymer nanocomposite [272-274].
Figure (3-23) Fitting interphase factor to the experiment data of direct mixing composite films.
Figure (3-24) shows the results of fitting our experimental data to the Ishai and Cohen model to estimate the modulus of composite which is developed based on using rules of mixture by the following equation [275]:

\[
\frac{E_c}{E_m} = 1 + \frac{V_f}{\delta V_f^{1/3}} \ldots \ldots (10)
\]

Where:

- \(E_c\) = represents composite modulus.
- \(\delta = E_f / E_m\).

Another model Verbeek provided (figure (3-25)) to calculate the composite modulus which is based on assuming perfect adhesion between phases and the stress transfer via a shear mechanism by introducing the following equation [276]:

\[
E_c = \chi_f E_f V_f + E_m (1 - V_f) \ldots \ldots (11)
\]

\[
\chi_f = 1 - \tanh(V_{f\text{ max}})/V_{f\text{ max}}.
\]

Finally, Einstein developed a model base on the concept of hydrodynamic which is expressed in equation (12) [277]. This model was simple and it valid at low concentration of filler with the assumption of perfect bonding between the used filler and matrix [278, 279]:

\[
\frac{E_c}{E_m} = 1 + (2.5 \times V_f) \ldots \ldots (12)
\]
Figure (3-24) Fitting Ishai-Cohen model to the experiment data of direct mixing composite films.
Figure (3-25) Fitting Verbeek model to the experiment data of direct mixing composite films.
From comparing the fitting results of all mentioned models to the experimental data, it becomes obvious that the effect of interphase was significant, and it should be included in the calculated models (as seen from comparing the results of the selected models with the experimental) [280, 281]. Figure (3-26) compared all three anticipated models with the experimental data fitting to interphase factor which can show the necessity of developing a new model that takes in consideration the effect of the interphase between the filler tubes and polymer matrix [282-284].

Many methods can be used to enhance the interfacial effect between the filler and matrix in the bulk scale such as oxidation, heat treatment or chemical functionalization of the fiber with certain material [285-287]. The major challenges for applying those methods in the nano level are their direct effect on the structure of the CNTs which is mainly sensitive to any chemical material because it will definitely modify it [144]. In addition to that, many factors which are considered in the bulk level cannot be applied to the nano level because new parameters should be taken into consideration with designing composites in the nano scale [8].

The properties of the produced films in the nano-level mainly depend on the surface energy for the aligned tubes in the produced composites. Therefore, developing a new composite theory to study the behavior in the nano level based on the surface energy became crucial.
Figure (3-26) Comparing three models to the experiment data of the direct mixing composite films.
3.4.1-2 Electrical Properties.

The same process which is applied in section (3.3-4) to measure the conductivity of the produced SWCNTs monolayer will be used in this section [211]. Figure (3-27) shows the conductivity in longitudinal and transverse directions of the deposited samples as a function of SWCNTs $V_f$. The conductivity in longitudinal direction is approximately 1.5 times its value in the transverse direction. The conductivity for the produced nanocomposite films is less than the value for a monolayer of well-aligned SWCNTs by four orders of magnitude. Figure (3-28) illustrated the difference between the conductivities values in both directions in the form of a histogram. The reason for the difference in the values of the measured conductivities in both directions can be related to losing the orientation by the effect of wrapping the polymer chains to SWCNTs which will enforce the tubes to orient in different directions. Another reason can be related to the effect of decreasing the SWCNTs volume fraction which will increase the insulation of the produced nanocomposite. Figure (3-29) shows ratios between the transverse to longitudinal conductivities. From comparing the differences between the bars ratios, it become clear that the tubes orientation didn’t have the major effect on decreasing the measured conductivities and the governing rule will be applied for increasing the percentage of the insulators added (decreasing SWCNTs $V_f$) which represents the most probable scenario [108, 138, 211].
Figure (3-27) conductivity (S/cm) in both direction as a function of SWCNTs \( V_f \) by direct mixing method.
Figure (3-28) Histogram comparison for the conductivity (S/cm) in both direction as a function of SWCNTs Vf.
Figure (3-29) Ratios between conductivities in the transverse and longitudinal directions for the direct mixing method.
3.4.2 Nanocomposite by the In-situ Polymerization technique.

3.4.2-1 Mechanical properties.

In-situ is a Latin idiom mean in position [127]. This process involves the formation of a stable thermodynamic phase within the matrix. A certain amount of monomer (MMA) is anticipated. After that, a mixing process for SWCNTs with MMA and UV initiator (2-HYDROXY-2-METHYLPROPIOPHENONE) takes place [248]. The process is handled in a dark place where no UV source is applied at this time. Due to the morphology of the liquid monomer used more freedom will apply for the SWCNTs to arrange and align themselves [121]. After anticipating certain amount of solution and dispersing on the surface of trough, UV light with a wavelength of 254 nm is exposed to the surface to allow for the bulk polymerization process to start. The produced composite represents a thermoset, so it cannot be reshaped after the polymerization process takes place [248]. Finally, the order will apply to start the compressing process and get the isotherm graph for the produced films to calculate their properties as used for the previous experiments. Figure (3-30) shows the values of the stiffnesses for the produced films after finishing the calculations processes [254]. The graph shows lateral modulus as a function of different volume fractions \( V_f \) of SWCNTs used in these experiments. The curing agent is not added because it may influence the properties of the produced films [28]. The main advantages of the in-situ polymerization are the surface of SWCNTs will
Figure (3-30) Average film stiffness as a function of SWCNTs Vf by in-situ polymerization.
be free from contaminations, the interaction between the reinforcement (SWCNTs) and matrix (PMMA in-situ) will hold a place in the molecular level of the nanocomposite and the dispersion will better hold place due to the low viscosity of the monomer in the pre-polymerization process [3, 248]. All those factors will contribute to improve the mechanical properties of the produced nanocomposite structure due to better control of the dispersion and alignment process. Meanwhile, the effect of the free radicals in the UV initiator influences the structure (unzipping) of SWCNTs and decreases the stiffnesses of the produced SWCNTs films and their composites because tubes will be broken into different irrelevant shapes and hexagons as shown in figure (3-30) [288-290].

3.4.2-2 Electrical Properties.

The same process which was applied to measure the electrical properties for the deposited direct mixing method mentioned in section (3.4.1-2) will be used [211]. Figure (3-31) shows the conductivity in the longitudinal and transverse directions of the deposited samples as a function of SWCNTs Vf-(in-situ). Figure (3-32) illustrates the difference between the conductivity measured values in the form of a histogram.

Conductivity in the longitudinal direction is about twice in average greater than the value of that in the transverse direction. Meanwhile to compare the values for the produced nanocomposite conductivities with the pristine SWCNTs film we will be lower by six order of magnitude, which is mostly due to the effect of the free radical on the structure of SWCNTs. Figure (3-33) shows the ratio of transverse to longitudinal
Figure (3-31) conductivity (S/cm) in both direction as a function of SWCNTs

\[ y = m1 + m2 \times \exp(m3 \times m0) \]

<table>
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<tr>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>m1</td>
<td>-0.087633</td>
</tr>
<tr>
<td>m2</td>
<td>0.1019</td>
</tr>
<tr>
<td>m3</td>
<td>1.1921</td>
</tr>
<tr>
<td>Chi sq</td>
<td>1.7021e-6</td>
</tr>
<tr>
<td>R^2</td>
<td>0.99454</td>
</tr>
</tbody>
</table>

\( V_f \) (in-situ) polymerization.
Figure (3-32) Histogram comparison for the conductivity (S/cm) in both direction as a function of SWCNTs Vf (in-situ).
Figure (3-33) Ratios between conductivities in the transverse and longitudinal directions for the (in-situ) polymerization method.
conductivities. The difference in the ratios values are small which can interperate as the effect of orientation of tubes will not have a significant effect on the measured values for conductivities. Therefore, the effect of increasing the percentage of insulator by decreasing SWCNTs Vf will directly impact the values of the measured conductivities. In addition to that, the present of the free radicals in the UV initiator mainly contributes in unzipping the carbon nanotubes and break the structure into different hexagonal shapes [291, 292]. Those newly produced shapes will contribute in improving the electrical properties for the insulator matrix and produce orthotropic material, but not have the same electronic structure as the pristine SWCNTs [293, 294]. Figure (3-34) shows schematic for the effect of the free radical on the structure of SWCNTs and how that will contribute in changing the grafting polymerization process for the produced composite as the percentage of PMMA-(in-situ) increases [108, 138, 211]. In addition to that, the effect of the free radicals in the UV initiator contributes to decrease the conductivity values due to their direct effect on damaging the structure of SWCNTs used and produced material had orthotropic structural properties with many defect points [292, 295].
Figure (3-34) Schematic for the effect of the free radical on the structure of SWCNTs in the (in-situ) polymerization process.
3.4.3 Comparing the Results for Direct Mixing and In-Situ Polymerization.

3.4.3-1 Comparing Mechanical Properties for Two Composites Production Methods.

Interfacial interaction between SWCNTs and PMMA matrix represents the main feature which can control the performance of the produced composite [296]. Good dispersion of SWCNTs in the PMMA matrix will contribute to provide more surface area for the filler to bond with the polymer matrix [296-298]. In addition to that, it will work on reducing SWCNTs agglomerations and aggregations in the polymer matrix which can work as stress concentration and mainly have a detrimental effect on the mechanical properties of the produced composite [296, 299, 300]. In our work dispersion process is achieved by sonicating both SWCNTs and polymer for a specific amount of time. The average stiffnesses values for the produced films by the direct mixing and in-situ polymerization are shown in figure (3-35). The stiffnesses values for the in-situ polymerization of nanocomposite are significantly reduced as compared with the direct mixing process because of the free radical (FRs) effects caused by the in-situ polymerization process (UV initiator) on the structure of SWCNTs [290, 295, 301]. The FRs are affecting the physical structure of SWCNTs and reacting with them easily [290, 295, 301], due to the natural structure of SWCNTs which nominate them to be excellent free radical scavengers [288].

SWCNTs exhibit strong reactivity toward free radicals because of the high
Figure (3-35) Average film stiffness as a function of SWCNTs $V_f$ by both direct mixing and in-situ polymerization methods.
electron affinity with the SP²- hybridization structure [288, 302]. The FRs will attach to the surface of SWCNTs which is usually stable and change their inactive state [288, 290, 302]. Our results confirm what is published by many researchers that free radicals tend to minimize the characterizations for SWCNTs because they mainly modify their structure [288, 302-305].

In addition to the effect of FRs on the structure of SWCNTs, they also have significant effects on the polymer properties [290, 306, 307]. The main disadvantage for the FRs on the polymer structure which has been used in the nanocomposite material is that it does not provide sufficient control over the produced polymer chain length during the polymerization process with SWCNTs [289, 290, 307].

3.4.3-2 Comparing Electrical Properties.

As mentioned before, the high aspect ratio with the excellent electrical properties for SWCNTs contribute to enhance conductivity for the insulator PMMA matrices [308]. Due to the structure and arrangement of SWCNTs in the produced composite with PMMA matrix they will form a continuous electron path or conducting network after reaching percolation limits which represent the way of arrangement of those networks in the PMMA matrix that will raise the values of conductivity in the polymer several orders of magnitude [308, 309]. Figure (3-36) shows the measured conductivities for both of the direct mixing and in-situ polymerization as a function of SWCNTs volume fraction in the longitudinal direction.
Figure (3-36) conductivity in the longitudinal direction as a function of SWCNTs Vf by both direct mixing and in-situ polymerization methods.

\[
y = m_1 + m_2(1 - \exp(-m_3m_0))...
\]

<table>
<thead>
<tr>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>m1</td>
<td>0.15912</td>
</tr>
<tr>
<td>m2</td>
<td>438.06</td>
</tr>
<tr>
<td>m3</td>
<td>0.011309</td>
</tr>
<tr>
<td>Chisq</td>
<td>0.055108</td>
</tr>
<tr>
<td>R²</td>
<td>0.98149</td>
</tr>
</tbody>
</table>
For the direct mixing method, conductivity values in the direction is approximately one order of magnitude higher than that for the in-situ polymerization due to the free radical effect on the structure of SWCNTs [301, 303, 307]. The orientation of SWCNTs in the produced composite is changed due to decreasing the values of the measured conductivities as compared with values of the pristine SWCNTs films. These changes in the orientation of the tubes in the produced composite also can result from the warping of the polymer chains to the SWCNTs while mixing together during the composite processing process [71]. SWCNTs are very sensitive to the conditions that surround them [309]. Therefore, during processing with the polymer, the structure sensitivity should be taken into consideration [308].

The conductivity in the transverse direction of the two methods also shows that direct mixing provides a better-measured value from the in-situ polymerization for the same reasons which are related to the free radicals provided in the in-situ polymerization [289, 302, 303, 306]. The conductivity decreased as the SWCNTs Vf decreased as shown in figure (3-37).
Figure (3-37) conductivity in the transverse direction as a function of SWCNTs Vf by both direct mixing and in-situ polymerization methods.
3.4.4 Comparing Results for Chemically and Physically linked SWCNTs in the Produced Monolayer Film.

3.4.4-1 Comparing Mechanical Properties.

SWCNTs can chemically link to produce a monolayer by adding UV initiator to the solution (SWCNTs and solvent) then polymerize all together. The free radical species (FRs) which are available in the UV initiator contain one or more unpaired electrons [292, 310, 311]. Those electrons will react with the surface of SWCNTs which is usually inert and modify tubes structure [292, 310, 311]. Carbon nanotubes can be represented as large arrays of conjugate double bond very active for receiving free radical effect, therefore they are named free radical scavengers [312]. FRs will work to unzip the cylindrical shape for SWCNTs and break it to pieces of different hexagonal shapes. This process will definitely affect the structure of SWCNTs and produce different types of defects which mainly reflect on the physical, mechanical, and electrical performance [313-316].

Physically linking SWCNTs to produce a monolayer has been studied in detail in section (3.3-3) for the mechanical properties of the produced monolayer film. The structure of the tubes was not affected because none of the chemical or physical methods was used to functionalize SWCNTs. Figure (3-38) shows the difference between the values of the calculated monolayer film stiffnesses in the transverse direction for the direct deposition (physically) of pristine SWCNTs and chemically linked SWCNTs.
Figure (3-38) Comparing between film stiffness (MPa) of the produced SWCNTs monolayer of physically linking VS chemically linking processes
For the chemically linked SWCNTs the value for the film stiffness is reduced by 40% due to the effect of the free radical associated with the UV initiators which mainly influence the structure of the SWCNTs deposited monolayer and directly appear on the performance [291, 317, 318].

3.4.4-2 Comparing Electrical Properties.

As shown in section (3.3-4) the values of measured conductivities vary within the range of (5 e4 and 1 e4) S/cm depending on the direction for the physically linked SWCNTs in the produced monolayer. The electronic structure of SWCNTs is unaffected because none of the chemical materials were included in the processing process.

Figure (3-39) shows the difference between the values of the measured conductivities for a monolayer film of physically and chemically linked SWCNTs. The effect of the free radical in the chemically linked SWCNTs was significant and can be observed from comparing the values for the measured conductivities. For the chemically linked process the conductivity was decreased by two order of magnitude from the physical process. The most probable scenario is the effect of free radicals on damaging the structure of the SWCNTs and produce defect regions which definitely will affect the electronic structure of the SWCNTs [319-323].
Figure (3-39) Comparing between conductivity values (S/cm) for the produce SWCNTs monolayer of physically linking VS chemically linking processes.
CHAPTER 4: Conclusions and Recommendations for Future works

4.1 Conclusion.

- A monolayer of highly oriented single-walled carbon nanotubes has been successfully processed using the Langmuir-Blodgett technique.
- Our current study shows a processing methodology that would enable the full recognition of the superior properties of nanotubes on a bulk scale.
- The compressive behavior of such highly orthotropic films demonstrated a linear stress/strain relationship up to 30% with an elastic modulus in the range of 10 MPa making its compressive behavior in the transverse direction similar to rubbery materials.
- The measured electrical properties show significant improvements as compared to metallic networks of SWCNTs.
- Our produced films can be deposited on different types of substrates with different shapes (flat or curve) depending on the required applications.
- Conductivity decreases as the number of stacked layers increases most probably due to the effect of the stacked layers on the tubes electronic structure up to 11 layers.
- Both the direct mixing method and the in-situ polymerization technique show that the conductivities of the produced films increase as the weight fraction of SWCNTs added to the nanocomposite is increased.
• The conductivity for the composite films for direct mixing in longitudinal and transverse directions is higher than the values for the in-situ polymerization due to the damaging effect of free radicals on the structure and properties of SWCNTs.

• The effect of dispersion of SWCNTs in the PMMA matrix for the two used methods of producing nanocomposite films was significant on the orientation of tubes. Also, the wrapping of polymer chains to SWCNTs can align them in different directions; those two issues can be recognized from comparing the conductivity values for the produced nanocomposite films with the pristine SWCNTs films.

• Depending on the applications at which the nanocomposite produced films can be used, our work shows that the free radicals from the UV initiator had a significant effect on damaging the structure of SWCNTs and should be taken into consideration.

• The produced films for pristine SWCNTs and nanocomposite both had excellent transparency to the visible and infrared radiation.

• CNTs-PMMA Interphase effect was significant and should be taken in consideration in the theoretical models which are used to estimate this type of nanocomposite mechanical constant.

• Free radical in the in-site polymerization should not be used to produce SWCNTs/PMMA nanocomposites because of the tremendous damage of the structure and, hence, the superior properties of the nanotubes.
4.2 Recommendations for Future Works.

- New multi-scale simulation models need to be developed to accurately understand the formation, properties, and the impact of the interphase in this class of nanocomposites.
- The effect of laminating the successful produced highly oriented SWCNTs films with different orientation is still uncharted field and needs to be investigated.
- The production of sandwiched fullerene films using the LB technique is now possible and should be explored.
References


154


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