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Investigation of mechanical properties of polyethylene-based Nano-composites.

By

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IN

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AT THE

UNIVERSITY OF JOHANNESBURG

SUPERVISOR: Prof N.A. Ahmed

25 September 2019
AUTHOR'S DECLARATION

I RONNY THAPELO TEBETA hereby declare that this master’s research dissertation is wholly my own work and has not been submitted anywhere else for academic credit either by myself or another person.

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Signed: ___________ Date: 25 September 2019
DEDICATION

TO MY LATE MOTHER
MY FATHER
MY GIRLFRIEND
MY TWO GRANNIES
AND
MY AUNT
ACKNOWLEDGEMENT

This report and the work in it would not have been successful without the following people, so I will like to thank them for their contribution.

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Finally, I would like to thank all those who contributed to my work directly or indirectly and I thank Lord, who have given me strength and opportunity to complete this work.

Thank You all

The following papers resulted from this thesis work:


• R.T. Tebeta, N.A. Ahmed, and A.M. Fattahi, ‘Experimental and numerical study on HDPE/SWCNT nanocomposite elastic properties considering the processing techniques effect’ DOI:10.1007/s00542-020-04784-y
ABSTRACT

Composites and nanocomposites materials are widely used in the newly developing technology for lightweight but strong materials such as in the automotive, aerodynamic, wind turbine and biomedical industries. The advantage of composites or nanocomposites is that they are made of a combination of two or more materials with distinct properties to achieve a new material with different properties from the constituent materials. This work covers the investigation of elastic properties of polymer-based nanocomposites whereby high-density polyethylene (HDPE) is reinforced with single-walled carbon nanotubes (SWCNT) at various weight fractions. SWCNTs nanoparticles are used with polymer HDPE to make composite which has remarkable properties, to enhance the elastic properties of polymer-based nanocomposites.

The reason why SWCNTs nanoparticles were used as the strengthening material for HDPE, is because they contain high strength, high melting temperature and are easy to mix with plastics due to their size which is in Nanoscale. On the other hand, polymers are low in strength and lightweight materials which are easy to shape during the manufacturing process and they are inexpensive. Strengthening HDPE with SWCNTs nanoparticles result with a nanocomposite material which is high in strength and low in weight. This composite material holds a great potential to be used in the future for strong but lightweight components application.

The objective of the current work was to prepare HDPE/SWCNTs nanocomposites using two different processing methods by reinforcing HDPE with SWCNT nanoparticles at the weight fractions of 0 wt%, 0.2 wt%, 0.4wt%, 0.6 wt%, 0.8wt%, and 1wt%. Then investigate its elastic properties at each weight fraction of SWCNTs and the effect of the processing techniques used on the elastic modulus of the composite. Injection and compression moulding were used to process the tensile test samples of HDPE/SWCNTs nanocomposites. The investigation was conducted used three approaches which include numerical, experimental and analytical.

Numerical results were obtained using the finite element method (FEM) incorporated with represented volume element (RVE) to generate the HDPE/SWCNT nanocomposite model with the aid of ANSYS software. The simulations were made using two density-fractions of HDPE and SWCNTs at the same given weight fractions of SWCNTs nanoparticles per HDPE matrix. The modelled results showed that elastic modulus of HDPE/SWCNTs nanocomposite improved by 74 % at the SWCNTs weight fraction of 1 wt% for the density fraction of 1.8 and at the same weight fraction for the density fraction of 2 the improvement was found to be 56 % compared to pure HDPE. This shows that the low-density fraction of SWCNTs fibre and
HDPE matrix results with higher improvement on elastic modulus HDPE/SWCNTs nanocomposite compare to the high-density ratio at the same weight fraction of SWCNTs. The modelling results also showed that adding of SWCNTs nanoparticles into the HDPE matrix enhance the elastic modulus of HDPE/SWCNTs nanocomposite.

The experimental tensile test samples of HDPE/SWCNTs nanocomposites were produced according to injection and compression moulding at different weight fractions of SWCNTs. The tensile test samples of pure HDPE and HDPESWCNTs nanocomposites were produced conferring to the ASTM D-638 and ISO 527. The Taguchi method was used to plan the experiment and to determine which parameters between the SWCNTs nanoparticles and processing methods influence the elastic properties of HDPE/SWCNTs nanocomposites the most. The results showed that SWCNTs has a higher effect on the elastic modulus of HDPE/SWCNTs nanocomposite compared to the processing techniques. This was done using the signal to noise ratio of the Taguchi technique which showed that SWCNTs at the weight fraction of 1 wt % increased the elastic modulus of HDPE/SWCNTs nanocomposite by 24 % compared to pure HDPE. However, at the same SWCNTs weight fractions processing methods improved the elastic modulus of HDPE/SWCNTs nanocomposite by 10% compared to pure HDPE. Furthermore, the experimental results also showed that yielding stress and maximum force of HDPE/SWCNTs nanocomposites increased by 3 % for injection moulded samples and by 25 % for compression moulded samples compared to pure HDPE respectively. The behaviour of the elastic properties of HDPE/SWCNTs nanocomposite was further predicted by theoretical models.

Three theoretical models which include approximation model Manera, model of Pan or fibres density equation and Hirsch’s model were used to predict the modulus of HDPE/SWCNTs nanocomposite. This was achieved by using the experimental elastic modulus results for both processing methods. The analytical results showed that the addition of SWCNTs nanoparticle increases the elastic modulus of HDPE/SWCNTs nanocomposite. Although they showed a big difference compared to that of experimental and FEM which was observed through the comparison study. The comparison study showed that FEM result has an acceptable and reasonable difference that can be useful for the prediction of the elastic modulus of HDPE/SWCNTs nanocomposite.

**Keywords:** Compression moulding; Elastic properties; High-density polyethylene; Injection moulding; Single-walled Carbon nanotubes
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<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>CSIR</td>
<td>Council for Science and Industrial Research</td>
</tr>
<tr>
<td>DMX</td>
<td>Maximum Displacement</td>
</tr>
<tr>
<td>DT</td>
<td>Destructive Testing</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite Element Method</td>
</tr>
<tr>
<td>GTT</td>
<td>Glass Transition Temperature</td>
</tr>
<tr>
<td>HDH</td>
<td>High-Density Homopolymer</td>
</tr>
<tr>
<td>HDPE</td>
<td>High-Density Polyethylene</td>
</tr>
<tr>
<td>IPPI</td>
<td>Iran Polymer and Petrochemical Institute</td>
</tr>
<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
</tr>
<tr>
<td>LCB</td>
<td>Long Chain Branching</td>
</tr>
<tr>
<td>LLDPE</td>
<td>Linear Low-Density Polyethylene</td>
</tr>
<tr>
<td>MDPE</td>
<td>Medium-Density Polyethylene</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular Weight</td>
</tr>
<tr>
<td>MWD</td>
<td>Molecular Weight Distribution</td>
</tr>
<tr>
<td>NDT</td>
<td>Non-Destructive Testing</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>RVE</td>
<td>Representative Volume Element</td>
</tr>
<tr>
<td>SCB</td>
<td>Short Chain Branching</td>
</tr>
<tr>
<td>SCL</td>
<td>Supercooled Liquid</td>
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<tr>
<td>SWCNT</td>
<td>Single-Walled Carbon Nanotube</td>
</tr>
<tr>
<td>TSE</td>
<td>Twin Screw Extruder</td>
</tr>
<tr>
<td>3D</td>
<td>Three-Dimensional</td>
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## NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>CH₄</td>
<td>Methane</td>
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<tr>
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<tr>
<td>C</td>
<td>Carbon</td>
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<td>Tₒₛ</td>
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<td>M</td>
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<td>Eᵢ</td>
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<td>P</td>
<td>Pressure</td>
<td>MPa</td>
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</tr>
<tr>
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<td>Yield Stress</td>
<td>MPa</td>
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CHAPTER 1

1.0 INTRODUCTION

1.1 Overview
This chapter provides a brief explanation of the present investigation at hand. This is reached by recognizing the important areas in determining where the elastic properties of polymer-based nanocomposites could be improved in relations to the developing processes, processing techniques, and identifying the problem statement, objectives, scope and methodology of the investigation.

1.2 General background
Enhancing polymer elastic properties by reinforcing it with nanoparticles such as graphene, carbon nanotubes (CNTs), nanoclay and other reinforcing nanoparticles have attracted the attention of many researchers and manufacturing industries in the past few years. This is due to the increase in the demand of improved materials in the new technological applications such as in automotive, energy and aeronautical industries for high strength but lightweight components, thermal insulators in electrical and electronics, coating and many others [1, 2]. The combination of two or more material in the form of reinforcing a matrix material of unique properties with another material that serve as fibres to achieve material of exceptional properties from constituent material is called composite [3]. However, when one or more dimensions of the added fibres in the matrix are less than 100 nm the subsequent composite material is said to be a nanocomposite material [4, 5, 2]. Nanocomposite materials are newly developed engineering materials under the field of nanotechnology, which is the area of research and innovation that have a great potential to produce materials on the scale of atom and molecules with unique properties and to manufacture the products form those materials for a great number of applications [6, 7, 8]. Developing and processing of new material with improved mechanical properties is an exciting topic in the research field these days that will lead the world into fourth industrial (4I) revolution on materials.

This study is mainly based on the development and the processing of polymer-based nanocomposites by looking at two processing methods. High-density polyethylene (HDPE) as a matrix will be reinforced with single-walled carbon nanotubes (SWCNTs) fibres at different weight fractions to produced nanocomposite with enhanced elastic properties. The produced HDPE/SWCNTs nanocomposites will then be processed using two techniques namely;
injection and compression moulding. The goal is to predict the elastic behaviour of HDPE reinforced with SWCNTs at various weight fractions as well as investigating the effect of the processing methods on the mechanical properties of HDPE/SWCNTs nanocomposites. This will be achieved using three approaches which include numerical, experimental and analytical.

The numerical analysis will be conducted using ANSYS software whereby finite element method FEM is used with the aid of represented volume element RVE to produce the three-dimensional (3D) HDPE/SWCNT nanocomposite model. The numerical approach has been used by many researchers in the past using different approaches such as molecular dynamics modelling, continuum mechanics methods, multiscale modelling, micromechanical analysis and others [9, 10, 11]. However, some of these approaches have proven to be accurate, economic and timesaving. Although there have been some challenges encountered along the way to figure out the suitable bonds between the fibre CNTs and the matrix. Liu et al. [12] managed to come up with a 3D model for CNTs reinforced composites with compatibility and accuracy between the CNTs and matrix. In this work, the elastic modulus of HDPE/SWCNTs nanocomposite will be investigated using Liu et al’s approach by creating RVE using FEM. The properties of the matrix, fibre and interface will be extracted from the atomic modelling results. The FEM simulated results will then be validated with the experimental and analytical results.

The experimentation will be conducted utilizing the tensile test for elastic properties of HDPE/SWCNTs nanocomposites. The properties such as elastic modulus, Yield strength, maximum force, maximum elongation and others will be investigated for each weight fractions of SWCNTs nanoparticle into HDPE matrix. This will also be done for both processing methods used to produce HDPE/SWCNTs nanocomposites. The tensile test experimentation for nanocomposites has been used by many researchers like Oztan et al. [13], Thakur et al. [14], and Najipour et al. [15]. They all managed to come up with the results that built the background of the nanocomposite especially CNTs, SWCNTs and multi-walled carbon nanotubes (MWCNTs) particles reinforced polymers literature. They used different approaches for their experimentation as well as various weight fractions and nanoparticle. This work will focus mainly on the effect of two processing method on the elastic properties of HDPE/SWCNTs nanocomposite and the effect of SWCNTs nanoparticles weight fraction on the elastic properties of HDPE/SWCNT nanocomposites.
1.3 Problem Statement
Composite and nanocomposite materials are increasingly in demand for various industrial application as mentioned, this is due to their lightweight and high strength properties which can be made artificially. Polymer nanocomposites are easy to shape and to manufacture especially for design purposes, but they turn to change behaviour under some operational conditions such as temperature changes and load subjection. It is impotent to investigate their elastic behaviour under a given load using different approaches to achieve required and necessary elastic properties for the specified application.

1.4 Research Questions
The following research questions can be asked based on the research topic:

- How will each processing methods affect the mechanical properties of the HDPE/SWCNTs nanocomposites?
- Which processing method will bring about better elastic and hardness properties of HDPE/SWCNTs nanocomposite at a low cost?
- Which parameter between the processing methods and the weight fractions of SWCNTs will result with better elastic properties of HDPE/SWCNT nanocomposites?

1.5 Objectives of the Research
The primary and secondary objectives of the research are presented as follows:

1.5.1 Primary Objective
The main aim of this research is to predict the elastic behaviour of HDPE reinforced with SWCNTs at different weight fractions and investigate the effects of two processing methods on the mechanical properties of HDPE/SWCNTs nanocomposites. The two processing techniques that will be focused on in this research project are:

- Injection moulding
- Compression moulding

1.5.2 Secondary Objectives
- Understanding the development and the manufacturing processes of polymer-based nanocomposites by conducting the relevant literature
- Identify mechanical properties, characteristics and industrial applications of polymer-based nanocomposites
• Understand the relationship between the matrix and reinforcement weight fractions in the nanocomposites
• Develop/design an HDPE/SWCNTs nanocomposites at different SWCNTs weight fractions using the injection and compression moulding
• Investigate the elastic behaviour of HDPE reinforced with SWCNTs at different weight fractions
• Investigate the effect of an injection and compression moulding on the elastic modulus of HDPE/SWCNTs nanocomposites

1.6 Research Motivation
This section discusses the two issues that motivate the investigation undertaken in this project. First, there is a necessity for high strength and lightweight components in automotive, aerodynamics and energy industries that are easy to manufacture especially for complex geometries. Second, there is a need to identify the effective processing method to produce polymer-based nanocomposites with desirable mechanical properties.

1.7 Significance of the Research
This research is very important especially in the field of nanotechnology, material sciences, engineering materials such as nanocomposites, and the strength of materials. It helps to study behaviour and mechanical properties (elastic properties) of materials as well as improving them for a suitable application. Most of the polymer-based nanocomposite are lightweight easy to fabricate and shape, and they have been applied in many industries because of such properties. This research will help to understand the effect of reinforcing HDPE with SWCNTs at different weight fractions as well as predicting the elastic behaviour of the nanocomposite. It will also help to come up with the recommendation of the effective and economical processing methods that can be used to produce HDPE/SWCNTs nanocomposites products.

1.8 Research Methodology
Nanotechnology and nanocomposite are newly developed field of science that requires basic general background and understanding. To be familiar in the field, relevant literature review based on polymer-based nanocomposites must be conducted. The conducted review of the literature will aid the researcher to become an expert on the topic. It will also help to come with the steps and procedures to be followed during the experimentation in the laboratories or workplace. Since the experimental, numerical and analytical approaches are required in this
study to investigate and predict the elastic behaviour of HDPE/SWCNTs nanocomposites, then several steps on the approaches and procedure need to be followed and applied.

To fulfil the research objectives, the following research steps will be followed:

1. Literature review
   - Conduct relevant literature regarding the development and the investigations showed based on polymer-based nanocomposites by looking at the following:
     o Identification of the knowledge gaps of the study topic
     o Identification of the potential benefits of the study
     o Formulation of the relevant solutions to the stated problem
     o Planning the conduction of experimental numerical and analytical analysis

2. Predicting model
   - Create an ANSYS model
   - Predict the elastic behaviour HDPE/SWCNTs nanocomposite using finite element method (FEM) using the ANSYS model created

3. Material development
   - Developing polyethylene-based nanocomposites by reinforcing HDPE with SWCNTs at different weight fractions to come up with an improved nanocomposite by focusing on the following:
     o Gathering of the materials to be used (HDPE and SWCNTs)
     o The mixing preparations of matrix and reinforcing nanoparticles
     o Tween screw extruder as the mixing equipment

4. Processing methods
   - Using two processing methods to manufacture the tensile test samples of HDPE/SWCNTs nanocomposite by looking at the following:
     o Cost and time required to produce a given number of samples from each processing method
     o Accuracy of each processing methods

5. Experimentation
   - Perform tensile tests using the samples made from each processing methods and do the followings:
     o Calculate the elastic properties for each produced sample
     o Relate the properties using calculations and interpretations
Validation of the results by Correlating the numerical results and experimental results using the existing literature results

Find out what do the results mean and how can they be used

6. Conclusion and further recommendations

- Draw a relevant conclusion and come with further recommendations based on the obtained results and their implications.

1.9 Scope of the Study

This research project is focusing on the development and the investigation of elastic properties of HDPE/SWCNTs nanocomposite and the examination of the effects of processing methods on its mechanical properties. The aspects to be studied are the SWCNTs weight fractions, the effect of the two processing methods, two melting points temperatures, testing conditions, and the sample sizes. This will be achieved by looking at the following points:

- **General-purpose:** To determine the elastic properties of HDPE/SWCNTs nanocomposite processed using two different technologies.
- **Subject matter:** The elastic properties of nanocomposites.
- **Topics studied:** The effect of SWCNTs nanoparticles weight fractions on the elastic properties of the nanocomposites, the outcome of the processing methods on the elastic properties of pure HDPE and reinforced HDPE/SWCNTs nanocomposites, the problems encountered during the production of the nanocomposites and the proposed solutions.
- **Population and sample:** Weight fractions, processing methods and elastic properties.
- **Limitations:** These are the factors that the researcher cannot control for example; the environmental conditions which include the temperature, pressures and humidity.
- **Delimitations:** These are choices made by the researches during the investigation, they include the description of the boundaries that have been set for the study. Most of the delimitations are included in the research methodology section, in that case, this is the place to explain the things that are not covered in this research and why. Things that will not be done are as follows:

This research is not looking at other polymer-based nanocomposites processing techniques except the Injection, and compression moulding. The reason being there are a lot of polymer processing techniques and it will require time and money to process samples using them all.
Having said that injection and compression moulding are selected because they are popular and available for processing of polymer-based nanocomposites.

1.10 Document Outline
This entire report outline is presented as follows:

Chapter 1: Introduction
- General research background
- Stating of the research problem
- Formulation of objectives
- Designing the research methodology
- Overview of the research study

Chapter 2: Literature Review
- General analysis of the existing literature on polymer-based nanocomposites (HDPE/SWCNTs nanocomposites)
- Recognizing specific key areas of scarcity in this works
- Planning of the study based on the accessibility of the research resources
- Improvement based on the previous experiment and numerical models conducted in the past

Chapter 3: Experimental Design
- Planning experimental steps to be followed and the numerical approach to be used
- Selection of the best experimental design technique and numerical software
- Preparation of the experimental matrix and numerical model
- Selecting data analysis tools and methods

Chapter 4: Results and Discussion
- Present and analyze the obtained results
- Discussion of the analyzed results, by highlighting the important findings of the experiment and numerical simulations
- Comparison of the experimental and numerical results with the analytical results

Chapter 5: Conclusion and Recommendations
Conclude by summarising the key findings of the entire investigation and give reasonable recommendations

1.11 Summary

Chapter 1 was focusing on the overview of the research project, problem statement, objectives of the research, significance of the research and the experimental methodology that must be followed to result with the great success of the investigation. The investigation is based on the development and examination of the mechanical properties of polyethylene-based nanocomposites. The next chapter will focus on the theoretical background of the polymer-based nanocomposite and the previous studies made, based on the elastic properties of polyethylene-based nanocomposites.
CHAPTER 2

2.0 LITERATURE REVIEW

2.1 Overview
The previous chapter provided a brief outline on the topic; the problem statement, together with the objectives as well as the significance of the research and the scope of the work. The current chapter presents the literature review on the introduced topic, which focuses on the previous investigations that were done on similar topics. The current chapter aims to gather and study relevant information on the topic, that will provide a clear knowledge on how to conduct the experiments, numerical (FEM) simulations, and analytical equations required for the research. It will also be helpful to come up with the improvements on the present investigations because knowing what happened in the past investigations based on the subject will help improve the results for new investigations, which is why literature review is very important in this type of project.

2.2 Composites
Engineering materials these days have evolved to such an extent that many of our modern industrial applications require a material with a rare combination of properties. These types of materials cannot be achieved by conventional metal alloy, ceramics, and polymeric materials only [16, 17]. This is particularly true for materials that are required for aerospace, automotive, household, and underwater applications. For example, the aerospace industries are increasingly in the demand of the structural materials that possess high strength properties, with low densities, stiff, and impact resistance, however, such material properties are not easily found in a pure material [18]. To achieve such properties, two or more materials with distinct properties should be combined. The development of a material with new properties by combining materials is influenced by composite materials.

The composite material is any multiphase material that shows a significant proportion of the properties of both constituent phases such that a better combination of properties is realized [16, 19]. According to the principle of combined action by Callister. Jr at al. [16], better property combination is twisted by the careful combination of two or more distinct materials. A composite, in short, is a multiphase material that is artificially made as opposed to one that forms or occurs naturally [20]. Most of the composite materials have been created to enhance the thermal, electrical, and mechanical properties of the material.
Many composite materials are composed of two phases namely, the Matrix (binder) phase and dispersed phase (reinforcement). Where matrix surrounds and binds together dispersed phases called reinforcements [16, 20], as shown in Figure 2.1.

![Figure 2.1 Schematic representation of the various geometrical of the composite [16]](image)

Figure 2.1 (a) illustrates the concentration of reinforcements within the matrix, (b) the size of reinforcements inside the matrix, (c) the shapes of reinforcements in the matrix, (d) the mode in which the reinforcements can be distributed within the matrix, and (e) the orientation of reinforcements within the composite. For every composite material, the matrix phase has a unique function and reinforcement has its exclusive functions as well. Their functions are as follows:

**Functions of the matrix phase in composites are:**

- Binds reinforcements together,
- Protect reinforcements from surface damage,
- Separated reinforcements and prevents a crack from one reinforcement material propagating through another,
- Acts as a medium through which externally applied stress are transmitted and distributed to the reinforcements.

**Functions of reinforcements in composites are:**

- It increases the coefficient of thermal expansion and the conductivity of the composite,
- It increases the mechanical properties of the composite,
- It also provides the stiffness and strength to the composite material.
Composites are being progressively established for a multitude of tasks. For example, fibre reinforced composites are being developed and used to replace materials such as metals and their alloys because their mechanical properties can be achieved with the correct combination of matrix and fibres. Metal and their alloys are heavy and difficult to shape so composite materials are designed to offer the following properties:

- Low weight but high stiffness and high strength,
- Resistance against fatigue and corrosion,
- Ease in manufacturing complex shapes,
- Low coefficient of expansion,
- Simple repair of damaged structures.

There are many different types or classes of composites based on the kind and size of the reinforcement. One simple arrangement for the classification of the composite materials is shown in Figure 2.2, which consists of three main divisions namely: particle-reinforced, fibre-reinforced, and structural composites; with at least two subdivisions exist for each division. This research looks at two classifications which are of major importance for this topic and are currently being developed for many applications:

- Particle-reinforced composites,
- Fibre-reinforced polymer composites.

![Classification arrangement for the various composite types](image-url)

**Figure 2.2** Classification arrangement for the various composite types [16]
2.2.1 Particle-reinforced Composites

As shown in Figure 2.2, particle-reinforced composite contains two main subdivisions which are large-particle and dispersion strengthened. The difference between these two subdivisions is based on reinforcement or strengthening mechanism. For large-particle, the term “large” is used to indicate that reinforcing particles cannot be treated on the atomic or molecular level [16, 21, 22]. For most of these composites, the particulate (reinforcing) phase is harder and stiffer than the matrix phase. These reinforcing particles tend to restrain movement of the matrix phase near each particle.

For dispersion-strengthened composites, particles are normally much smaller with diameters between 0.01 and 0.1 μm (10 and 100 nm). Particles of such size are said to be nanoparticles [23, 16]. For such composites, Particle-matrix interactions that lead to strengthening, occur on the atomic or molecular level. The matrix phase bears the major portion of an applied load and the small-dispersed particles delay the motion of dislocations. Therefore, plastic deformation is restricted such that yield and tensile strength, as well as hardness, improve [16].

2.2.2 Fibre-reinforced polymer composites

Fibre-reinforced polymer composites (FRP) or fibre-reinforced composite is a composite material made of the dispersed phase in a polymer matrix in the form of fibres [16, 24, 25]. The fibres in this kind of composite are usually carbon, epoxy, glass, vinyl ester, and others. The goal of designing a fibre-reinforced composite is to achieve high strength and stiffness on a weight basis [26].

2.3 Nanocomposites

Nanocomposite organic/inorganic materials are a fast-expanding area of material research, which is part of the growing field of nanotechnology [27]. The term “nanocomposite” encompasses a wide range of materials mixed at the nanometer scale (normally dimensions less than 100 nm), combining the best properties of matrix phase material and dispersed nanomaterials to come up with the unique properties of nanocomposite materials [28, 29, 27]. This process improves the mechanical properties of nanocomposite materials such as elastic modulus, stiffness, hardness, toughness, and heat distortion temperature [28, 30]. The properties of nanocomposite materials depend not only on the properties of their components but also on their morphology and interfacial characteristics.
According to Knauth et al. [27], the previous experimental work has shown that almost all types and classes of nanocomposite materials lead to new and improved properties when compared to their macro-composite counterparts. They tend to improve the electrical conductivity, especially the ionic conductivity, and thermal conductivity of the original material as well as other properties that might undergo substantial improvements such as thermal stability and chemical resistance, decreased permeability to gases, water and hydrocarbons, surface appearance and optical clarity [27, 31]. Consequently, nanocomposites promise new application in many fields such as mechanically reinforced lightweight components, battery cathodes and solid-state Ionics, nonlinear optics, sensors, nanowires and many others. However, much effort is going on to develop efficient combinations of materials at a proper weight fraction and to report multi functionalities to the nanocomposites.

Previous researchers such as Knauth et al. [27], and Comargo et al. [4] reported on the properties and application of materials with characteristic dimensions in the nanometre scale. These reports were, though, devoted to inorganic single-phase materials. However, recent researchers have seen extensive development of polymer and hybrid organic/inorganic systems, which improve the inconsistency of the properties of the materials and give extra freedom for the understanding of the previously unachievable combination of properties.

In this report, the focus is on the investigation of mechanical properties (especially elastic properties) of polymer-based nanocomposites. HDPE will be reinforced with SWCNTs at different weight fraction to achieve better mechanical properties. It is very important to look at the previous studies made based on polymers and nanoparticles mentioned above, to come up with a clear understanding of how to improve the mechanical properties of the polymer-based nanocomposites.

2.4 Polymers

Without the discovery and varied applications of polymers, the daily life would have not been easier and colourful as it is these days. The use of polymers in the manufacturing of plastic buckets, automobile tyres, electrical insulating materials, machine parts, packaging bags, synthetic clothing materials, and children’s toys has completely revolutionised the industrial development as well as the daily life. Engineering materials such as rubber, plastic, and adhesives are commonly referred to as polymers. There are over 15,000 various types of commercially available polymer and are categorised into 20 diverse families [32]. Polymers
are commonly light and corrosion-resistant materials with low stiffness and strength. They are typically not appropriate for high-temperature applications but are reasonably cheap and can be easily formed into a variety of shapes and designs [33, 31].

### 2.4.1 Polymer Structure

The word ‘polymer’ comes from two Greek words: ‘poly’ means many and ‘mer’ means unit or part. The term polymer is defined as a chemical species of very high molecular mass (10³-10⁷u) made up from many units of low molecular mass covalently linked together [31, 34, 35]. These are also referred to as macromolecules, which are formed by linking of repeating structural units on a large scale. The repeating structural units (a long chain of repeating molecules) are derived from simple and reactive molecules called monomers and are linked to each other by covalent bonds [31].

The backbone of these repeating structural units is the carbon (C) atom. According to Cooper [36], from valence theory it is identified that carbon has 4 electrons in its outer shell, therefore to complete its atomic structure it can share further 4 electrons. To achieve this, it must bond covalently with other atoms around it [31]. One of the commonly known atoms that carbon is likely to bond with is hydrogen (H). From valence theory, it is known that hydrogen can share one electron to complete its outer shell [31, 36]. Consequently, it is easy for a carbon atom to bond with 4 hydrogen atoms at maximum. Figure 2.3 shows methane structure formed by four hydrogen atoms and one carbon atom as explained by valence theory.

![Figure 2.3 Methane formed by 4 hydrogen atoms and 1 carbon atom](image)

However, Polymers are derived from the long chain of monomers (molecules) that results from adding another carbon atom methane. The next section will explain how the polymer is formed from monomers.
2.4.2 Polymer Chains

Adding carbon to methane by removing two hydrogen atoms, carbon atom will then bond with another carbon atom to form a double bond which results as a monomer shown in Figure 2.4. If another carbon atom is continually added to the monomer with hydrogen atoms attached to them, they then form a polymer as illustrated in Figure 2.5. The polymer is however formed from a sequence of monomers bonded together to form a molecular chain. A simple example is polyethylene, which consists of many ethylene units, -CH₂CH₂-, bonded covalently to one another to form long-chain molecules consisting of thousands of ethylene units [31].

Figure 2. 4 Illustrate Lewis molecular structure of the ethylene monomer unit (ethylene) [34]

Figure 2. 5 Illustrate Lewis molecular structure of a polymer unit (polyethylene) [34]

In short, a sequence of monomers attached forms a molecular chain is known as a polymer. Most of the polymers exist in the functional groups

2.4.3 Monomer Combinations

A polymer can be composed of a mixture of diverse monomers since there is no reason for every monomer in a polymer molecular chain to be the same [37, 38]. If a polymer is composed of a single type of monomer is said to be homopolymer whereas a polymer composed of two or more various types of monomers is known as a copolymer illustrated in Figure 2.6
Monomers are important when it comes to the enhancement and the development of dental filling composite materials. Monomers applied in dental filling composites are strongly related to stability, viscosity, reactivity, polymerisation shrinkage of the composite, and mechanical properties [39]. Since this study is based on the mechanical properties of polymer-based nanocomposite especially elastic properties, them it is important to gain knowledge on how monomer affects the elastic behaviour of the polymer-based nanocomposites. These are due to the polymerization and the functional groups of polymers.

### 2.4.4 Crystalline or Amorphous of Polymer

As explained, a polymer is a series of long-chain molecules composed into a complex arrangement to make a solid. It exists in two possible arrangements of the molecular chains which are either crystalline or amorphous [40, 41, 42]. Crystalline is a polymer molecular chain array with a long-range straight-line order as shown in Figure 2.7 (a). Amorphous is randomly packed polymer molecular chains with no obvious order shown in Figure 2.7 (b). Though a polymer can never be crystalline instead it will contain the amorphous regions or ales it can be completely amorphous. A polymer with a molecular structure that is partly crystalline and partly amorphous are said to be semi-crystalline.
The degree of crystallinity in a polymer structure may range from completely amorphous to up to 95% crystalline [42]. The presence of both crystalline and amorphous regions in a polymer is like a two-phase metal-alloy as presented in Figure 2.8.

All polymers contain the mix of crystalline and amorphous structure like the one shown in Figure 2.8. The proportion of each structure in a polymer is influenced by the temperature, how the resulting polymer is processed and its composition.

2.4.5 Viscosity and Specific Volume of Polymer
Viscosity is the resistance of the fluid to change in shape. The viscosity of a polymer depends on the size and the concentration of the dissolved polymer [44].

2.4.5.1 Viscosity in Crystalline Polymers
The amorphous and crystalline polymers behave quite different under applied heat. A crystalline polymer in the solid-state is rigid with high viscosity. As it is exposed to heat that is past its melting point, the viscosity drops shortly to that of a flowing liquid the same as ice melt into water [45, 46]. Figure 2.9 illustrates the behaviour of the crystalline polymer under different temperature.
Specific volume is defined as the number of cubic meters occupied by one kilogram of matter which is the same as the reciprocal of its density or the ratio of the volume of a material to its mass [47]. When heating a crystalline polymer from the solid-state it expands at a constant rate depending on its coefficient of thermal expansion. The polymer usually undergoes a large increase in volume at the melting point and then expand at a constant rate in the liquids state. This large expansion in the free volume of the polymer occurs as the chains in the crystalline state back down into an amorphous structure [47, 46]. Figure 2.10 demonstrates the temperature effect on the specific volume of crystalline polymers.

Figure 2. 9 Temperature effect of the viscosity of crystalline polymer [47]

2.4.5.2 Specific Volume in Crystalline Polymers

Figure 2. 10 Effect of temperature on the specific volume of the crystalline polymer [47]
2.4.5.3 Viscosity in Amorphous Polymers

Most of the amorphous polymers in the solid-state are brittle and hard but when exposed to heat they will first transform to a soft leathery state then forming into a viscous liquid as illtreated in Figure 2.11. This transformation of amorphous polymer from solid-state to the soft leathery state happens at the Glass Transition Temperature GTT ($T_g$) of the polymer [47]. However, at this temperature change, there is no sharp transition in viscosity of the amorphous polymer.

![Figure 2.11 Effect of temperature of the viscosity of amorphous polymer [47]](image)

2.4.5.4 Specific Volume in Amorphous Polymers

Amorphous and semi-crystalline polymers do not melt the same way when exposed to high temperature. Instead, the amorphous polymer becomes progressively low in viscosity as it is heated above ($T_g$) as shown in Figure 2.12. When an amorphous polymer undergoes cooling from a liquid state, it contracts gradually based on the coefficient of thermal expansion and its viscosity increases at a content relative rate [47]. If the temperature is below ($T_g$), then the rate of reduction falls below the rate that the viscosity increases due to structural change of the molecular chains into the glassy amorphous state.
2.4.6 Types of Polymers

Polymers are formed from monomers and the process of forming polymers is called polymerization [31]. There are two different types of the polymerisation reaction, for example, the transformation of ethylene to polyethylene and interaction of hexamethylene diamine and adipic acid leading to the formation of Nylon 6,6 [34]. Polymers have several classifications based on special considerations such as the origin of source, the structure of polymers, molecular forces and mode of polymerisation as shown in Figure 2.13.

**Figure 2.12** Effect of the temperature on the specific volume of the amorphous polymer [47]

**Figure 2.13** Classification arrangement for polymers [34]
From Figure 2.13, Polymers that we are focusing on for this research are polyethylene high-density polyethylene (HDPE). It means under the classifications of polymers illustrated in Figure 2.13, we will be focusing on the subcategories highlighted in yellow which are synthetic polymers, linear polymers, thermoplastics, and additional polymers. Because these subcategories explain polyethylene characteristics and their formation.

The following are explanations of subcategories as highlighted in Figure 2.13:

### 2.4.6.1 Synthetic polymers

Synthetic polymers are subcategory three, under the classification based on the source of polymers shown in Figure 2.13. These are man-made polymers extensively used in industries and daily life, an example of such polymers is plastic (polyethylene or polythene), nylon 6.6, synthetic rubbers and synthetic fibres [31, 48]. Figure 2.14 shows the daily application and common types of synthetic polymers.

![Synthetic Polymers](image)

**Figure 2. 14 Application of synthetic polymer [49]**

### 2.4.6.2 Linear polymers

Linear polymers are subcategories one, found under the classification based on the structure of polymers illustrated in Figure 2.13. These types of polymers consist of long and straight chains. They are well packed and contains high density, high melting point and high tensile strength. The good examples are high-density polythene or polyethylene, polyvinyl chloride and many more [34]. Figure 2.15 shows three different types of polymer structures.
From Figure 2.15 (a) is a linear polymer as defined, (b) is branched-chain polymers structure which is irregularly packed and has a lower melting point and lower tensile strength compared to linear polymer structure, and (c) is cross-linked polymers structure which is rigid, brittle and hard [31, 34]. Linear polymers differ from branched-chain and cross-linked polymers as explained, and it is the strongest among them. Polymers like polyethylene have a linear structure, which makes them materials of interest in the engineering material research and structural materials.

2.4.6.3 Thermoplastics
Thermoplastics are found under sub-category three of classification based on molecular forces of polymers illustrated in Figure 2.13. These are the linear or slightly branched long-chain molecules capable of repeatedly softening at high temperature (heating) and hardening at low temperature (cooling). These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres. Examples of such polymers are polyethylene, polyvinyl, polystyrene and many more [31, 34].

2.4.6.4 Addition polymers
Addition polymers are found under subcategory one of classification based on the mode of polymerization for polymers [31]. These are polymers formed by linking together many monomer molecules possessing double or triple bond [31, 51]. For example, the formation of polyethylene from ethylene and polypropene from propane.

As above-mentioned subcategories form the classification of polymer defines and characterize polyethylene, it is important to take a step further to look at the essence of polyethylene to better understand the formation and the behaviour of polyethylene.
2.4.7 The Essence of Polyethylene

Polyethylene in its simplest molecular form consists of a long backbone of an even number of covalently linked pair of hydrogen atoms attached to each carbon atom; with chain ends terminated by methyl groups [52]. The structure of chemically pure polyethylene is shown in Figure 2.16.

![Chemical structure of pure polyethylene](image)

**Figure 2.16** Chemical structure of pure polyethylene [52]

Chemically pure polyethylene resins consist of alkanes with the formula shown in equation 1.

\[ C_{2n}H_{4n+2} \]

*equation 1*

Where \( n \) is the degree of polymerization, for example, the number of ethylene monomers are polymerized using a catalyst to form the long chain of polymers (polyethylene). Polyethylene is unlike conventional organic materials; it does not consist of identical molecules. However, polyethylene resins comprise chains with a variety of backbone length. According to Peacock [52], naturally, the degree of polymerization (\( n \)) in equation 1 cannot characterize polyethylene properties.

For example, the degree of polymerization is regarded as well in excess if it’s around 100 and can be claimed as high if it’s 250,000 or more. If equated to molecular weights it varies from 1400 to more than 3,500,000. Low molecular weight polyethylene like oligomer which has the degree of polymerization ranging between 8 and 100, are regarded as waxy solids meaning they do not possess plastic properties and when the degree of polymerization is less than 8, alkane groups are liquids or gases at normal temperatures and pressure [52]. Polyethylene molecules can be classified based on the classification of polymers as illustrated in Figure 2.13. There are several principal classes of polyethylene that formed under the classification of polymers.
2.4.7.1 Types of Polyethylene

All different types of polyethylene retain the same basic reiterating unit (-CH₂CH₂-). However, they consist of diverse properties and applications due to their structural variations. Main properties that play a role in distinguishing various types of polyethylene are density, molecular weight (MW), percentage crystallinity, degree of long-chain and short-chain branching, and molecular weight distribution (MWD) [53, 52].

The major factors that affect the mechanical properties and processability of polyethylene are molecular weight distribution and molecular weight. Wide MWD material consist of shorter chain that acts as a lubricant and they are easier to process due to such chains. Short-chain branching (SCB) are introduced into polyethylene through the process of using comonomer such as 1-hexene. During the process, the short-chain branches interfere with the lamellae formation and consequently affect the density and crystallinity of semi-crystalline polymer [54]. According to the American Society for Testing and Materials (ASTM) standards, polyethylenes are classified into four density categories. Table 2.1 shows Four classifications of polyethylene based on density.

Table 2.1 Classification of polyethylene by density [53, 55].

<table>
<thead>
<tr>
<th>Type of PE</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear Low-Density Polyethylene (LLDPE)</td>
<td>0.910 – 0.925</td>
</tr>
<tr>
<td>Medium-Density polyethylene (MDPE)</td>
<td>0.926 - 0.940</td>
</tr>
<tr>
<td>High-Density Polyethylene (HDPE)</td>
<td>0.941 – 0.959</td>
</tr>
<tr>
<td>High-Density Homopolymer (HDH)</td>
<td>0.960 and above</td>
</tr>
</tbody>
</table>

Linear low-density polyethylene (LLDPE) and HDPE consist of spherulitic and lamellar morphology, although elastomer and plasterer have bunch-like crystals implanted in amorphous material. An increase in crystallinity causes an increase in the density of polyethylene, which increases the tensile yield strength and stiffness of the material [56]. High-density polyethylene (HDPE) is the preferred choice in the pipe and other applications, because of its high strength of the material [57].

The variation in material densities shown in Table 2.1 is due to branching in polyethylene chains and other properties. There are two types of branching as mentioned, Long-chain branching (LCB) usually formed from side reactions during polymerization, and short-chain branching (SCB) mostly formed due to introduction of comonomer. Figure 2.17 illustrates the
branching types for HDPE, LLDPE, and LDPE respectively. In Figure 2.17 (a) represents HDPE branching type which is generally linear with low SCB, (b) is LLDPE that have higher SCB compared to HDPE and it contains few or no long chain branches, (c) is LDPE which is known to have both high SCB and LCB contents [58, 31].

![Branch Structures of Polyethylene](image)

**Figure 2.17** Branch structures of Polyethylene [58]

In this research project, we are focusing on HDPE as the matrix of the nanocomposite. It is very important to know its characteristics and mechanical properties as well as the factors that might affect them.

### 2.5 Production of Polyethylene

Polyethylene (PE) is one of the largest synthetic product polymers in terms of annual production and it is globally used due to its chemical properties and versatile physical [55]. The American Society for Testing and Materials (ASTM) has classified PE into four groups as stated in Table 2.1. Polyethylene and other polymers are formed from their basic monomers through the process of polymerization. Polymerization in polymer chemistry is defined as the process whereby monomer molecules react together in a chemical reaction to form polymers chains [59, 60]. There are two mechanisms in which polymers can be produced from polymerization which are either additive or condensation polymerization. In additional polymerization mechanism, the ethylene monomers physically link together in a sequence form whereas in condensation polymerization big molecules attach through a chemical reaction.
2.5.1 Addition Polymerization

Addition polymerization mechanism occurs through a chain reaction that takes place under three steps which are initiation, propagation and termination. It is also known as chain growth which requires the activation of ethylene monomers so that they can connect [61, 62]. For example, if ethylene monomer that contains carbon to carbon double bond as shown in Figure 2.18 is broken through heat, pressure and catalyst to create free attachment of electron on either side of the monomer.

![Reaction of ethylene monomer to polyethylene](image)

**Figure 2.18** Reaction of ethylene monomer to polyethylene [61]

In Figure 2.18 the n term represents the degree of polymerisation, naturally in the thousands. The chemical reaction in Figure 2.18 takes place in three steps as mentioned and these steps are as follows:

2.5.1.1 Initiation Process

Initiation simply means the chemical reaction gets started. It starts through the addition of a free-radical which acts to fragment the carbon to carbon double bond by joining to one side of the ethylene monomer. This gives the ethylene monomer chance to react with other open ethylene monomers on the other side. The main initiator is the free radicals which are formed from hydrogen peroxide by the addition of heat [61]. The chemical reaction process is illustrated in Figure 2.19.
Figure 2.19 Two steps initiation reaction for the formation of the free electron [61]

Figure 2.19 (a) presents the chemical reaction of the production of a free electron from hydrogen peroxide and (b) shows the production of free radical from the chemical reaction of free electron and ethylene.

2.5.1.2 Propagation Process

Propagation just means how the reaction keeps going. The majority of addition polymerization time is spent on the propagation phase as the polymer chain grow. Propagation process takes place to lower the overall energy of the chemical system. In this phase, the newly-formed free radical monomers attacks and attach to the carbon to carbon double bond of another ethylene monomer molecule [62, 63]. The form of addition occurs time and again to make the long polymer chain. Figure 2.20 summarises the process of propagation chemical reaction process.

Figure 2.20 Propagation chemical reaction process [61]
2.5.1.3 Termination process

This is the third and final stage in the addition polymerisation process. It simply means how the reaction stops. Termination process occurs when two chains combine or through the addition of dismissing free radical. This makes sense because two free radicals could bond to make a stable promise that ends the reaction [63, 61] as illustrated in Figure 2.21.

\[
\begin{align*}
\text{H-O} & \quad \text{C-C} \quad \text{H-H} \\
\text{H-H} & \quad \text{C-C} \quad \text{H-H} \\
\text{H-H} & \quad \text{C-C} \quad \text{H-H} \\
\end{align*}
\]

Figure 2.21 The joining of two free radicals [61]

It is important to bear in mind that chemists can control how the polymer is formed from these three steps by varying the reactions, the reaction conditions, and the reaction time [64].

2.6 Polyethylene Properties and Deformations

Polyethylene (PE) is a plastic or polymer material that is known technically as a thermoplastic as stated. Thermoplastic materials are plastic materials that turn into liquid when heated, and when cooled the turn into a solid [65, 66]. PE is usually used in numerous industrial applications ranging from plastic grocery bags to heavy-duty plastic containers. PE is like all plastics, it is a polymer-based material as stated, this means that it is comprised of long chains of matching molecules. PE serves as a material that can be cast, compressed, injected and moulded in varying shapes and thicknesses to produce usable products it is in its liquid form. In its solid state is serving many proposes [55, 67]. According to history, PE was first synthesized by Hans von Pechmann, a German chemist who accidentally discovered it by heating diazomethane [55]. Its purposeful methods of production were introduced by Michael Perrin in 1939 and the low-density polyethylene variant production was introduced for industrial application. The main benefits of PE since it was discovered are its several desirable engineering characteristics. It possesses a semi-crystalline structure as stated which prevents it from dissolving at room temperature. It also extremely chemically resistant which makes it perfect for storage of corrosive materials. The main advantage of PE is that it can be used in the situation when metallic materials are not needed such as when corrosion due to different metals [68]. The significance of PE is then it is extremely resistant to chemical solutes and
caustics. It remains a durable recyclable material for numerous plastic shaped application. Its ability to be recyclable helps to reduce landfill production also lowering the material cost [67, 55].

When considering polyethylene or a polymer for use in any industrial application ii is important to understand its behaviour concerning the change in temperature. Polymers are unlike ceramics or metals that have high melting points. Polymers can experience a significant number of changes in state at the temperature ranging between -20 °C and 200 °C [47]. Properties of a polymer such as strength and stiffness depend on the temperature variation. Under different temperatures, a polymer can exist as plastic, leathery, viscoelastic, viscous or rubber. Temperature is the main factor that affects the state of polymer which in turn affect its modulus and strength by the factor up to $10^3$ [47, 55]. It is essential to look at the effect of temperature on the polymer’s properties.

### 2.6.1 Temperature Effects on Polyethylene

As stated, that change in temperature affects polyethylene properties, Figure 2.22 presents the graph which illustrates the changes in a polyethylene modulus of elasticity concerning temperature variation. Figure 2.22 shows the behaviour of polyethylene as the temperature is regularized against the glass change temperature $T_g$.

![Figure 2.22 Polyethylene elastic modulus against normalised temperature](image)

---

**Figure 2.22** Polyethylene elastic modulus against normalised temperature [47]
When designing a polymer or polyethylene, the temperature is a very important factor. This is because the secondary Van Der Waals forces which bind the chains together in a polyethylene molecule can be stunned with small increases in temperature [55]. If the temperature is increased to above $T_g$, a polyethylene can change from a rigid brittle material to a viscoelastic material that displays both elastic and viscous abilities [47, 55] as presented in Figure 2.23.

![Figure 2.23](image)

**Figure 2.23** temperature effect on the crystalline and amorphous of polyethylene [47]

Polyethylene states such as viscoelasticity state, glassy state, rubbery state and liquid state are significantly to look at as they are affected by temperature change.

2.6.1.1 Viscoelasticity State

Viscoelasticity, as defined, is the property of the material that shows both viscous and elastic characteristics when experiencing distortion [69]. For thermoplastic viscoelasticity refer to the deformation under applied stress at a given time. The stress that is vital to deform the polyethylene or polymer is related to the level of strain and the rate of strain. It is distorted at a fast rate where the is no enough time for polymer chains to unpick then the polymer behaves in a brittle way with low fracture toughness [70, 71]. A large amount of stress and creep can be experienced by polyethylene if stress is applied over a long period.
2.6.1.2 Glassy State

The glassy state usually occurs at a low temperature of which is a non-crystalline and nonequilibrium condensed state of a matter that shows a glass transition. The structure of glassy material appears as solid for a short time scale but spontaneously relax toward the supercooled liquid (SCL) state [72, 73, 71]. Glassy polymers are normally more dimensionally stable, brittle but strong and rigid, they are also resistance to creep. Glassy polymers result with high elastic modulus because of their elastic deformation which is limited to stretching of the bonds in their state.

2.6.1.3 Rubbery State

Most of the amorphous polymers at the temperature above $T_g$ retains the properties of leathery or rubbery depending on their temperature. The rubbery state takes place just above the temperature at which viscous occurs. The rubbery polyethylene has some elasticity and strength [74]. It experiences both elastic and plastic deformation under the applied stress. In rubbery polyethylene molecular chain movements are easy and therefore large elongation is possible and they are easy to extrude and former for complex geometries. At a lower temperature polyethylene is stronger and stiffer and it also takes more leathery form than rubbery [75]. This is due to the stability in the molecular chain.

2.6.1.4 Liquid State

At the temperature greater than 1.4 $T_g$, polyethylene exists in a completely viscous state without any elasticity [76]. In this case, the molecular chains are not stable, they are free to move over one another without the presence of the applied force. This type of polyethylene is suitable for forming and casting processes. At very high temperatures polyethylene may degrade as the covalent bond its network are destroyed [77].

2.6.2 HDPE Mechanical Properties

HDPE is characterized as closest to pure polyethylene because of its chemical structure. It contains mainly of LCB or sometimes unbranched molecules with very few defects to ruin its linearity. Table 2.2 presents the classification and properties of HDPE conferring to the ASTM D 3350 standard.
Table 2.2 Properties of HDPE according to ASTM D 3350 standard [78, 79, 80]

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM Specification</th>
<th>Classification</th>
<th>Classification Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>ASTM D 1505 – Test Method Density for Density of Plastics by the Density-Gradient Technique</td>
<td>3</td>
<td>0.941-0.959 g/cm³</td>
</tr>
<tr>
<td>Melt index (MI)</td>
<td>ASTM D 1238 – Test Method for Flow Rates of Thermoplastics by Extrusion Plastometer</td>
<td>3</td>
<td>0.4 &gt; MI ≥ 0.15</td>
</tr>
<tr>
<td>Flexural modulus (Ef)</td>
<td>ASTM D 790 – Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials</td>
<td>5</td>
<td>758 MPa ≤ Ef &lt;1103 MPa</td>
</tr>
<tr>
<td>Tensile strength (ft)</td>
<td>ASTM D 638 – Test Method for Tensile Properties of Plastics</td>
<td>4</td>
<td>21 MPa ≤ ft &lt; 24 MPa</td>
</tr>
<tr>
<td>Slow crack growth resistance</td>
<td>ASTM D 1693 – Test Method for Environmental Stress-Cracking of Ethylene Plastics</td>
<td>2</td>
<td>test condition B, 24 hr duration 50% failure (max)</td>
</tr>
<tr>
<td>Hydrostatic Strength Classification</td>
<td>ASTM D 2837 – Obtaining Hydrostatic Design Basis for Thermoplastic Pipe Materials</td>
<td>0</td>
<td>(not pressure rated)</td>
</tr>
<tr>
<td>Colour (C)</td>
<td>(not specified by ASTM)</td>
<td>C</td>
<td>2% ≤ C ≤ 5%</td>
</tr>
</tbody>
</table>

Table 2.2 is useful when it comes to the experimental preparation of the tensile testing of HDPE or any other polymers because it provides the guidance and the standards to be met during the preparation of the samples.
2.6.3 Mechanical Behaviour

There are mainly three different types of stress-strain behaviours that can be observed on polymeric materials which are Brittle, plastic or elastic as presented in Figure 2.24.

![Stress-strain graph showing brittle, plastic, and elastic behaviour](image)

**Figure 2.24** Three various stress-strain behaviours for polymeric materials [16]

According to Figure 2.24, the brittle polymeric materials distort elastically before fracturing, the plastic polymeric materials buckle first and then yields into a region of plastic distortion, and the elastic polymeric materials display completely elastic deformation at large strain levels [16].

### 2.6.3.1 Brittle or Ductile Polyethylene

At the temperature below the glass, transition thermoplastics deform mainly by elastic distortion this kind of materials are said to be brittle. The thermoplastics materials with the temperature above \( T_g \) they distort chiefly by plastic deformation and they are said to be ductile. However, thermoplastics go through a brittle to ductile change when heated over their \( T_g \) [81].

The temperature influences the strength of the of a thermoplastic as discussed. Normally, a thermoplastic loses strength because of temperature change. For example, if it is heated the secondary attachment forces between the molecular chains become weaker [82].

### 2.6.3.2 Brittle Polyethylene

Thermoplastics or polyethylene that are well at the temperature below \( T_g \) \((0.75T_g)\), display brittle behaviour [82, 83]. Polyethylene is a brittle state contains molecular chains that are
locked in one place through a strong interlocking system that make plastic to flow difficultly. Brittle polyethylene or thermoplastics behaves like ceramics and glasses, they contain faults that cause them to fracture prematurely during the applied load [16]. Figure 2.25 represents the stress-strain curve of the mechanical behaviour of a brittle polyethylene.

![Stress-strain curve](image)

**Figure 2.25** Mechanical behaviours of a brittle polymer [16]

### 2.6.3.3 Ductile Polyethylene

Thermoplastic with the temperature above their $T_g$ frequently exhibits ductile behaviour. This kind of polymers usually plastically deform and yield strength in a way known as cold drawing under an applied tensile load [82, 84]. Cold drawing is a process which includes viscous flow where the molecular chains slide past one another. At first, the molecular chain may be highly twisted but when the load is applied it forces them to elongate and align in a single direction as shown in Figure 2.26. Once the molecular chains are fully stretched higher stress is needed for fracture [16].
2.6.5 Polymeric Material Testing

Various types of tests can be made on materials to determine their qualities or properties. These types of tests can be either destructive or non-destructive. The destructive tests (DT) are frequently conducted to determine an exact property of the material that is being tested. They usually need a specific shaped test part to be made that will be damaged during the testing. Examples of destructive tests are impact tests, bending tests, fatigue tests and tensile test [16].

Non-destructive testing (NDT) is the process of examining, evaluating or testing materials for discontinuities or characteristics without damaging the serviceability of the part [85]. Since this work is based on the investigation of the mechanical behaviour of polymer-based nanocomposites, so tensile testing method is the type of test that is going to be used.

2.6.5.1 Tensile Testing

Tensile testing is the test method that covers the determination of the tensile properties of unreinforced and reinforced materials [86]. The tensile samples shapes that are used for this method are in the form of standard dumbbell-shaped and can be tested under defined conditions of temperature, humidity, pressure and testing machine speed. The standard test method for tensile properties of plastics is ASTM D638-02a and ISO 527-1 [87]. In the tensile test, the test sample is required to break with a slowly increasing uniaxial tensile load to determine the
resistance of the material to the load. The typical test sample shapes that are usually used are presented in Figure 2.27. They are generally flat but may be circular, their standard test section diameter or thickness is 12.5 mm with the gauge length of 50 mm.

![Figure 2.27 Typical tensile test pieces][86, 37]

### 2.6.5.2 Tensile Test Machine

The tensile test machine is designed to measure the load cell and the extension of the tensile test sample by an extensometer. The tensile test sample is initially mounted into the grips of the tensile machine and the grips pull the test sample apart hydraulically at a constant rate. This kind of test is normally destructive as mentioned because the test piece is permanently deformed and normally fracture in the test. Figure 2.28 shows the schematic of the tensile test machine.

![Figure 2.28 Schematic of the tensile test machine][37]
2.6.5.3 Tensile Test Curve

Tensile test curve is mainly generated by stress versus strain of the tensile sample results. The tensile test curve is divided into five regions which are elastic region, elastic limit, plastic region, necking region and point of fracture as shown in Figure 2.29 [16].

![Figure 2.29 Tensile-strain curve](image)

**Elastic region** presented by OA in Figure 2.29, is the point where the stress-strain curve is at its straight line and the material will return to its original shape when the load is released in that region. The slope of the stress-strain curve at that area provides the stiffness of the material which is known as the young’s modulus or modulus of elasticity [89, 88].

**Elastic limit** presented by B in Figure 2.29, is the point in a stress-strain curve where the elastic region ends, and plastic deformation of the material begins. When the load is released beyond this point, the materials will be permanently distorted [88].

**Plastic region** presented by BE in Figure 2.29, is the area in the stress-strain curve where material deforms plastically, for example, the material does not return to its original shape.
Though, it becomes stronger and harder with more stress required to deform the material [88, 37].

**Necking region** presented by DE in Figure 2.29, is the area in the stress-strain curve after reaching maximum stress. At this region, the tensile test sample will have a localised reduction in the cross-sectional area of the test section where the distortion will be focused [90].

**Point of fracture** presented by E in Figure 2.29, is a point in stress-strain curve tensile test sample fails via fracture it is also known as breaking strength [37].

### 2.7 Polymer Design

There are many ways commonly employed in the industry to change the key properties of polymers. These include varying the degree of crystallinity, copolymerization, addition of plasticizers, fibre-reinforcement, blending and many more [91, 92]. However, this study based on the designing polymer using fibre-reinforcement as stated. This is targeting to alter polymers properties such as modulus, toughness, strength, environmental resistance and wear.

#### 2.7.1 Fibre-Reinforcement

Fibre-reinforcement is one of the most commonly used methods of increasing the elastic modulus and strength of a polymer. This result with the composite material where the main rigidity and strength are resulting from the presence of the fibres. In this case, the polymer acts as a means of transporting load between the fibres and it as well protect them from corrosive damage [93]. As stated in chapter 1, the main material for this investigation is HDPE and the reinforcing fibre is SWCNTs.

#### 2.7.1.1 SWCNTs as the Reinforcing Fibre

Carbon nanotubes (CNTs) are materials that possess amazing properties and offer a strange possibility. It is important to look at and the characteristics of Single-walled carbon nanotubes (SWCNTs). SWCNTs have inspired plenty of activities in both industry and global research community since its discovery in 1991 [94]. It has also stimulated much investment in application development, characterisation and manufacturing methods [95]. The reasons for this are due to its outstanding properties.

#### 2.7.1.2 SWCNTs Structure

According to Jansen et al. [95]. SWCNTs are an allotrope of sp² hybridized carbon which is like fullerenes. The structure can be understood as a cylindrical tube contained six-membered carbon rings, as in graphite. To understand the structure of SWCNT one requires knowledge
on the concept of nanotube Chirality since it dictates many of its properties. Figure 2.30 illustrates the concept of recognized as a Chirality Map.

Figure 2. 30 Graphical display of Chirality Map of SWCNT [95]

An SWCNT can be assumed as a chirality map sheet of graphite one atom thick rolled into a tube as shown in Figure 2.30. The chirality describes both the diameters and the orientation in which the sheet is rolled. Each SWCNT chirality map in Figure 2.30 is distinct from two integers, (n and m). The chirality in the map defines many of the properties of the separate SWCNT. For instance, SWCNT presented on the blue chirality map are metallic in nature and they are normally armchair tubes where $n = m$ or $n - m = 3i$ where (i) is an integer. Those showed in yellow are semiconducting and they display various band gaps depending on the length of the chiral vector [95, 96, 97].

2.7.2.3 Unique Properties of SWCNTs

Mechanical properties: Separate SWCNTs are stronger than steel with the calculated tensile strength of 100 times greater the steel at 1/16th the weight. The highest measured strength value of SWCNTs is approximately half of the estimated theoretical strength, maybe due to the defects in the structure [98].

Thermal properties: Thermal conductivity of SWCNTs at room temperature may be compared to that of in-plane graphite or diamond, which are usually through to show the
maximum measured the thermal conductivity of any known material at a reasonable temperature [95].

**Electrical properties**: Individual SWCNTs have current-carrying potential of $10^9$ amp/cm$^2$, which is higher than those of gold and copper with the semiconducting species exhibiting higher electron mobility than silicon [99]

### 2.8 Polymer Forming Methods

Many different methods are commonly used for the manufacturing of polymers. These methods depend on the large extent on whether the polymer is thermoset or thermoplastic. Thermosets polymers do not fully polymerize during the forming process. However, they are moulded into required shapes and then finished into a solid through a chemical reaction to achieve cross-links in their molecular chains [37]. Commonly forming method for such polymers is transfer moulding, Injection moulding and compression moulding. Thermoplastics like HDPE are usually melted from a solid-state and reshaped before cooling. Common methods of shaping thermoplastics include extrusion, injection moulding, and blow moulding [37]. For this work, the focus is on extrusion, injection moulding and compression moulding as the processing methods of HDPE-based nanocomposites.

#### 2.8.1 Extrusion

The extrusion process is widely used in the production of plastic parts that are normally continuous and simple in shapes such as sheets and pipes. Is the same forming process as injection moulding, because for both processes the melted polymer is moved along by rotating screw (auger) or screws towards the die [100, 101]. However, for extrusion the molten polymer in continually threading through an opening of a die to produce a cautious part with constant cross-sectional area [37, 102]. Figure 2.31 illustrates the schematic of the extruding machine.

![Figure 2.31 Schematic of extruding machine [37]](image-url)
2.8.2 Injection Moulding

Injection moulding is the most important method of processing polymer materials. Polymer pellets are fed into a rotating screw or auger. The auger moves the pallets towards the mould as they are heated by the walls shown in Figure 2.32. The heated polymer pellets are melted into a viscous liquid [37]. At the moulding, the molten polymer is injected into a required shaped mould at a given pressure and cooled until solid. The difference between injection moulding and extrusion is the output shapes. Extrusion produces limited shapes as stated but injection moulding can produce a variety of shapes.

![Figure 2.32 Schematic of injection moulding machine [37]](image)

2.8.3 Compression Moulding

Compression moulding is mainly used for thermosetting polymers. In the compression moulding process preheated balm is positioned into a hot mould cavity as shown in Figure 2.33. Where the upper heated segment of the mould is then forced down onto the balm to create the required product shape. The applied load and the heat on the segment force the dissolved polymer to fill the cavity [103].

![Figure 2.33 Schematic of compression moulding machine [103]](image)
2.9 Summary

Chapter 2 has presented the most important issues for achieving the production and the testing of the polymer-based nanocomposites. The chapter also focused on the temperature effect on the mechanical properties of the polymer materials during the processing. The method of designing a polymer composite was established as well as the relevant processing that can be used. The standard tensile test standers for plastics were also covered and demonstrated the results that should be expected and the classifications of the mechanical properties. Chapter 2 helped to understand the behaviour of polymer, relevant polymer manufacturing methods and the necessary tensile testing methods. Chapter 3 which is the research methodology was planned based on chapter 2.
CHAPTER 3

3.0 RESEARCH METHODOLOGY

3.1 Overview

Chapters 1 and 2 covered the introduction and the theoretical background of the study which identified the investigations conducted in the past based on the polymer-based nanocomposites as well as the improvements that can be made. Chapter 3 will focus on the materials, methods and three main approaches used to obtain the results of this project which includes numerical, experimental, and analytical approaches.

3.2 Numerical approach

Numerical methods are mathematical techniques incorporated with computer software’s used to answer mathematical problems that are hard to solve analytically [103]. The numerical solutions are approximate, and they can be very accurate. This section presents the application of a numerical approach to predict the elastic modulus of HDPE/SWCNTs nanocomposite with finite element method (FEM). To achieve this, the representative volume element (RVE) will be generated to serve as a model for HDPE/SWCNTs nanocomposites. The RVE plays a vital role in the physics and the mechanics of random heterogeneous materials with an understanding to predict their effective properties [104].

Since HDPE/SWCNTs nanocomposites are heterogeneous composites materials with randomly scattered nanoparticles through the matrix, then RVE will be a useful tool to help predict its elastic modulus. The RVE of HDPE/SWCNTs nanocomposite will be used as a representing model on ANSYS 19.2 to help to solve stress distribution and the displacement with FEM.

3.2.1 Finite Element Modelling Approach

The finite element method (FEM) is an arithmetical technique for solving engineering and mathematical physics problems such as structural analysis, fluid flow, heat transfer electromagnetics and others [105, 106]. For this investigation, structural analysis was applied when solving the elastic properties of the nanocomposites. The types of elements used in the modelling for the HDPE matrix and SWCNTs fibre were 3D tension elements of C3D83R and for the intermediate phase which is the bond between matrix and fibre was an adhesive element of COH3D8 as illustrated in Figure 3.1.
To achieve the properties affecting HDPE nanocomposites reinforced with SWCNTs, Cylindrical representative volume element (RVE) was created and used in the simulation of an SWCNT in an HDPE matrix. The intermediate phase is the most important region in studying the probability of tension transfer and other properties of nanocomposites. In most of the investigations, the bond between SWCNTs fibre and matrix is presumed to be complete in analyses based on continuums media. But to make the simulation more accurate, spring elements are used to model the intermediate phase [11]. In this study, an intermediate phase with small thickness has been modelled to determine in the simulation. To determine its properties, the results from the atomic modelling were used. The separate region in the form of a tube was created to assign the properties and the area of the intermediate phase. This physical separation section between the SWCNT and matrix did not mean the existence of a phase or third material. It was the only type of an adjustment for modelling force transfer properties form the HDPE matrix to SWCNTs fibre.

The intermediate phase properties used in this work were determined from the atomic simulation results of Namilae and Chandra. [107]. To determine this, a displacement of 0.05 Å was applied on the terminal atoms of the CNTs with a primary length of 15 Å. The system was set for the time interval of 0.2 Fs for each displacement. These simulations were made until some hydrocarbon chains from CNTs terminals broke, and these generally lasted for 500000 to 800000-time intervals. Figure 3.2 demonstrates the fitted elongating separations of Namilae and Chandra. [107], where the slope of the primary section gives hardness to length units of the intermediate phase. The slope of the graphs in Figure 3.2 was used to determine the elastic modulus of the intermediate phase.
Figure 3.2 Traction movement plot attained from atomic simulation [107]

\[ M = \frac{(0.1-0)}{(3-0)} = 0.03333 \ \text{GPa} \ \text{Å} \]  

\[ L_{CNT} = 122 \ \text{Å} \]

Where \( M \) is the gradient of the graph and \( L_{CNT} \) is the length of CNT element which was assumed to be 122 Å because of molecular dynamics results. The elastic modulus of the intermediate phase was calculated by multiplying the slope of the graph by the length of CNT which gives:

\[ E_i = M \times L_{CNT} = 0.03333 \ \frac{\text{GPa}}{\text{Å}} \times 122 \ \text{Å} = 4.06 \ \text{GPa} \]

Where \( E_i \) is the intermediate phase elastic modulus, which was extracted for the primary section of the graph in Figure 3.2 from zero until the displacement of 5 Å. This region selection
seemed to be reasonable for the maximum displacement of 0.5. The thickness and Poisson’s ratio of the intermediate phase were 0.4 nm and 0.3 respectively. These properties were used for modelling of HDPE matrix reinforced with SWCNTs using RVE.

3.2.2 Representative Volume Element Generation
The RVE was created using the test section of the HDPE/SWCNTs nanocomposite tensile test sample which is represented by randomly dispersed SWCNTs nanoparticles as demonstrated in Figure 3.3. The SWCNTs nanoparticles were assumed to be homogeneously dispersed through the HDPE matrix and that there is no presence of SWCNTs nanoparticle combination in the nanocomposite [108]. The RVE was assumed to have contained three phases if magnified, which includes HDPE matrix, SWCNT fibre, and intermediate phase located between fibre and matrix. Based on the existing literature and researches, it is famous that the SWCNTs nanoparticles are modelled as nanofibers surrounded by the intermediate phase regions [109, 110, 111, 112]. To acquire the elastic modulus of the HDPE/SWCNTs nanocomposite, a uniform pressure of -100 MPa was presumed to be acting on the edge of the tensile test sample, while the opposite edge was fixed along the z-direction as illustrated in Figure 3.4.

![Figure 3.3 Tensile test sample with the magnified RVE](image)

Figure 3.3 Tensile test sample with the magnified RVE

Figure 3.4 shows the two views of the magnified cylindrical geometry of the RVE obtained from the reinforced tensile test section model in Figure 3.3. Illustrated in Figure 3.4 is the load and boundary conditions on the RVE of HDPE/SWCNTs nanocomposite. It has been assumed
that the microstructure of RVE was obtained from the centre of the test sample where x and z are fixed so that it can respond to the applied load the same way as the reinforced tensile test sample due to the symmetry along z-x region [113].

Figure 3.4 Magnified RVE with the boundary conditions

The three-dimensional (3D) model for RVE of HDPE/SWCNTs was generated using a quarter of magnified RVE presented in Figure 3.4. Figure 3.5 exemplifies the 3D RVE of the short SWCNT fibre in an HDPE matrix and intermediate phase. The presented RVE of HDPE/SWCNT nanocomposite was made from three layers of different colours to demonstrate the bonding of SWCNT fibre and HDPE matrix with an intermediate phase. Figure 3.6 shows the assembling order of the three layers that make up the RVE of HDPE/SWCNT nanocomposite. It displays that SWCNT was model as a tube-like structure enclosed with the layer of the intermediate phase.

Figure 3.5 3D views of RVE of HDPE/SWCNT nanocomposite
3.2.3 Modelling the RVE of HDPE/SWCNT Nanocomposite

HDPE and SWCNTs are materials with different properties that will be combined to yield a composite material of new properties. The investigation of the effect of reinforcing HDPE matrix with SWCNTs at different weight fractions wt% was conducted using the material properties listed in Table 3.1. The last two rows of Table 3.1 contain the densities for both HDPE and SWCNTs which are different. This is because of the quality and the manufacture of the product of HDPE and SWCNTs, for example, HDPE has a density of 0.940 g/cm$^3$ to 0.959 g/cm$^3$ [114] which are available in the marketplaces. SWCNTs also exist with a density of 1.65 g/cm$^3$ to 1.90 g/cm$^3$. Since HDPE and SWCNT exist in various ranges of densities, then two ranges of their densities were used for the investigation.

Table 3.1 The properties HDPE matrix, SWCNTs, and the intermediate phase as well as their dimensions in the RVE [11]

<table>
<thead>
<tr>
<th>Properties</th>
<th>Intermediate phase</th>
<th>(HDPE) Matrix</th>
<th>(SWCNT) Fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (nm)</td>
<td>150</td>
<td>Change with x</td>
<td>150</td>
</tr>
<tr>
<td>Internal radius (nm)</td>
<td>5</td>
<td>4.6</td>
<td>5</td>
</tr>
<tr>
<td>Outer radius (nm)</td>
<td>5.4</td>
<td>2.020</td>
<td>1000</td>
</tr>
<tr>
<td>Elastic modulus (GPa)</td>
<td>4.06</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.3</td>
<td>0.940</td>
<td>1.68</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>--</td>
<td>0.950</td>
<td>1.90</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>--</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.7 represents the schematic of HDPE/SWCNT nanocomposite with the dimensioned listed in Table 3.1. The x parameter in Figure 3.7 characterizes the volume of HDPE matrix which changes as the weight fraction of the SWCNTs change within the nanocomposite. In achieving the different weight and volume fractions of HDPE/SWCNTs nanocomposite RVE model, calculations were made based on Figure 3.7 dimensions. The calculating equations were used such that change in x parameter effect the weight fractions of the RVE. This was used to investigate the effect of the addition of SWCNTs nanoparticles into an HDPE matrix. It was assumed in the study that the material properties of RVE in Table 3.1 resembles the real properties of the HDPE/SWCNT nanocomposite [115, 116, 117].

\[
V_{SWCNT} = \pi((5)^2 - (4.6)^2)(150) = 576\pi \\
\]

\[
V_{RVE} = \pi \left(\frac{(2x+10)^2}{2}\right)(2x + 150) \\
\]

Where \(V_{SWCNT}\) is the volume of SWCNT inside HDPE/SWCNT nanocomposite RVE, and \(V_{RVE}\) is the volume of RVE of the nanocomposites. The relating equation between the volume of SWCNT and the volume of RVE is their volume fraction \(V_f\) presented in equation 7.
\[ V_f = \frac{V_{SWCNT}}{V_{RVE}} = \frac{wt\%}{wt\% + \left(\frac{\rho_f}{\rho_m}\right)(1 - wt\%)} \]

Where \( wt\% \) is the given weight fraction of SWCNT fibre into an HDPE matrix, \( \rho_f \) is the density of SWCNT fibre, and \( \rho_m \) is the density of an HDPE matrix.

Equation 6 provides the density-fraction of WSCNT fibre and HDPE matrix as \( \left(\frac{\rho_f}{\rho_m}\right) \). Since in this investigation the two densities for SWCNT fibre and HDPE matrix were used, then the two density-fractions were calculated for each \( x \) parameter as:

\[
\left(\frac{\rho_f}{\rho_m}\right) = \left(\frac{1.68}{0.940}\right) = 1.8 \text{ for the first RVE of HDPE/SWCNTs nanocomposite properties and the second RVE of HDPE/SWCNTs nanocomposite properties was found to be } \left(\frac{\rho_f}{\rho_m}\right) = \left(\frac{1.90}{0.950}\right) = 2. \text{ These density fractions were used in equation 6 to calculate the volume fractions of each HDPE/SWCNTs nanocomposite at a given weight fraction of SWCNT nanoparticles.}

Equations 5, 6 and 7 were then associated to come up with the equation 8 that was used to compute the \( x \) parameter in Figure 3.7 as follows:

\[ V_{RVE} = \frac{V_{SWCNT}}{V_f} \times 100 = \pi \left(\frac{\left(\frac{2x + 10}{2}\right)^2}{2x + 150}\right) = \frac{576\pi}{V_f} \times 100 \]

The simplified form of equation 8 is presented by the third-order equation as:

\[ 2x^3 + 170x^2 + 1550x + 3750 = \frac{576}{V_f} \times 100 \]

The overall dimensions of the RVE on HDPE/SWCNT nanocomposite for a given weight fraction of SWCNT nanoparticle was obtained by calculating the value of \( x \) parameter using equation 9. The length and the diameter were calculated as:

\[ D_{RVE} = 2x + 10, \quad L_{RVE} = 2x + 150 \]

Where \( D_{RVE} \) and \( L_{RVE} \) are the diameter and the length of RVE.
For the FEM results to conform with the experimental results of [14, 118] and the numerical results of [11]. The calculated values of the x parameter for each given weight fraction was used to obtain the dimensions of the RVE of HDPE/SWCNT nanocomposite for each density-fraction as presented in Table 3.2 and Table 3.3.

Table 3.2 Presents the volume fractions, x parameters and the dimensions of the RVE of HDPE/SWCNT nanocomposite at different weight fractions for the density fraction of 1.8.

<table>
<thead>
<tr>
<th>SWCNTs weight fraction (wt%)</th>
<th>Volume Fraction</th>
<th>Parameter x (nm)</th>
<th>The diameter of RVE (nm)</th>
<th>Length of RVE (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.112</td>
<td>41.9</td>
<td>93.8</td>
<td>233.8</td>
</tr>
<tr>
<td>0.4</td>
<td>0.224</td>
<td>29.99</td>
<td>69.98</td>
<td>209.98</td>
</tr>
<tr>
<td>0.6</td>
<td>0.337</td>
<td>24.33</td>
<td>58.66</td>
<td>198.66</td>
</tr>
<tr>
<td>0.8</td>
<td>0.449</td>
<td>20.87</td>
<td>51.74</td>
<td>191.74</td>
</tr>
<tr>
<td>1</td>
<td>0.562</td>
<td>18.42</td>
<td>46.84</td>
<td>186.84</td>
</tr>
</tbody>
</table>

Table 3.3 Presents the volume fractions, x parameters and the dimensions of the RVE of HDPE/SWCNT nanocomposite at different weight fractions for the density fraction of 2.

<table>
<thead>
<tr>
<th>SWCNTs weight fraction (wt%)</th>
<th>Volume Fraction</th>
<th>Parameter x (nm)</th>
<th>The diameter of RVE (nm)</th>
<th>Length of RVE (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.1</td>
<td>44.16</td>
<td>98.32</td>
<td>238.32</td>
</tr>
<tr>
<td>0.4</td>
<td>0.201</td>
<td>31.65</td>
<td>73.3</td>
<td>213.3</td>
</tr>
<tr>
<td>0.6</td>
<td>0.301</td>
<td>25.81</td>
<td>61.62</td>
<td>201.62</td>
</tr>
<tr>
<td>0.8</td>
<td>0.402</td>
<td>22.16</td>
<td>54.32</td>
<td>194.32</td>
</tr>
<tr>
<td>1</td>
<td>0.503</td>
<td>19.6</td>
<td>49.2</td>
<td>189.2</td>
</tr>
</tbody>
</table>

3.2.4 ANSYS Simulation of the RVE

The dimensions and parameters presented in Table 3.2 and Table 3.3 together with the material properties in Table 3.1, were used to produce the ANSYS model for FEM simulation using ANSYS Mechanical APDL 19.2 file. The setting of preferences on ANSYS mechanical was adjusted to structural and the Element type selected was solid 10 nodes 187. The material properties were assumed to be elastic, linear, and isotropic. The model was created to
characterize a quarter of a cylinder as demonstrated in Figures 3.5 and 3.6. Shown in Figure 3.8 are the lead applications on the RVE of HDPE/SWCNTs nanocomposite.

Figure 3.8 Load applications on the RVE of HDPE/SWCNT nanocomposite

Figure 3.9 illustrates the meshed RVE of HDPE/SWCNT nanocomposite with the two longitudinal sides along z-direction assumed to be symmetric. The load of -100 MPa was applied to the red striped area and the opposite area was fixed as shown by the purple arrows.

Figure 3.9 Meshed RVE of HDPE/SWCNT nanocomposite geometry

The mesh size of the model was improved by reducing mesh size starting from 10 nm to 1 nm as illustrated in Table.3.4. This was done to achieve a better global independence mesh for the model that can be used for the calculation of the results. The elastic modulus of the meshed results in Table 3.4 was obtained using equation 11:
\[ E_c = \frac{PL}{DMX} \]

Where \( E_c \) is the elastic modulus of the HDPE/SWCNT nanocomposite, \( P \) is the applied load, \( L \) is the length of the RVE of HDPE/SWCNT nanocomposite, and \( DMX \) is the FEM maximum displacement.

The pressure of -100 MPa was applied to the HDPE/SWCNT nanocomposite RVE as demonstrated in Figure 3.8. The length used was 186.84 nm of which is that of the weight fraction of 1 w\% with the \( x \) parameter of 18.42 nm shown in Table 3.2.

**Table 3.4** Data for global mesh independence

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>4.6369</td>
<td>4.03</td>
</tr>
<tr>
<td>9</td>
<td>4.6708</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>4.68801</td>
<td>3.99</td>
</tr>
<tr>
<td>7</td>
<td>4.71619</td>
<td>3.94</td>
</tr>
<tr>
<td>6</td>
<td>4.75358</td>
<td>3.93</td>
</tr>
<tr>
<td>5</td>
<td>4.75265</td>
<td>3.93</td>
</tr>
<tr>
<td>4</td>
<td>4.75923</td>
<td>3.93</td>
</tr>
<tr>
<td>3</td>
<td>4.75657</td>
<td>3.93</td>
</tr>
<tr>
<td>2</td>
<td>4.75445</td>
<td>3.93</td>
</tr>
<tr>
<td>1</td>
<td>4.75169</td>
<td>3.93</td>
</tr>
</tbody>
</table>
Figure 3. 10 Mesh independence for RVE of HDPE/SWCNT nanocomposite model

Figure 3.10 was generated from Table 3.4; it displays the relationship between the mesh sizes and the elastic modulus of the meshed HDPE/SWCNTs nanocomposite RVE. It can be seen in Figure 3.10 that elastic modulus stabilizes from the mesh size of 6 nm to 1 nm due to the maximum displacement. The mesh size of 3 nm was used as the global mesh for all the weight fractions for RVE models because it was found to be within the range of stable elastic modulus.

Figure 3.11 presents the fine-meshed RVE of HDPE/SWCNT nanocomposites with the global mesh of 3 nm.

Figure 3. 11 Improved mesh of HDPE/SWCNTs nanocomposite RVE
The results obtained using a mesh size of 3 nm for all given weight fractions of SWCNTs nanoparticles were recorded and will be discussed under chapter 4 of results and discussions.

3.3 Processing of the samples

This section describes the materials, devices, tools and methods used in this research project. The methods and devices used to produce HDPE/SWCNTs nanocomposites samples, the measuring instruments and testing, together with the designing of experiments are specified in this unit.

3.3.1 Materials

The material used to produce HDPE/SWCNTs nanocomposites are:

- High-density polyethylene (HDPE),
- Single-walled carbon nanotubes (SWCNTs),
- Maleic anhydride.

HDPE material was produced by Goodfellow Cambridge Limited at Huntingdon PE29 6WR England and provided by Sigma-Aldrich form 1 Friesland Drive, Longmeadow Business Estate South Modderfontein, Johannesburg 1645 South Africa. The physical and the chemical properties of the HDPE used as a matrix during the manufacture of HDPE/SWCNTs nanocomposites are illustrated in Table 3.5.

Table 3.5  The physical and the chemical properties of HDPE

<table>
<thead>
<tr>
<th>Physical state</th>
<th>Clear to white Pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.950 g/cm³ or 950 Kg/m³</td>
</tr>
<tr>
<td>Melting point temperature</td>
<td>125 – 135°C</td>
</tr>
<tr>
<td>Weight impact</td>
<td>250 gm</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>1000%</td>
</tr>
<tr>
<td>Yield strength</td>
<td>25 MPa</td>
</tr>
<tr>
<td>Flesh Ignition temperature</td>
<td>335°C</td>
</tr>
<tr>
<td>Auto Ignition temperature</td>
<td>350°C</td>
</tr>
<tr>
<td>Odour</td>
<td>Slight waxy odour</td>
</tr>
</tbody>
</table>
SWCNTs nanoparticles used was produced by Sigma-Aldrich at 3050 Spruce Street, St. Louis, MO 63103 USA and has provided by Sigma-Aldrich 1 Friesland Drive, Longmeadow Business Estate South Modderfontein, Johannesburg 1645 South Africa. Illustrated in Table 3.6 are the physical and the chemical properties of SWCNTs nanoparticles used as the reinforcements during the production of HDPE/SWCNTs nanocomposites.

Table 3.6 The physical and the chemical properties of SWCNTs

<table>
<thead>
<tr>
<th>Physical state</th>
<th>Black fine powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.7 - 1.9 g/cm³ at 25°C (lit.)</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.1 g/cm³</td>
</tr>
<tr>
<td>Purity/assay</td>
<td>90% carbon basis and 99% as carbon nanotubes</td>
</tr>
<tr>
<td>Average diameter</td>
<td>0.83 nm</td>
</tr>
<tr>
<td>Median length</td>
<td>1 µm</td>
</tr>
<tr>
<td>Chirality</td>
<td>7.6</td>
</tr>
<tr>
<td>Impurities</td>
<td>5% moisture content</td>
</tr>
<tr>
<td>Surface area</td>
<td>700 m²/g</td>
</tr>
<tr>
<td>Melting point temperature</td>
<td>3652 – 3697 °C (lit.)</td>
</tr>
<tr>
<td>Elastic modulus</td>
<td>200 GPa</td>
</tr>
</tbody>
</table>
Maleic anhydride is the acid anhydride of maleic acid which was provided by Iran Polymer and petrochemical institute. Lister in Table 3.7 is the physical and chemical properties of the maleic anhydride that was used mix HDPE and SWCNTs before processing of HDPE/SWCNTs nanocomposites.

Table 3.7 Presents the physical and the chemical properties of Maleic anhydride

<table>
<thead>
<tr>
<th>Physical state</th>
<th>Clear to white Pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass</td>
<td>98.06 g/mol</td>
</tr>
<tr>
<td>Melting point</td>
<td>52.6 °C</td>
</tr>
<tr>
<td>Density</td>
<td>1.48 g/cm³</td>
</tr>
<tr>
<td>Boiling point</td>
<td>202 °C</td>
</tr>
<tr>
<td>Chem Spider ID</td>
<td>7635</td>
</tr>
</tbody>
</table>
3.3.2 The Preparation Methods

During the preparation of the HDPE/SWCNTs nanocomposites, several steps including weighting, mixing and chemical treatments were followed. The preparation and the processing of the HDPE/SWCNTs nanocomposites were done at the Iran Polymer and Petrochemical Institute (IPPI) and some at in South Africa at the Council for Scientific and Industrial Research (CSIR).

3.3.2.1 Mixing of HDPE with SWCNTs

The following apparatuses and procedures were used to measure and mix HDPE unprocessed pellets with SWCNTs nanoparticle are listed as follows:

3.3.2.2 The apparatuses used for weighting and mixing are:

- stamp weighing scale,
- CAS weighing scale,
- Beaker,
- Steering rod,

3.3.2.3 Preparation and the mixing procedure were as follows:

Two major processes were followed to produce the requires samples of pure HDPE and HDPE/SWCNTs nanocomposites. The goal of this section was to produce HDPE samples reinforced with SWCNTs at the weight fractions of 0 wt%, 0.2 wt%, 0.4 wt%, 0.6 wt%, 0.8 wt%, and 1 wt%. To achieve these subsequent steps were taken:

➢ Preparation of Pure HDPE samples
Pure HDPE unprocessed pellets were measured to a mass of 400 g using Stamp weighting scale as showed in Figure 3.15. The 400 g weighted was declared to be used to produce 100 % HDPE sample with zero weight fractions (0 wt%) of SWCNTs.

Figure 3.15 weightings of HDPE on the stamp weighing scale

➢ Preparation of HDPE/SWCNTs nanocomposites

The preparation of HDPE/SWCNTs nanocomposites was different from that of pure HDPE. For HDPE/SWCNTs nanocomposites, SWCNTs were added into HDPE at different weight fractions as well as maleic anhydride to create a clear bond between HDPE matrix and SWCNTs reinforcements [119, 120, 121]. To produce HDPE based nanocomposites by adding 0.2 wt% weight fraction of SWCNTs nanoparticles into HDPE unprocessed pellets measurement and the calculation was essential. To calculate how many grams of HDPE unprocessed pellets, SWCNTs nanoparticles, and maleic anhydride will be required to produce HDPE/SWCNTs nanocomposites of specific weight fraction of SWCNTs, the following steps were followed:

- Step 1, the mass of maleic anhydride was measured to be 5 g using CAS weighing scale,
- Step 2, To achieve HDPE/SWCNTs nanocomposite of the weight fraction of 0.2 wt% SWCNTs, 400 g of HDPE was multiplied with the given weight fraction of SWCNTs to calculate the mass of SWCNTs inside the nanocomposite. For example, (400 g x 0.2% = 0.8 g) which gives 0.8 g of SWCNTs at the weight fraction of 0.2wt%,
- Step 3, To calculate the mass of HDPE inside the HDPE/WSCNTs nanocomposites, masses of maleic anhydride and SWCNTs were subtracted from 400 g were mass of
maleic anhydride was kept at 5 g. For example, (400 g – 5 g – 0.8 g = 394.2 g) which gives 394.2 g of HDPE at the weight fraction of 0.2 wt%.

- Step 4, HDPE reinforced with SWCNTs nanoparticles at the weight fraction of 0.2 wt% was then performed by measuring 394.2 g of HDPE, 5 g of maleic anhydride and 0.8 g of SWCNTs nanoparticles as demonstrated in Figure 3.16. They were then added into one beaker and mixed with the steering rod.

Figure 3.16 demonstrate the equipment used during the preparation of HDPE/SWCNTs nanocomposites.

![Figure 3.16](image)

**Figure 3. 16** The weighted HDPE pellets, maleic anhydride, and SWCNTs nanoparticles

The preparation steps for production of HDPE/SWCNTs nanocomposites was also followed throughout to prepare for 0.4 wt%, 0.6 wt%, 0.8 wt% and 1 wt% weight fractions of SWCNTs nanoparticles in the HDPE matrix. Table 3.8 Illustrate the measurements carried out for each weight fraction of SWCNTs in the HDPE matrix.
Table 3.8 Mass compositions of each material for a specific weight fraction of SMCNTs nanoparticles inside HDPE/SWCNTs nanocomposite

<table>
<thead>
<tr>
<th>SWCNTs weight fractions (wt%)</th>
<th>HDPE mass (g)</th>
<th>Maleic anhydride mass (g)</th>
<th>SWCNTs mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>400</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.2</td>
<td>394.2</td>
<td>5</td>
<td>0.8</td>
</tr>
<tr>
<td>0.4</td>
<td>393.4</td>
<td>5</td>
<td>1.6</td>
</tr>
<tr>
<td>0.6</td>
<td>392.6</td>
<td>5</td>
<td>2.4</td>
</tr>
<tr>
<td>0.8</td>
<td>391.8</td>
<td>5</td>
<td>3.2</td>
</tr>
<tr>
<td>1</td>
<td>391.0</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

After the mixing process, products of HDPE/SWCNTs appeared as coated pellets but differ in colour because of the amount of the weight fractions of SWCNTs as per Table 3.8. The HDPE/SWCNTs coated pellets were then processed further to make required experimental test samples.

3.3.3 Equipment for Samples Making
The equipment and the processing of the HDPE/SWCNTs nanocomposites samples for the tensile test are discussed in detail under this section. The flow diagram in Figure 3.17 shows all the steps to be followed during the samples production.

Figure 3.17 Flow diagram for samples preparation
According to Figure 3.17, the coated pellets of HDPE/SWCNTs nanocomposites were first fed to a twin-screw extruder to mix and fuse them, and extruded filaments turned into granules by a milling machine. The acronyms and the weight ratio of the presence of various materials are indicated in the formulations given in Table 3.8. The tensile test samples for both injection and compression moulding were produced conform to the American Society for Testing and Materials (ASTM) Designation: ASTM D638, which is the Standard Test Method for tensile properties of plastics [86]. The process of the samples was conducted using the following equipment:

3.3.3.1 Twin-Screw Extruder

Twin-screw extruder (TSE) is a machine that plays an essential role in the materials applications technique such as melting, mixing, and devolatilization. It is normally used to mix or melt materials that are more viscous after melting such as polymers [122]. The extruder used in this research is a German-made model zsk25 with double copper shear extruder as presented in Figure 3.18. It has the screw diameter of 25 mm with the ratio of L/D = 40 and the 6 thermal areas.

![Twin screw extruder used](image)

This twin-screw extruder was used because of its distinct rotational direction and intermeshing structure and it was set for the regulating temperatures of 170 °C to 190 °C, the pressure of 120 MPa and the screw rotating speed of 250 RPM, creating a homogeneous and uniform mixture of HDPE/SWCNT nanocomposites as a solid strip of 1.75 mm diameter. Table 3.9 presents the effective parameters of the extruder machine that are important in the production of nanocomposites.
Table 3.9 Extruder regulatory parameters

<table>
<thead>
<tr>
<th>Regulatory parameters</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heaters Temperature</td>
<td>170 - 190</td>
<td>°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>120</td>
<td>MPa</td>
</tr>
<tr>
<td>Screw speed</td>
<td>250</td>
<td>rpm</td>
</tr>
</tbody>
</table>

3.3.3.2 Grinding Machine
The grinding machine shown in Figure 3.19 was used to cut the HDPE/SWCNTs nanocomposites strips produced from the twin-screw extruder into smaller pellets so that they fed to injection and compression moulding.

3.3.3.3 Humidifier/Oven
After the extruded nanoparticles were cut into small pellets, they were then dried using oven since they were exposed to water. The machine used to dry the HDPE/SWCNTs nanocomposites pellets is shown in Figure 3.20. The reason why nanocomposites pallets were dried was to prevent the creation of bobbles during the compression and injection moulding. The setting temperature of the drying machine is between 0 °C to 250 °C with a capacity of 750 litres.
The pellets were dehumidified for a period of 9 hours at a temperature of 60°C before they can be ready for the injection and compression moulding.

### 3.3.3.4 Plastic Injection Machine

Plastic injection or injection moulding machine is a manufacturing process that is wildly used and accepted to produce plastic parts. It is regarded as 3D “negative” of the desired part because it involves taking molten plastic material and inject it into a mould that contains the negative shape of the part then result with the needed one [123, 124]. The model of the plastic injection machine used to prepare the tensile, bending, and Charpy samples of HDPE/SWCNTs nanocomposites for this work is EM80. Presented in Figure 3.21 is the type of the plastic injection machine used which was set to operate under the specification stated in Table 3.10 during the processing of the samples.

![Figure 3.20 types of the humidifier/oven used](image1)

![Figure 3.21 Injection moulding machine and its control screen display](image2)
Table 3.10 The operating specifications of the injection moulding machine

<table>
<thead>
<tr>
<th>Regulatory parameters</th>
<th>Operating conditions</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mould temperature</td>
<td>60</td>
<td>°C</td>
</tr>
<tr>
<td>Regulating temperatures for cylinder heater</td>
<td>175,190,200</td>
<td>°C</td>
</tr>
<tr>
<td>Injection speed</td>
<td>53</td>
<td>cm³/s</td>
</tr>
<tr>
<td>Injection pressure</td>
<td>9</td>
<td>MPa</td>
</tr>
<tr>
<td>Storage pressure</td>
<td>7</td>
<td>MPa</td>
</tr>
<tr>
<td>Pressure keeping time</td>
<td>8</td>
<td>seconds</td>
</tr>
<tr>
<td>The cooling time of the mould</td>
<td>4</td>
<td>seconds</td>
</tr>
</tbody>
</table>

The tests samples obtained from the injection moulding machine after the processing are presented in Figure 3.22, which shows three different shaped samples for three tests.

Figure 3.22 Three different test samples from the injection moulding machine

3.3.3.5 Compression Moulding

Compression moulding is one of the oldest material processing methods for plastics, is regarded as one of the first industrial techniques of moulding [125]. Accordant to Kwon. [126], Compression moulding method is known by producing large and thin polymeric parts robustly. Figure 3.23 demonstrates the type of compression moulding machine used to prepare the samples. Compression moulding machine is different from injection moulding machine, a
A compression moulding machine is designed to produce specific types of test samples at a time. For this investigation only, tensile test samples were made from compression moulding. The operating parameters of the compression moulding machine were as listed in Table 3.11.

![Tensile samples shaping sheet](image1)

![Compression machine used](image2)

![Resulting tensile test samples](image3)

**Figure 3.23** Compression moulding machine and its resulting tensile test samples

**Table 3.11** The operating specifications of the compression moulding machine

<table>
<thead>
<tr>
<th>Regulatory parameters</th>
<th>Operating conditions</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compression load</td>
<td>2000</td>
<td>N</td>
</tr>
<tr>
<td>Upper heated plate temperature</td>
<td>197</td>
<td>°C</td>
</tr>
<tr>
<td>Lower heated plate temperature</td>
<td>194</td>
<td>°C</td>
</tr>
</tbody>
</table>
3.4 Experimental approach

The experimental approach is usually a quantitative tactic designed to determine the effects of presumed causes. The main feature of this approach is that one object/parameter is deliberately varied to understand what happens or how it affects other controlled object/parameters or to discover the effect of supposed causes [127, 128]. An experiment is a study or process that usually results in the collection of data and data analysis. Normally the results of the experiment are not known in advance, so it is very important to reduce or minimize all possible errors that could be encountered during the experiment. Usually, to minimize possible errors during the experiment, researchers can manipulate the condition or the experimental environment and can also control the factors that are irrelevant to the research objectives. For example, tensile testing of two different types of polyethylene-based nanocomposites, while also controlling the type of sample sizes and shapes, material properties, applied load, environmental temperature, and other conditions.

It is always important to plan or come up with the right methods of experimental design to achieve reasonable experimental results. To achieve these, the following entails are required:

- Outlining the required experimental design method to be followed,
- Proper planning of the experiments,
- Determine the most influential variables on the response,
- Highlighting all the basic parts of the apparatus required to experiment,
- Outlining all the methods followed during the conduction of the experiment.

To achieve the objectives of this study, the Taguchi method [129, 130, 131] which is one of the most popular approaches of statistical analysis were used to evaluate the stets. The weight fractions of SWCNTs in six levels and the processing methods in two levels were considered in designing the experiment for tensile testing.

3.5 Experimental design

3.5.1 Scope

The process of reinforcing HDPE with SWCNTs nanoparticles is investigated by evaluating the effect of SWCNTs weight fractions and processing technologies used on the elastic properties of the nanocomposites. The independent variables for this study are weight fractions of SWCNTs and the processing methods. The experimental design will be based on the
processing techniques used to produce HDPE/SWCNTs nanocomposites and SWCNT at different weight fractions.

3.5.2 Designing an Experiment

The effect of reinforcing polymer and other materials with nanoparticles such as carbon nanotubes CNTs have been widely investigated. Different analysis and experimental tests have been conducted to evaluate nanocomposite behaviours among which tensile test has attracted great attention. The main goal of this experiment is to investigate tensile properties of the unreinforced and reinforced polymer (HDPE reinforced with SWCNTs at various weight fractions). The tensile test specimens are prepared in the form of standers dumbbell-Shapes and they will be tested under the defined condition of humidity, temperature, and testing machine speed. The experimental test will be conducted intending to examine the effect of weight fraction and processing method on the elastic properties of HDPE/SWCNTs nanocomposites. The hypothetical questions that one can ask for this experimental test are as follows:

- How will the elastic modulus of HDPE/SWCNTs nanocomposites improve compare to that of pure or unreinforced HDPE?
- Which other tensile or material properties will HDPE/CNT nanocomposite retain?
- At which weight fraction can the best improvement of elastic properties of HDPE/SWCNTs nanocomposites obtain?
- And for which industrial application can they be implemented?

The tensile test method is designed to yield tensile properties data for the control and requirement of materials like plastics and metals. The data obtained from this test method are beneficial for the qualitative description and research and development. Since it is known that tensile properties vary with the specimen environment of testing, machine speed, and preparation, of which all the mentioned factors can affect the data. It is important to carefully control these factors so that the precise comparative results can be obtained.

According to Designation: D638 – 14 [86] It is understood that a material cannot be tested without testing its method of preparation. So, it is necessary to ensure that all material samples are prepared the same way, except the test is to contain the effect of sample preparation. It is very important to consider the sample shapes, dimensions, and processing method during the preparation. According to ASTM standard D882 [86], The method of tensile test is appropriate
for testing materials of any thickness up to 14 mm and including thin samples with less than 1.0 mm in thickness.

3.5.3 Experimental Matrix

3.5.3.1 Title of the Experiment

The effect of various weight fractions of SWCNTs on the elastic properties of HDPE based nanocomposite processed with two processing techniques namely injection and compression moulding.

3.5.3.2 Hypothesis

If the weight fraction of SWCNTs is increased as reinforcement in the HDPE matrix, then the elastic modulus of HDPE based nanocomposite will improve.

Injection moulding will result in better elastic properties compared to compression moulding.

3.5.3.3 Independent Variable

SWCNTs nanoparticles weight fractions per samples and processing methods

3.5.3.4 Experimental Parameters and Their Levels

Table 3.12 presents the experimental parameters and their levels

<table>
<thead>
<tr>
<th>Levels</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNTs weight fractions (wt%)</td>
<td>0</td>
<td>0.2</td>
<td>0.4</td>
<td>0.6</td>
<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td>Processing methods</td>
<td>Injection moulding</td>
<td>Injection moulding</td>
<td>Injection moulding</td>
<td>Injection moulding</td>
<td>Injection moulding</td>
<td>Injection moulding</td>
</tr>
<tr>
<td></td>
<td>Compression moulding</td>
<td>Compression moulding</td>
<td>Compression moulding</td>
<td>Compression moulding</td>
<td>Compression moulding</td>
<td>Compression moulding</td>
</tr>
</tbody>
</table>

3.5.3.5 Dependent Variable

Elastic properties of HDPE/SWCNTs nanocomposites such as elastic modulus, tensile strength, ultimate strength and others.

3.5.3.6 Controlled Factors

All sample shapes and size are identical,
All sample are tested under the same environmental temperature using the same testing machine,

Tensile testing machine speed is constant for all samples.

3.5.3.7 Control or Explanation of Why it is a Controlled Experiment
The experiment must be carefully controlled so that precise comparative results can be obtained.

3.5.3.8 Experimental Design According to Taguchi’s Method
Table 3.13 Presents Experimental design according to Taguchi’s method

<table>
<thead>
<tr>
<th>Sample number</th>
<th>SWCNTs weight fraction (wt%)</th>
<th>Processing methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>Injection moulding</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>Compression moulding</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>Injection moulding</td>
</tr>
<tr>
<td>4</td>
<td>0.2</td>
<td>Compression moulding</td>
</tr>
<tr>
<td>5</td>
<td>0.4</td>
<td>Injection moulding</td>
</tr>
<tr>
<td>6</td>
<td>0.4</td>
<td>Compression moulding</td>
</tr>
<tr>
<td>7</td>
<td>0.6</td>
<td>Injection moulding</td>
</tr>
<tr>
<td>8</td>
<td>0.6</td>
<td>Compression moulding</td>
</tr>
<tr>
<td>9</td>
<td>0.8</td>
<td>Injection moulding</td>
</tr>
<tr>
<td>10</td>
<td>0.8</td>
<td>Compression moulding</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>Injection moulding</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>Compression moulding</td>
</tr>
</tbody>
</table>

3.6 Tensile Test of Specimen
The tensile testing of HDPE/SWCNTs nanocomposites samples was carried out using the ASTM standards D638 -14 which is the standard test method for tensile properties of plastic.
This test method includes the resolution of the tensile properties reinforced and unreinforced plastics such as tensile stress, tensile strength, modulus of elasticity and tensile strain. For this work, all these tensile properties are obtained using Zwick/Roell Z250 tensile testing machine using the tensile sample presented in Figure 3.24.
The Zwick/Roell Z250 tensile testing machine used was designed to provide the relationship between the tensile stress and the applied load to a specimen and the change in its test section shape at a constant temperature. The test can be performed by stretching the sample on the machine using two methods. One method is a tension with a constant rate of stress and the other is a stretch with a constant strain rate. The tensile testing is normally conducted by pulling the standard sample until it breaks. During the testing process, the testing machine generates data that can be used to generate the stress-strain curve. From this curve information such as material behaviour, the strength of submission and others as mentioned are obtained. The stress-strain curve in Figure 3.25 illustrates the general behaviour of plastic materials under tensile testing for International Organization for standardization ISO 527 -1 standard [87].
In Figure 3.25 The line incline in the linear region at low strain indicates the elastic modulus of the material which can be obtained between strains $\varepsilon_1$ and $\varepsilon_2$ and their relative stresses $\sigma_1$ and $\sigma_2$. The area under the stress/strain curve represents the energy required to break the material. The elastic modulus can be obtained using equation 12 as:

$$E_t = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1}$$

Where $E_t$ is Young’s modulus elasticity/elastic modulus expressed in megapascals (MPa), $\sigma_1$ is the stress expressed in MPa measured at the relative strain value $\varepsilon_1 = 0.0005$ according to ISO 527-1:1996, and $\sigma_2$ is the stress in (MPa) measured at the relative strain value $\varepsilon_2 = 0.0025$ according to ISO 527-1:1996.

The stress and strain are calculated using equations 13 and 14 as:

$$\sigma = \frac{F}{A}$$
Where \( \sigma \) is the calculated tensile stress value expressed in MPa, \( F \) is the applied force on the cross-sectional area expressed in newtons (N), and \( A \) is the initial cross-sectional area of the test sample at test section expressed in square millimetres (mm\(^2\)).

\[
\varepsilon = \frac{\Delta L_0}{L_0}
\]

Where \( \varepsilon \) is the calculated strain value expressed as a dimensionless ration or sometimes in percentage, \( \Delta L_0 \) is the change in the sample length between the gauge marks expressed in millimetres (mm), and \( L_0 \) is the gauge length of the test sample expressed in millimetres (mm).

Since it is not easy to accurately calculate the slope of the line and the linear region concerning the experimental data, then these can be determined using Figure 2.26 according to ISO 527-1:1996 for the diversity of plastics.

The tensile modulus:

- It is the slope in the stress-strain diagram between 0.05% and 0.25% strain
- It can be calculated as a secant between 2 points or by a linear regression calculation.

\[ E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} \]

\[ E = \frac{d\sigma}{d\varepsilon} \]

**Figure 3.26** How to compute the elastic modulus for plastics [87, 132]

To conduct the experimental tests for the samples the Zwick/Roell Z250 tensile testing machine in Figure 3.27 was set to the test standard of ASTM D-638 for plastic testing with the operating parameters illustrated in Table 3.14
Figure 3.27 The Zwick/Roell Z250 tensile testing machine with the control computer

Table 3.14 Operating parameters of Zwick/Roell Z250 tensile testing machine

<table>
<thead>
<tr>
<th>Regulatory parameters</th>
<th>Operating conditions</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grip to grip separation at the start position</td>
<td>83</td>
<td>mm</td>
</tr>
<tr>
<td>Speed, start position</td>
<td>5</td>
<td>Mm/min</td>
</tr>
<tr>
<td>Pre-load</td>
<td>0.1</td>
<td>MPa</td>
</tr>
<tr>
<td>Speed, pre-load</td>
<td>5</td>
<td>mm/min</td>
</tr>
</tbody>
</table>

3.6.1 Testing Procedure

To perform the tests, the testing machine in Figure 3.27 was calibrated by using the two test samples of pure HDPE out of five made samples. First, the sample was measured at the test section using a Vernier caliper to check if they meet ASTM D-638 standard. The sample was put into the machine with the relevant operation parameters according to Table 3.14. Then the door of the testing machine was closed, and the test begins.
Figure 3.28 Measured test specimen ready for testing

Based on the experimental matrix in Table 3.13, which demonstrate that 12 experiments must be made due to 12 levels, three tests were made for each level and the average results were considered. This means the total number of the test made was 36. The raw data collected from the tensile testing machine are interpreted and discussed in chapter 4.

3.7 Summary

Chapter 3 discussed the research methodology which includes the approaches, materials, and the processing methods used. Two approaches such as numerical and experimental were implemented aiming to come up with a different way of achieving the results. For the numerical approach, RVE model was created with the relevant parameters to conduct FEM analysis to predict the elastic behaviours of HDPE reinforced with SWCNTs at various weight fractions. Furthermore, the experimental approach was carried out by first processing the pure HDPE and HDPE/SWCNTs nanocomposites tensile test samples using the injection and compression moulding. The numerical and the experimental results will be discussed in chapter 4 together with the theoretical results.
CHAPTER 4

4.0 RESULTS AND DISCUSSIONS

4.1 Overview
This chapter presents and discusses the results of the study based on the methodology applied to gather the information in chapter 3. The key parameters investigated were SWCNTs nanoparticles weight fractions (wt%) and the two processing methods which are: injection and compression moulding. This chapter includes the numerical, experimental, and analytical results that state the findings of the research as well as the validation of the results.

4.2 Numerical Results
The modelling results obtained from the FEM model and rule of the mixture are summarized in Table 4.1 and 4.2. These results were attained using the model presented in chapter 3 section 3.2. The elastic modulus of HDPE/SWCNTs nanocomposites RVE was calculated using the nodal displacement and the nodal stress transfer of the model as presented in Figures 4.1 and 4.2. Figure 4.1 and 4.2 presents the results of the RVE model for the SWCNTs weight fraction of 1 wt% from the last row of Table 3.2.

Figure 4.1 Nodal displacement of HDPE/SWCNTs nanocomposite RVE model in the z-direction
Figure 4.2 Nodal stress transmission in the HDPE/SWCNTs nanocomposite RVE

Figure 4.2 shows the maximum displacement of HDPE/SWCNTs nanocomposite which is 4.96128 nm at the weight fraction reinforcement of 1 wt% SWCNTs with the x parameter of 18.42 nm. The elastic modulus of this model was calculated using these parameters as:

\[
E_c = \frac{PL}{DMX} = \frac{(100 \times 10^6)(186.84)}{4.96128} = 3765.964 \text{ MPa} = 3766 \text{ MPa}
\]

This equation and procedure were used to calculate the elastic modulus of other HDPE/SWCNTs nanocomposites at different weight fractions of SWCNTs and density fractions as illustrated in Table 4.1 and 4.2. The pressure applied was kept constant which was -100 MPa for each weight fraction of SWCNTs to yield various DMX based on the FEM model parameters.

The Rule of mixture elastic modulus of HDPE/SWCNTs nanocomposites RVE were calculated using equation 15 as:

\[
E_c = V_f E_f + V_m E_m + V_I E_I
\]
Where, $E_f$ in the elastic modulus of the nanocomposite, $V_f$ is the volume fraction of SWCNT fibre, $E_f$ is the elastic modulus of SWCNT fibre, $V_m$ is the volume fraction of the HDPE matrix, $E_m$ is the elastic modulus of the HDPE matrix, $V_I$ is the volume fraction of the intermediate phase, and $E_I$ is the elastic modulus of the intermediate phase.

The parameters in equation 15 such as the volume fractions of fibre, matrix and intermediate phase were calculated for each weight fraction of SWCNTs using equations 16, 17, and 18 where the elastic modulus is kept constant as illustrated in Table 3.1.

$$V_f = \frac{\pi((r_{of})^2 - (r_{if})^2)(150)}{\pi((r_{im} + x)^2 - (r_{im})^2)(150) + \pi((r_{im} + x)^2)(2x)}$$

$$V_I = \frac{\pi((r_{oi})^2 - (r_{ii})^2)(150)}{\pi((r_{im} + x)^2 - (r_{im})^2)(150) + \pi((r_{im} + x)^2)(2x)}$$

$$V_m = 1 - V_f - V_I$$

Where, $r_{of}$ is the fibre outer radius, $r_{if}$ is the fibre inner radius, $r_{im}$ is the matrix inner radius, $r_{oi}$ is the intermediate phase outer radius, $r_{ii}$ is the intermediate phase inner radius, 150 is the intermediate phase and fibre length in (nm), and $x$ is the changing parameter with the weight fractions as shown in Table 4.1 and Table 4.2.

**Table 4.1** Elastic modulus of HDPE/SWCNTs nanocomposite RVE at different weight fractions for the density fraction of 1.8 obtained from the FEM and rule of mixture.

<table>
<thead>
<tr>
<th>SWCNT Weight fraction [wt%]</th>
<th>Parameter x [nm]</th>
<th>FEM [MPa]</th>
<th>RULE OF MIXTURE [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>41.90</td>
<td>2160</td>
<td>3130</td>
</tr>
<tr>
<td>0.4</td>
<td>29.99</td>
<td>2600</td>
<td>4250</td>
</tr>
<tr>
<td>0.6</td>
<td>24.33</td>
<td>2980</td>
<td>5380</td>
</tr>
<tr>
<td>0.8</td>
<td>20.87</td>
<td>3410</td>
<td>6520</td>
</tr>
<tr>
<td>1</td>
<td>18.42</td>
<td>3766</td>
<td>7690</td>
</tr>
</tbody>
</table>
Table 4.2 Elastic moduli of HDPE/SWCNTs nanocomposite RVE at different weight fractions for the density fraction of 2 obtained from the FEM and rule of mixture.

<table>
<thead>
<tr>
<th>SWCNT Weight fraction [wt%]</th>
<th>Parameter x [nm]</th>
<th>FEM [MPa]</th>
<th>RULE OF MIXTURE [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>44.16</td>
<td>2307</td>
<td>3010</td>
</tr>
<tr>
<td>0.4</td>
<td>31.65</td>
<td>2690</td>
<td>4020</td>
</tr>
<tr>
<td>0.6</td>
<td>25.81</td>
<td>3000</td>
<td>5020</td>
</tr>
<tr>
<td>0.8</td>
<td>22.16</td>
<td>3300</td>
<td>6040</td>
</tr>
<tr>
<td>1</td>
<td>19.60</td>
<td>3600</td>
<td>7080</td>
</tr>
</tbody>
</table>

Density fraction of 1.8

Figure 4.3 The effect of SWCNTs weight fractions on the elastic modulus of HDPE/SWCNTs nanocomposite
Figure 4.4 The effect of SWCNTs weight fractions on the elastic modulus of HDPE/SWCNTs nanocomposite

Figures 4.3 and 4.4 are generated from Tables 4.1 and 4.2 respectively, which present the relationships of the FEM results and the rule of mixture results for both density fractions. The results of the FEM and the rule of mixture in Figure 4.3 for the density fraction of 1.8 shows that an increase in the weight fraction of SWCNTs nanoparticles inside the HDPE matrix result with the increase of the elastic modulus of HDPE/SWCNTs nanocomposites. However, the prediction error between FEM results and the Ruler of mixture results was higher and increase as the SWCNTs weight fractions rise, of which it might have caused by the assumptions made for FEM modelling or inaccuracy of the rule of mixture equation. Figure 4.4 of the density fraction of 2 displays the same results and behaviour as of Figure 4.3 the different is the effect of density fraction. It demonstrated in Tables 4.1 and 4.2 that for 1.8 density fraction high elastic modulus is achieved at the same SWCNTs weight fraction compared to that of 2 density fractions.

In overall the addition of SWCNTs weight fractions into HDPE matrix is directly proportional to the enhancement of the elastic modulus of HDPE/SWCNTs nanocomposites irrespective of density fractions. However, the effect of density fractions for FEM results play a role in the elastic modulus of HDPE/SWCNTs nanocomposites at a given weight fraction of SWCNTs. At the SWCNTs weight fractions, 0.2 wt% and 0.4 wt% it looks like the density fraction of 2 shows more improvement on the elastic modulus compared to the density fraction 1.8, then at
the weight fractions, 0.6 wt%, 0.8 wt%, and 1 wt% improvement on the elastic modulus was shown by HDPE/SWCNTs nanocomposite with density fraction of 1.8. This results line with the existing literature results of [11, 14]. The FEM results were used to predict the elastic modulus of the HDPE/SWCNTs nanoparticles, and they have proved to be working based on the obtained results. The next section is focusing on the experimental results.

4.3 Experimental Results

4.3.1 Tensile Tests

The tensile tests of HDPE/SWCNTs nanocomposites samples were assumed to contain the random orientation and uniform distribution of SWCNTs in the HDPE matrix, they were also assumed to behave like solid isotropic homogenous material. With these assumptions, the mechanical behaviour of the HDPE/SWCNTs nanocomposites can be investigated experimentally through tensile test only in one direction. Mostly, the tensile test is done by placing a standard test sample in a tensile testing machine and pulling on the sample in one direction (normally vertically) until it fractures. Data points found during the tensile test provides the strength and mechanical properties of the nanocomposite material such as tensile-modulus, Yield strength, maximum force, breakpoint and strain results. For each property of HDPE/SWCNTs nanocomposites, the average of the values was obtained for six experiments for each weight fraction of SWCNTs.

4.3.2 Results of Tensile Tests

The tensile tests results were obtained from the tensile test machine used as a raw data as indicated in chapter 3 section 3.5. The raw data for both injection and compression moulding are presented in Appendix A as an excel sheet. Three tests were done for each weight fraction of SWCNTs nanoparticle according to the experimental matrix in Table 3.12 and 3.13. Table 4.2 present the three-elastic modulus from each test and their average as well as their standard deviations. In Table 4.3 samples members 1,3,5,7,9, and 11 present the elastic modulus of injection moulded samples at the SWCNTs weight fractions of 0 wt%, 0.2 wt%, 0.4 wt%, 0.6 wt%, 0.8 wt%, and 1 wt%, respectively. Compression moulded tensile test samples are presented by sample members 2,4,6,8,10, and 12 at the SWCNTs weight fractions of 0 wt%, 0.2 wt%, 0.4 wt%, 0.6 wt%, 0.8 wt%, and 1 wt% respectively.
Table 4.3 Tensile test results for the elastic modulus for injection and compression moulding

<table>
<thead>
<tr>
<th>Sample number</th>
<th>SWCNTs weight fractions [wt%]</th>
<th>Elastic modulus [MPa]</th>
<th>Average elastic modulus [MPa]</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Test 1</td>
<td>Test 2</td>
<td>Test 3</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>545.881</td>
<td>579.671</td>
<td>618.044</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>550.545</td>
<td>500.441</td>
<td>553.579</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>594.272</td>
<td>562.010</td>
<td>604.866</td>
</tr>
<tr>
<td>4</td>
<td>0.2</td>
<td>564.607</td>
<td>571.933</td>
<td>472.906</td>
</tr>
<tr>
<td>5</td>
<td>0.4</td>
<td>573.793</td>
<td>643.710</td>
<td>588.833</td>
</tr>
<tr>
<td>6</td>
<td>0.4</td>
<td>502.837</td>
<td>667.260</td>
<td>519.568</td>
</tr>
<tr>
<td>7</td>
<td>0.6</td>
<td>588.843</td>
<td>589.317</td>
<td>666.981</td>
</tr>
<tr>
<td>8</td>
<td>0.6</td>
<td>595.185</td>
<td>582.773</td>
<td>535.370</td>
</tr>
<tr>
<td>9</td>
<td>0.8</td>
<td>577.004</td>
<td>667.450</td>
<td>690.309</td>
</tr>
<tr>
<td>10</td>
<td>0.8</td>
<td>615.141</td>
<td>607.285</td>
<td>526.915</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>748.498</td>
<td>720.125</td>
<td>742.473</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>815.630</td>
<td>604.502</td>
<td>525.045</td>
</tr>
</tbody>
</table>

The stress-strain curves of the results in Table 4.3 were found to be brittle according to their curve characteristics compare to Figure 3.25 of ISO 527 and ASTM D638 standard. Brittle materials are characterized as the materials that tend to break without appreciable plastic deformation when subjected to a tensile load [133, 134, 135]. Figure 4.5 represents the stress-strain curve of the sample obtained from the Zwick/Roell Z250 tensile test machine used. This cured demonstrate the properties of the brittle materials according to stress-strain curve an in Figure 3.25.
Figure 4.5 Stress-strain curve for the HDPE/SWCNTs nanocomposite

Figure 4.6 shows some of the test samples after tensile tests, it displays that the samples did not elongate plastically they just fractured without deforming plastically.

Figure 4.7 Tensile test samples after tests

Figure 4.7 which was generated from Table 4.3 that summarized the tensile results obtained from the laboratory presents the effect of SWCNTs weight fractions on the elastic modulus of injection and compression moulded samples. According to Figure 4.7, by increasing the weight fraction of SWCNTs nanoparticles, the elastic modulus of both injection and compression moulded sample increased.
According to the results in Figure 4.7, injection moulding proves to yield high elastic modulus compared to compression moulding at the same SWCNTs weight fractions. At the 0 wt % weight fraction of SWCNTs, injection moulding yield 9 % improvement on the elastic modulus of pure HDPE relates to that of compression moulding at the same SWCNTs weight fraction. At the SWCNTs weight fraction of 1 wt %, injection moulding gives 14 % enhancement in the elastic modulus of HDPE/SWCNTs nanocomposite compare to compression moulding at the same SWCNTs weight fraction. This shows that Injection moulding enhances the elastic modulus of nanocomposite better than compression moulding.

Since the investigated parameters are the SWCNTs weight fractions and the processing methods, to examine which parameters affect the improvement of the elastic modulus of the HDPE/SWCNTs nanocomposites, signal to noise ratio $S/N$ (Montgomery, 2013) [118] was used. Signal to noise ratio in equation 19, is a loss function which is ultimately introduced in the experimental design according to Taguchi’s method.

**Equation 19**

$$
\frac{S}{N} = -10 \log \left( \frac{1}{n} \sum_{i=1}^{n} \frac{1}{y_i^2} \right)
$$
Where \( S/N \) is the signal to noise ratio, \( n \) is the number of the observation on the specific product and \( y \) is the respective characters in this case in the elastic modulus presented by \( E \). According to the Taguchi method, the parameter that has the biggest \( S/N \) has a better effect on the experiment. Table 4.4 was generated using data from Table 4.3 by calculating the signal to noise ratio, where levels 1, 2, 3, 4, 5, and 6 under the effect of SWCNTs weight fractions present the elastic modulus of HDPE/ SWCNTs nanocomposites at a different weight fraction of SWCNTs. For example, level 1 represents 0 wt %, level 2 represent 0.2 wt % up to level 6 which represent 1 wt %. For Levels 1 and 2 under the effect of processing methods presents represent injection and compression moulding elastic modulus at different weight fractions of SWCNTs respectively.

**Table 4.4** Signal to noise ratio \( S/N \) for tensile test elastic modulus data

<table>
<thead>
<tr>
<th>Effect of SWCNTs weight fraction [wt %]</th>
<th>Effect of processing methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level</td>
<td>Elastic modulus (MPa)</td>
</tr>
<tr>
<td>1</td>
<td>( E_1=581.198 ) ( E_2=534.855 )</td>
</tr>
<tr>
<td>2</td>
<td>( E_1=587.050 ) ( E_2=536.482 )</td>
</tr>
<tr>
<td>3</td>
<td>( E_1=602.114 ) ( E_2=563.222 )</td>
</tr>
<tr>
<td>4</td>
<td>( E_1=615.047 ) ( E_2=571.109 )</td>
</tr>
<tr>
<td>5</td>
<td>( E_1=644.921 ) ( E_2=583.114 )</td>
</tr>
<tr>
<td>6</td>
<td>( E_1=737.032 ) ( E_2=648.392 )</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>56.8 – 54.9 = 1.9</td>
</tr>
<tr>
<td>Rank</td>
<td>1</td>
</tr>
</tbody>
</table>
The signal to noise ratio data was obtained according to Table 4.4 using elastic modulus for each parameter, where $\Delta$ is the change between the maximum and the minimum $S/N$ data per parameter, and Rank express the impact of each parameter concerning the magnitude of $\Delta$. According to signal to noise ratio results in Table 4.4, SWCNTs weight fractions had much more effect on the elastic modulus of the HDPE/SWCNTs nanocomposites samples compared to the processing methods. By increasing SWCNTs weight fractions up to level 6 (1 wt % of SWCNTs), the elastic modulus of the HDPE/SWCNTs nanocomposites samples were increased by 24 % which was obtained by taking the average elastic modulus per level and substitute them in equation 20.

$$\frac{692.712 - 558.027}{558.027} \times 100 \approx 24 \%$$

These means that the best level for SWCNTs weight fractions was at level 6 with the SWCNTs weight fraction of 1 wt % in which the highest value for the signal to noise ratio and elastic modulus were obtained. The most optimum state for the elastic modulus among the experiments was achieved when the SWCNTs weight fraction was at level 6 and processing method was at level 1, which correspond to test sample 11. Figure 4.8 illustrates the effect of SWCNTs weight fraction on the mean of $S/N$ ratio and Figure 4.9 shows the effect of processing methods on the mean of $S/N$ ratio.

![Signal to noise diagram of the elastic modulus data for SWCNTs weight fractions with percentage error shown](image)

Figure 4.8 Signal to noise diagram of the elastic modulus data for SWCNTs weight fractions with percentage error shown
According to Figure 4.8, when the HDPE/SWCNTs nanocomposites samples are processed by injection moulding, the highest elastic modulus was achieved at the weight fraction of 1 wt % SWCNTs. Rendering to the results of the signal to noise analysis, the processing method affected the elastic modulus, which through processing the HDPE/SWCNTs nanocomposites samples by injection moulding instate of compression moulding, increased the elastic modulus of the samples by 10 %.

Table 4.5 and 4.6 present the yielding stress, elongation at the yielding point and maximum force of HDPE/SWCNTs nanocomposite for both injection and compression moulding respectively. These results were obtained through a tensile test together with the elastic modulus as mentioned. According to the obtained results, the minimum and the maximum elastic values were attained for pure HDPE and HDPE with 1 wt % of SWCNTs for both processing methods correspondingly. The yielding stress, maximum force and the percentage of ultimate elongation of the tensile samples against the variation in SWCNTs weight fractions for both injection and compression moulding are presented in Figures 4.10, 4.11 and 4.12 respectively.
Table 4.5 Tensile test results for injection moulding HDPE/SWCNTs nanocomposite samples

<table>
<thead>
<tr>
<th>SWCNT weight fraction [wt%]</th>
<th>Yielding stress [MPa]</th>
<th>Elongation at yield point [%]</th>
<th>Area [mm²]</th>
<th>Maximum force [N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>23.156</td>
<td>9.038</td>
<td>38.1</td>
<td>882.242</td>
</tr>
<tr>
<td>0.2</td>
<td>23.237</td>
<td>15.088</td>
<td>38.1</td>
<td>885.330</td>
</tr>
<tr>
<td>0.4</td>
<td>23.399</td>
<td>11.907</td>
<td>38.1</td>
<td>891.499</td>
</tr>
<tr>
<td>0.6</td>
<td>23.490</td>
<td>11.071</td>
<td>38.1</td>
<td>894.963</td>
</tr>
<tr>
<td>0.8</td>
<td>23.510</td>
<td>10.875</td>
<td>38.1</td>
<td>895.727</td>
</tr>
<tr>
<td>1</td>
<td>23.879</td>
<td>11.362</td>
<td>38.1</td>
<td>909.796</td>
</tr>
</tbody>
</table>

Table 4.6 Tensile test results for compression moulding HDPE/SWCNTs nanocomposite samples

<table>
<thead>
<tr>
<th>SWCNT weight fraction [wt%]</th>
<th>Yielding stress [MPa]</th>
<th>Elongation at yield point [%]</th>
<th>Area [mm²]</th>
<th>Maximum force [N]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19.305</td>
<td>5.763</td>
<td>38.1</td>
<td>735.505</td>
</tr>
<tr>
<td>0.2</td>
<td>19.954</td>
<td>5.804</td>
<td>38.1</td>
<td>760.260</td>
</tr>
<tr>
<td>0.4</td>
<td>20.336</td>
<td>6.711</td>
<td>38.1</td>
<td>774.785</td>
</tr>
<tr>
<td>0.6</td>
<td>21.162</td>
<td>6.912</td>
<td>38.1</td>
<td>806.264</td>
</tr>
<tr>
<td>0.8</td>
<td>22.138</td>
<td>6.293</td>
<td>38.1</td>
<td>843.464</td>
</tr>
<tr>
<td>1</td>
<td>24.194</td>
<td>7.410</td>
<td>38.1</td>
<td>921.788</td>
</tr>
</tbody>
</table>

Tables 4.5 and 4.6 where used to generates Figures 4.10, 4.11 and 4.12 as follows:

Figure 4.10 Variation of the yield stress of HDPE/SWCNTs nanocomposite with SWCNTs weight fraction for both processing methods with percentage error shown.
Figure 4.10 demonstrates the variation of the yield stress of HDPE/SWCNTs nanocomposites for different weight fractions of WSCNTs produced using the injection and compression moulding. It shows in Figure 4.10, that the injection moulded samples of HDPE/SWCNTs nanocomposite show hardly any change in yield stress at different wt % fractions. However, when compared to compression moulded samples, the injection moulded samples contain higher yield stress for pure HDPE compared to HDPE reinforced samples at approximately 0.8 wt % of SWCNTs. The compression moulded samples show an increase or improvement of yield stress as the weight fraction of 1 wt %. In general, the yield stress of HDPE/SWCNTs nanocomposites increases when the weight fraction of SWCNTs is increased in the HDPE matrix for both processing methods but compression moulded sample shows better improvement at high weight fractions of SWCNTs.

Figure 4.11 Variation of maximum force of HDPE/SWCNTs nanocomposite with SWCNTs weight fraction for both processing methods with percentage error shown

Figure 4.11 present the variation of maximum force of HDPE/SWCNTs nanocomposites for various SWCNTs weight fractions. Figure 4.11 has almost the same behaviour as Figure 4.10 for both processing methods which shows that an increase in the SWCNTs weight fraction result with the increase in the maximum force of HDPE/SWCNTs nanocomposites samples for both processing methods. However, injection moulded sample shows higher maximum force for pure HDPE till the strengthening of 0.8 wt % of SWCNTs over compression moulding. But
compression moulded samples display the improvement in maximum stress at the WSCNTs weight fraction of 1 wt %. These show that the yielding stress and the maximum force of the HDPE/SWCNTs nanocomposites are directly proportional to the increment of SWCNTs weight fractions in the HDPE matrix.

Figure 4.12 Variation of ultimate elongation of HDPE/SWCNTs nanocomposite with SWCNTs weight fraction for both processing with percentage error shown

Figure 4.12 present the variation in the ultimate elongation percentage of HDPE/SWCNTs nanocomposites samples with weight fractions of SWCNTs for injection a compression moulding. Once again, the trend is very similar to that observed in Figure 4.10.

However, it is worth pointing out that in Figure 4.12 injection moulding shows high but fluctuating results of ultimate elongation percentage compared to that of compression moulding. These ultimate elongation percentage simply shows that the elongation of the HDPE/SWCNTs nanocomposites does not depend on the weight fractions of SWCNTs. However, the average tensile test samples of injection moulding elongate more compare to the compression moulded samples.

In overall the tensile test results showed that the addition of SWCNTs at concentrations up to 1 wt % increased the elastic properties of HDPE/SWCNTs nanocomposite compare to pure HDPE for both processing methods. Though, injection moulding showed to have more effect on the improvement of elastic properties of HDPE/SWCNTs compared to compression moulding at the same weight fractions of SWCNTs nanoparticles weight fractions.
HDPE/SWCNTs nanocomposites containing 1 wt % of SWCNTs nanoparticles had the yielding tensile stress which was about 3 % for injection moulding and 25 % for compression moulding higher than that of pure HDPE. The Increase of tensile stress can be credited to increased crystallinity of the HDPE/SWCNTs nanocomposite. Also, the contact of the HDPE matrix and SWCNTs nanoparticles was beneficial due to the high specific surface area of SWCNTs nanoparticles. The improve contact of HDPE matrix and SWCNTs nanoparticles can better transfer the stress from the HDPE matrix to SWCNTs nanoparticles and increase tensile strength. However, finding a preparation with the correct distribution of SWCNTs nanoparticles in the HDPE matrix is always among the most vital points in attaining high-quality HDPE/SWCNTs nanocomposites. Therefore, despite achieving proper approaches for distributing SWCNTs nanoparticles in HDPE matrices, experimental approaches have always suffered from inconsistent reports and results as well as costly and even contradictory test and error efforts. These do not apply only for HDPE matrix and SWCNTs nanoparticles, it also applies to most of polymer matrix and nanoparticles that can be used for reinforcements. To minimize the experimental errors numerical and analytical which are theoretical results are used for validation.

4.4 Analytical Results

Analytical or theoretical models are usually used for describing the general situations of material and they are intended to express the material behaviour. At this point, four theoretical models are gathered to help predict the elastic modulus of HDPE/SWCNTs nanocomposites produced using the injection and compression moulding at different weight fractions of SWCNTs. In all collected modelling equations, the elastic modulus of the HDPE/SWCNTs nanocomposite is $E_c$, the elastic modulus of the HDPE matrix is $E_m$, the elastic modulus of SWCNTs nanoparticles is $E_n$, the volume fraction of the HDPE matrix is $V_m$, and the volume percentage of SWCNTs nanoparticles is $V_n$.

The elastic modulus used for pure HDPE matrix in the modelling equations, where obtained from the experimental results for both injection and compression moulding as $E_m = 581.198$ MPa and $E_m = 534.855$ MPa respectively as illustrated in Table 4.3. The elastic modulus of SWCNTs was used as $E_n = 1000$ GPa as presented in Table 3.1 [11]. Four models used are as follows:

**Model 1: Approximation Model Manera [136, 137]:**
This model is usually used to predict the elastic properties of composites and nanocomposites materials with short fibres reinforcements which are inadvertently orientated through the matrix.

\[ E_c = V_n \left( \frac{16}{45} E_n + 2E_m \right) + \frac{8}{9} E_m \]

Where \( E_c \), \( V_n \), \( E_n \) and \( E_m \) are the nanocomposite elastic modulus, nanoparticle volume percentage, nanoparticles elastic modulus and matrix elastic modulus respectively as stated.

**Model 2: Model of Pan or fibres density equation [138, 139]:**

This model is effective for the composite materials with long fibres and consistent orientation of nanoparticle through the matrix. In this model, Pan recognized an equation based on the uneven orientation of fibres in two-dimensional and three-dimensional space by using extended simple mixing rule and a hypothetical density equation. The three-dimensional 3D model of Pan was used for the prediction of the elastic modulus of HDPE/SWCNTs nanocomposites materials.

\[ 3D: E_c = E_n \frac{V_n}{\pi} + E_m \left( 1 - \frac{V_n}{\pi} \right) \]

Where \( E_c \), \( V_n \), \( E_n \) and \( E_m \) are the nanocomposite elastic modulus, nanoparticles volume percentage, nanoparticles elastic modulus and matrix elastic modulus respectively as stated.

**Model 3: Hirsch’s model [140, 141]:**

This model presents the equation of the elastic modulus of nanocomposites with the combination of vertical longitudinal modulus of nanocomposite as the following:

\[ E_c = \frac{3}{8} \left[ V_n E_n + (1 - V_n)E_m \right] + \frac{5}{8} \left[ \frac{E_n Y_m}{E_m V_n + (1 - V_n)E_n} \right] \]

Where \( E_c \), \( V_n \), \( E_n \), \( E_m \) and \( Y_m \) are the nanocomposite elastic modulus, nanoparticle volume percentage, nanoparticles elastic modulus, matrix elastic modulus and yield stress of the matrix respectively as stated. The first term in the equation is the constant of the longitudinal modulus and the second term is the constant of the vertical modulus of the nanocomposite.
4.5 Comparison of the Results

For the comparison of the experimental, numerical and theoretical results, first, the numerical results were obtained from the ANSYS FEM model as presented in section 4.2. Secondly, the experimental results were obtained according to section 4.3 and their elastic properties (elastic modulus of pure HDPE for both processing methods) were used to improve the numerical model in section 4.2. Thirdly, the elastic modulus of the HDPE/SWCNTs nanocomposite samples were estimated using the three stated models in section 4.4 together with the experimental elastic modulus of pure HDPE for injection and compression moulding. Experimental, numerical and theoretical results obtained are summarized in Tables 4.7 and 4.8.

Table 4. 7 Experimental, numerical and theoretical results of elastic modulus of HDPE/SWCNTs nanocomposite processed with injection moulding

<table>
<thead>
<tr>
<th>SWCNT wt%</th>
<th>Experimental</th>
<th>FEM</th>
<th>Approximation model Manera</th>
<th>Model of Pan or fibres density equation</th>
<th>Hirsch’s model</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>587.050</td>
<td>717.427</td>
<td>1230.056</td>
<td>1217.448</td>
<td>764.502</td>
</tr>
<tr>
<td>0.4</td>
<td>602.114</td>
<td>846.405</td>
<td>1944.492</td>
<td>1853.698</td>
<td>1514.531</td>
</tr>
<tr>
<td>0.6</td>
<td>615.047</td>
<td>968.791</td>
<td>2656.928</td>
<td>2489.947</td>
<td>2264.560</td>
</tr>
<tr>
<td>0.8</td>
<td>644.921</td>
<td>1087.519</td>
<td>3370.364</td>
<td>3126.197</td>
<td>3014.580</td>
</tr>
<tr>
<td>1</td>
<td>737.032</td>
<td>1247.596</td>
<td>4083.800</td>
<td>3762.447</td>
<td>3764.619</td>
</tr>
</tbody>
</table>

Table 4. 8 Experimental, numerical and theoretical results of elastic modulus of HDPE/SWCNTs nanocomposite processed with compression moulding

<table>
<thead>
<tr>
<th>SWCNT wt%</th>
<th>Experimental</th>
<th>FEM</th>
<th>Approximation model Manera</th>
<th>Model of Pan or fibres density equation</th>
<th>Hirsch’s model</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>536.482</td>
<td>664.038</td>
<td>1188.677</td>
<td>1171.134</td>
<td>762.090</td>
</tr>
<tr>
<td>0.4</td>
<td>563.222</td>
<td>781.992</td>
<td>1901.928</td>
<td>1807.414</td>
<td>1512.114</td>
</tr>
<tr>
<td>0.6</td>
<td>571.109</td>
<td>902.139</td>
<td>2615.178</td>
<td>2443.693</td>
<td>2262.139</td>
</tr>
<tr>
<td>0.8</td>
<td>583.114</td>
<td>1005.693</td>
<td>3328.429</td>
<td>3079.972</td>
<td>3012.163</td>
</tr>
<tr>
<td>1</td>
<td>648.392</td>
<td>1112.084</td>
<td>4041.679</td>
<td>3716.251</td>
<td>3762.188</td>
</tr>
</tbody>
</table>

Figure 4.13 which was generated from Table 4.7 display the relationship between the experimental, numerical and analytical elastic modulus results obtained for HDPE/SWCNTs nanocomposites samples processed with injection moulding.
Figure 4.13 Comparison of experimental results with the numerical FEM and predicted analytical models results for the elastic modulus of HDPE/SWCNTs nanocomposites with SWCNTs weight fractions processed with injection moulding with percentage error shown.

It shows in Figure 4.13 that the FEM model results have the acceptable percentage ability to predict the elastic modulus of HDPE/SWCNTs nanocomposites. As for Approximation model, a model of Pan and Hirsh’s model results, they can only show with the high percentage error, that the elastic modulus of HDPE/SWCNTs nanocomposites increases as the SWCNTs weight fractions increases in an HDPE matrix. FEM model proves to contain the favourable and reliable results that can be used for the prediction of elastic modulus of HDPE/SWCNTs nanocomposites for this investigation.
Figure 4.14 Comparison of experimental results with the numerical FEM and predicted analytical models results for the elastic modulus of HDPE/SWCNTs nanocomposites with SWCNTs weight fractions processed with compression moulding with percentage error shown.

Figure 4.14 which was produced from Table 4.8 demonstrate the relationship between the experimental, numerical and analytical elastic modulus results obtained for HDPE/SWCNTs nanocomposites samples processed with compression moulding. Figure 4.14 contains the curves with similar behaviour as of the one in Figure 4.13. These results show that the FEM model results have a reasonable percentage of the ability to predict the elastic properties of HDPE/SWCNT nanocomposites.

Among the vital conclusions was that by increasing the weight fraction of SWCNTs, the errors of analytical models were increased as shown in both Figures 4.13 and 4.14. The experimental results also show the same behaviour which is more related to the FEM model although they have small errors against each other. Such errors might have occurred during the processing of the samples that might have caused the agglomeration of SWCNTs nanoparticles in the samples, or the experimental errors that may have occurred during testing and measuring or calibration of the machine used. In overall, the results are as expected, and they are in line with the existing literature results.
4.6 Summary

Based on the results and the discussions of the relative investigation, the following conclusions can be drawn:

In this work, HDPE/SWCNTs nanocomposites were produced according to injection and compression moulding methods. The effect of the two processing methods and the effect of the addition of SWCNTs at six different levels of 0 wt %, 0.2 wt %, 0.4 wt %, 0.6 wt %, 0.8 wt % and 1 wt % on the elastic properties of the nanocomposite samples was investigated using numerical, experimental and analytical approaches. It showed that by adding SWCNTs nanoparticles into the HDPE matrix significantly increases the elastic properties such as elastic modulus, yield stress, and maximum force of samples.

Also, according to the comparison results, the FEM model showed to have reliable and favourable results that can be used to predict the elastic modulus and other elastic properties of the HDPE/SWCNTs nanocomposites.
CHAPTER 5

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Overview

This research study was proposed as a steppingstone to establish and identify the effect of two different processing techniques namely; injection and compression moulding as well as the consequences of adding SWCNTs nanoparticles weight fractions on the elastic properties of HDPE matrix. The aim of this study was therefore to develop HDPE/SWCNTs nanocomposites reinforced at various weight fractions of SWCNTs and processed using two distinct methods as mentioned and investigate their effect on its elastic properties.

To achieve the above remarks, an appropriate literature review on the polymer, polymer-based nanocomposites, particle reinforcements, the processing of polymer-based nanocomposites and the experimental set up was conducted. The experimental set up was developed to investigate all the parameters that might affect the elastic properties of HDPE. Several approaches such as numerical and analytical including experimental were implemented in the study of HDPE/SWCNTs nanocomposites elastic properties. The numerical approach was performed to predict the elastic properties of HDPE/SWCNTs nanocomposites reinforced at different weight fractions of SWCNTs nanoparticles which served as trial simulations. The main part of the study which is the development and the investigation through the experimentation was performed and the results were validated with that of numerical and theoretical results. The comparison or the validation study was carried out aiming to establish the relationship between the elastic modulus of HDPE/SWCNTs nanocomposites using the FEM model, experimental and analytical models.

This chapter summarizes the conclusions and the recommendations made regarding the parameters affecting the elastic properties of HDPE/SWCNTs nanocomposites. The conclusion addresses the aim stated within the scope of study in chapter 1. This is followed by the recommendations that may arise from the current research and the opportunity of future work.

5.2 Numerical FEM

Firstly, numerical simulation was conducted to predict the elastic modulus of HDPE/SWCNTs nanocomposites using the existing literature results with the given parameter of SWCNTs nanoparticles weight fractions. This study aimed to evaluate the behaviour of the elastic modulus of HDPE reinforced with SWCNTs nanoparticles at different weight fractions using
3D represented volume element (RVE). The RVE was then computed using finite element method (FEM) using ANSYS 19.2 software and its elastic behaviour was simulated. The properties of fibre, matrix and interface were extracted by using the results of atomic modelling to present the model for prediction of the elastic modulus of HDPE/SWCNTs nanocomposites. The effects of geometric and mechanical properties of the matrix, fibre, and interfaces such as elastic modulus and density fractions on the stress transformation, displacement and elastic modulus of HDPE/SWCNTs nanocomposites were investigated. The results of the FEM model displayed the following about the elastic modulus of HDPE/SWCNTs nanocomposites at various weight fractions of SWCNTs nanoparticles:

5.2.1 Effect of SWCNTs weight fractions on the elastic modulus of HDPE/SWCNTs nanocomposites
The results showed that the increase of weight fraction of SWCNTs nanoparticle in the HDPE matrix results with an increase in the elastic modulus of HDPE/SWCNTs nanocomposites.

5.2.2 Effect of density fraction on the elastic modulus of HDPE/SWCNTs nanocomposites
It was also found that at the density fraction of 1.8 and the SWCNTs weight fraction of 1 wt %, the elastic modulus of HDPE/SWCNTs nanocomposite improved by 74 %. Once more at the same SWCNTs weight fraction for the density fraction of 2, it was found that the improvement in the elastic modulus of HDPE/SWCNTs nanocomposite is 56 %. These show that the low-density fraction of SWCNTs fibre and HDPE matrix yield higher elastic modulus of HDPE/SWCNTs nanocomposites at given SWCNTs nanoparticles weight fraction compare to the high-density fraction.

In general, the modelling results displayed that the elastic modulus of polymers or polymer-based nanocomposites (HDPE) can be enhanced by the addition of the nanoparticles (SWCNTs) weight fractions. These were also shown by the rule of mixture results.

5.3 Experimental Investigation
The investigated parameters during the experiment were two processing methods and the SWCNTs nanoparticles weight fractions on the elastic modulus of HDPE/SWCNTs nanocomposites samples. The levels of SWCNTs nanoparticles used were 0 wt %, 2.0 wt %, 0.4 wt %, 0.6 wt %, 0.8 wt %, and 1 wt %. These SWCNTs weight fractions were used as the reinforcements for the HDPE matrix in the two processing methods. HDPE/SWCNTs nanocomposites were produced according to injection and compression moulding to prepare
the samples for tensile tests. The tensile tests of HDPE/SWCNTs nanocomposites samples were then tested using Zwick/Roell Z250 tensile testing machine and the results were obtained in excel sheet data form. The results obtained from the testing machine presented tensile properties such as tensile modulus, yield stress, maximum force, breakpoint and strain as well as the stress-strain curve for each sample. For each SWCNT weight fraction and processing method, three samples of HDPE/SWCNTs nanocomposites were made and the average test results were taken. The tensile test results of HDPE/SWCNTs nanocomposites showed the following effects:

5.3.1 Comparison of the effect of SWCNTs weight fractions and the processing method on the elastic modulus of HDPE/SWCNTs nanocomposites

To compare which parameter between the SWCNTs nanoparticles weight fractions and the two-processing method affect the elastic modulus of the HDPE/SWCNTs nanocomposites, the signal to noise ratio from the Taguchi’s method was applied. According to the Taguchi technique, the parameter with the larger signal to noise ratio among the compared parameters is the one that has a bigger effect on the experiment. The results of the signal to noise ratio showed that SWCNTs weight fractions have the signal to noise ratio of 1.9 and the processing method with the signal to noise ratio of 0.8. This means that SWCNTs weight fractions have more effect on the elastic modulus of HDPE/SWCNTs nanocomposites. In general, reinforcing polymers by adding nanoparticles is better than just processing it using various techniques when targeting to enhance its elastic properties.

5.3.2 The effect of SWCNTs weight fractions on the elastic properties of HDPE/SWCNTs nanocomposites

The obtained results of the signal to noise ratio showed that SWCNTs nanoparticles at the weight fraction of 1 wt % improve the elastic modulus of HDPE/SWCNTs nanocomposite by 24% compared to the two processing methods which are 20 %.

5.3.3 The effect of processing method on the elastic properties of HDPE/SWCNTs nanocomposites

The effect of an injection and compression moulding on the elastic properties of HDPE/SWCNTs nanocomposite samples were divided into four sections as follows.
5.3.3.1 Their effect of the processing methods on the elastic modulus of HDPE/SWCNTs nanocomposites

The results showed clearly that at 0 wt % weight fraction of SWCNTs, injection moulding yield 9 % improvement on the elastic modulus of pure HDPE compared to that of compression moulding at the same SWCNTs weight fraction. Again, at the SWCNTs weight fraction of 1 wt %, injection moulding gives 14 % enhancement in the elastic modulus of HDPE/SWCNTs nanocomposite liken to compression moulding at the same SWCNTs weight fraction. This means that Injection moulding improves the elastic modulus of HDPE/SWCNTs nanocomposites better than compression moulding at a given SWCNTs nanoparticles weight fractions.

5.3.3.2 Their effect of processing techniques on the yielding stress and the maximum force of HDPE/SWCNTs nanocomposites

Both yielding stress and the maximum force results displayed that the injection moulded samples of HDPE/SWCNTs nanocomposites holds high yield stress and maximum force for pure HDPE up until it is reinforced with 0.8 wt % of SWCNTs weight fraction compared to that of compression moulded samples. The compression moulded samples show the improvement of yield stress and the maximum force at the weight fraction of 1 wt %. This means the yield stress and the maximum force of HDPE/SWCNTs nanocomposites increases as the weight fraction of SWCNTs increase in the HDPE matrix for both processing methods, but compression moulded samples show better improvement at high weight fractions of SWCNTs.

5.3.3.3 Their effect processing methods on the ultimate elongation of HDPE/SWCNTs nanocomposites

The results of ultimate elongation for both processing technologies presented the fluctuating behaviour for each SWCNTs weight fractions. However, injection moulded samples showed to have high ultimate elongation compare to that of compression moulded samples at each given SWCNTs weight fraction.

5.4 Theoretical Study

Three theoretical models of which are approximation model Manera, model of Pan or fibres density equation, and Hirsch’s model were used to predict the elastic modulus of the HDPE/SWCNTs nanocomposite using the experimental elastic modulus results of pure HDPE processed with injection and compression moulding. The analytical results showed for both
injection and compression moulded samples of HDPE/SWCNTs nanocomposites, that by addition of SWCNTs nanoparticle weight fraction into the HDPE matrix significantly increased the elastic modulus on the nanocomposites.

5.5 Comparative Study

The comparison study was conducted to compare the numerical, experimental and theoretical results of the elastic modulus of HDPE/SWCNTs nanocomposites. All these results have something in common of which is the increase in the elastic modulus of HDPE/SWCNTs nanocomposite as the SWCNTs weight fractions increases. However, theoretical models result such as the approximation model Manera, model of Pan or fibres density equation, and Hirsch’s model results showed a bigger difference compared to the experimental and FEM results. This means the FEM results show the reliable and acceptable difference of ability to predict the elastic properties of HDPE/SWCNTs nanocomposites. In general, the following conclusions can be made based on the investigation:

- The elastic modulus of the polymer can be enhanced by reinforcing it with nanoparticles because it has been shown by the obtained results, that addition of SWCNTs nanoparticles weight fractions into the HDPE matrix improved the elastic modulus of the HDPE/SWCNTs nanocomposites.
- Injection moulding yield better elastic properties of HDPE/SWCNTs nanocomposites compare to compression moulding at the same weight fractions of SWCNTs nanoparticles.
- Yielding stress and the maximum force of the HDPE/SWCNTs nanocomposites increases as the SWCNTs nanoparticle weight fraction increased in the HDPE matrix.
- Addition of 1 wt % SWCNTs nanoparticle at the ambient temperature of 25 °C increased the elastic modulus of HDPE/SWCNTs nanocomposites by 27 % for injection moulded samples and 21 % for compression moulded samples compare to pure HDPE respectively.
- Addition of 1 wt % SWCNTs nanoparticle at the ambient temperature of 25 °C increased the yield stress and the maximum force of HDPE/SWCNTs nanocomposites by 3 % for injection moulded samples and 25 % for compression moulded samples compare to pure HDPE respectively.
5.6 Recommendations for Future Work

The recommendation for future work in the associated fields of this present study are as follows:

➢ There was evidence of improvement in elastic properties of HDPE/SWCNTs nanocomposite as the weight fractions of SWCNTs nanoparticles increased in the HDPE matrix. These results were valuable for this investigation and future work, the following parameters can be investigated to build upon the current study:

• Further research can be conducted to investigate the elastic properties of polymer-based nanocomposites using different nanoparticles or polyethylene,

• Additional examinations on the effect of other processing techniques such as 3D-printing on the elastic modulus of nanocomposite can be shown,

• Study the effect of changing the injection pressure or compression load of the processing methods of the elastic properties of the nanocomposites.

• Furthermore, the examination and minimizing the effect of processing method defects that may occur during the production of samples should be conducted.
REFERENCES


[119] N. Hasegawa, M. Kawasumi, M. Kato, A. Usuki and A. Okada, "Preparation and mechanical properties of polypropylene-clay hybrids using a maleic anhydride-


## 6.1 Appendix A: Project Plan

Table 6.1 Present project tasks, dated and their days to complete

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Figure 6.1 The Project Gantt Chat

- Problem Definition
- Literature Study
- Finding Quotation for the Materials Required
- Finding Quotation for the Equipment
- Planning Experimental Design
- Conducting Experiment
- Performing FEM Analysis
- Validating the Results
- Presentation Preparation
- Final Project Report
- Review of Project Report for Final Submission
- Reporting

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6.2 Appendix B: Material Test Certificates

SPECIFICATION CERTIFICATE

**Product:** Single Walled Nano Tubes (SWCNT)

**Description:** Sample purity of NANOSHEL SWCNT is 90-98 Vol%, as determined by Raman Spectrophotometer and SEM Analysis. Nanoshel Nano material contains no residual catalyst impurities. Tubes occur in bundles of length ~1 - 10μm. (±1.5μm). Individual tube length has not been determined.

**Quality Control:** Each lot of NANOSHEL SWCNT’s was tested successfully.

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<td>Amorphous carbon</td>
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<tr>
<td>Residue (calcinations in air)</td>
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<td>Volume Resistivity</td>
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Signed By:
NANOSHEL LLC
www.nanoshel.com
sales@nanoshel.com

---

Figure 6.2 SWCNTs specification certificate
### Appendix C: Experimental Data and Stress-Strain Curves Results

![Table of Injection Moulding Tensile Test Experimental Data](image)

**Figure 6.3** Injection moulding tensile test experimental data (raw)
### Figure 6.4: Compression moulding tensile test experimental data (raw)

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Figure 6.5 Stress-strain curves for all injection moulded samples
Figure 6.6 Stress-strain curves for all compression moulded samples
Figure 6.7 Stress-Strain curves for 0 wt% injection moulded samples

Figure 6.8 Stress-Strain curves for 0.2 wt% injection moulded samples
0.4 wt% SWCNTs weight fraction for injection moulding

Figure 6.9 Stress-Strain curves for 0.4 wt% injection moulded samples

0.6 wt% SWCNTs weight fraction for injection moulding

Figure 6.10 Stress-Strain curves for 0.6 wt% injection moulded samples
0.8 wt% SWCNTs weight fraction for injection moulding

![Graph showing Stress-Strain curves for 0.8 wt% injection moulded samples.](image)

**Figure 6.11** Stress-Strain curves for 0.8 wt% injection moulded samples

1 wt% SWCNTs weight fraction for injection moulding

![Graph showing Stress-Strain curves for 1 wt% injection moulded samples.](image)

**Figure 6.12** Stress-Strain curves for 1 wt% injection moulded samples
0 wt% SWCNTs weight fraction for compression moulding

Figure 6.13 Stress-Strain curves for 0 wt% compression moulded samples

0.2 wt% SWCNTs weight fraction for compression moulding

Figure 6.14 Stress-Strain curves for 0.2 wt% compression moulded samples
Figure 6.15 Stress-Strain curves for 0.4 wt% compression moulded samples

Figure 6.16 Stress-Strain curves for 0.6 wt% compression moulded samples
0.8 wt% SWCNTs weight fraction for compression moulding

Figure 6. 17 Stress-Strain curves for 0.8 wt% compression moulded samples

1 wt% SWCNTs weight fraction for compression moulding

Figure 6. 18 Stress-Strain curves for 1 wt% compression moulded samples
6.4 Appendix D: Numerical results

Figure 6.19 Maximum displacements for 0.2 wt% injection moulding

Figure 6.20 Maximum stress for 0.2 wt% injection moulding
Figure 6. 21 Maximum displacements for 0.4 wt% injection moulding

Figure 6. 22 Maximum stress for 0.4 wt% injection moulding
Figure 6. 23 Maximum displacements for 0.6 wt% injection moulding

Figure 6. 24 Maximum stress for 0.6 wt% injection moulding
Figure 6. 25 Maximum displacements for 0.8 wt% injection moulding

Figure 6. 26 Maximum stress for 0.8 wt% injection moulding
Figure 6. 27 Maximum displacements for 1 wt% injection moulding

Figure 6. 28 Maximum stress for 1 wt% injection moulding
Figure 6. **29** Maximum displacements for 0.2 wt% compression moulding

Figure 6. **30** Maximum stress for 0.2 wt% compression moulding
Figure 6.31 Maximum displacements for 0.4 wt% compression moulding

Figure 6.32 Maximum stress for 0.4 wt% compression moulding
Figure 6. 33 Maximum displacements for 0.6 wt% compression moulding

Figure 6. 34 Maximum stress for 0.6 wt% compression moulding
Figure 6.35 Maximum displacements for 0.8 wt% compression moulding

Figure 6.36 Maximum stress for 0.8 wt% compression moulding
Figure 6.37 Maximum displacements for 1 wt% compression moulding

Figure 6.38 Maximum stress for 1 wt% compression moulding