INVESTIGATION OF STRUCTURAL, MECHANICAL, AND ELECTRICAL PROPERTIES OF CARBON NANOTUBE REINFORCED RUBBER NANOCOMPOSITES

A dissertation submitted to the Department of Physics, Bangladesh University of Engineering and Technology, Dhaka in partial fulfillment of the requirements for the degree of Master of Science (M.Sc.) in physics

SUBMITTED

BY

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CANDIDATE’S DECLARATION

It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

Signature of the candidate

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Roll No.: 1015142503F
Session: October, 2015
Dedicated to

My Beloved Parents and Teachers

Who have inspired and influenced me in higher study
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Abstract

Natural rubber (NR) is an interesting biopolymer. But the modulus and durability of a neat rubber is very low and therefore, addition of reinforcing agents is essential to improve different properties of NR for its specific application. Recently, Carbon nanotubes (CNTs) have also been reported as reinforcing filler in different polymers, because of its unique mechanical, thermal and electrical properties. In this study multiwalled CNTs is used as filler components to reinforce the NR. To realize uniform dispersion of CNTs in the NR matrices MWCNTs are functionalized using HNO$_3$:H$_2$SO$_4$ acid refluxing. Owing to this treatment oxygen containing groups were introduced in the MWCNTs which help the dispersed as well as interact more with the NR matrix.

The CNT-NR composites were prepared by simple solution casting method introducing 0.5, 1.0, 1.5 wt% of MWCNTs in NR. For this NR and f-MWCNTs were dispersed in toluene individually and then mixed together and casted in glass tray.

From scanning electron microscope (SEM) images it is observed that all the CNTs are well embedded inside the rubber matrix, and no individual CNTs were visible under SEM. It may be due to the uniform dispersion of CNTs which were wrapped by the molecules of NR. EDX spectra confirmed 100% presence of carbon in the composites signifying less or no impurity in it. From XRD a broad peak is observed for NR and CNT-NR composites and therefore indicating that CNT-NR composites are amorphous in nature. FTIR spectra of the MWCNTs confirm the attachment of functional groups (-OH, -COOH) on the surface of the CNTs during acid refluxing of the CNTs. The FTIR spectrum of NR and CNT-NR composites remain similar confirming uniform dispersion of CNTs in the NR matrices. Tensile strength was observed to increase with increasing wt% of CNTs in NR matrices. TG-DTA data shows thermal stability of the composites improved slightly, and degradation of NR delayed with the concentration of CNTs in NR. From DC electrical measurement the current density is observed to increase with increasing wt% of CNTs in the NR matrices at room temperature, also observed to increase with the temperature. Therefore, resistivity decreases with increasing wt% of CNTs in the NR matrices. The activation energy of the experimental composites is observed to vary from 0.17 to 0.26 eV, and observed to decrease with increasing wt% of CNTs in the NR matrices, though slight increase trend shown in the lower voltage region (<20V).

The fabricated NR nanocomposites will find interesting applications in different engineering products like robotic arms, tubes, tyres, high charge storage capacitors, electronic packaging, seal pad, electromagnetic interference shielding, etc.
## CONTENTS

<table>
<thead>
<tr>
<th>Candidate’s Declaration</th>
<th>ii</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dedication</td>
<td>iii</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>iv</td>
</tr>
<tr>
<td>Abstract</td>
<td>vi</td>
</tr>
<tr>
<td>List Of Figures</td>
<td>ix</td>
</tr>
<tr>
<td>List Of Tables</td>
<td>xii</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>xiii</td>
</tr>
</tbody>
</table>

### Chapter I

#### GENERAL INTRODUCTION

1.1 Introduction
1.1.1 Properties of Carbon Nanotubes
1.1.2 Importance of carbon nanotubes
1.2 Literature Review
1.3 Objectives
1.4 Thesis Layout

### Chapter II

#### THEORETICAL BACKGROUND

2.1 Polymers
2.1.1 Classification of Polymer
2.1.2 Natural Rubber (NR)
2.1.3 Applications of Polymer Composites
2.2 Different Methods of Nanocomposite Preparation
2.2.1 Freeze Drying
2.2.2 Spray drying
2.2.3 Latex stage compounding
2.2.4 Hetero coagulation approach
2.2.5 In-situ polymerization
2.2.6 Melt blending/Extrusion
2.2.7 Solid state shear pulverization
2.2.8 Solution Casting
2.2.8.1 Advantages of Solvent Casting Method
2.2.8.2 Advantages of the resulting film

2.3 Functionalization of CNTs

2.4 Theory of Surface Morphology
2.4.1 Scanning Electron Microscope
2.4.2 Transmission Electron Microscopy
2.4.3 Energy Dispersive X-Ray Spectroscopy

2.5 Theory of Structural Analysis
2.5.1 Fourier Transform Infrared Spectroscopy
2.5.2 X-ray Diffraction Analysis

2.6 Thermal Analysis

2.6.1 Differential Thermal Analysis

2.6.2 Thermogravimetric Analysis

2.7 Mechanical Properties of Composites

2.7.1 Engineering Strain

2.7.2 Stress

2.7.3 Tensile Strength

2.7.4 Elongation-at-Break or Breaking Strain

2.7.5 Young’s Modulus

2.8 Conduction mechanisms

2.8.1 Introduction

2.8.2 Below percolation threshold

2.8.3 When the mean distance is less than 2nm-5nm

2.8.4 Particle to particle contact

2.8.5 Electrical contact between filler

2.8.6 Thermally activated conduction processes

References

Chapter III
MATERIALS AND METHODS

3.1 Raw Materials

3.1.1 Natural Rubber Ribbed Smoked Sheet (1, 4-cis poly isoprene)

3.1.2 Multiwall Carbon Nanotubes

3.1.3 Acids Used for CNT Functionalization

3.1.4 Toluene

3.2 Equipment for the Preparation of Composites Samples

3.2.1 Electric Balance

3.2.2 Reflux System (Lebig Condenser Round Bottom Flux)

3.2.3 Centrifuge Machine

3.2.4 Hot Plate with Magnetic Stirrer

3.2.5 Glass Tray

3.3 Preparation of Composites Samples

3.4 Surface Morphology Test

3.4.1 Surface Morphology Test by FESEM

3.5 Structural Measurement of Rubber Nanocomposites Samples

3.5.1 Fourier Transform Infrared Spectroscopy

3.5.2 X-ray Diffraction

3.6 Methods of Measuring Mechanical Properties
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.6.1</td>
<td>Universal Testing Machine</td>
<td>64</td>
</tr>
<tr>
<td>3.6.2</td>
<td>Measurement by Universal Testing Machine</td>
<td>65</td>
</tr>
<tr>
<td>3.7</td>
<td>Electrical Measurements</td>
<td>66</td>
</tr>
<tr>
<td>3.8</td>
<td>Thermal Measurements</td>
<td>67</td>
</tr>
<tr>
<td>3.8.1</td>
<td>Thermogravimetric Analysis and Differential Thermal Analysis</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>69</td>
</tr>
</tbody>
</table>

Chapter IV
RESULTS AND DISCUSSION

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>71</td>
</tr>
<tr>
<td>4.2</td>
<td>Surface Morphology</td>
<td>71</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Transmission Electron Microscopy</td>
<td>71</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Field emission scanning electron microscopy</td>
<td>72</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Energy dispersive X-ray analysis</td>
<td>78</td>
</tr>
<tr>
<td>4.3</td>
<td>Structural Analyses</td>
<td>80</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Fourier Transform Infrared Spectroscopy Analyses</td>
<td>80</td>
</tr>
<tr>
<td>4.4</td>
<td>XRD Analyses</td>
<td>81</td>
</tr>
<tr>
<td>4.5</td>
<td>Thermal Analyses</td>
<td>83</td>
</tr>
<tr>
<td>4.6</td>
<td>DC Electrical Properties of Natural Rubber CNTs Polymer Composites</td>
<td>84</td>
</tr>
<tr>
<td>4.6.1</td>
<td>Current density-voltage characteristics</td>
<td>84</td>
</tr>
<tr>
<td>4.6.2</td>
<td>Dependence of current density on temperature</td>
<td>89</td>
</tr>
<tr>
<td>4.7</td>
<td>Mechanical Properties</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>93</td>
</tr>
</tbody>
</table>

CHAPTER V
CONCLUSIONS

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Conclusions</td>
<td>95</td>
</tr>
<tr>
<td>5.2</td>
<td>Suggestions for Future Work</td>
<td>96</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Fig. No.</th>
<th>Figure Captions</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>(a) SWCNT and MWCNT, (b) Different types of SWCNTs</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Applications of CNTs</td>
<td>5</td>
</tr>
<tr>
<td>1.3</td>
<td>SEM micrographs of the NR/MWCNT composites: (A) p-MWCNT (1 wt %) dispersed in an NR matrix, (B) f-MWCNT (1 wt %) dispersed in an NR matrix, (C) MWCNT-PDDA (0.5 wt %) dispersed in an NR matrix, (D) MWCNT-PDDA (2 wt %) dispersed in an NR matrix, and (E) MWCNT-PDDA (5 wt %) dispersed in an NR matrix</td>
<td>6</td>
</tr>
<tr>
<td>1.4</td>
<td>(a) TG curves of the NR and NR/MWCNT composites in N2 and (b) DTG curves of the NR and NR/MWCNT composites in N2</td>
<td>7</td>
</tr>
<tr>
<td>1.5</td>
<td>TEM images composites at 1% filler loading (a) NR/CNT and (b) NR/m-CNT</td>
<td>8</td>
</tr>
<tr>
<td>1.6</td>
<td>TGA and DTG curves of NR/CNT composites</td>
<td>8</td>
</tr>
<tr>
<td>1.7</td>
<td>DSC thermograms of NR/CNT composites (a) unmodified CNT and (b) m-CNT</td>
<td>9</td>
</tr>
<tr>
<td>1.8</td>
<td>TEM images of CNT/NR composites containing 1 wt % filler (a) CNT and (b) phenol functionalized CNT</td>
<td>9</td>
</tr>
<tr>
<td>1.9</td>
<td>DSC thermograms of NR composites with (a) CNT and (b) phenol functionalized CNT</td>
<td>10</td>
</tr>
<tr>
<td>1.10</td>
<td>TEM images of NR filled with 3 phr of MWNTs taken at different (a, b, c) scales. d) shows the graphene layers of an individual tube</td>
<td>11</td>
</tr>
<tr>
<td>1.11</td>
<td>Volume resistivity against nanotube loading for NR composites</td>
<td>11</td>
</tr>
<tr>
<td>2.1</td>
<td>Chemical structure of Poly-Chloroethene</td>
<td>16</td>
</tr>
<tr>
<td>2.2</td>
<td>Chemical structure of Nylon 6, 6</td>
<td>17</td>
</tr>
<tr>
<td>2.3</td>
<td>(a) Linear Chain Polymers (b) Branched Chain Polymers</td>
<td>17</td>
</tr>
<tr>
<td>2.3</td>
<td>(c) Crosslinked or Network Polymers Polymers</td>
<td>18</td>
</tr>
<tr>
<td>2.4</td>
<td>Chemical structure of NR</td>
<td>18</td>
</tr>
<tr>
<td>2.5</td>
<td>Major application of CNT/elastomer composites a) Home appliances b) switches c) pressure sensing skin in robotics d) strain sensor attached to tyre engineering e) energy storage application as capacitors and f) cables</td>
<td>22</td>
</tr>
<tr>
<td>2.6</td>
<td>Functionalization possibilities for SWNTs: A) defect-group functionalization, B) covalent sidewall functionalization, C) noncovalent functionalization with surfactants, D) noncovalent exohedral functionalization with polymers, and E) endohedral functionalization</td>
<td>27</td>
</tr>
<tr>
<td>2.7</td>
<td>Functionalization of CNTs with acid modification</td>
<td>29</td>
</tr>
<tr>
<td>2.8</td>
<td>Scanning Electron Microscope</td>
<td>30</td>
</tr>
<tr>
<td>2.9</td>
<td>Transmission electron microscope</td>
<td>31</td>
</tr>
<tr>
<td>2.10</td>
<td>Elements in an EDX spectrum are identified based on the energy content of the X-rays emitted by their electrons as these electrons transfer from a higher energy shell to a lower energy one</td>
<td>33</td>
</tr>
</tbody>
</table>
2.11 Fourier Transform Infrared spectroscopy
2.12 (a) Stretching vibrations (b) Bending vibrations
2.13 Diffraction of X-rays from a set of planes
2.14 Schematic diagram of an X-ray diffractometer
2.15 Block diagram of a DTA instrument
2.16 A pictorial set-up for TGA measurements
2.17 Deformation of a Bar Produce by an Axial Load
2.18 Diagram of electron-transfer mechanisms between adjacent sites separated by a potential-energy barrier
3.1 (a): A photograph of NR (RSS) and (b) Chemical structure of NR(cis-1,4-polyisoprene)
3.2 A photograph of an electric balance
3.3 A photograph of Reflux system of MWCNTs
3.4 A photograph of centrifuge machine
3.5 A photograph of hot plate with magnetic stirrer
3.6 A photograph of the glass tray
3.7 Flow chart of CNT-NR composites preparation
3.8 Field emission scanning electron microscope, (JEOL JSM 7600F)
3.9 Fourier Transform Infrared Spectroscopy, (SIMADZU, FTIR-8400)
3.10 (a) The photograph of an X-ray diffractometer (b). Schematic diagram of an X-ray diffractometer
3.11 Photograph of the tensile strength measurement samples
3.12 Universal Testing Machine Instron 3369
3.13 (a): A schematic circuit diagram of DC measurement (b): Arrangement for DC measurement
3.14 The TG/DTA 6300 system which was used to study the thermal properties
4.1 TEM micrographs of MWCNTs
4.2 FESEM micrographs of pure Natural Rubber (NR) film of with (a) ×3k (b) ×10k
4.2 FESEM micrographs of pure Natural Rubber (NR) film of with (c) ×30k
4.3 FESEM micrographs of 0.5 wt% CNT-NR composites film of with (a) ×3k
4.3 FESEM micrographs of 0.5 wt% CNT-NR composites film of with (b) ×10k (c) ×30k
4.4 FESEM micrographs of 1.0 wt% CNT-NR composites film of with (a) ×3k (b) ×10k
4.4 FESEM micrographs of 1.0 wt% CNT-NR composites film of with (c) ×30k
4.5 FESEM micrographs of 1.5 wt% CNT-NR composites film of with (a) ×3k
4.5 FESEM micrographs of 1.5 wt% CNT-NR composites film of with (b) ×10k (c) ×30k
4.6 EDX spectra of NR, and 0.5 wt% CNT-NR composites
4.6 EDX spectra of 1.0 wt% and 1.5 wt% CNT-NR composites
4.7 Fourier Transform Infrared Spectroscopy spectra of p-CNTs and f-CNTs
<table>
<thead>
<tr>
<th>Section</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.8</td>
<td>Fourier Transform Infrared Spectroscopy spectra of NR and CNTs-NR composite</td>
</tr>
<tr>
<td>4.9</td>
<td>(a) XRD spectra of NR, 0.5 wt%, 1.0 wt% and 1.5 wt% CNT-NR composites (b) XRD spectra of NR and CNT-NR composites in 10-30° range (c) XRD spectra of NR, NR-CNT, NR-CG200 and NR-CG600 composites</td>
</tr>
<tr>
<td>4.10</td>
<td>TGA and DTG thermographs of NR</td>
</tr>
<tr>
<td>4.11</td>
<td>TGA and DTG thermographs of NR, 0.5, 1.0, 1.5 wt% CNT-NR composites in N2 environment</td>
</tr>
<tr>
<td>4.12</td>
<td>J-V plots for NR, 0.5 wt% CNT-NR, 1.0 wt% CNT-NR and 1.5 wt% CNT-NR polymer composites samples at room temperature</td>
</tr>
<tr>
<td>4.13</td>
<td>J-V plots for NR polymer sample at different temperature</td>
</tr>
<tr>
<td>4.14</td>
<td>J-V plots for 0.5 wt% CNT-NR polymer composite sample at different temperature</td>
</tr>
<tr>
<td>4.15</td>
<td>J-V plots for 1.0 wt% CNT-NR polymer composite sample at different temperature</td>
</tr>
<tr>
<td>4.16</td>
<td>J-V plots for 1.5 wt% CNT-NR polymer composite sample at different temperature</td>
</tr>
<tr>
<td>4.17</td>
<td>J vs wt% of CNTs in NR matrices</td>
</tr>
<tr>
<td>4.18</td>
<td>(a) Current density vs inverse of absolute temperature for NR polymer sample (b) Current density vs inverse of absolute temperature for 0.5 wt% CNT-NR polymer composite sample (c) Current density vs inverse of absolute temperature for 1.0 wt% CNT-NR polymer composite sample (d) Current density vs inverse of absolute temperature for 1.5 wt% CNT-NR polymer composite sample</td>
</tr>
<tr>
<td>4.19</td>
<td>Activation energy vs wt% of CNTs in NR matrices</td>
</tr>
<tr>
<td>Table No.</td>
<td>Table Captions</td>
</tr>
<tr>
<td>----------</td>
<td>--------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1.1</td>
<td>Theoretical and experimental properties of CNTs in comparison to graphite.</td>
</tr>
<tr>
<td>4.1</td>
<td>Mass percentages of the elements for NR, 0.5 wt%, 1.0 wt% and 1.5 wt% CNT-NR composites achieved by EDX analysis</td>
</tr>
<tr>
<td>4.2</td>
<td>Weight loss calculation for different sample by TG-DTG</td>
</tr>
<tr>
<td>4.3</td>
<td>The ‘n’ in $J \alpha V^n$ at different temperatures for NR, 0.5, 1.0 and 1.5 wt% CNT-NR polymer composites</td>
</tr>
<tr>
<td>4.4</td>
<td>Values of activation energy $\Delta E$ (eV) for CNT-NR polymer composite samples.</td>
</tr>
<tr>
<td>4.5</td>
<td>Tensile strength and Elongation at breaking% for NR, 0.5, 1.0 and 1.5 wt% CNT-NR polymer composites</td>
</tr>
<tr>
<td>SYMBOLS</td>
<td>LIST OF ABBREVIATIONS</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon Nanotubes</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Multiwalled Carbon Nanotubes</td>
</tr>
<tr>
<td>p-CNTs</td>
<td>Pristine Carbon Nanotubes</td>
</tr>
<tr>
<td>f-CNTs</td>
<td>Functionalized Carbon Nanotubes</td>
</tr>
<tr>
<td>NR</td>
<td>Natural Rubber</td>
</tr>
<tr>
<td>RSS</td>
<td>Ribbed Smoked Sheet</td>
</tr>
<tr>
<td>d-NR</td>
<td>Dissolved Natural Rubber</td>
</tr>
<tr>
<td>CB</td>
<td>Carbon Black</td>
</tr>
<tr>
<td>NP</td>
<td>Nano Particle</td>
</tr>
<tr>
<td>GE</td>
<td>Graphene</td>
</tr>
<tr>
<td>θ</td>
<td>Bragg angle</td>
</tr>
<tr>
<td>D</td>
<td>Crystallite size</td>
</tr>
<tr>
<td>ε</td>
<td>Microstrain</td>
</tr>
<tr>
<td>δ</td>
<td>Dislocation density</td>
</tr>
<tr>
<td>N</td>
<td>Crystallite per unit area</td>
</tr>
<tr>
<td>β</td>
<td>Full width half maximum</td>
</tr>
<tr>
<td>A</td>
<td>Absorbance</td>
</tr>
<tr>
<td>T</td>
<td>Transmittance</td>
</tr>
<tr>
<td>J</td>
<td>Current density</td>
</tr>
<tr>
<td>h</td>
<td>Plank’s constant</td>
</tr>
<tr>
<td>ρ</td>
<td>Electrical resistivity</td>
</tr>
<tr>
<td>σ</td>
<td>Electrical conductivity</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>ΔE</td>
<td>Activation energy</td>
</tr>
<tr>
<td>t</td>
<td>Thickness</td>
</tr>
</tbody>
</table>
Chapter-I

GENERAL INTRODUCTION
1.1 Introduction to Carbon Nanotubes

Since the discovery of carbon nanotubes (CNTs) by Japanese scientist Sumio Iijima in 1991[1], these have been attracted immense interest from a wide variety of disciplines such as chemistry, physics, biology, medicine and engineering. CNTs are allotropes of carbon with a nanostructure of cylindrical shape that can be viewed as seamless rolls of graphitic sheets. Their name is derived from their size, since the diameter of a CNT is on the order of a few nanometers (approximately 50,000 times smaller than the width of a human hair), while they can be up to several millimeters in length.

There are mainly two types of CNTs: Single Walled Carbon Nanotubes (SWCNTs) and Multi Walled Carbon Nanotubes (MWCNTs); however various nanotube related structures do exist and are reported. Fig. 1.1(a) shows the structural forms of SWCNT and MWCNT. SWCNTs result when one layer of graphene is wrapped into the form of a cylinder. These tubes have diameter of about 1.2-1.4 nm which may vary due to strain and different mode of wrappings. Both the side walls and the end caps of SWCNTs have different physical and chemical properties. As radius of the tube decreases, the partial sp$^3$ character of carbon atoms increases and thus leads to more reactivity. SWCNTs can be named by a chiral vector denotation (n, m) which describes how to roll up a graphene layer to make CNTs in an infinite graphene sheet (n and m denote unit vectors along two different directions in the graphene crystal lattice) [2-3]. Depending upon these chiral vectors, SWCNTs show difference in their properties such as optical activity, mechanical strength and electrical conductivity. Based on the chirality, CNTs can be again classified as given in Fig. 1.1(b). When n=m, it is called armchair form, when n-m=0, it is zigzag and all the others. Also for zig zag, n is a multiple of 3 whereas for chiral, n-m is a multiple of 3. The nanotubes could be metallic (armchair CNTs) and semiconducting (n-m=3i). In the case of semi metallic/semiconductor, the band gap can vary from 0–2eV.

CNTs show thermal conduction along the tube axis and also exhibit ballistic conduction (unimpeded flow of charge or energy carrying particles over high distances) [4]. However they are insulators laterally to the tube axis. This helps in tuning the properties. Table 1.1 gives a comparison in properties of CNTs with graphite [5].
Table 1.1: Theoretical and experimental properties of CNTs in comparison to graphite [5].

<table>
<thead>
<tr>
<th>Property</th>
<th>CNTs</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>0.8 gm/cm$^3$ for SWCNT; 1.8 gm/cm$^3$ for MWCNT (theoretical)</td>
<td>2.26 gm/cm$^3$</td>
</tr>
<tr>
<td>Elastic modulus</td>
<td>1 TPa for SWCNT; 0.3–1 TPa for MWCNT</td>
<td>1 TPa (in-plane)</td>
</tr>
<tr>
<td>Strength</td>
<td>50–500 GPa for SWCNT; 10–60 GPa for MWCNT</td>
<td>9.6 GPa</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>5–50 $\mu\Omega$ cm</td>
<td>50 $\mu\Omega$ cm (in-plane)</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>3000 W m$^{-1}$ K$^{-1}$ (theoretical), 3000 W m$^{-1}$K$^{-1}$ (in-plane)</td>
<td>6 W m$^{-1}$ K$^{-1}$ (c-axis)</td>
</tr>
<tr>
<td>Magnetic susceptibility</td>
<td>$22 \times 10^6$ emu/gm (perpendicular with plane) $0.5 \times 10^6$ emu/gm (parallel with plane)</td>
<td>$6 \times 10^6$ emu/cm$^3$</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>$&gt;700$ °C (in air); 2800 °C (in vacuum)</td>
<td>450–650 °C (in air)</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>10–20 m$^2$/gm</td>
<td>0.6 m$^2$/gm</td>
</tr>
</tbody>
</table>
Among all the various types of nanotubes discussed, the most important ones that attracted much attention are SWCNTs and MWCNTs due to their high stability and ease of preparation. And therefore focus is given on their properties and composites in this study. Moreover, its mechanical and electronic properties vary remarkably depending on the tube radius and the type.

1.1.1 Properties of Carbon Nanotubes

Mechanical Properties
Carbon nanotubes are one of the strongest materials in nature. Carbon nanotubes (CNTs) are long hollow cylinders of graphene. CNTs by geometry have different properties in axial and radial directions. It has been shown that CNTs are very strong in the axial direction. Young's modulus of the order of 270-950 Gpa and tensile strength of 11-63 GPa were obtained [6]. The strong in-plane graphitic carbon - carbon bonds make them exceptionally strong and stiff against axial strains.

Thermal Conductivity and Expansion
Many applications of CNTs, such as in nanoscale molecular electronics, sensing and actuating devices, or as reinforcing additive fibers in functional composite materials, have been proposed. CNTs in polymer suggest modest enhancements in strength characteristics of CNT-embedded matrixes as compared to bare polymer matrixes. Preliminary experiments and simulation studies on the thermal properties of CNTs show very high thermal conductivity. It is expected, therefore, that nanotube reinforcements in polymeric materials may also significantly improve the thermal and thermomechanical properties of the composites.

Electrical Conductivity
CNTs can be highly conducting, and hence can be said to be metallic. Their conductivity has been shown to be a function of their chirality, the degree of twist as well as their diameter. CNTs can be either metallic or semi-conducting in their electrical behavior.
1.1.2 Importance of Carbon Nanotubes:
CNTs having a number of valuable and unique properties, including high thermal and electrical conductivity, unique optical properties, high flexibility, increased stiffness, high tensile strength, light weight, etc. are useful for the following applications

- Micro- and nano-electronics
- Structural composite materials
- Flat-panel displays
- Conductive plastics
- Atomic Force Microscope (AFM) tips
- Ultra-capacitors
- Radar-absorbing coating
- Technical textiles such as conductive cotton textiles
- Gas storage
- Power applications (e.g. batteries with improved lifetime, photovoltaic)
- Sensors and Biosensors
- Extra strong fibers

Fig. 1.2 Applications of CNTs [from web].
When applied to products, these properties provide tremendous advantages. For example, when used in polymers, bulk CNTs can improve the thermal and electrical properties of the products.

1.2 Literature review

Fig. 1.3 SEM micrographs of the NR/MWCNT composites: (A) \( p \)-MWCNT (1 wt \%) dispersed in an NR matrix, (B) \( f \)-MWCNT (1 wt \%) dispersed in an NR matrix, (C) MWCNT–PDDA (0.5 wt \%) dispersed in an NR matrix, (D) MWCNT–PDDA (2 wt \%) dispersed in an NR matrix, and (E) MWCNT–PDDA (5 wt \%) dispersed in an NR matrix [7].
Peng et al. [7] investigated natural rubber/multiwalled carbon nanotube (NR/MWCNT) composites were prepared by a combination of the latex compounding and self-assembly techniques. The morphological structures of the composites depended on the loadings of f-MWCNTs which were modified with Poly diallyl dimethylammonium (PDDA) chloride as an intermedium. MWCNTs were dispersed well in NR when the loading was lower than 3 wt% but aggregation was observed when more MWCNTs were added. These structural and morphological effects contributed directly to the thermal and mechanical properties of the composites. Significant improvements in the tensile strength and modulus was demonstrated when the MWCNT loading was between 1 and 2 wt% whereas a further increase in the loading showed only limited reinforcement.

![Graphs](image)

Fig.1.4 (a) TG curves of the NR and NR/MWCNT composites in N₂ and (b) DTG curves of the NR and NR/MWCNT composites in N₂ [7].
Abdulateef et al. [8] studied NR composites compounded with both unmodified and acid-modified CNT were investigated with respect to mechanical and dynamic mechanical properties. There is improvement in mechanical properties due to the efficient stress transfer between the matrix and filler. The dynamic mechanical properties showed enhancement especially in the low temperature region. Both storage and loss moduli showed many-fold increase for the composites with modified CNT, along with drop in the tan δ value. Crystallization of NR from DSC studies showed two different regions of crystallization due to the CNT reinforcement and coiling of NR chains over the surface of CNT. TEM studies confirm better dispersion of modified CNT in the matrix as there is drop in the aggregating tendency of CNT. In general, the acid modification of CNT improved the dynamic mechanical and mechanical properties of NR composites over a range of filler loading especially at the lower end.

Fig. 1.5 TEM images composites at 1% filler loading (a) NR/CNT and (b) NR/m-CNT [8].

Fig. 1.6 TGA and DTG curves of NR/CNT composites [8].
Fig. 1.7 DSC thermograms of NR/CNT composites (a) unmodified CNT and (b) m-CNT [8].

Fig. 1.8 TEM images of CNT/NR composites containing 1 wt % filler (a) CNT and (b) phenol functionalized CNT [9].
Thomas et al. [9] studied on the effect of phenol functionalization of CNTs on the mechanical and dynamic mechanical properties of NR composites. To weaken the filler-filler agglomeration in CNT, the CNT surface was phenol functionalized. The CNT-NR nanocomposites were prepared by solvent mixing followed by two-roll compounding. Incorporation of CNT in NR matrix causes an increase in static modulus with consequent decrease in elongation at break. But the tensile strength reaches a maximum at a loading of 5 phr, beyond which the strength decreases. The dynamic modulus of the nanocomposites increases with increase in CNT loading and the effect is more pronounced in the case of functionalized CNT. Functionalization of CNT causes manifold increase in the ratio of storage modulus of the CNT/NR composite at room temperature to that of neat NR at all CNT loadings, indicating improved filler-matrix adhesion. This is corroborated by the drop in the ratio of the tangent loss at $T_g$ of the CNT/NR composite to that of the neat NR at all CNT loadings. TEM and electrical resistivity measurements indicate improved dispersion of CNT in NR matrix upon phenol functionalization.

![Fig. 1.9 DSC thermograms of NR composites with (a) CNT and (b) phenol functionalized CNT [9].](image)

Bokboza [10] investigated Electrical and Mechanical properties of MWCNT-NR composites. The volume resistivity of the composites decreases with increasing the MWCNTs content and the electrical percolation threshold is reached at less than 1 phr of MWCNTs (phr = parts of filler by weight per hundred parts of rubber). This is caused by the formation of conductive chains in the composites. The presence of a small number of agglomerates acting as defects is responsible of the lack of improvement in rupture properties. The high aspect ratio of MWCNTs is the main parameter for mechanical reinforcement and electrical conduction. The high aspect ratio also explains the formation of a filler network at a low nanotube loading.
Fig. 1.10 (a, b, c) TEM images of NR filled with 3 phr of MWNTs taken at different scales. d) shows the graphene layers of an individual tube [10].

Fig. 1.11 Volume resistivity against nanotube loading for NR composites [10].

1.3 Objective of This Study

Nowadays, rubber technology has become an important part in industry. Because of the remarkable properties of rubber, it is used extensively in industrial and societal fields. The essential modulus and strength of neat rubber is low, it is necessary to introduce an additional reinforcing phase to achieve optimum properties for practical purposes. The use of CNTs for the reinforcement of NR composites is a new technology that gives high expectations because it has shown enhancement in the
composites, especially in its mechanical properties. The main purpose of this work is to develop efficient methods of nanotube functionalization using acid modification and dispersed CNTs in NR homogeneously.

**Objectives of this research are-**

1. To prepare polymer nanocomposite incorporating different percentages of CNT in NR using solution casting method.
2. To obtain the crystallite size and structural phase of the CNT-NR composites by XRD.
3. To investigate the surface morphology of the neat NR and CNT-NR nanocomposites by SEM and EDX.
4. To study the variation of electrical conductivity of the CNT-NR nanocomposites for different percentages of CNT in it by DC electrical measurements.
5. To investigate the melting, decomposition and thermal stability of the casted films by TG/DTA.
6. To obtain the tensile strength and elongation at break of the CNT-NR nanocomposites from mechanical study.

**1.4 Thesis Layout**

This thesis paper has been represented by five chapters. Chapter one contains general introduction, review of previous works where a considerable number of literatures are reviewed to recognize the importance of those investigations for the present work, and it also contains objectives of the research work.

Functionalization methods of CNTs is presented in chapter two. Different characterization processes are discussed in this chapter.

In chapter three, the experimental details are narrated including the details of the solution casting set up, nanocomposite preparation method. A brief description of the instrumentation of the different characterization techniques has been also mentioned in this chapter.

Results and Discussion which is presented in chapter four. The morphological, elemental, structural, thermal properties of CNT-NR polymer composites are discussed in this chapter. The mechanical and DC electrical conduction mechanism are also studied in this chapter.

Finally, the conclusions of the research work, outcome of the work and suggestion for the future research on this material are included in chapter five.
References


Chapter-II
THEORETICAL BACKGROUND
2.1 Polymers

Polymers are defined as macromolecules composed of one or more chemical units (monomers) that are repeated throughout a chain. The basic part of a polymer are the monomers, the monomers are the chemical units that are repeated throughout the chain of a polymer containing ten or less atom in a row. Carbon and hydrogen are the most common atoms in monomers, but oxygen, nitrogen, chlorine, fluorine, silicon and sulfur may also be present. Think of a polymer as a chain in which the monomers are linked (polymerized) together to make a chain with at least 1000 atoms in a row. It is this feature of large size that gives polymers their special properties. Polymers are created through chemical reactions known as polymerizations, and the majority is produced through two basic reaction types. The first type of polymerization reaction is known as a condensation polymerization. The second type of reaction is known as chain-growth polymerization.

2.1.1 Classification of Polymer

The following are some of the common classifications of polymers:

<table>
<thead>
<tr>
<th>Basis of Classification</th>
<th>Polymer Type</th>
<th>Basis of Classification</th>
<th>Polymer Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Natural</td>
<td>Tacticity</td>
<td>Isotactic</td>
</tr>
<tr>
<td></td>
<td>Semi synthetic</td>
<td></td>
<td>Syndiotactic</td>
</tr>
<tr>
<td></td>
<td>Synthetic</td>
<td></td>
<td>Atactic</td>
</tr>
<tr>
<td>Thermal response</td>
<td>Thermoplastic</td>
<td>Polarity</td>
<td>Polar</td>
</tr>
<tr>
<td></td>
<td>Thermosetting</td>
<td></td>
<td>Nonpolar</td>
</tr>
<tr>
<td>Mode of formation</td>
<td>Addition</td>
<td>Chain</td>
<td>Hetero</td>
</tr>
<tr>
<td></td>
<td>Condensation</td>
<td></td>
<td>Homochain</td>
</tr>
<tr>
<td>Line Structure</td>
<td>Linear</td>
<td>Crystallinity</td>
<td>Noncrystalline</td>
</tr>
<tr>
<td></td>
<td>Branched</td>
<td></td>
<td>Semicrystalline</td>
</tr>
<tr>
<td></td>
<td>Cross-linked</td>
<td></td>
<td>Crystalline</td>
</tr>
<tr>
<td>Application &amp; Physical Properties</td>
<td>Rubber</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Plastic</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fiber</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

On the basis of Origin, polymers can be classified into three groups

1. Natural polymer: The polymers, which occur in nature are called natural polymer known as biopolymers. Examples of such polymers are: natural rubber, natural cellulose, starch, proteins, etc.
2. **Semi synthetic polymer:** They are the chemically modified natural polymers such as hydrogenated natural rubber, cellulose, cellulose nitrate, methyl cellulose, etc.

3. **Synthetic polymer:** The polymer which has been synthesized in the laboratory is known as synthetic polymer. These are also known as manmade polymers. Examples of such polymers are polyvinyl alcohol, polyethylene, polystyrene, polysulfone, etc.

**Classification Based on Thermal Responses**

On the basis of thermal response, polymers can be classified into two groups

1. **Thermoplastic polymers:** They can be softened or plasticized repeatedly on application of thermal energy, without much change in properties if treated with certain precautions. Example of such polymers are Polyolefins, nylons, linear polyesters and polyethers, PVC, sealing wax etc.

2. **Thermosetting polymers:** Some polymers undergo certain chemical changes on heating and convert themselves into an infusible mass. The curing or setting process involves chemical reaction leading to further growth and cross linking of the polymer chain molecules and producing giant molecules. For example, Phenolic, resins, urea, epoxy resins, diene rubbers, etc.

**Mode of Formation**

On the basis of mode of formation, polymers can be classified as

1. **Addition Polymers:** They are formed from olefinic, diolefinic, vinyl and related monomers. They are formed from simple addition of monomer molecules to each other in a quick succession by a chain mechanism. This process is called addition polymerization. Examples of such polymers are polyethylene, polypropylene, polystyrene.

   ![Chemical structure of Poly-Chloroethene](image)

   **Fig. 2.1** Chemical structure of Poly-Chloroethene.

2. **Condensation Polymer:** They are formed by the combination of two monomers by removal of small molecules like water, alcohol or NH₃, Nylon 6,6, Nylon6, etc. For example, Nylon 6, 6 is formed by the condensation of hexamethylene diamine with adipic acid.
Classification based on structure of polymer

1. **Linear polymers on Structure**: In these polymers monomers are linked with each other and form a long straight chain. These chains have no any side chains, ex. Polyethylene, PVC, NYlons, Polyesters etc. Their molecules are closely packed and have high density, tensile strength. These are represented in Fig. 2.3(a).

2. **Branched Chain Polymers**: They have a straight long chain with different side chains. Their molecules are irregularly packed hence they have low density, tensile strength and melting point, ex. polypropylene, amylopectin and glycogen.

3. **Crosslinked or Network Polymers**: These polymers in which two linear chains are joined together by covalent bonds and they have three dimensional. Degree of crosslinking is a number of junction point per unit volume. Polymers crosslinking are hard, rigid and brittle due to their network structure. Polymers cross linked do not dissolve in solvents because all the polymer chains are covalently tied together, but they can absorb solvents. Ex. Bakelite, melamine, formaldehyde resins, vulcanized rubber etc. These polymers are depicted in Fig. 2.3(c).
2.1.2 Natural Rubber (NR)

Natural rubber is the prototype of all elastomers. It is extracted in the form of latex from the bark of the Hevea tree. The rubber is collected from the latex in a series of steps involving preservation, concentration, coagulation, dewatering, drying, cleaning, and blending. Because of its natural derivation, it is sold in a variety of grades based on purity (color and presence of extraneous matter), viscosity, viscosity stability, oxidation resistance, and rate of cure. Modified natural rubbers are also available, with treatment usually performed at the latex stage. These include:

1. Epoxidized natural rubber (ENR).
2. Deproteinized natural rubber (DNR).
3. Process oils have been incorporated.
4. Heveaplus MG rubber
   – natural rubber with grafted poly(methyl methacrylate) side chains.
5. Thermoplastic natural rubber (TNR) – blends of natural rubber and polypropylene.

The natural rubber polymer is nearly 100% cis-1,4 polyisoprene with $M_w$ ranging from 1 to $2.5 \times 10^6$ PP. Due to its high structural regularity, natural rubber tends to crystallize spontaneously at low temperatures or when it is stretched. Low temperature crystallization causes stiffening, but is easily reversed by warming. Crystallization gives natural rubber high tensile strength and resistance to cutting, tearing, and abrasion.
Like other high polymers, natural rubber can be pictured as a tangle of randomly oriented sinuous polymer chains. The “length” of these chains is a function of their thermodynamic behavior and is determined as the statistically most probable distance between each end. This chain length reflects the preferred configuration of the individual polymer molecule. The application of force to a rubber sample effectively changes the chain length. When the force is removed, the chain tries to regain its preferred configuration. In simple terms, this can be compared to the compression or extension of a spring. This effect is the basis of rubber’s elasticity.

Elasticity is one of the fundamentally important properties of natural rubber. Rubber is unique in the extent to which it can be distorted, and the rapidity and degree to which it recovers to its original shape and dimensions. It is, however, not perfectly elastic. The rapid recovery is not complete. Part of the distortion is recovered more slowly and part is retained. The extent of this permanent distortion, called permanent set, depends upon the rate and duration of the applied force. The slower the force, and the longer it is maintained, the greater is the permanent set. Because of rubber’s elasticity, however, the permanent set may not be complete even after long periods of applied force. This quality is of obvious value in gaskets and seals.

The rubber’s polymer network allows elasticity and flexibility to be combined with crystallization-induced strength and toughness when stretched. The elastic nature of this network also accounts for the exceptional resilience of cured rubber products. This resilience means less kinetic energy is lost as heat during repeated stress deformation. Products made from natural rubber are less likely than most other elastomers to fail from excessive heat buildup or fatigue when exposed to severe dynamic conditions. This has secured the place of natural rubber as the preferred sidewall elastomer in radial tires.

As already noted, the rubber polymer network was originally an impediment to rubber processing. Mixing additives with a tough, elastic piece of raw rubber was a substantial challenge. The solution came with the discovery of its thermoplastic behavior. High shear and heat turn the rubber soft and plastic through a combination of extension, disentanglement, and oxidative cleavage of polymer chains. In this state it is considerably more receptive to the incorporation of additives so that the rubber's natural attributes can be modified and optimized as desired. The commercial utility of natural rubber has in fact grown from the ease with which its useful properties can be changed or improved by compounding techniques.
Another important and almost unique quality of uncured natural rubber compounds is building tack. When two fresh surfaces of milled rubber are pressed together they bond into a single piece. This facilitates the building of composite articles from separate components. In tire manufacture, for example, the separate pieces of uncured tire are held together solely by building tack. During cure they fuse into a single unit.

Natural rubber is used in the carcass of passenger car cross-ply tires for its building tack, ply adhesion, and good tear resistance. It is also used in the sidewalls of radial ply tires for its fatigue resistance and low heat buildup. In tires for commercial and industrial vehicles, natural rubber content increases with tire size. Almost 100% natural rubber is used in the large truck and earthmover tires which require low heat buildup and maximum cut resistance. Natural rubber is also used in industrial goods, such as hoses, conveyor belts, and rubberized fabrics; engineering products, for resilient load bearing and shock or vibration absorption components; and latex products such as gloves, and adhesives.

2.1.3 Applications of Polymer Composites

Elastomer composites containing conducting fillers such as CB, carbon fiber, and metal fiber have been extensively investigated for multi-functional applications such as structural reinforcement [1], EMI shielding, electronic packaging, radar absorbing materials and high charge storage capacitors. Addition of CNTs is promising in improving the flame retardancy of elastomers as well [2]. These nanofillers have the unique ability to delay ignition, reduce smoke emissions and eliminate slumping and dripping of the molten polymer by formation of a strong, stable char. Some applications such as flame retardant material include wire and cable covers, battery jars and electrical enclosures, small appliances and home interior decoration materials. The CNT composites have potential applications in automotive industry that could lead to better quality, lower cost, less fuel consumption and lower environmental emissions. Those applications include electrostatic painting of exterior panels, shielding of automotive electronics and addition of nanofibers to tyres to improve stiffness. Recent researches developed a high performance rubber sealing material resisting 260°C / 240 MPa using a special composite of surface controlled MWCNT, which can act as a sealing material. This composite material can be used at low temperatures in a real oil field, which can avoid the energy crisis [3]. High
performance CNT composites out of NR and aligned MWCNTs with large elastic modulus and thermal and electrical conductivities were reported by Sui et al. [1] and Kim et al. [4].

Recently, Hata and co-workers [5] developed a new viscoelastic material from CNTs that is similar to SR, but maintains temperature independent viscoelasticity at a range of temperatures from -196 to 1000°C in an oxygen-free environment, unlike the traditional composites. Among many other applications, temperature-invariant rubbery material made from CNTs could be used as dampeners (anti-vibration mounts) for high-vacuum furnaces and even aerospace vehicles that travel to the cold interstellar space. These composites remain flexible over the entire temperature range. This CNT rubber can be stretched in the direction of applied stress up to 5% strain and the porous network structure, coupled with excellent thermal transport properties intrinsically associated with CNTs, allows the CNT rubber for rapid and efficient heat dissipation to prevent significant heat accumulation. CNT rubber composite materials with exotic viscoelastic properties can outperform the existing elastomers. Even though it is difficult to picture all the applications of elastomer composites, a few of them are illustrated in Fig. 2.5.

In addition, conducting rubber composite out of EPDM, MWCNT and clay is used as strain sensors [6]. In the same way, MWCNT/SR composite gives a positive piezoresistance both parallel and perpendicular to the direction of applied pressure [7]. Conductive thermoplastic elastomer composites of PP/EPDM with three kinds of carbon fillers including CB, MWCNT and hybrid CNT-CB show piezoresistive properties depending on the nature of filler, concentration and percolation threshold [8]. At low filler concentration high pressure-resistance sensitivity and at high concentration low pressure-resistance sensitivity is observed. These composites are well suited for fabricating pressure sensors, the detailed study of which is given in the next section. There are certain other kinds of sensors useful for health monitoring [9] and for detecting dangerous deformations and vibrations of vehicle parts as well.

CNTs having high dielectric constant are very effective for synthesising composite dielectrics. Such composites are very beneficial as actuators for artificial muscles, capacitors for energy storage, sensors for mechanical strain, humidity, and gases and in flexible electronics [10-15]. CNTs can act as the electric or light induced heating sources for liquid crystalline elastomers. They are efficient heat absorbers and can convert heat energy to light energy [16]. This is really important in the field of
electronics specifically in solar cells or light emitting diodes. The three dimensional network structure formed by boron doping of CNTs by CVD behaves like elastomer solids and these materials have unique properties. These oil absorbing sponge-like solids possess multi functionalities such as ultra-light weight, super-hydrophobicity, high porosity, thermal stability and mechanical flexibility [17]. Moreover photo-actuating materials based on the commercial elastomer EVA filled with well-dispersed MWCNTs were also developed as potential materials for the fabrication of smart actuators [18].

Figure 2.5 Major application of CNT/elastomer composites a) Home appliances b) switches c) pressure sensing skin in robotics d) strain sensor attached to tyre engineering e) energy storage application as capacitors and f) cables [5].

2.2 Different Methods of Nanocomposites Preparation Techniques

The major composite manufacturing methods usually employed are explained here in detail.

2.2.1 Freeze drying

Freeze drying is a process whereby solutions are frozen in a cold bath and then the frozen solvents are removed through sublimation under vacuum, leading to the formation of porous structures. The nature, size, volume and morphology of pores depend on freeze temperature, solution concentration, nature of solvent and solute, and the control of the freeze direction. Aqueous, organic, colloidal and supercritical CO$_2$ solutions are used in this technique generally to produce porous structures [19].
A dispersion of filler in the polymer matrix is prepared by simple mixing and is allowed to condense in liquid $\text{N}_2$ and then it is compression molded. Up to now, this technique is not widely used to synthesize CNT/elastomer composites. Yu et al. [20] effectively synthesized CNT polystyrene latex composites using freeze drying followed by compression molding method. The same technique can be proposed to prepare elastomer latex composites also.

### 2.2.2 Spray drying

A suspension of CNTs in elastomer can be converted to CNT/elastomer powder composites by spray drying process. For this, the suspension of CNTs (with or without functionalization)/elastomer/vulcanizing reagents is homogeneously mixed, atomized and dried by means of spray drying to obtain powders of composites. By means of spray drying process, uniform globules of polymers (diameter less than 10 $\mu$m) could be fabricated in which CNTs are well dispersed. Zhou et al. [21-22] synthesized SBR powders containing CNTs with uniform diameters of about 5-10$\mu$m using spray drying process. Compared with those of pure SBR composites, the hardness and tear strength of the composites filled with 60phr CNTs are enhanced by 70 and 250% respectively, and the tensile strength of the composites with 50phr CNTs improved remarkably by 600%.

### 2.2.3 Latex stage compounding

Rubber latex can be compounded with CNTs along with curing agents. The main crosslinking method is using sulphur in the presence of ZnO, stearic acid, Tetramethyl Thium Disulfide (TMTD), 2,2'-Dithiobis(benzothiazole) (MBTS) etc. This process improves crosslinking between the polymer chains in the composites. In this process, at first the curing agents are mixed well with the latex by milling methods, which is called compounding and then the compounded latex is mixed with the CNTs [23]. This method is successfully utilised by Anand et al. [24] for preparing MWCNT/NR latex composites. They compounded the NR latex using ball milling and thereafter composites are formulated using mechanical mixing and noticed good improvement in mechanical, rheological and electrical properties.

### 2.2.4 Hetero coagulation approach

The typical heterocoagulation process is based on depositing small charged particles on the surface of larger particles of opposite charge. The method is based on ion exchange between cationic latex particles and anionic (oxidized) nanoparticles [25]. The electrostatic interaction between the filler and polymer is believed to enhance the
filler–polymer adhesion [26]. Heterocoagulation method was also successfully used to prepare exfoliated clay filled polymer composites [27-28]. This technique is employed by Peng et al. [29] while preparing functionalized MWCNT/NR composites. The interaction between the charged particles binds them together to give well dispersed composite materials.

2.2.5 In-situ polymerization

In situ polymerization to fabricate CNT based composites involves the polymerization of corresponding monomers in situ within the CNT suspensions. This offers an easy and efficient method to disperse CNTs uniformly in the polymer matrix. The type of polymerization reaction, nature of solvents used, reaction conditions etc. may vary based on the type of composite required. Curing of elastomers can be done by directly adding curing agents also in situ. When the monomers polymerize in the presence of CNTs, covalent bonds can be formed between the monomer units as well as with the functionalized CNTs. These strong matrix-filler bonds enhance the interfacial interaction and lead to highly improved properties like mechanical strength of the composites [30-32]. This method is particularly used for polymers that cannot be prepared by solution processing (insoluble polymers) and melt mixing (thermally unstable polymers).

2.2.6 Melt blending/Extrusion

As the name indicates melt blending offers a high temperature shear mixing for composite fabrication. In this method, elastomers are melted in internal mixers or two roll mills by adding CNTs. This is the most industrially preferred method of composite manufacturing since it avoids the usage of solvents. The machines used for this purpose are designed such a way that the screws inside it can move at high speeds which in turn results in efficient dispersion of CNT bundles inside the elastomer matrix. Even though this method is the best suited one for commercial scale, it has two disadvantages. One is the high possibility of efficient dispersion of CNTs only at higher concentration inside the elastomer matrix [33] and the second is the difficulty to add curing agents to elastomers at high processing temperatures. So this method is more concentrated on thermoplastics reinforced composites. However there are a few works reported on fabrication of elastomer composites also. For instance, Das et al. obtained good dispersion of CNTs in SBR and butadiene rubber (BR) blend following melt mixing [34]. They also fabricated [35] MWCNT/CR composites by adding the
CNT dispersion using ethanol as dispersion agent in to mill mixed CR and obtained excellent mechanical properties.

2.2.7 Solid state shear pulverization
Polymer and CNTs were mixed and pulverized by pan mill or twin screw extruder and the polymers are grafted on CNTs. The major advantage of this technique includes its easy scale-up. This is a solvent less process [36]. Xia et al. [37] and Masuda et al. [38] prepared CNT/polymer composites via solid state shear pulverization and proved that this technique improves the dispersion rate of the nano fillers in the matrix and results in a major property enhancement. By this process powders of the composites are obtained. Other methods of composite manufacture include growing a pre aligned array of CNTs in a substrate by CVD and then infiltration of a monomer in to these arrays and its polymerization. The resulting composite film showed good dispersion of nanotubes in the polymer and gave enhanced thermal stability. Electrophoretic deposition method is also possible by moving the charged particle dispersed in a suitable solvent towards an electrode under an applied electric field. The functional groups on CNTs can solubilize them in water and can create a negative charge which helps them to move towards anode [39]. This offers advantages of low cost, uniformity of the coatings and possibility of depositing on complex shaped substrates. The techniques for CNT dispersion are not limited to those described above. Many of the recent studies are often based on the use of a combination of aforementioned techniques, such as ultrasonication plus ball milling [40], and ultrasonication plus extrusion [41–42] etc. By combining the latex stage compounding with self-assembly technique, Peng et al. synthesized MWCNT/NR latex composites and obtained good adhesion behavior at <3 % CNTs content [43]. They suggested the enhanced state of dispersion based on morphology and thermal analyses as a result of the combined techniques.

2.2.8 Solvent casting
This method involves dispersion of both filler and matrix in separate suitable solvents and thereafter mixing the two. The solvent evaporates to get dry samples of the composite. Following this method, Bokobza et al. [44] formulated CNT/styrene butadiene rubber (SBR) composites and achieved a 45% increase in modulus and a 70% increase in the tensile strength with 1 phr (per hundred rubber) MWCNT. Solvent casting is found to be the most useful and effective method in the case of latex matrices as this does not require the dissolution of the elastomer in any
additional solvent depending on the nature of the filler. But if the filler is not compatible with the aqueous elastomer matrix, both the elastomer and filler dispersions are made in other suitable solvents. Khalid et al. [45] also dispersed CNTs in NR by solvent casting using toluene.

### 2.2.8.1 Advantages of Solvent Casting Method

Manufacturing process advantages of polymer solution casting over traditional film extrusion methods include:

- Processing at low temperatures, which is valuable for thermally activated films or applications incorporating temperature-sensitive active ingredients.
- Ability to produce high-temperature resistant films from non-thermoplastic soluble raw materials.
- Simplified incorporation of additives and fillers.
- Quicker changeovers for platforms with many part numbers that are differentiated based on formula.
- Single pass manufacturing of multi-layer films (e.g., the ability to cast a film, then coat an adhesive and laminate release liner on one side, and coat a top coat on the other side).
- Wider range of material choices with casting from either aqueous or solvent-based solutions.

### 2.2.8.2 Advantages of the resulting film

- Greater film thickness uniformity, as tight as +/-2%.
- Wider range of film thickness, from 150 microns down to less than 12 microns.
- Films that are gel and pinhole free.
- Excellent flatness and dimensional stability.
- Isotropic orientation (mechanical and optical) as film is not stretched during manufacture.
- Absence of typical extrusion process lubricants.

### 2.3. Functionalization of Carbon Nanotubes

The carbon nanotube unique properties make it desirable for different applications. For most of these applications nanotubes require functionalization, such as changing some of the graphite properties to make nanotubes soluble in different media, or
attaching different groups or even inorganic particles for future utilization of modified nanotubes.

All functionalization methods of carbon nanotubes can be divided into two major groups (Fig. 2.6):

1. Functionalization from inside (endohedral), [46] shown in Fig. 2.6 (E), meaning that nanotubes are functionalized by filling them with different nanoparticles, this can be achieved either by
   i) Exploiting the phenomenon of spontaneous penetration when nanotubes are filled with colloidal suspensions followed by evaporation of the carrier liquid; or by
   ii) Wet chemistry, when the nanotubes are filled with some compounds, which react under particular thermal or chemical conditions and produce nanoparticles. These nanoparticles then become trapped in the nanotubes.

Fig. 2.6: Functionalization possibilities for SWNTs: A) defect-group functionalization, B) covalent sidewall functionalization, C) noncovalent functionalization with surfactants, D) noncovalent exohedral functionalization with polymers, and E) endohedral functionalization [46].

2. Chemical functionalization from outside (exohedral), [46] Fig. 2.6 (A-D). This group also can be subdivided into three subgroups based on the mechanism of attachment of different groups or compounds to the sidewall of the nanotube:
   i) Covalent functionalization by attaching functional groups to the nanotube ends or defects;
   ii) Covalent functionalization through “sidewall functionalization”.
iii) Non-covalent exohedral functionalization, for example, wrapping nanotubes by polymers [46].

Dujardin with coworkers made the first experiments on filling MWNTs with cesium, selenium, and sulfur and empirically found that materials with surface tension less than 200 mN/m could fill the nanotubes by capillary action [47]. In 1994, Tsang and coworkers produced nanotubes filled with corresponding metal oxide compounds while opening a nanotube with nitric acid solution containing metal (cobalt, nickel, iron, uranyl) nitrate [48]. Chu et al. showed the filling of MWNTs with gold and silver by the same wet chemistry method [49].

**Exohedral Functionalization**

The purpose of the chemical functionalization of the outer walls of nanotubes, or exohedral functionalization, is to make nanotubes soluble in different media. This is needed, for example, to make composites, and to attach different groups or metals for use in sensors.

Two major groups of chemical functionalization of CNTs via covalent attachment can be selected:[50]

i) First is the functionalization via “end and defect-side chemistry” [51]. When the nanotubes were discovered, Iijima described the structure of carbon nanotubes as perfect graphite sheets rolled into nanocylinders. In reality, there are no perfect nanotubes rolled from the perfect graphitic sheets. Some nanotubes are bent or have defects; for example, Stone-Wales defects, which are comprised of 5 and 7 rings.

ii) The second group of covalent attachment is modification through “sidewall functionalization”. By treatment of nanotubes in an oxidizing environment, for example in a mixture of concentrated nitric and sulfuric acids, the oxygen-containing groups are introduced to the ends and sidewalls of the tubes. These groups, which are chemically attached to the tubes, are mostly represented by –COOH groups, less by –C=O, and –OH groups [52-53]. These groups can serve as starting points for further functionalization of the nanotubes [54-56].

Among these functionalization processes I have been used covalent functionalization through sidewall functionalization. For sidewall functionalization I have been used acidic treatment because it can damage the sidewall of carbon nanotubes and the outer layer of MWCNTs is covalently functionalized to become non-conducting, whereas the unmodified inner layers remain conducting. This leads to increase the dielectric
constant while lessening the increase in electrical conductivity and dielectric loss of the CNT-polymer composites.

CNT composites with high dielectric constant are increasing attention in many technological fields. But, though there is an increase in dielectric constant, these composites show an increase in dielectric loss and a significant decrease in dielectric strength, which are undesirable for many practical applications. To increase the dielectric constant by minimizing the increase in dielectric loss in CNT-polymer composites is a matter of great importance. It should also be noted that covalent functionalization on CNT surface can damage their intrinsic properties like electrical conductivity.

For functionalization of MWCNTs I have been taken 1gm of MWCNTs, 20 mL concentrated (98%) H₂SO₄ and 20 mL concentrated (65%) HNO₃. Then steering the solution 6 h with a magnetic stirrer on an oil-bath. The temperature was kept at 80°C and water flow into the condenser to condense acid. To remove excess acid from CNTs washed with distilled water. The functionalized CNTs were kept in a beaker. Then it was washed with distilled water by centrifuge machine. Finally, it was dried in an oven at 50°C.

![Reflux in HNO₃+H₂SO₄ → f-CNTs → Centrifuge → Drying in Oven at 50°C](image)

Fig. 2.7 Functionalization of CNTs with acid modification.

### 2.4 Theory of Surface Morphology

Morphology is a qualitative evaluation of the three dimensional shape of a surface, i.e., “what a sample looks like,” and also evaluate the size of a line, an area, or a volume; the texture or topography of a surface; the habit of a crystal; the distribution of phases in a system material is best evaluated using imaging techniques, such as optical microscopy or Scanning Electron Microscopy SEM. These methods can also provide layer thickness and other quantitative information.
2.4.1 Scanning Electron Microscope

SEM scans a focused electron beam over a surface to create an image. The electrons in the beam interact with the sample, producing various signals that can be used information about the surface topography and composition.

Fig. 2.8 Scanning Electron Microscope.

Electrons are generated at the top of the microscope by metallic filament. This region is referred to as the electron gun. The filament is very similar to what we see inside a light bulb. The emitted electrons are then formed into a beam and accelerated down the column toward the specimen. The beam is further focused and directed by electromagnetic lenses as it moves down the column. When the beam reaches the specimen, electrons are knocked loose from the surface of the specimen. These electrons are referred to as secondary electrons. These electrons are "seen" by a detector that amplifies the signal and sends it to a monitor. The electron beam scans back and forth across the sample building up an image from the number of electrons emitted from each spot on the sample.
2.4.2 Transmission Electron Microscopy

![Diagram of Transmission Electron Microscope]

TEM is an imaging technique whereby a beam of electrons is focused onto a specimen causing an enlarged version to appear on a fluorescent screen or on a photographic film or to be detected by a CCD camera. Electrons are generated by a process known as thermionic discharge in the same manner as in a cathode ray tube, or by field emission; they are then accelerated by an electric field and focused onto the sample. The electrons can be focused onto the sample providing a resolution far better than that possible with light microscopes, with improved depth of vision. Details of a sample can be enhanced in light microscopy by the use of stains. Similarly with electron microscopy, compounds of heavy metals such as osmium, lead or uranium can be used to selective deposit on the sample to enhance structural details. The electrons that remain in the beam can be detected using a photographic film or fluorescent screen. So areas where electrons are scattered appear dark on the screen, as on a positive image. TEM is a straight forward technique to determine the size and shape of the nanostructure materials as well as to obtain structural information. In TEM, electrons accelerated to 100 keV or higher are projected on to a
thin specimen by means of a condenser lens system and they penetrate into the sample [57].

TEM uses transmitted and diffracted electrons which generate a two dimensional projection of the sample. The principal contrast in this projection or image is provided by diffracted electrons. In bright field images, the transmitted electrons generate bright regions while the diffracted electrons preferentially form the image. In TEM, one can switch between imaging the sample and viewing its diffraction pattern by changing the strength of the intermediate lens. The great advantages that TEM offers are the high magnification ranging from 50 to 106 and its ability to provide both image and diffraction information of the same sample. The schematic of a TEM is shown in Fig. 2.9.

2.4.3 Energy Dispersive X-Ray Spectroscopy

The EDX analysis system works as an integrated feature of a scanning SEM and cannot operate on its own without the latter. During EDX analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atoms own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell. To be able to do so, however, the transferring outer electron must give up some of its energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases X-rays with unique amounts of energy during the transferring process. Thus, by measuring the amounts of energy present in the X-rays being released by a specimen during electron beam bombardment, the identity of the atom from which the X-ray was emitted can be established.

The output of an EDX analysis is an EDX spectrum. The EDX spectrum is just a plot of how frequently an X-ray is received for each energy level. An EDX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to a single element is in the specimen.

An EDX spectrum plot not only identifies the element corresponding to each of its peaks, but the type of X-ray to which it corresponds as well. For example, a peak corresponding to the amount of energy processed by X-rays emitted by an electron in the L-shell going down to the K-shell is identified as a K-Alpha peak. The
peak corresponding to X-rays emitted by M-shell electrons going to the K-shell is identified as a K-Beta peak.

Fig. 2.10 Elements in an EDX spectrum are identified based on the energy content of the X-rays emitted by their electrons as these electrons transfer from a higher energy shell to a lower energy one.

2.5 Theory of Structural Analysis
Many of the analytical techniques used to determine the molecular structure of unknown organic compounds are also used in polymer characterization. Spectroscopic techniques of such as ultraviolet–visible spectroscopy, infrared spectroscopy, Raman spectroscopy, nuclear magnetic resonance spectroscopy, electron spin resonance spectroscopy, X-ray diffraction, and mass spectrometry are used to identify common functional groups.

2.5.1 Fourier Transform Infrared Spectroscopy
Infrared spectroscopy is non-destructive technique for materials analysis and used in the laboratory for over seventy years. Infrared absorption spectroscopy is the study of interaction of infrared radiation with matter as a function of photon frequency. Fourier Transform Infrared Spectroscopy (FTIR) provides specific information about the vibration and rotation of the chemical bonding and molecular structures, making it useful for analyzing organic materials and certain inorganic materials. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared
Spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis.

Fig. 2.11 Fourier Transform Infrared spectroscopy.

The IR region is commonly divided into three smaller areas: near - IR (400 - 10 cm⁻¹), mid - IR (4000 - 400 cm⁻¹), and far - IR (14000 - 4000 cm⁻¹). Infrared photons have enough energy to cause groups of atoms to vibrate with respect to the bonds that connect them. Like electronic transitions, these vibrational transitions correspond to distinct energies, and molecules absorb infrared radiation only at certain wavelengths and frequencies. Chemical bonds vibrate at characteristic frequencies, and when exposed to infrared radiation, they absorb the radiation at frequencies that match their vibration modes. Measuring the radiation abs frequency produces a spectrum that can be used to identify functional groups and compounds. Some impurities produce their own characteristic bands in infrared region. Spectral measurements of these bands are used to determine the impurities and their bonding with the host materials. Identification, the measured interferogram signal cannot be interpreted directly. A means of "decoding" the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the transformation is performed by the computer which then presents the user with the desired spectral information for analysis.
Fundamentals of Fourier transform infrared absorption

IR radiation does not have enough energy to induce electronic transitions as seen with UV. Absorption of IR is restricted to compounds with small energy differences in the possible vibrational and rotational states. For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule. The alternating electrical field of the radiation (remember that electromagnetic radiation consists of an oscillating electrical field and an oscillating magnetic field, perpendicular to each other) interacts with fluctuations in the dipole moment of the molecule. If the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a change in the amplitude of molecular vibration. The energy of a molecule consists of translational, rotational, vibrational and electronic energy

\[ E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{translational}} \]

Fig. 2.12(a) Stretching vibrations.

The major types of molecular vibrations are stretching and bending. The various types of vibrations are illustrated in Fig. 2.12(a) and Fig. 2.12(b). IR radiation is absorbed and the associated energy is converted into these types of motions. The absorption involves discrete, quantized energy levels. However, the individual vibrational motion is usually accompanied by other rotational motions. These combinations lead to the absorption bands, not the discrete lines, commonly observed in the mid IR region.

Fig. 2.12(b) Bending vibrations.
2.5.2 X-Ray Diffraction Method (XRD)
Absorption is a continuous process with respect to X-ray wavelength due to the scattering of the radiation. Along with this background there are sharp absorption peaks when the energy of the X-rays couples with certain electronic transitions in the material. We looked at crystalline solids and their properties. In X-ray diffraction we focus on a combination on both, how X-rays interact with crystalline solids, specifically the phenomenon of diffraction. Diffraction by light waves is a well-known phenomenon.

![Diffraction of X-rays from a set of planes.](image)

The theory was put forward by Dutch physicist Christian Huygens and refined by French physicist Augustin-Jean Fresnel. If we have a ruled grating with the spacing of the order of the wavelength of light (400-700 nm) each point on the grating can be considered to be a source of secondary waves. These secondary waves can interfere forming alternate maxima and minima i.e. diffraction pattern. X-rays have wavelength of the order of 0.1 – 10 Å. Crystals have lattice constants and hence interplanar spacing around 2 – 6 Å. Thus a crystalline material naturally serves as a ruled grating with the ability to scatter X-rays producing maxima and minima i.e. diffraction. Diffraction using X-rays was first shown by German physicist von Laue in 1912 where he used a copper sulphate crystal (CuSO₄ with a triclinic structure) to get diffraction patterns from X-rays.

This work was carried forward by a father-son scientist team W.H. Bragg and W.L. Bragg who managed to express the condition for diffraction in a mathematical form this was called Bragg’s law. They were also able to solve the structure of sodium chloride (with 2 interpenetrating fcc structures) using X-rays thus proving the power of X-ray diffraction to solve crystal structures. 2 Bragg’s law Bragg’s law in the simplest sense gives the condition for constructive interference for X-rays incident on a set of lattice planes. Constructive interference occurs when the intensities of the
waves add to each other while the opposite is destructive interference where the intensities cancel each other. Bragg’s law can be derived from the general set of diffraction conditions derived by von Laue, which we shall see in the context of electron diffraction. Consider a set of planes as shown in Fig.2.13. the inter planar spacing between the planes is denoted by d. If the Miller indices of the plane is (hkl) and the system is cubic then d is related to a by

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{a^2}$$  \hspace{1cm} (1)

For a tetragonal system with two lattice parameters a and c the equation is modified as

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$ \hspace{1cm} (2)

For a hexagonal system where γ = 120° the relation between d-spacing and lattice parameters are

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$ \hspace{1cm} (3)

From Fig. 2.13 x-rays are incident at an angle θ on 2 planes with spacing d. Xrays reflected from the bottom plane have to travel an extra distance, which is given by 2dsinθ (from geometry). This is the then the path difference between the x-rays reflected from the material. For constructive interference this path length has to be an integral multiple (nλ) of the wavelength.

Thus, Bragg’s law can be stated as 2dsinθ = nλ  \hspace{1cm} (4) Here, n is an integer and can take values 1, 2, 3 and so on. This represents the order of reflection. Bragg’s law is the most important law in diffraction. It is not only used for XRD but also when we look at diffraction in an electron microscope. For a given set of planes there are reflected waves in all possible directions but these are not reinforced (the waves are not in phase) and hence the intensity is weak. The strongest reflected intensity is when the angle is equal to the Bragg angle i.e. the diffracted wave.
2.6 Thermal Analysis

Thermal analysis is used to establish thermodynamic properties which are essential for understanding the behavior of material under different heating and cooling rates, under inert, reduction or oxidation atmosphere or under different gas pressures. Thermal analysis comprises a group of techniques in which a physical property of a substance is measured to a controlled temperature program.

2.6.1 Differential Thermal Analysis

A technique in which the difference in temperature between the sample and a reference material is monitored against time or temperature while the temperature of the sample and reference material is subjected to the same controlled temperature programmers.

Fig. 2.15 shows the block diagram of DTA instrument. In DTA the material under study and an inert reference are made to undergo identical thermal cycles, while recording any temperature difference between sample and reference. The technique is based on the fact that as a substance is heated it undergoes reactions and phase changes that involve absorption or emission of heat.
In DTA the temperature of the test material is measured relative to that of an adjacent inert material. A thermocouple imbedded in the test piece and another in the inert material are connected so that any differential temperatures generated during the heating cycle are graphically recorded as a series of peaks on a moving chart. The amount of heat involved and temperature at which these changes take place are characteristic of individual elements or compounds; identification of a substance, therefore, is accomplished by comparing DTA curves obtained from the unknown with those of known elements or compounds.

Moreover, the amount of a substance present in a composite sample will be related to the area under the peaks in the graph, and this amount can be determined by comparing the area of a characteristic peak with areas from a series of standard samples analyzed under identical conditions. The DTA technique is widely used for identifying minerals and mineral mixtures.

2.6.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time in a controlled environment. It is suitable for use with all types of solid materials, including organic or inorganic materials.
TGA can provide information about physical phenomena, such as second-order phase transitions, including vaporization, sublimation, absorption, adsorption, and desorption. Likewise, TGA can provide information about chemical phenomena including chemisorption, desolvation (especially dehydration), decomposition, and solid-gas reactions (e.g., oxidation or reduction). TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles (such as moisture). Common applications of TGA are (1) materials characterization through analysis of characteristic decomposition patterns, (2) studies of degradation mechanisms and reaction kinetics, (3) determination of organic content in a sample. Thermal stability, oxidation, and combustion, all of which are possible interpretations of TGA traces, will also be discussed.

2.7 Mechanical Properties of Composites

2.7.1 Engineering Strain
We have just briefly described the response of atoms to deformation by mechanical forces. If this concept of atomic displacement is extended to bulk engineering materials, we can define the deformation in terms of original dimensions of the materials under consideration in other words, the ratio of dimensional change to original dimension.

Engineering strain is the amount that a material deforms per unit length in a tensile test (also known as normal strain).
For example, consider a bar of length $l_0$ as shown in figure. Under the action of an applied load $P$ this bar experiences deformation and elongates to a new length $l_f$. The ratio of this change in length to the original length $l_0$ is the “average linear strain” ($\varepsilon$) and can be expressed as follows [58].

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{l_f - l_0}{l_0} \tag{2.1}$$

This quantity is referred to as the average linear strain because only the dimensional change in the axial direction is considered and it is considered over the entire length of the sample. In reality, because its volume remain constant, the bar diameter does decrease slightly, resulting in a decrease in the cross-sectional area, but for small strain and expressed in units of in/in or mm/mm. However, strain may also be treated as a dimensionless quantity because these units cancel. From equation (2.1), it is clear that is unitless.

### 2.7.2 Stress

The response of an engineering material to impose forces on it has been discussed in terms of deformation and strain. Now let us analyze the resistance of a material for deformation. We know that, the net force on an atom is zero only for the equilibrium position. Displacement in either direction produces an increase in the forces (tensile or compressive) that oppose the deformation. This resistance is due to the inter-atomic attraction and repulsive forces that operate in a particular material. Stress $\sigma$ is the result of the internal response that a material exhibits when forces are imposed on it.

To simplify matters at this point, we will assume that the forces acts uniformity over a certain area, Then we can state that the stress is a force per unit area. Consider the load $P$ is applied to a cylindrical bar. The bar remains intact, indicator that the external force is balanced internally by a response of the material. If we section this bar at any particular location (normal to the axis of the applied load) $P$ must be opposed by the stress produced in each elemental area $dA$. Since it is previously
assumed that the force uniformly applied over the cross section, the summation of stress over the entire area may be expressed as follows \[ P = \sigma \int_{0}^{A} dA \]

\[ P = \sigma A \]

Therefore, the stress can be expressed as,

\[ \sigma = \frac{P}{A} \]

Where, \( P \) = load or force

\( A \) = cross sectional area over which the force act.

Stress is commonly denoted in unit’s lb/in\(^2\) (psi) or in international unit (SI) of Pascal (Pa). Since the Pascal is a rather small value of stress, it is customary to express stress values in megapascals (MPa).

2.7.3 Tensile Strength

The maximum load (or force) to which a material is subjected during stretching divided by its original cross-sectional area is called the tensile strength.

Let the maximum load or force = \( F_{\text{max}} \) and original cross-sectional area = \( A \)

\[ \therefore \text{Tensile strength, } TS = \frac{F_{\text{max}}}{A} \]

2.7.4 Elongation-at-Break or Breaking Strain

Elongation-at-break or breaking strain is defined as the strain at which the material under study breaks. If length of the original material is \( l_0 \) and its length after stretching is \( l \), then

\[ \text{Strain} = \frac{l - l_0}{l} \]

Elongation-at-break (%) is defined as

\[ EB(\%) = \frac{l - l_0}{l} \times 100\% \]

2.7.5 Young’s Modulus

The elastic limit of an engineering material is the highest stress that can be produced without experiencing any plastic (Permanent) deformation. In most materials for values of stress below the elastic limit, stress is proportional to strain as follows.

\[ \sigma = Y \varepsilon \]

This relationship is known as Hooke’s law, and the proportionality constant \( Y \) is the modulus of elasticity or Young's modulus. Young’s modulus is a measure of the
stiffness of an isotropic elastic material. It is defined as the ratio of the uniaxial stress over the uniaxial strain in the range of stress in which Hooke's Law holds. This can be experimentally determined from the slope of a stress-strain curve created during tensile tests conducted on a sample of the material. Young's modulus is the ratio of stress, which has units of pressure, to strain, which is dimensionless; therefore Young's modulus itself has units of pressure. The SI unit of Young’s modulus is the Pascal (Pa or N/m\(^2\)); the practical units are megapascals ( MPa or N/m\(^2\)) or gigapascals (GPa or KN/m\(^2\)). In United States customary units, it is expressed as pounds (force) per square inch (psi).

2.8 Conduction mechanisms

2.8.1 Introduction

Electrical properties of insulating polymers are there responses when an electric field is applied to them. In contrast to metals, in which the electrical field response is one of electronic conduction, polymers may respond in a more varied manner, and a whole set of delicate electrical effects may be observed. No known polymer is completely free of conduction processes, however small the quantity of charge carriers it may possess. Low level conduction in insulating polymers can take a variety of forms.

Conduction may very often be contributed by impurities that provide a small concentration of charge carriers in the form of electrons or ions. At high fields, the electrodes may inject new carriers (holes and electrons) into polymers. At very high fields, these and other processes will lead to complete breakdown of polymers as insulating materials. The imposition of an electrical field upon a polymer will cause a redistribution of any charges in the polymer, provided they are mobile enough to respond in the time scale in the applied field. If some of the mobile charges are able to diffuse throughout the specimen and charge migration through the electrode sample interface is possible, then the charges will support a dc conductance. A well-judged study of electrical conduction in vacuum deposited thin films cannot be accomplished without consideration of these possibilities [60]. A power law can express the variation of current density with voltage in a material generally:

\[ J \propto V^n \]  

(2.20)

Where, \( n \) is a power factor. When \( n \) is unity, the conduction is Ohmic. If the value of \( n \) is less or more than unity, then the conduction process is other than Ohmic.
Medalia (1986) and Strumpler and Glatz-Reichenback (1999) have reviewed the various possible conduction mechanisms which include electron tunnelling and electron hopping in a filled composite. According to Strumpler and Glatz-Reichenback (1999) there are three different cases,

1. Filled polymer below the percolation threshold.
2. Filled polymer in which the mean distance between fillers is below 2-5nm.
3. Polymers containing particles in direct contact.

2.8.2 Below percolation threshold

In filled polymers, which are below the percolation threshold the particle to particle contact is ruled out as the primary conduction mechanism. Hence, the limited conduction mechanism can only result from electron tunnelling, Rubin et al. (1999). The electron tunnelling occurring between filler particle is related to the mean separation distance. Electron tunnelling occurs if the mean particle to particle separation is around 2nm-5nm [61]. In the case of polymer below the percolation threshold and in the insulating zone, the conductivity may be mainly due to intrinsic conductivity of polymer. The conductivity in this polymer material could also be due to the impurities which tend to enhance the conductivity.

2.8.3 When the mean distance is less than 2nm-5nm

In polymer composites when the mean distance is less than 2nm-5nm but not touching two possible mechanism of conduction has been suggested. Beek (1962) suggested that when the average particle distance is less than 2nm-5nm then electrical field assisted tunnelling takes place.

\[ j_{\text{Tunneling}} = A E_s^n \exp \left( -\frac{B}{E_s} \right) \]  \hspace{1cm} (2.21)

Where \( A, B \) and \( n \) are the constants whose values vary from 1 to 3, \( j_{\text{Tunneling}} \) is tunnelling current and \( E_s \) is the applied electrical field strength. The probability that charges carriers can move between the filler and the polymer is indicated by ratio \( B/E_s \). The term \( B \) represents the measurement of energy barrier between polymer and filler. Another model of conduction model was suggested by Frenkel (1930),

\[ j_{\text{Hopping}} = A_r T^2 \exp \left( \frac{K_e B}{k_b T} \right) \]  \hspace{1cm} (2.22)

Where, \( A_r \) is the Schottky Richardson constant, a work function of the filler material. \( k_b \) is the Boltzmann constant \( j_{\text{Hopping}} \) is the Hopping current and \( T \) is the temperature.
Accordingly, the conduction takes place due to electron hole separation; known as hopping transfer assisted by the electrical field. The mechanism of hopping transport of electrical conduction has been usefully applied in printing. Factors such as the properties of the filler, the polymer and the interfacial contact area are all very important.

2.8.4 Particle to particle contact
When the filler volume fraction is greater than the critical percolation threshold then filler to filler contact takes place. In this case the primary conduction mechanism is conduction through the filler aggregate network.

2.8.5 Electrical contact between filler
When there is a contact between two conducting fillers there is a contact resistance which contributes to overall resistivity. This contact resistance can be described as the constriction resistance and tunnelling resistance between the particles. Contact resistance acts as a spot where maximum energy loss takes place. This energy loss is mostly in the form of heat. Assume two spherical particles which are in contact. If the Young’s modulus is assumed to be to infinite then contact between the spheres is only at a single point. If these assumptions are used to calculate the constriction resistance then it results in a singularity. Holm (1967) considered that a more realistic macroscopic contact be used with a finite radius a. Accordingly the constriction resistance is as follows,

\[ R_c = \frac{\rho_t}{2a} \]  

(2.23)

Here \( \rho_t \) is the bulk resistivity of the filler. If the radius of the filler is larger than the radius of contact than a constriction resistance will be of greater effect than the filler resistance. This equation can be applied only to the fillers which are homogenous, having no surface contamination and which do not show any dependence on a large temperature gradient. Contact resistance estimation depends on an accurate estimation of the contact area. In calculating the contact area the mechanical properties of filler are very important.

If we assume that a sharp protrusion of a filler is in contact with a flat surface of the filler, then the elastic force between them for a small deformation is given by Bush (1982),

\[ F = \frac{2}{3} \frac{E}{1-\nu^2} \frac{a^3}{r} \]  

(2.24)
Where E is Young’s modulus and v is Poisson’s ratio. From Equation (2.23) and (2.24) we get:

\[ R_c = \frac{\rho_f}{2} \left( -\frac{E}{3(1-v^2)} \right)^{\frac{1}{2}} F\left( -\frac{1}{3}, r^{\frac{-1}{3}} \right) \]  

(2.25)

The contact resistance between filler particle decreases as the force applied increases. The contact resistance will also decrease if the protrusion radius increases. According to the above equation softer materials tend to have a higher constriction resistance.

**2.8.6 Thermally activated conduction processes**

Electronic conduction in organic, molecular compounds differs in several important ways from the more familiar kind in metals and semiconductors. An important feature of the band system is that electrons are delocalized and spread over the lattice. Some delocalization is naturally expected when an atomic orbital of any atom overlaps appreciably with those of more than one of its neighbors, but delocalization reaches an extreme form in the case of a regular 3 dimensional lattice. The band theory assumes that the electrons are delocalized and can extend over the lattice. When electronic conduction is considered in polymers, band theory is not totally suitable because the atoms are covalently bonded to one another, forming polymeric chains that experience weak intermolecular interactions. But macroscopic conduction will require electron movement, not only along the chain but also from one chain to another. As the temperature is increased the charge carrier concentration increases strongly with temperature. This dominates the temperature dependence of the conductivity, giving it an Arrhenius - like character.

It is difficult to generalize about the temperature dependence of dc conduction whether it is ionic or electronic since so many processes are possible. Ohmic (low field) conduction whether ionic or electronic, gives exponential temperature dependence, given by

\[ J = J_0 e^{\frac{-\Delta E}{kT}} \]  

(2.26)

Where, \( J_0 \) is a constant and \( \Delta E \) is the activation energy for carrier generation. Now

\[ J = N e \mu \]  

(2.27)

Where, N is the number of charge carriers, e their charge, and \( \mu \) their mobility. With extrinsic ionic conduction, it is the mobility i.e. the activated process, \( \Delta E \) being the energy for the ion to hop. With extrinsic electronic conduction, the electrons may move by hopping. However, if the electronic conduction is by excitation into the
conduction band, the production of free electrons, not their mobility, $\mu$ is activated. Whatever the Ohmic mechanism, a log $J$ vs. $1/T$ plot (Arrhenius plot) will usually exhibit increasing linear slopes (activation energies) as $T$ is raised [62].

For variable range hopping the electrical conductivity is given by

$$\sigma = \sigma_0 \exp \left( \frac{T_o}{T} \right)^{-d+1} \quad \text{(2.28)}$$

Where “$d$” is the dimensionality of transport, $\sigma$ is the conductivity, $\sigma_0$ is the initial value of conductivity, $T$ is the absolute temperature and $T_o$ is the activation energy in terms of temperature.

In bulk material ionic conduction occurs due to the drift of defect under the influence of an applied electric field. The degrees of ionic impurities that may be totally ignored in the context of other properties may have a significant effect on conductivity. A theoretical expression may be derived for the current density.

$$J = \sin h \left( \frac{eaE}{2kT} \right) \quad \text{(2.9)}$$

Where $E$ is the electric field, $a$ is the distance between neighboring potential wells, $e =$ electronic charge.

Fig. 2.18 Diagram of electron-transfer mechanisms between adjacent sites separated by a potential-energy barrier.
References


Chapter-III
MATERIALS AND METHODS
3.1 Raw Materials
In the recent year application of the composites are worldwide, in this research work composites were prepared from natural rubber (NR) and multiwalled carbon nanotubes (MWCNTs). Ribbed smoked sheet (RSS) natural rubbers were used to prepare polymer nanocomposites. The composites have particular ratios of MWCNTs at different percentages. Brief descriptions of NR and MWCNTs, which are used in this study is given below.

3.1.1 Natural Rubber Ribbed Smoked Sheet (1, 4-cis poly isoprene)
Natural rubber (NR) is a hydrocarbon diene monomer whose repeating unit is cis-isoprene. The outstanding strength of natural rubber has maintained its position as the preferred material in many engineering applications. It has a long fatigue life, good creep and stress relaxation resistance and low cost.
Ribbed Smoked Sheet Rubber is commonly known as RSS Fig. 3.1. It is made directly from latex which is treated and then made to coagulate. The coagulated latex sheets are then air dried or smoked in ovens. The smoked sheets are visually graded on the basis of certain parameters and then packed in bales.

![Fig. 3.1(a) A photograph of NR (RSS) and (b) Chemical structure of NR(cis-1,4-polyisoprene).](image)

3.1.2 Multiwalled Carbon Nanotubes (MWCNTs)
MWCNTs obtained from Shizuoka University Japan. The purity of CNTs above 90%. CNT growth from chemical vapor deposition method.

3.1.3 Acids Used for CNT Functionalization
Nitric acid 67% concentration is manufactured by Merck KGaA, 64271 Darmstadt, Germany, which was collected from local market. Sulfuric acid 98% concentration is manufactured by RCI LABSCAN LIMITED, V.S.CHEM HOUSE, THAILAND, which was collected from local market.
3.1.4 Toluene
The solvent Toluene is manufactured by Merck KGaA, 64271 Darmstadt, Germany, purity >99%, which was collected from local market. Toluene is a methylbenzene with the molecular formula C₇H₈.

3.2 Equipment for the Preparation of Composite Samples
Several types of equipment were used in the fabrication of composites. The main equipment is as follows:

(a) Electric Balance
(b) Reflux Systems
(c) Centrifuge
(d) Magnetic Stirrer
(e) Glass Tray

3.2.1 Electric Balance
In Fig.3.2 is shown an electric balance used for measurement of weight the sample. The balance is sensitive and has a measuring capacity of 0.001 gm.

Fig.3.2: A photograph of an electric balance.

3.2.2 Reflux System (Lebig Condenser Round Bottom Flux)
Reflux systems have a lebig condenser, round bottom flux, oil-bath, hot plate and water input output system. Fig. 3.3 shows the reflux system. For functionalization of MWCNTs I had taken 1gm of MWCNTs, 20 mL concentrated (98%) H₂SO₄ and 20 mL concentrated (67%) HNO₃. Then steering 6 h with a magnetic stirrer in an oil-bath. The temperature was kept at 80°C and water flow in the condenser to condense acid. To remove excess acid from CNTs washed with distilled water. The functionalized CNTs were kept in a beaker. Then it was washed with distilled water by centrifuge machine.
3.2.3 Centrifuge Machine

Centrifugation is the process where a mixture is separated through spinning. A mixture where there are two different sized particles. If we left this mixture out, over time the larger particles would settle to the bottom. Centrifugation uses a centrifuge, or a device that can rapidly spin, to speed up this process. In this process we put the mixture into test tubes, and those tubes into the centrifuge. The centrifuge holds the top of the tubes, and the bottom is allowed to angle out. As it spins, the larger particles would get flung out further, and smaller particles would stay close to the center. Fig. 3.4 shows the centrifuge machine.

In this processes we take the functionalized MWCNTs ($f$-MWCNTs) with distilled water in 4 falcon tubes and each tube hold on 10 ml solution. Then it has been centrifuged for 5 minutes and the spinning speed was 4500 revolution per minute. Finally we got $f$-MWCNTs and the $P^H$ was 5. Then the $f$-MWCNTs kept in an oven at $50^\circ$C.
Fig. 3.4 A photograph of centrifuge machine.

3.2.4 Hot Plate with Magnetic Stirrer

In Fig.3.2.4 is shown a magnetic stirrer used for stirring the natural rubber (NR), toluene and sonicated f-MWCNTs in different percentages in beakers on the hot plate.

Fig.3.5 A photograph of hot plate with magnetic stirrer.

3.2.5 Glass Tray

In Fig. 3.6 is shown the glass tray. The lengths of this glass tray 12 inches, wide 4 inches and height 4 inches and the tray have four chambers. By this tray, we can prepare 4 samples at a time.
3.3 Preparation of Composites Samples

At first 10 gm. of NR RSS washed with distilled water in an ultrasonic bath. Then the rubbers were dried in air. Then toluene (400 ml) and rubbers (10 gm.) take in beakers and stirring with the magnetic stirrer on a hot plate until the rubber dissolved in toluene. The temperature was kept at 70°C. Secondly, the f-MWCNTs sonicated with toluene in the sonicator (AS ONE) and sonication for 1 hour. When the f-MWCNTs were dispersed homogeneously in toluene then it was added with rubber solution and mixed by a glass rod. The mixture mixed 1 hour, when the mixture mixed homogeneously then it was cast on the glass tray. Then it was kept for dry at room temperature. After 20 days letter the sample is ready for characterization.

Fig.3.6: A photograph of the glass tray.
3.4 Surface Morphology Test

3.4.1 Surface Morphology Test by FESEM

The surface morphology of the Carbon nanotube Natural Rubber polymer composites have been investigated by the field emission scanning electron microscopy (FESEM) [JEOL JSM 7600F, Japan] with an operating voltage of 3kV and with five magnification (×3,000, ×10,000 and ×30,000). The energy dispersive analysis of X-rays (EDAX) which connected to the microscope also performed for the elemental analysis of the samples. Micrographs were taken varying points for different magnifications. Fig. 3.8 shows the different parts of the Scanning Electron microscope used in the study of the surface morphology.
The data generated by EDAX consist of spectra showing peaks corresponding to the elements making up the true composition of the sample being analyzed. In a multi-technique approach EDAX becomes very powerful, particularly in contamination investigations. EDAX of the polymer composites were performed by using an energy dispersive X-ray detector attached to the FESEM instrument. EDAX spectra were recorded at various points of the polymer composite samples to identify the percentage of carbon and oxygen present in this samples and carbon is almost 100%.

3.5 Structural Measurement of Rubber Nanocomposites Samples

3.5.1 Fourier Transform Infrared Spectroscopy
Fourier transform infrared (FTIR) spectra of NR-CNTs composites were recorded at room temperature by using a double beam IR spectrophotometer (SIMADZU, FTIR-8400 spectrophotometer, Japan) in the wave-number range of 400-4000 cm\(^{-1}\). The FTIR spectra of the composites were obtained by putting solid samples in a potassium bromide (KBr) measuring cell. Composites sample were sliced and then pellets of composites powder mixed with KBr were prepared for recording the FTIR spectra of composites sample. The FTIR spectra of the composites were recorded in transmittance (%) mode.
3.5.2 X-ray Diffraction

XRD can be used as a powerful tool for the study of materials because of its ability to give a broad range of information such as crystal structure, composition and defects. It is a non-destructive technique and does not require any specific sample preparation methods.

In the present study, the structural analysis of material was done for using XRD technique. The bar samples having the same thickness were used for XRD measurements. Wide-angle XRD (WAXD) studies were performed by an X-ray diffractometer (model JDX-8P, JEOL Ltd., Tokyo, Japan) using CuKα radiation of wavelength, \( \lambda = 1.5418 \) Å for the crystallographic analysis, through a step-wise scan over the scattering angle (2θ) from 10° to 70°, with a step of 0.02°. Fig 3.9(a) shows the photograph of an X-ray diffractometer. The operating voltage and the tube current of the X-ray generator were 30 kV, 200 mA, respectively. Small-angle (SAXD) measurements of the samples were performed using a rotating anode type high-intensity Rotaflex, RU-300 X-ray generator (40 kV×200 mA; Rigaku Corporation Tokyo, Japan). The incident X-ray beam, monochromatized by a graphite single crystal, had a wavelength of 1.54 Å. The X-ray beam was passed through a collimation system with a pinhole of 100 µm in diameter. The camera length of SAXD was 460 mm. The diffraction intensity was recorded by a Rigaku Display System imaging plate (IP) (Rigaku Corporation, Tokyo, Japan). The exposure time was set as 60 min in every X-ray measurements.
The standard JCPDS data cards were used for comparative purpose. The schematic diagram of X-ray diffractometry is shown in the Fig. 3.9(b). X-ray diffraction is based on the constructive interference of monochromatic X-rays caused by crystalline materials. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation collimated to concentrate and directed towards the sample. The interaction of the incident rays with the sample produces constructive interference when Bragg’s law \((n\lambda = 2d\sin\theta)\) conditions are satisfied. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the
lattice spacing in a crystalline sample. SAXD and WAXD measurements are usually carried out to study the lamellar and crystalline structure of polymers, respectively [1, 2].

3.6 Method of Measuring Mechanical Properties
The mechanical properties, such as tensile stress, tensile strain, tensile strength and Elongation at break of the prepared samples were evaluated by a universal testing machine (UTM).

3.6.1 Universal Testing Machine
UTM (Instron UTM 50kN; ASTM D-412) can be used for measuring the mechanical properties such as, tensile stress, tensile strain, tensile strength and elongation at break of the composites. The load range, speed, measuring unit, gauge length etc. can be selected over a wide range. The maximum speed, load range and gauge length to be used in this machine are 1.0 mm-min⁻¹, 0.00639 kN and 33mm respectively for NR sample. The maximum speed, load range and gauge length to be used in this machine are 1.0 mm-min⁻¹, 0.0143 kN and 33mm respectively for 0.5 wt% CNTs-NR composite sample. The maximum speed, load range and gauge length to be used in this machine are 1.0 mm-min⁻¹, 0.00385 kN and 33mm respectively for 1.0 wt% CNTs-NR composite sample. The maximum speed, load range and gauge length to be used in this machine are 1.0 mm-min⁻¹, 0.00562 kN and 33mm respectively for 1.5 wt% CNTs-NR composite sample. A photograph of the Instron UTM 10kN is shown in Fig. 3.12. This machine contains grips to hold a sample, which is stretched by the application of a continuously increasing load to measure the tensile properties. The gap between the grips is maintained according to ISO standard. The maximum load that can be employed in this machine is 50kN. The measuring conditions are set by the programmed software. The data acquisition and analyses can be performed by the software.

Sample Die
We cut the sample for tensile strength measurement and the die shape was ASTM D 412 model. Fig. 3.11 shows the tensile strength measurement samples [3].

Fig.11 Photograph of the tensile strength measurement samples.
3.6.2 Measurement by Universal Testing Machine

Tensile strength (TS), tensile strain (\(\varepsilon\)), tensile stress (\(\sigma\)) and percentage of elongation-at-break [EB(\%)]) of the samples were measured by a software controlled universal testing machine [Instron UTM 10 kN(3369)]. Four samples of each composition were used in the mechanical testing.

(i) **Tensile Stress**

Tensile stress was evaluated using the following formula (2.2)

\[
\sigma = \frac{F}{A} \tag{3.1}
\]

Where, \(F\) = Load applied to the sample

\(A\) = Cross sectional area of the test sample

The value of \(F\) was obtained from the UTM. The value of \(A\) was obtained by a slide calipers by measuring the width and thickness at least three points in the narrow zones of the sample.

(ii) **Tensile Strength**

Tensile strength was estimated by the following formula (2.3)

\[
TS = \frac{F_{\text{max}}}{A} \tag{3.2}
\]

Where, \(F_{\text{max}}\) = Maximum load applied to the sample

\(A\) = Cross sectional area of the test sample
(iii) **Tensile Strain**

Tensile strain was calculated using the following formula (2.4)

\[ \varepsilon(\%) = \left( \frac{\Delta L}{L_0} \right) \times 100\% \]

Where, \( \Delta L \) = Extension due to applied load

\( L_0 \) = Gauge length or original length of the sample

The value of \( \Delta L \) was obtained from the UTM.

### 3.7 Electrical Measurement

For electrical measurements, First a Thick NR-CNTs polymer composites film cut into 7 mm × 7 mm and 1 mm thick sample was prepared and then coated both sides of the sample with low temperature silver paste. Then the film was placed inside a pressure conductor. Al electrodes were deposited on the both sides of the pressure conductor, i.e. after the lower electrode was deposited, the pellet was deposited onto the electrode and then the upper electrode was deposited on the opposite direction of the lower electrode using an Edward coating unit, E-306A (Edward, UK). Silver paste is used in both surface of the film. The current across the film was measured by a high impedance Keithley 614 electrometer and the dc voltage was applied by an Agilent 6545A stabilized dc power supply. The block diagram for dc measurements and dc measurement set up are shown in Fig. 3.13 (a) and Fig. 3.13 (b). The thermally activated current or the temperature dependence of current across the pellets was measured at applied voltages of 20 and 50 V using the above mentioned electrometer. The measurements were performed from 25°C to 100°C. For these measurements the samples were heated by a heating coil which was wrapped around the specimen chamber. The temperature was measured by a Chromel-Alumel (Cr-Al) thermocouple placed very close to the sample which was connected to a 197 A digital microvolt (DMV) meter.

Fig. 3.13(a): A schematic circuit diagram of DC measurement.
DC power supplies use AC main electricity as an energy source. Such power supplies will sometimes employ a transformer to convert the input voltage to a higher or lower AC voltage. A rectifier is used to convert the transformer output voltage to a varying DC voltage, which in turn is passed through an electronic filter to convert it to an unregulated DC voltage. The instrument was used for measuring current for increasing voltage to investigate that whether the sample was Ohmic or not.

The Ohm’s law is, \( V = IR \)
Where, \( V, I, R \) denotes voltage, current and resistance respectively.

The formula can be modified as,
\[ J = GV \]
Where, \( J \) and \( G \) are current density and conductance respectively.

Taking log on both sides we get,
\[ \ln J = \ln V + \ln G \]
If we plot \( \ln J \) versus \( \ln V \) curve, and compare it with equation \( y = mx + c \), we get a slope. If the value of slope is approximately one then the sample will be ohmic.

Fig. 3.13(b): Arrangement for DC measurement.

### 3.8 Thermal Measurements

Thermal analysis comprises a group of techniques in which a physical property of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature programed. In differential thermal analysis, the temperature difference that develops between a sample and an inert reference material
is measured, when both are subjected to identical heat treatments. Melting and degradation temperatures of the neat CNTs-NR polymer composites were monitored by a DTA and thermogravimetric analyzer (TGA) [Seiko-Ex-Star-6300, Japan]. The measurements using DTA and TGA were carried out from room temperature 25 °C to 600 °C at a heating rate of 20 °C/min under nitrogen gas flow. While the DTA traces give the melting and degradation temperatures as determined from the endotherm versus temperatures curves, the TGA runs exhibit the weight-loss of the sample with temperature.

3.8.1 Thermogravimetric Analysis and Differential Thermal Analysis

Thermal analysis is one of the most important investigations for CNTs-NR polymer composites samples for their different applications [4]. For thermal analysis the CNTs-NR polymer composites samples were kept on the metallic electrodes. Then the samples were used for the investigations of differential thermal analysis and thermogravimetric analysis. The DTA/TGA scans of CNTs-NR polymer composites samples were recorded using a computer controlled TG/DTA 6300 system connected to an EXSTAR 6000 station, Seiko instruments Inc, Japan. The investigation was performed at nitrogen atmosphere. The measurement specifications of the DTA/TGA traces were as follows:

Fig. 3.14 The TG/DTA 6300 system which was used to study the thermal properties.
References

Chapter-IV
RESULTS AND DISCUSSION
4.1 Introduction
This chapter gives a comprehensive discussion of the results of structural, thermal, electrical and mechanical properties of the CNT-NR composites films. The surface morphology, structural, thermal behavior of CNT-NR composites films were investigated by FESEM, FTIR, TG-DTA respectively. DC electrical conduction mechanism was measured from the current density-voltage (J-V) characteristics curves.

4.2 Surface Morphology
4.2.1 Transmission Electron Microscopy
TEM micrographs of CNTs are displayed in Fig. 4.1. From TEM micrograph it can be seen that MWCNTs have good quality and they are highly pure. The purity of MWCNTs is more than 90%.

Fig. 4.1 TEM micrographs of MWCNTs in two different magnifications.
4.2.2 Field Emission Scanning Electron Microscopy

The FESEM micrographs of the CNT-NR composites were recorded at various points with various magnifications (×3k, ×10k and ×30k) at accelerating voltages of 3kV, 5kV and 10 kV are shown Fig 4.2–4.5. From SEM images it is observed that the surfaces of the CNT-NR composites films are pinhole free and homogeneous and it also show that CNTs are embedded inside the NR matrices.

Fig. 4.2 FESEM micrographs of Natural Rubber (NR) film of with (a) ×3k (b) ×10k.
Fig. 4.2 FESEM micrographs of pure Natural Rubber (NR) film of with (c) ×30k.

Fig. 4.3 FESEM micrographs of 0.5 wt% CNT-NR composites film of with (a) ×3k.
Fig. 4.3 FESEM micrographs of 0.5 wt% CNT-NR composites film of with (b) ×10k (c) ×30k.
Fig. 4.4 FESEM micrographs of 1.0 wt% CNT-NR composites film of with (a) x3k (b) x10k.
Fig. 4.4 FESEM micrographs of 1.0 wt% CNT-NR composites film of with (c) ×30k.

Fig. 4.5 FESEM micrographs of 1.5 wt% CNT-NR composites film of with (a) ×3k.
Fig. 4.5 FESEM micrographs of 1.5 wt% CNT-NR composites film of with (b) ×10k (c) ×30k.
4.2.3 Energy dispersive X-ray analysis

The compositional analysis was achieved for the same samples by EDX which is attached to the FESEM. EDX spectra of CNT-NR composites are shown in Fig 4.6. The observation indicates mass percentages of the components of CNT-NR composites which are noted in Table 4.1.

![EDX spectra of NR and 0.5 wt% CNT-NR composites.](image)

Fig 4.6 EDX spectra of NR and 0.5 wt% CNT-NR composites.
Table 4.1 Mass percentages of the elements for NR, 0.5 wt%, 1.0 wt% and 1.5 wt% CNTs-NR composites achieved by EDX analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>NR</th>
<th>0.5 wt% CNT-NR</th>
<th>1.0 wt% CNT-NR</th>
<th>1.5 wt% CNT-NR</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

The observation indicates the presence of C is almost 100% in pure NR and its composites. Although cis-1,4-polyisoprene is composed of C and hydrogen (H), but
hydrogen is not noted in Table 4.1, because the main obstacle of EDX is that it cannot detect the presence of H, He, etc. Because EDX is related to the K-shells which are not the valence shell. H does not have a K shell or better to say, it has only one shell which is valance shell.

4.3 Structural Analyses

4.3.1 Fourier Transform Infrared Spectroscopy Analyses
The FTIR spectra of pristine (p) and functionalized MWCNTs are shown in the Fig. 4.7 absorption bands at 3432 cm\(^{-1}\) FTIR spectra of both the p-MWCNTs and f-MWCNTs assigned to the stretching vibrations of hydroxyl groups (–OH). In case of p-MWCNTs this might have been caused by the residual water absorbed on the surface of the MWCNTs. The absorption band centered at 3432 cm\(^{-1}\) for the f-MWCNTs was stronger than in the spectra of the p-MWCNTs; therefore, it can be considered that a certain number of –OH groups are introduced onto the surface of the MWCNTs. Compared with the p-MWCNTs, new bands appeared at 1724 and 1403 cm\(^{-1}\) in the spectra of the f-MWCNTs; these were assigned to the stretching vibrations of carbonyl groups (–C=O) and carboxylic acid groups (–COOH), respectively. So, it can be said that –COOH groups were successfully introduced onto the surface of the MWCNTs. With these hydrophilic groups, the f-MWCNTs disperse well in toluene as well as in natural rubber solution [1-3].

![FTIR spectra of p-MWCNTs and f-MWCNTs.](image-url)
Fig. 4.8 FTIR spectra of NR and CNT-NR composite.

From Fig. 4.8 it can be seen that absorption bands for NR assigned at 1257 and 1670 cm\(^{-1}\) correspond to (C–H) twisting and carbon carbon double bond (C=C) stretching vibrations. The bands at 2853 cm\(^{-1}\) represents the (C–H\(_2\)) symmetric stretching vibration and the band at 2926 cm\(^{-1}\) corresponds to (C–H\(_2\)) asymmetric stretching vibration. The band at 2962 cm\(^{-1}\) represents the (C–H\(_3\)) asymmetric stretching vibration [4]. It is noted that in case of CNT-NR composites absorption peaks appear at the same wavelength. Therefore, it can be said that CNT did not influenced the structure of NR and disperses well in the NR matrices.

4.4 XRD Analyses

Fig.4.9 shows the XRD spectra of the NR and CNT-NR composites show a broad peak around $\theta = 20^\circ$. This is an important crystalline peak which is diffused, which is originated from the amorphous nature of NR. The broad diffused peak suggests that NR chains are poorly ordered with a low degree of crystallinity due to evaporation of solvent (toluene) from the solution.
Ponnam et al. [5] also reported XRD pattern confirming amorphous nature for the, NR, NR-CNT, NR-CG600 and NR-CG200 composites. The absence of characteristic peaks of fillers in the spectrum reveals their well dispersion in the composites.

Fig 4.9 (a) XRD spectra of NR, 0.5 wt%, 1.0 wt% and 1.5 wt% CNT-NR composites (b) XRD spectra of NR and CNT-NR composites 10-30° range (c) XRD spectra of NR, NR-CNT, NR-CG200 and NR-CG600 composites [4].
4.5 Thermal Analyses

Fig. 4.10 represents the TGA and DTG thermocurves of natural rubber in N\textsubscript{2} environment. The TGA curves show that the weight losses in A, B, C and D regions are 0.3\% at 127.1 °C temperature, 17\% at 366.02 °C, 41.9\% at 395.3 °C and 37.7\% at 424.6 °C respectively and remaining weight is 3.1\%. In region A, the 0.3\% weight loss up to about 127.1 °C may be due to the removal of water content or moisture in the natural rubber. The corresponding DTG traces show a small peak in this region. In region B, up to temperature 366.02 °C in TGA curve with a weight loss of about 17\% which may due to the removal of some unreacted monomers or oligomers. In region C, the thermal decomposition of NR is observed as a large weight loss of about 79.6\% from 366.02 °C to about 426.6 °C in TG trace and corresponding DTG trace has indicated the same phenomenon by a broad peak. From DTG, it was calculated that the maximum weight loss has been occurred in temperature 396.9 °C. From Fig. 4.11 it is observed that the degradation in the region B is delayed owing to incorporation of CNTs in NR composites. But in case of 1.5 wt\% of CNTs in NR the degradation in this region again start at lower temperature signifying deterioration of thermal stability of the CNT-NR composites. This may be when more CNT was introduced some of the CNT become coagulated in the NR matrices.

![Figure 4.10 TGA and DTG thermographs of neat NR.](image-url)
Table 4.2 Weight loss calculation for different samples from TG-DTG.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Region A</th>
<th>Region B</th>
<th>Region C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>Weight Loss%</td>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>NR</td>
<td>25-120</td>
<td>0.49</td>
<td>120-360</td>
</tr>
<tr>
<td>0.5 wt% CNTs-NR</td>
<td></td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>1.0 wt% CNTs-NR</td>
<td></td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>1.5 wt% CNTs-NR</td>
<td></td>
<td>0.49</td>
<td></td>
</tr>
</tbody>
</table>

4.6 DC Electrical Properties of CNT-NR Polymer Composites

4.6.1 Current density-voltage characteristics

In the literatures various conduction mechanisms have been suggested for the carrier transport in polymer thin films based on the dependence of current density (J) on voltage (V), temperature (T) and thickness (d). In filled polymers, which are below the percolation threshold the particle to particle contact is ruled out as the primary conduction mechanism. Hence, the limited conduction mechanism can only results from electron tunnelling, Rubin et al. [6]. The electron tunnelling occurring between filler particle is related to the mean separation distance. Electron tunnelling occurs if
the mean particle to particle separation is around 2 nm-5 nm [7]. To elucidate the existence of any conduction mechanism in CNT-NR composites, dependence of J on above mentioned parameters have been observed on CNT-NR composites of the voltage rage 0.1-110 V in the temperature of 298, 323,348 and 373K. The J-V characteristics of CNT-NR composites at room temperature are shown in Fig. 4.12. The observed J-V characteristics of the CNT-NR composites at various temperatures are presented in Fig. 4.13-4.16 for different wt% of CNTs in NR.

![Graph showing J-V plots for NR, 0.5 wt% CNT-NR, 1.0 wt% CNT-NR and 1.5 wt% CNT-NR polymer composites samples at room temperature.](image)

Fig. 4.12 J-V plots for NR, 0.5 wt% CNT-NR, 1.0 wt% CNT-NR and 1.5 wt% CNT-NR polymer composites samples at room temperature.
Fig 4.13 J-V plots for NR polymer sample at different temperature.

Fig 4.14 J-V plots for 0.5 wt% CNT-NR polymer composite sample at different temperature.
Fig 4.15 J-V plots for 1.0 wt% CNT-NR polymer composite sample at different temperature.

Fig 4.16 J-V plots for 1.5 wt% CNT-NR polymer composite sample at different temperature.
It is observed from Fig.4.12–4.16 that J increases with increasing wt% of CNTs in NR and increasing temperature [Fig. 4.13-4.16] for CNTs-NR composites. Each J-V curve have approximately same shape having ohmic section in the lower and higher voltage regions according to the power law of the form \( J \alpha V^n \), where ‘n’ being power index. The values of the slopes are tabulated in Table 4.3. The slope \( 0.921 \leq n \leq 1.037 \).

Table 4.3 The ‘n’ in \( J \alpha V^n \) at different temperatures for NR, 0.5, 1.0 and 1.5 wt% CNTs-NR polymer composites.

<table>
<thead>
<tr>
<th>Samples Name</th>
<th>Measurement temperature (K)</th>
<th>Values of ‘n’ in ( J\alpha V^n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>298</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.927</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>1.037</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>1.013</td>
</tr>
<tr>
<td>0.5 wt%</td>
<td>298</td>
<td>0.921</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>1.009</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>1.011</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>1.033</td>
</tr>
<tr>
<td>1.0 wt%</td>
<td>298</td>
<td>1.000</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>1.000</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>1.002</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>1.016</td>
</tr>
<tr>
<td>1.5 wt%</td>
<td>298</td>
<td>1.002</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>1.007</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>0.995</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>1.012</td>
</tr>
</tbody>
</table>

Fig. 4.17 J vs wt% of CNTs in NR matrices.
Fig. 4.17 shows the current density vs wt% of CNTs in NR matrices. From this graph we can see current density is increases with increasing of CNTs in NR at both low and high voltage region.

4.6.2 Dependence of current density on temperature

The dependence of J on inverse absolute temperature, 1/T, for CNTs-NR composites, with an applied voltage, 20 V and with an applied voltage, 50 V are shown in Fig. 4.18 (a-d). The activation energies calculated from the slopes of curves of Fig. 4.18 for all samples are tabulated in Table 4.4.

![Graph showing current density vs inverse of absolute temperature for NR polymer sample.](image-url)
Fig. 4.18 (b) Current density vs inverse of absolute temperature for 0.5 wt% CNT-NR polymer composite sample.

Fig. 4.18 (c) Current density vs inverse of absolute temperature for 1.0 wt% CNT-NR polymer composite sample.
Fig. 4.18 (d) Current density vs inverse of absolute temperature for 1.5 wt% CNT-NR polymer composite sample.

Fig. 4.19 Activation energy vs wt% of CNTs in NR matrices.
Table 4.4 Values of activation energy $\Delta E$ (eV) for CNTs-NR polymer composite samples.

<table>
<thead>
<tr>
<th>Samples Name</th>
<th>Activation energies $\Delta E$ (eV)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20V</td>
<td>50V</td>
<td></td>
</tr>
<tr>
<td>NR</td>
<td>0.144</td>
<td>0.259</td>
<td></td>
</tr>
<tr>
<td>0.5 wt% CNT-NR</td>
<td>0.174</td>
<td>0.255</td>
<td></td>
</tr>
<tr>
<td>1.0 wt% CNT-NR</td>
<td>0.185</td>
<td>0.246</td>
<td></td>
</tr>
<tr>
<td>1.5 wt% CNT-NR</td>
<td>0.178</td>
<td>0.226</td>
<td></td>
</tr>
</tbody>
</table>

From Table 4.4, activation energy was calculated at two different voltages. In the low voltage region (20V) activation energy increases with increasing wt% of CNTs in the NR matrices but in the high voltage region (50V) activation energy decreases with increasing wt% of CNTs in the NR matrices.

4.7 Mechanical Properties

Table 4.5 Tensile strength and Elongation at breaking% for NR, 0.5, 1.0 and 1.5 wt% CNT-NR polymer composites

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Average Thickness at Gauge mm</th>
<th>Ultimate Tensile Strength MPa</th>
<th>Elongation at Break (G.L.=33mm) %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exp.</td>
<td>Ref[8]</td>
<td></td>
</tr>
<tr>
<td>NR</td>
<td>1.09</td>
<td>1.17</td>
<td>0.284</td>
</tr>
<tr>
<td>0.5 wt% CNT-NR</td>
<td>1.04</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>1.0 wt% CNT-NR</td>
<td>1.04</td>
<td>0.87</td>
<td>0.564</td>
</tr>
<tr>
<td>1.5 wt% CNT-NR</td>
<td>1.04</td>
<td>1.16</td>
<td></td>
</tr>
</tbody>
</table>

The tensile strength and elongation at break of the neat NR and CNT-NR composite are measured from mechanical testing. It is observed that tensile strength increase with increasing CNT content in NR. Our study supports the results of Atieh et al. [8] who investigated the tensile strength for NR and NR-CNTs composition. The maximum tensile strength they got for NR was 0.28 MPa, but in our case we are able to increase the tensile strength to 1.16 MPa. The values of it are tabulated in Table 4.5. The EB is observed to decrease with increasing CNT wt% in NR.
References


Chapter-V
CONCLUSIONS
5.1 Conclusions

In this work the properties of natural rubber (NR) biopolymer and its composite with MWCNTs have been studied. CNTs-NR polymer composites are prepared by solution casting method incorporating 0.5, 1.0, 1.5 wt% of CNTs in NR. Then structural, mechanical and electrical properties of the NR and its composites are studied.

To obtain uniform dispersion of MWCNTs they are refluxed in concentrated (67%) nitric acid (HNO₃) and concentrated (98%) sulfuric acid (H₂SO₄). Thus MWCNTs are observed to be functionalized by the attachments of oxygen containing groups as observed by the FTIR spectra.

From the SEM images it is observed that no MWCNTs are visible and all the CNTs are embedded inside the NR matrix. This may be due to that the CNTs inside the matrix are wrapped by the molecules of rubbers. EDX spectra confirmed 100% presence of carbon in the composites signifying less or no impurity in it.

XRD spectra for NR and CNT-NR composites show broad amorphous peak near 2θ = 20° which indicates amorphous nature of all the samples.

The absorption peaks in the FTIR spectra of NR and CNT-NR composites are observed to appear at similar position confirming the uniform dispersion of CNTs in the NR matrices.

Tensile strength of the composites is observed to be slightly increased with the increase in wt% of CNTs in NR matrices. This may due to the stronger interaction of the CNTs with the NR molecules.

TG-DTA data shows thermal stability of the composites gets improved with the increase in CNTs percentages in the NR matrix, the decomposition of the NR is delayed due to the incorporation of more thermally sable CNTs in it.

From the DC electrical measurement it is calculated that current density in the CNT-NR composites is of the order of several Am⁻², which is observed to increase with increasing wt% of CNTs in the NR matrices at room temperature. When measurement temperature increases the current density is observed to increase indicating that the conduction is semiconducting in nature. The resistivity decreases with increasing wt% of CNTs in the NR matrices. The activation energy is observed to vary between 0.175 – 0.250 eV for the experimental samples.
In conclusion, it can be inferred that incorporation of the modified CNTs reinforced the structural, mechanical, thermal and electrical properties of the NR. The fabricated NR nanocomposites may find interesting applications in different engineering products like robotic arms, tubes, tyres, high charge storage capacitors, electronic packaging, seal pad, electromagnetic interference shielding, etc.

5.2 Suggestions for Future Works

More investigations are needed to explain different characteristics elaborately, which will help to reveal suitable applications of CNTs-NR polymer composites. For further understanding of this material the following studies may be carried out:

- AC electrical measurement of CNTs-NR polymer composites.
- Tensile strength measurement for Volcanized CNTs-NR polymer composites.
- To study the variation of $P^H$ of the functionalized CNTs and its composites.
- Study of the CNT dispersion in the CNTs-NR polymer composites by transmission electron microscopy.