EVALUATION OF MECHANICAL PROPERTIES IN THERMOPLASTIC POLYMER NATURAL RUBBER FILLED WITH HYBRID FILLERS

This report is submitted in accordance with requirement of the University Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Hons.)

by

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2021

DECLARATION

I hereby, declared this report entitled "Evaluation of Mechanical Properties in Thermoplastic Polymer Natural Rubber Filled With Hybrid Fillers" is the result of my own research except as cited in references.

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Hons). The member of the supervisory committee is as follow:

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ABSTRAK

Penggunaan barangan elektronik yang meningkat masa kini telah menyebabkan berlakunya satu pencemaran baru iaitu gangguan frekuensi radio atau gangguan elektromagnetik yang boleh menyebabkan gangguan pada alatan elektronik dan juga komponen dalamannya. Perkara ini berlaku dalam semua sektor termasuk industri, tentera, komersial dan sektor pengguna. Oleh itu, penggunaan pelindung elektromagnetik diperlukan bagi mencegah pencemaran ini daripada berlaku. Pengisi tambahan nano yang akan digunakan dalam kajian ini adalah nanotiub karbon (CNT) dan nanoplatelet grafen (GNP). Bahan-bahan ini akan dicampur ke dalam gabungan karbon hitam (CB) bagi mengkaji bagaimana kesan hidbridisasi ke atas tingkah laku polipropelina (PP) dan getah asli (NR) termoplastik elastomer. PP/NR pada 75/25 dijangka mempunyai kekuatan impak yang lebih tinggi tetapi mempunyai kekuatan tegangan, modulus keanjalan dan kekerasan yang lebih rendah berbanding PP asli sahaja. PP/NR pada 75/25 bersama 30 phr karbon hitam dan 1 phr CNT dan GNP. Berdasarkan tinjauan kritikal, fokus utama adalah pada sifat mekanikal dan fizikal sesebuah komposit. Terdapat dua jenis gabungan hibrid pengisi nano yang digunakan iaitu CB/CNT dan CB/GNP. Berdasarkan keputusan yang beralasan, PP/NR yang berhibrid pengisi nano CB/CNT mempunyai kekuatan tegangan yang sama seperti CB/GNP, modulus kenjalan yang lebih baik dan kekuatan impak yang lebih baik berbanding CB/GNP. Sementara itu, CB/GNP mempunyai kekerasan yang lebih baik. Konklusi ini disokong oleh analisis mikroskop electron pengimbas (SEM) dan difraksi sinar-x (XRD)

ABSTRACT

Growth in electronic devices nowadays has created a new form of pollution which is radio frequency interference (RFI) or electromagnetic interference (EMI) that can cause equipment to malfunction and cause interference towards the components. This is applicable in all sectors such as industrial, military, commercial and consumer sectors. Therefore, the usage of EMI shielding is needed to prevent this pollution from occurring is needed. The nanofillers that is used in this study are graphene nanoplatelet (GNP) and carbon nanotube (CNT). They will be employed in combination with carbon black to evaluate how the hybridization affects the properties of PP/NR thermoplastic elastomers. PP/NR of 75/25 is predicted to have better impact strength but have lower tensile, Young's modulus and hardness compared to pure PP. PP/NR composition is at 75/25 with 30 phr of carbon black and 1 phr of CNT and GNP. In the evaluation based on critical review, the main focus is the mechanical and physical properties of the composites. There are two different pair of hybrid fillers which is CB/CNT and CB/GNP. In the postulated result, PP/NR with hybrid fillers of CB/CNT has the same tensile strength as CB/GNP blend, better Young's modulus, and better impact strength compared to CB/GNP. Meanwhile CB/GNP has better hardness. The conclusion is supported by the scanning electron microscopy and X-Ray Diffraction analysis.

DEDICATION

Only

my beloved father, Ahmad bin Daud

my appreciated mother, Afizah binti Ahmad

my adored brothers, Muhammad Haziq and Izzat Harith

my dearest best friends

for giving me moral support, financial support, cooperation, encouragement and also understanding

Thank You So Much & Love You All Forever

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LIST OF ABBREVIATIONS

EMI	-	Electromagnetic Interference
RFI	-	Radio Frequency Interference
ESD	-	Electrostatic Discharge
NR	-	Natural Rubber
CB	-	Carbon Black
CNT	-	Carbon Nanotube
GNP	-	Graphene Nanoplatelet
PP	-	Polypropylene
XRD	-	X-Ray Diffraction
SEM	-	Scanning Electron Microscopy
SE	-	Shielding Effectiveness
PEDGE	-	Polyethylene Glycol Diglycidyl Ether
PVC	-	Polyvinyl Chloride
EVA	-	Ethylene-Vinyl Acetate
SCF	-	Short Carbon Fiber
CVD	-	Chemical Vapor Deposition
SWCNT	-	Single-Walled Carbon Nanotube
MWCNT	-	Multi-Walled Carbon Nanotube
PSA	-	Particle Size Analyzer

LIST OF SYMBOLS

℃ - Degree Celsius

cm - Centimeter

mm - Millimeter

% - Percent

H - Magnetic Field

E - Electric Field

V - Volt

Amp - Ampere

λ - Lambda

π - Pi

TPa - Tera Pascal

MPa - Mega Pascal

GPa - Giga Pascal

n - Nano

g - Gram

W - Watt

K - Kelvin

Ω - Ohm

T_g - Transition Temperature

kg - Kilo Gram

µ	-	Micro
ASTM	-	American Society for Testing and Materials
min	-	Minute
Q	-	Mass of Toluene Absorbed in each Rubber Compound
phr	-	Parts Per Hundred Rubber

CHAPTER 1

INTRODUCTION

This chapter contains the background, problem statements, objectives and scope of the study, as well as the organization of the report.

1.1. Background of Study

Electromagnetic interference is the unwanted noise that occurs when a supersensitive electronic device receives an electromagnetic radiation emitted from the usage of electronic devices such as laptop, microwaves, speaker and phones too. This noise is undesirable as it will affect the overall performance of the electronic devices. A striking example of that is the dysfunction of pacemakers when in the vicinity of certain electronic device. The unnecessary EMI is an electromagnetic disturbance that affects the unit, transmission channel, or system performance. It is also called as radio frequency interference (RFI) when the interference is in the radio frequency spectrum. This problem occurs in operation of any electrical devices when the proximity of the electromagnetic field to the spectrum of radio frequencies derived from other electronic devices.

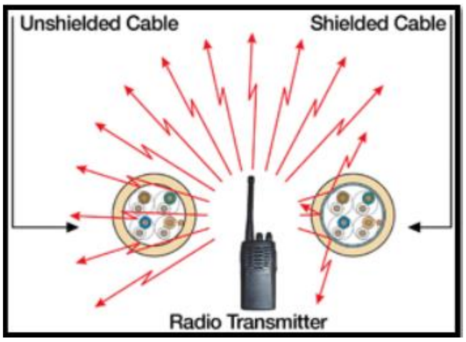


Figure 1.1: Shielded and non-shielded cable from EMI.

Furthermore, interference also frequently happened to mobile phone, aircraft and medication too. Electromagnetic interference (EMI) occurring to medical devices has been widely established (Klein AA, 2003), but its clinical consequences remain controversial (Myerson SG, 2003). The electromagnetic interference (EMI) also occurs when making a call when noise from the cellphone handshaking with the communication tower. In military sector, EMI can cause jamming of enemy radio tower network to disable their communication which is considered as a useful EMI. The EMI can cause disturbance of communication between control tower and their aircraft.

This will also increase the demand for injection moldable thermoplastic for the housing of the component. The features and specifications require improvement, making them lighter, smaller and better at preventing electromagnetic interference (EMI). The fact that plastic is not able to replace metal as a conductive material due to the electrical conductivity, one application where conductivity requirement is not as severe as in electromagnetic interference (EMI) shielding (Grady, 2011). To prevent system failure, most electronic gadgets need to be shielded from electromagnetic interference (EMI). Due to its lightweight, low cost and ease of process, the housing of the unit is typically made of plastic. However, most of the plastic cannot prevent electromagnetic interference (EMI) from occurring. As a result, plastic housing, especially in the electronics and communications industries, has posed some serious problems. Since communication devices have become increasingly sensitive, dense, and abundant, EMI shielding has become one of the most important concerns in optical-electronic packaging.

On top of that, the main solution to this particular problem is the electrical conductive properties in plastics are required to ensure adequate EMI shielding to enhance the EMI shielding for the electronic housing of a device. The current available techniques for EMI shielding are including conductive sprays, conductive fillers, electro-plating or electrolysis-plating on housing surface, modification of electrical properties during molding stage and other metallization process (M. Murt, 1990). Among these methods, the most popular for EMI shielding is compound plastics with discontinuous electronic conductive fillers, such as metal particles, metal flakes, stainless fiber, graphitized carbon particles, graphitized carbon fibers, and metal-coated glass and carbon fibers (J. Bell et al, 1992).

Conductive polymer is recommended which small volume fractions of electrically conductive filler are added into a non-conducting polymer matrix such as engineering polymers through melt blending process (Jou et al, 2001). Carbon black/fibres was one of the first materials used for the purpose of conductive filler. Since carbon black is a semiconductor, the typical resistivity of carbon black is in range of 20-0.5Ω cm and when used as a filler in polymer matrix composites it endowed the compound with conductive properties (Guo et. al.,2013). So, there is other material that can be used as conductive filler such as carbon nanotube and graphene nanoplatelets.

1.2. Problem Statement

In modern era nowadays, the market for electronic devices has been growing rapidly in various fields, such as military, entertainment, industrial and medical. Electromagnetic interference (EMI) or radio frequency interference (RFI) that is not really necessary can cause plenty of issues, such as system interference and failure, as a result of this situation. Since EMI usually occur in daily routine such as noise on microphones from the cell phones, distortion of television broadcast reception and interference of radio frequency. Most of electronic gadget must be protected against these EMI and electrostatic discharge (ESD) especially in sectors involved.

Thus, development of EMI shielding using thermoplastic elastomer with nanofillers as housing component is introduced in order to prevent EMI from occurring. Besides its lightweight and easy to shape characteristics, the usage of elastomers such as polypropylene integrated with nanofillers can reduce and eliminate seam and has better properties than normal metal EMI shielding material that is heavy and expose to corrosion. In order to become EMI shielding materials, thermoplastic elastomer added with various conductive filler such as carbon black, carbon nanotube and graphene nanoplatelets which allows current flow and can both absorb and reflect EMI.

Generally, thermoplastics elastomer is not a good electrically conductive material. Metal is the most common and suitable material for EMI shielding which metal has a very high electrical conductivity (106 Siemens/cm). However, the disadvantages of the usage of metal are the weight of the metal itself which is heavy will increase the weight of the whole product compared to plastics. Other than that, there is also a possibility of corrosion of metal could occur in a certain amount of time. This can be solved by providing metal coating but it will be costly. The electrical conductivity can be improved with additional carbon black, carbon nanotube and graphene nanoplatelets. Therefore, the main objective of the research is to study the impact of additional nanofillers on the thermoplastic elastomer to be used as EMI shielding.

1.3. Objectives

The overall objective of this study is to evaluate the mechanical properties in thermoplastic polymer natural rubber filled with nanofillers such as carbon black, carbon nanotubes and graphene nanoplatelets. There are several objectives listed below that need to be achieved in this study:

1. To postulate the effect of NR content to the physical and mechanical properties of PP/NR thermoplastic elastomer.
2. To predict the impact of filler hybridization on the physical and mechanical properties of the thermoplastic elastomer.
3. To correlate the morphological properties of the nanofiller filled PP/NR composites with their mechanical behavior.

1.4. Scope

In order to achieve the objectives, this project is depending on both experimental data and critical review. Thermoplastic elastomer filled with various nanofillers such as carbon black, carbon nanotubes and graphene nanoplatelets will be fabricated and tested. Initially, blends of polypropylene and natural rubber will be prepared using internal mixer and extrusion before compressed using hot compression moulding. The PP/NR compositions will be varied at 100:0, 75:25 and 50:50 wt%. Subsequently, conventional and nanofiller will be loaded to the premixed 75:25 thermoplastic elastomer. The amount of filler loadings is 30 phr CB, 29:1 phr (CB/CNT) and. 29:1 phr (CB/GNP). Sonication will be performed on the nanofiller prior to the mixing with the thermoplastic elastomer in order to exfoliate it. The resulted composites then will be characterized to study the effects of different hybrid fillers to the PP/NR thermoplastic elastomers. The mechanical and physical tests that will be performed are tensile test, hardness test, impact test, swelling test, X-Ray Diffraction (XRD) test and Scanning Electron Microscopy (SEM).

1.5. Significant of Study

There is some potential benefit that can be gained from this study, which is the better solution in order to create a better EMI shielding with a stronger composite and a better mechanical property of thermoplastics elastomers. As we know, material such as metal used in preventing EMI is good but have their own downside such as heavy in weight and exposed to corrosion. By doing this study, we can propose a better solution other than metal with a cheaper material, lighter and does not corrode easily but still having a good characteristic in preventing EMI.

1.6. Organization of Report

Chapter 1: Introduction

This chapter discuss the background of the study. Problems are identified through past research and academic journals. Followed by the objectives of the study and scope to narrow down the area of the study. The significant of the study is also discussed.

Chapter 2: Literature Review

This chapter covers the basic theories regarding the topic and previous studies from journal, book and the internet.

Chapter 3: Methodology

This chapter consists of methodology. It contains the information about proposed material specification, equipment, materials preparations and procedure in this study.

Chapter 4: Results and Discussion

The chapter consist of the results and discussion of this study. The results from the proposed testing in Chapter 3 will be in this chapter. The analysis of the results of various mechanical testing such as tensile test, tear test, hardness test, impact test, swelling test, X-Ray Diffraction (XRD) test and Scanning Electron Microscopy (SEM) will be carried out in order to investigate the mechanical properties. The results will be analyzed and discussed in relative to the problem statement.

Chapter 5: Conclusion and Recommendation

This chapter consist of conclusion and recommendation. The whole research was concluded in this chapter and the suggestion for future study will be stated here.

CHAPTER 2

LITERATURE REVIEW

2.1. Introduction

This chapter revises the earlier research works that has been done from a few years back which related on Electromagnetic Interference (EMI) shielding and its material. One of the objectives of this research is to study the impact of filler hybridization on the physical and mechanical properties of the thermoplastic elastomer. In recent years, there is some research of conductive fillers applied in the industry. However, until today there are limited source of information especially on Polypropylene added with carbon black, carbon nanotube and graphene nanoplatelets.

2.2. Electromagnetic Interference (EMI) Shielding

The application of electronic devices in entertainment, military and industrial has been rocketing since 2000s, also comes with it is radio frequency interference (RFI), electromagnetic interference (EMI) or categorized as noise pollution that can cause malfunctioning and interference to the electronic device. One of the most common EMI that occurred in our daily life is electrostatic discharge (ESD) which is distortion of the television broadcast reception, radio static and disturbing sound from audio system such as speakers. Besides, EMI contains many unwanted radiated signals that can cause these disturbances. Other than that, EMI can cause health hazards to human being too. Thus, effective shielding of components from its adverse effects is very indispensable and nowadays there are so many EMI shielded products.

Since EMI came from electromagnetic waves with high frequency signal that transmitted out of electronic devices to the surrounding environment, the EMI shielding's function is to prevent the interference either from the incoming or outgoing from and to the devices. In order to prevent EMI, shielding effectiveness have been studied. Shielding effectiveness (SE) is a ratio of impinging energy to residual energy. When an electromagnetic wave passes through the shield, it is absorbed and reflected. Residual energy is the energy that is not reflected or absorbed by the shield but instead appears to be ejected from it. Magnetic field (H) and electric field (E) are two essential components of electromagnetic waves. Magnetic field and electric field are perpendicular to each other and the direction of wave is at right angles to the plane containing two components. It is shown in Figure 2.1. Wave impedance also known as ratio of electric field (E) to the magnetic field (H). SE is a function of frequency and can be expressed as:

$$SE = 20\, log \frac{E_t}{E_i} \qquad \text{Equation 2.1}$$

$$SE = 20\, log \frac{H_t}{H_i} \qquad \text{Equation 2.2}$$

Where E and H are electric field and magnetic field respectively. Subscripts t and i refers to the transmitted and incident waves. E is measured in volts/m and H in amps/m.

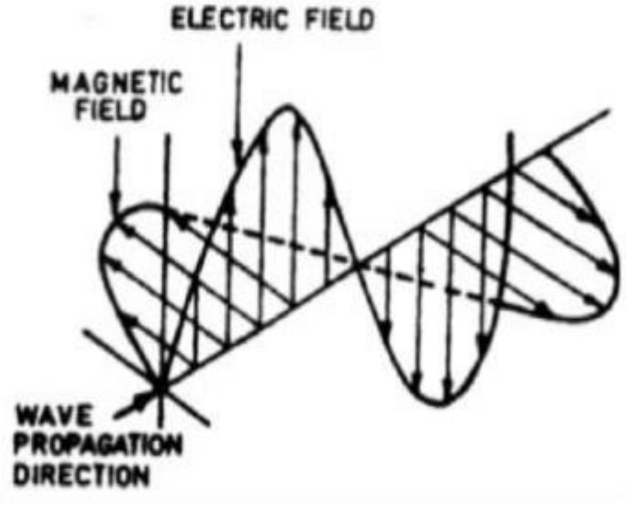


Figure 2.1: Electromagnetic Radiation Vector (Guo et al., 2013)

EMI shielding comprises the near field shielding region and far shielding region which is distance between radiation source and the shield is less than $\lambda/2\pi$ is near field shielding region and at this region, electric and magnetic dipoles is used for EMI shielding. When the distance is larger than $\lambda/2\pi$, it is a far shielding region and the EMI shielding based on electromagnetic plane wave is applied in this region.

EMI shielding effectiveness can be measured by 4 method which is Open Field or Free Space Method, Shielded Box Method, Shielded Room Method and Coaxial Transmission Line Method. The open field or free space method is used to evaluate the practical shielding effectiveness of electronic assembly. Shielded Box Method is used for comparative measurements of test specimens of different shield materials. Next, Shielded Room method is the most advanced and has been developed to overcome the limitations of the Shielded Box Method. Lastly, Coaxial Transmission Line Method is commonly used for the measurement of shielding effectiveness which overcome the limitations of the shielded box technique and it is the most recommended method.

2.2.1. EMI Shielding Materials

To prevent electromagnetic interference (EMI), EMI shielding materials need to have conductivity properties. Even with high conductivity does not required in order to block EMI which is a volume of resistivity of the order of 1 $\pi\Omega$ cm is good enough (Chung, 2001), but the better the conductivity of materials, the better they are at absorbing, reflecting, and transmitting the EMI. EMI shielding materials usually consist of metals and plastic that are embedded with metal foil as a shield due to their conductivity properties. Generally, metal is a good conductor of electricity, they can protect electrical equipment from static charge and heat obliterated which is can be related to the high frequency electromagnetic radiation can be prevented from escaping the equipment or the equipment is shielded from stray radiation by using metal as a shield and covers.

Commonly, material used for shields and covers is mu-metal. Mu-metal is a nickel-iron soft magnetic alloy with high permeability which is very suitable for shielding sensitive electronic devices against static charge and low-frequency magnetic field. It has a few compositions used in industry. One of them is 14% iron, 5% copper, 1.5% chromium and 79.5% nickel (Guo et. al.,2013). In addition, brass, aluminium, silver, nickel, stainless steel, and conductive carbon or graphite composites are also the type of metals material that is used in EMI shielding and their electrical conductivity is shown in the Table 2.1 below. Nevertheless, these conductive composites have their own distinctive limitation such as high density of metal which means it is heavy, brittleness for carbon and graphite and low impact resistance for aluminium based material. Usually, metals will not corrode easily which can affect the shielding effectiveness of the metallic shields.

Table 2.1: Electrical Conductivity of Metals

Metals	**Conductivity (S/cm)**
Silver	$6.8x10^5$
Copper	$6.4\ x10^5$
Aluminium	$4.0\ x10^5$
Brass	$1.7\ x10^5$
Nickel	$9.7\ x10^5$

2.2.2. Polymer Composite as EMI Shielding Material

Rubber and plastics nonconducting material and transparent to EMI. Basically, plastic housing act as insulators whereby they do not reflect nor absorb EMI and most of the EMI can pass through the plastics easily which can cause interference problem. In the polymer matrix, embedded thin metal foils of aluminium, copper or silver are in vogue with sufficient grounding provisions. The shielding efficiency depends on the foil material, the thickness of the embedded foil and the effectiveness of the grounding arrangement. In order to shield the component or devices from EMI by using this material, the electrical conductivity must be considered by the way of the conductive coating on plastic, compounding with conductive filler and intrinsically conductive polymer.

Conductive coating on plastics is a method used for metalizing the plate surface for the purpose of shielding from EMI. However, this particular method has its own limitation which is coating operations are secondary to the moulding operation and hence demanding some addition in the preparation and special equipment in order to execute this operation.

Compounding with conductive filler is the most common method used for conducting the polymer composites and become one of the EMI shielding material. Generally, plastic is an excellent electrical insulator. This method is applied by incorporating the plastic materials with the conducting material as the fillers. Supri et al., 2016 have studied in polyethylene glycol diglycidyl ether (PEDGE) as surface modifier and type of conductive fillers into polyvinyl chloride (PVC). According to them, the addition of PEDGE shows lower tensile strength but higher modulus of elasticity and electrical conductivity for all compositions of PVC/PEO conductive films which is to prevent the EMI from incoming or outgoing. According to Bowyer and Bader, 1972, the composites of very high specific strength and stiffness produced by incorporating continuous aligned filaments of glass and carbon into matrices of thermosetting plastics like epoxy or polyester. Das et al., 2000 have reported that the EMI shielding characteristics of natural rubber and Ethylene-vinyl acetate (EVA) filled with conductive carbon black (Vulcan XC-72) and short carbon fiber (SCF). In their research, they stated that ethylene-vinyl acetate (EVA), also known as polyethylene-vinyl acetate (PEVA) based composite is more effective in EMI shielding when used with short carbon fiber (SCF) as the conductive filler. The shielding effectiveness of the composites is also higher compared to carbon black.

In the interim, intrinsically conducting polymer method is technological uses of conducting polymers as active electrode materials in energy storage, display equipment and their intended use for electromagnetic radiation control and electrostatic charge dissipation. Therefore, intrinsically conducting polymer is a method that is affective for EMI shielding applications.

2.3. Classification of Composite

Figure 2.2 shown the classification of composites materials (Campbell, 2010). Composite are divided into two main groups which are Fiber-reinforced composite and Particle-reinforced composite. The example of particle-reinforced is cubic, and irregular shape. The arrangement of particulate reinforced is random and preferred arrangement. Single layer composites can be divided into two which are continuous fibers and discontinuous fibers. The continuous fiber have high aspect ratio and the discontinuous fiber low aspect ratio. Aspect ratio is the length of the cross-sectional area. The suitable orientation for continuous fiber composite is by unidirectional and the corresponding random that from woven reinforcement. For multi-layered composite, it is classified as laminates or hybrids. The laminates are a sheet constructed by stacking layers in the sequence. It may be between 4 to 40 layers and different degrees of orientation. While the hybrids are multi-layered composites with mix fiber in manner of ply or layer by layer.

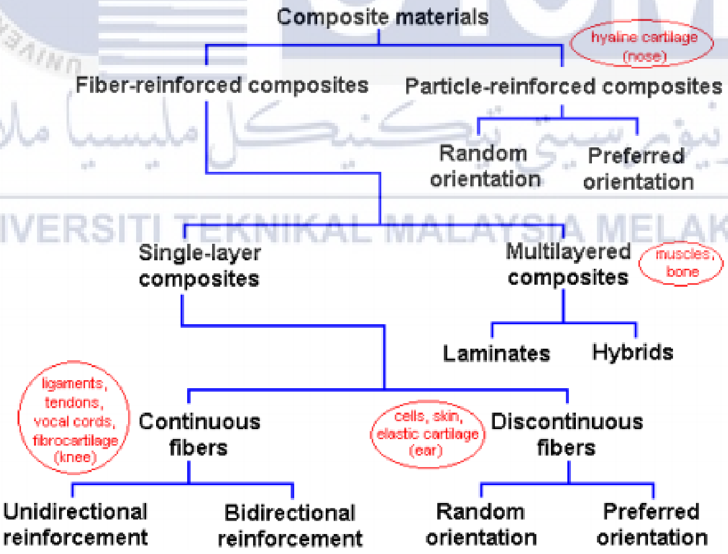


Figure 2.2: The Classification of Composites

2.3.1. Basic Element of Composites

2.3.1.1. Matrix

The matrix phase of fibrous composites may be a metal, polymer, or ceramics. For this research, the matrix of the composites is polypropylene which from thermoplastic polymers group. Since polymers are ductile, they are employed as matrix materials in ceramic-matrix composites. A reinforcing component is added to improve fracture toughness. The matrix provided several capabilities for fiber-reinforced composites. First, it acts as a medium via which an externally imposed stress is transferred and dispersed to the fibres; nevertheless, only a tiny portion of the applied load is sustained by matrix phase. In addition, the matrix material must be ductile. Furthermore, the elastic modulus fibre should have a significantly greater value than the matrix. The matrix's second purpose is to shield individual fibres from surface damage caused by mechanical abrasion or chemical reactions with the environment. Lastly, the matrix acts as a barrier to the fibres, preventing the propagation of brittle breaks from one fibre to the next, resulting in catastrophic failure.

2.3.1.2. Reinforcement

Reinforcement composites existed in type of particulate and fibres form. In this research, the reinforcement that has been chosen is graphene nanoplatelets, carbon black and carbon nanotubes. Whiskers, fibres, and wires are the three different types of reinforcement available. Graphene reinforcement was classified in whisker group. The whiskers are made up of incredibly thin single crystals with significant length-to-diameter ratios. They are also free of defects and have a high degree of crystalline perfection, impacting their incredibly high strength. They are among the most effective materials known. Since whiskers are very costly, they are not completely usable as a reinforcement medium. In addition, it is difficult and not necessary to integrate the whiskers into a matrix. The example of whiskers material including graphite, silicon carbide and aluminium oxide. The fiber material are polycrystalline or amorphous and consist small of diameter.

2.4. Filler

In polymer engineering, filler is described as relatively inert, finely divided substance such as calcium carbonate, carbon or graphite, glass spheres, kaolin, silica or wood floor (Harald, 2004). The filler is incorporated into a polymer in relatively huge proportions to increase bulk. It is also proven that it will decrease the cost, modify the physical, mechanical, thermal, electrical or other properties.

To be effective as a reinforcing agent in rubber, a filler must be evenly dispersed and form a large polymer filler interface with higher surface adhesion between rubber and filler. Chemical compatibility is necessary for filler dispersion (Munirah et al., 2016). The presence of reinforcement fillers will influence the processing characteristic and network structure of rubber as well. Particulate fillers are often incorporated into rubber to increase various desirable properties needed for different applications and to reduce cost.

Rubber reinforcement by rigid entities such as carbon black, clays, silicates, and calcium carbonate are one of the most important phenomena in material science (Sobhy, El-Nashar, and Maziad 2003). These fillers or reinforcement aids are added to rubber formulations to optimise qualities that meet a certain service application or set of performance standards. Although the initial goal is to reduce the cost of the moulding compounds, the selective active fillers and their quantity, which produce specific improvements in the physical properties of rubber, are now of primary importance.

2.4.1. Conventional Fillers

Since the start of twentieth century, conventional fillers which is specially layered silicates have been used as effective reinforcing agents in rubber formulation to produce conventional composites for a variety application (Jayaraj et al. n.d.). With the help of modern techniques, layered silicates as nanofillers are now implement into rubber with important enhancement in physical properties.

Filler is also known as reinforcing agent which defined as a material such as carbon black, kaolin or zinc oxide in finely divided form is added to elastomers or plastic usually in relatively high percentages to increase strength, hardness and abrasion resistance (Harald 2004).

Particulate fillers have long been used as additions in a variety of rubber products (Pangamol et al. 2018). Reinforcing and non-reinforcing fillers are the two types of fillers that can be used in rubber. Reinforcing fillers are chosen over non-reinforcing fillers in engineering applications due to their ability to improve rubber characteristics. Silica and carbon black are examples of reinforcing fillers used in the rubber industry, both of which can improve the mechanical qualities of rubber products. The tensile strength, abrasion resistance, modulus of elasticity, and hardness of rubber containing such fillers have all increased. Precipitated silica, made by precipitating an aqueous sodium silicate solution, and fume silica, made by the pyrogenic process, are two types of silica used in the rubber business.

2.4.2. Types of Conductive Filler

Since electronic devices become part of daily routine nowadays, many researches related to type of conductive filler have been done in the past. Generally, there are several types of conductive filler commonly used which are silver-plated aluminium. This type of filler is considered as the best conductive filler in terms of galvanic corrosion compatibility with aluminium alloy components. This filler also has a very good high temperature performance. Besides, nickel coated carbon is a conductive filler with excellent high temperature resistance and very good electrical or shielding performance. This filler also low in cost with is make it most commonly used. Furthermore, silver-plated copper also acts as conductive filler with excellent conductivity, and low contact resistance. Carbon which is has a low costing and can be used for some less demanding EMI shielding application also one of type of conductive filler. Subsequently, silver-plated nickel, silver-plated glass and pure silver also type of conductive filler that commonly used nowadays with a different of their properties.

Carbon black/fibres was one of the first materials used for the purpose of conductive filler. Since carbon black is a semiconductor, the typical resistivity of carbon black is in range of 20-0.5Ω cm and when used as a filler in polymer matrix composites it endowed the compound with conductive properties (Guo et. al.,2013). Aluminium fibres also one of the conductive fillers with the advantage of low specific gravity. However, this material is a subject to surface oxidation under normal environment. Aluminium flakes which are a various flakes and powder that also considered as filler have a high aspect ratio and achieved commercial significant in EMI shielding composites. Nickel coated graphite fibres is the type of filler that used as conductive additive for plastics and by combination of advantages of the conductivity of the metal coating with reinforcing properties of carbon/graphite fibres. Therefore, the insulator plastic material or polymer matrix composites can be change to conductive material by these metals or metallised filler which is a conductive material and at once make these material act as EMI shielding applications. However, these conductive fillers not widely use due to their own limitation.

2.4.3. Functionalization of Conductive Filler

The process of altering a material's surface chemistry to introduce new features, functions, capabilities, or qualities is known as functionalization. In other words, by functionalizing conductive filler, polymer matrix composites or plastics can be conductive materials that can be used as EMI shielding materials. The process of functionalization entails attaching molecules or nanoparticles to the surface of a material, either chemically or via adsorption. Georgakilas et. al., 2012 have studied about functionalization of graphene. In their research, conductivity properties of graphene have been found in the functionalization of pristine graphene sheets with organic functional groups. This research can be related to the functionalization of conductive filler for the purpose of EMI shielding application.

2.4.4. Advantages of Functionalization

The advantages of functionalization are dependent on the properties of two different materials to be used since functionalization is the process of introducing new functions or properties to a substance by modifying the surface chemistry of the material. P. Ma et. al.,2007 have been studied about effects of silane functionalization of Multi-wall carbon nanotubes (CNTs) on properties of CNT/epoxy nanocomposites. In their research, results showed that grafting silane molecules onto the CNT surface improved the dispersion of CNTs in epoxy along with much enhanced mechanical and thermal properties as well as fracture resistance of nanocomposites compared to those containing CNTs without functionalization. However, due to the wrapping of CNTs with non-conductive silane molecules, electrical conductivity of nanocomposites decreased. According to Kuila et. al.,2012 which is have done the research about chemical functionalization of graphene and its application, functionalization can be perform by covalent and noncovalent modification techniques. Functionalization of graphene can overcome the tendency toward aggregation and processing difficulty of the problematic using pure graphene. Very low graphene content is the most important aspect of these nanocomposites and by functionalization graphene, it provides good mechanical properties such as high strength and modulus are required with only small amount of fillers. However, with this form of alteration, the electric conductivity of the functionalized graphene is greatly reduced. Electrophilic substitution of diazonium salt on the surface of partially reduced graphene is suggested in order to obtain graphene conductivity. Noncovalent alteration on a pre-reduced graphene surface of a small organic polymer can also produce improved electrical conductivity.

2.5. Graphene Nanoplatelets

A monolayer of graphene has been found really high which is more than 1 TPa through intrinsic Young’s modulus but it cannot be fully utilized in bulk nanocomposite due to inefficient stress transfer from low modulus matrix to high modulus filler by shear at the filler/matrix interface (Liu et al., 2018). Graphene is consisting of single graphite layer having a thickness of one atom. GNPs are exfoliated graphite stacks with a high aspect ratio. The method utilized to combine GNPs inside the matrix of composite materials and the capacity to create chemical connections with polymers are two obstacles that arise with the single nanoplatelet, despite its high characteristics. (Elmarakbi et al, 2020). GNPs have remarkable electrical, thermal and mechanical properties which containing dozens of carbon-atomic stacking layers (Liu et al., 2020). GNPs also have excellent thermal and electrical conductivities, as well as outstanding mechanical qualities, including an elastic modulus of 1100 GPa and a tensile strength of 125 GPa, according to reports (Matalkah et al, 2019). Nowadays, because of its remarkable improvement in characteristics at minimal filler concentration, graphene has piqued academic and industry interest. Graphene, a single-layer carbon sheet with a hexagonal packed lattice structure that was discovered in 2012, has a number of unique properties, including the quantum Hall effect (QHE), high carrier mobility at room temperature, a large theoretical specific surface area, good optical transparency, high Young's modulus, and excellent conductivity. Graphene also has a zero-gap structure. Graphene has become popular in industry for applications such as electronic devices, energy storage, sensors, ESD and EMI shielding, and biological applications because to its numerous unique features. Graphene is a one-atom-thick sheet of carbon atoms arranged in a two-dimensional honeycomb lattice formed of carbon that is the world's thinnest, strongest, stiffest, and best heat and electricity conductor. The scanning probe microscopy of graphene honeycomb lattice pattern shown in Figure 2.2.

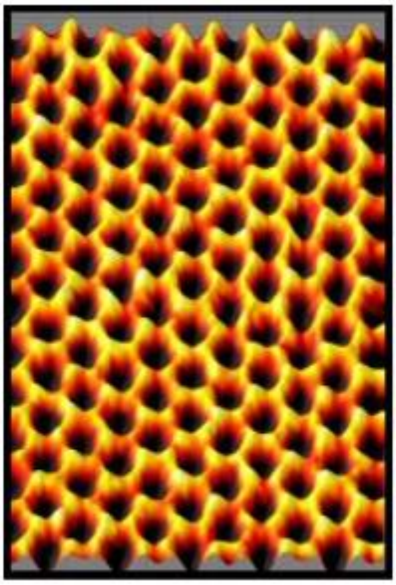


Figure 2.3: Scanning Probe Microscopy of Graphene Honeycomb Lattice Pattern (T. Das and S. Prusty, 2013)

Graphene-based polymer composites are made with graphene as a nanofiller. The polymeric utilised determines the type of graphene-based polymer composite. Polyaniline/graphene nanocomposites, poly 3,4-ethyldioxythiophene/graphene, epoxy/graphene nanocomposites, polystyrene (PS)/graphene nanocomposites, polyurethane (PU)/graphene nanocomposites, polyvinyl alcohol (PVA)/graphene nanocomposites, and polyethylene terephthalate (PET)/graphene nanocomposites. According to T. Das and S. Prusty, 2013, graphene-based polymer composites show superior mechanical, thermal, gas barrier, electrical and flame-retardant properties compared to the neat polymer. Improvement in mechanical and electrical properties of graphene-based polymer composites also show much better in comparison to that of clay or other carbon filler- based polymer composites. Graphene show better nanofiller than carbon nanotubes (CNTs) in certain aspect such as thermal and electrical conductivity.

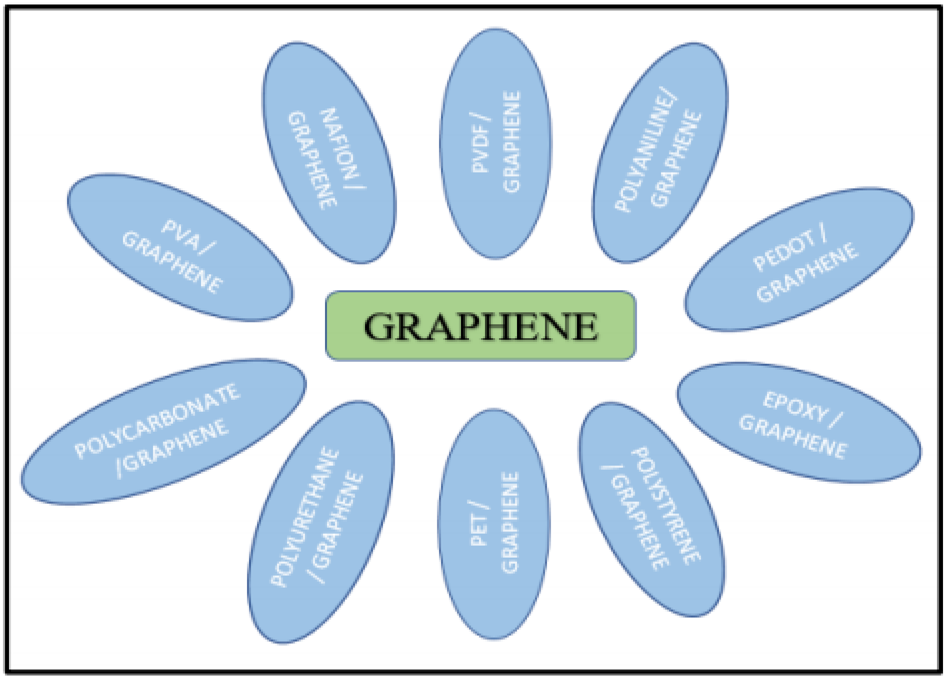


Figure 2.4: Type of Graphene-Based Polymer Composites (T. Das and S. Prusty,2013)

2.5.1. Properties of Graphene

2.5.1.1. Density of Graphene

With the unit of hexagonal shape that consist of two carbon atoms, graphene has an area of 0.052 nm^2. Due to this area, the density of the graphene should be 0.77 mg/m^2. A hypothetical hammock has measured 1 m^2 made from graphene have weight of 0.77 mg.

2.5.1.2. Optical Transparency of Graphene

Graphene has a unique optical property which is absorbing 2.3% red light and 2.6% green light. This value can be approximately by $\pi\alpha$ where α = fine structure constant. Due to its optical properties, this one atom thick crystal can be seen with the naked eye that shown in Figure 2.5. However, suspended graphene will not have any colour.

Figure 2.5: Photograph of Graphene in Transmitted Light.

2.5.1.3. Thermal Conductivity of Graphene

Due to the potential for thermal management applications, graphene has been attracted attention for research. In the past research, thermal conductivity of suspended graphene has been reported that an extremely large thermal conductivity with approximately 5300 $W.m^{-1}K^{-1}$. The large range of the thermal conductivity can be caused by large measurement uncertainties also by variations in the graphene quality and processing conditions. Thermal conductivity of graphene can reduce to about 500-600 $W.m^{-1}K^{-1}$ at room temperature when single-layer graphene supported on an amorphous material.

2.5.1.4. Electrical Conductivity of Graphene

This two-dimensional honeycomb lattice graphene sheet conductivity is given by $\sigma = en\mu$ where mobility, μ have a theoretically limit to 200,000 cm^{2}V^{-1} s^{-1} and acoustic phonons at a carrier density of $n = 1012$ cm^{-2}. Layer thickness bulk conductivity of graphene is 0.96x106 Ω^{-1} cm^{-1} which is higher than the conductivity of metal copper that only 0.60x106 Ω^{-1} cm^{-1}.

2.5.2. Application of Graphene Nanoplatelets

Advances in graphene preparation processes have resulted in a focus on novel material characteristics. The remarkable electrical properties of this material can be used in a variety of applications, including sensors, conductive materials, and supercapacitors. (Platnieks et al., 2020). Graphene has dramatic improvement in properties which make graphene have numerous application such as in biomedical or bio-engineering, energy technology or energy storage, electronic device, sensors, ESD and EMI shielding and nanotechnology as shown in Figure 2.6.

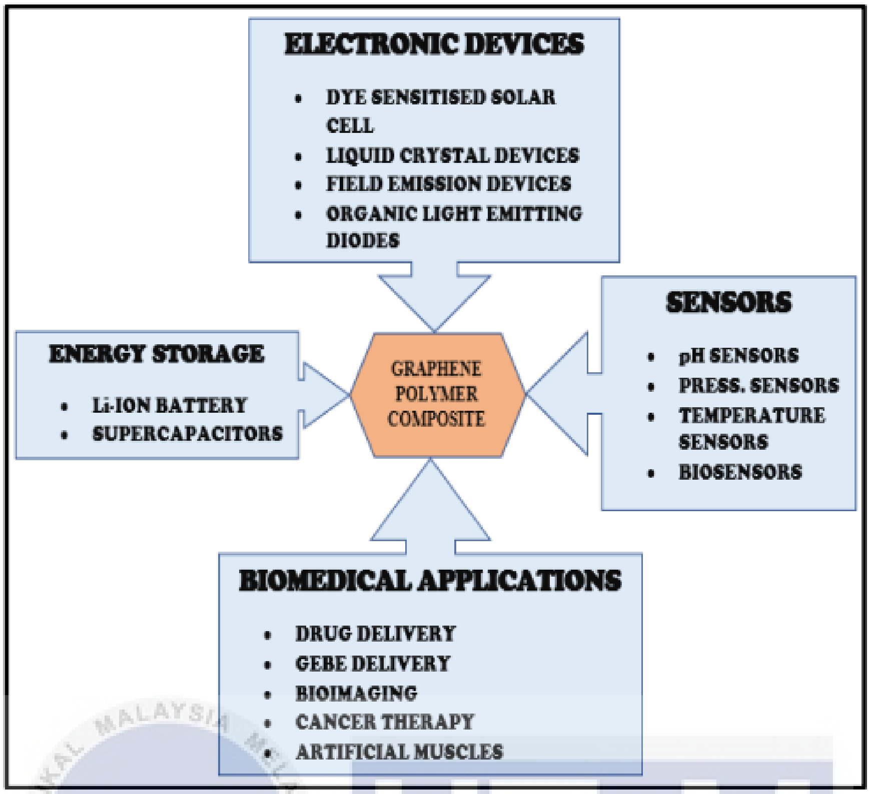


Figure 2.6: Application of Graphene-Based Polymer Composites (Yoo, E,2008)

Since graphene have high electrical conductivity, high carrier mobility and moderately high optical transmittance in visible range of spectrum, graphene have been used in solar cells, touch panels, smart windows or phones, light emitting diodes (LED) or organic light emitting diodes and (OLED) and field emission devices. Besides, Graphene/CNT composites have also prepared via solution blending in situ chemical vapor deposition (CVD) growth and have been applied in lithium-ion batteries (Yoo, E,2008). Due to this, graphene is also considered as one of the most promising energy storage systems. Furthermore, graphene has the properties of conductance changing as a function of extent of surface absorption and large specific area which leads to detect a variety of molecules gases and bio-molecules. It’s also can detect the pH, pressure, and temperature which make graphene good sensors application. In addition, graphene also a good ESD and EMI shielding materials. With intrinsic high conductivity and aspect ratio of graphene, it enables to absorb, reflect and transmitted the EMI. ESD and EMI shielding material can be applied to many applications such as carpeting floor mats, electronics packing to telecommunication antenna, mobile phone parts and frequency shielding coating for aircraft and electronics.

2.6. Thermoplastics

Thermoplastic can be melted easily and soften by heating, reshaped and reform it and solidified by cooling. This process may be reversible or can be repeated. Thermoplastics did not create a cross-linking like thermosetting material. This proved that they are can be reformable shape. It also can be amorphous or semi-crystalline, each with their properties. The amorphous type of thermoplastics materials has no order and it long chain of molecules can be totally entwined and also randomly arranged. Amorphous thermoplastics also have a temperature that variable range that can change from a hard and relatively at brittle to a viscous, and rubber state. The change of the states as mentioned before is known as the glass transition temperature (T_g) and the optimum temperature that amorphous plastics materials must be above of the polymer chains. This will enable to flow over other for processing.

Table 2.2: Classification of Thermoplastics

Name	Properties	Principal uses
Polypropylene	Light, hard but scratches easily, tough, good resistance.	Medical equipment, laboratory equipment, rope, kitchen equipment.
Polymethyl methacrylate (Acrylic)	Stiff, hard but scratches easily, durable, brittle, good electrical insulator, polishes well.	Aircraft canopies and windows, covers for car lights.
Polystyrene	Light, hard, stiff, transparent, brittle, water resistance.	Toys, especially model kits, packaging, and containers.
Low density polythene (LDPE)	Tough, good resistance to chemicals, flexible, fairly soft.	Packaging, especially bottles, toys, packaging film
High density polythene (HDPE)	Hard, stiff, able to be sterilized.	Plastic bottles, tubing, household equipment.

2.7. Rubber

Generally, rubbers are divided into two types. First type is thermosets and second type is thermoplastics. Three dimensional molecular networks, with the long molecules control along by chemical bonds known as thermosets. The three-dimensional molecular networks absorb swell and solvent. However, the three-dimensional molecular networks do not dissolve. Moreover, heating cannot reprocess the three-dimensional molecular networks. Primary chemical bonds do not connect the molecules of thermoplastic rubbers. Rather, they are linked by the physical aggregation of molecular components into difficult domains. As a result, thermoplastic rubbers dissolve incompatible solvents and soften when heated, allowing them to be treated several times. Thermoplastic and thermoset rubbers can be used interchangeably in a number of situations. Thermoset elastomers, on the other hand, are employed exclusively in demanding applications such as tyres, engine mounts, and springs due to their superior elasticity, set resistance, and durability. Rubber combination or formulation is the process of adding various compounds to raw rubber to give it interesting qualities. Rubber and elastomers are a number of the foremost common materials considerably acknowledged for its flexibility and their ability to soak up particle like carbon black, silica and clay in enhancing and getting the required properties for specific applications wherever resistance to impact or toughness are desired (Mohamed, Mohd Nurazzi, and Huzaifah 2017).

2.7.1. Natural Rubber

Natural rubber is an elastic substance contained in the milky juice (latex) of any various plants of the genus Hevea, especially the rubber tree (H. Brasiliensis) (Harald 2004). Latex consists of an aqueous dispersion of cis-1, 4-polyisoprene, (C5H8)n, an unsaturated, high molecular weight hydrocarbon for commercial purposes. This latex is coagulated by adding acetic or formic acid or sodium hexaflurosilicate and subsequently concentrated by evaporation or centrifugation. The processed latex is usually dried and converted into sheets of crude rubber. Besides, unvulcanised natural rubber has poor mechanical properties and chemical and environmental resistance but these are significantly improved by crosslinking (or vulcanizing). Usually, the improvement through treatment with sulphur or special chemicals. Natural rubber (NR) is the second largest type of rubber utilized in the world (Jayaraj et al. n.d.). NR based product have a high demand due to remarkable properties of NR that not exist in other materials. Excellent mechanical properties are maintained by NR with the addition of fillers, vulcanizing system and other specialty chemicals.

NR was a well-known polymer that has been widely used in a spread of commercial and engineering applications (George et al. 2000). The strain-induced crystallization behaviour makes NR distinctive among elastomers as so much as strength properties are concerned. NR has better strength and lower heat build-up and shows better performance at low temperature (Aprem et al. 2003). Natural rubber is well-known for its strain- induced crystallization behaviour (Ismail et al, 2010). It then shows outstanding properties, such as green strength. Furthermore, NR exhibits abrasion resistance and strong hysteric properties as well. It is, however, necessary for NR to be strengthened to achieve specific properties with the fillers.

CHAPTER 3

METHODOLOGY

3.1. Introduction

This chapter describes the proposed/suggested methodology as this study is based on critical review which consist of the principles of methods that performed to complete the research. The selection of material, processing, methods, equipment and testing are presented as well after refer attentively to the specification and particular of previous research.

3.2. Process Flowchart

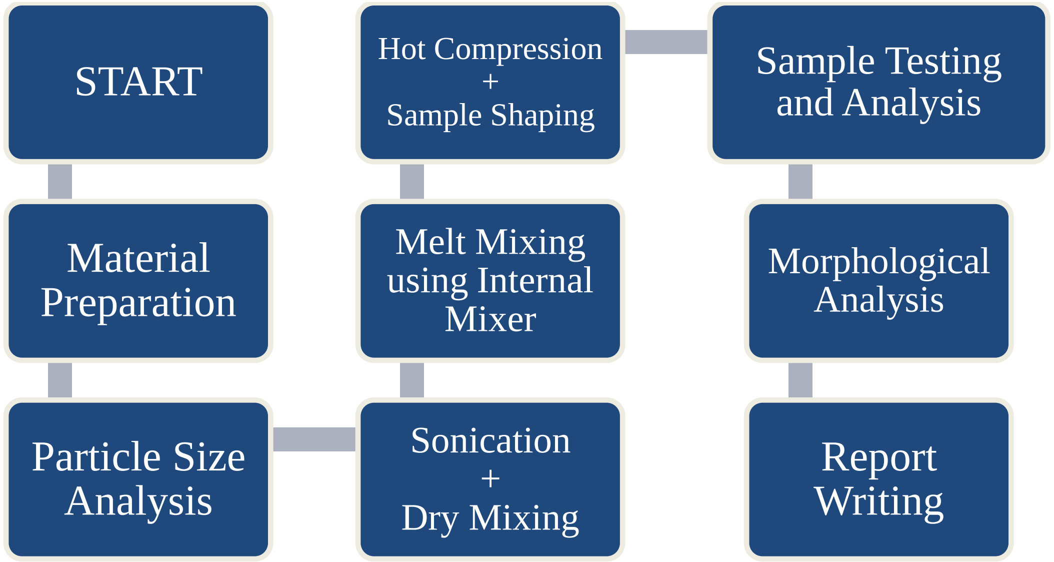


Figure 3.1: Research Methodology Flow Chart

3.3. Materials

In this research, polypropylene is proposed to be used as a polymer matrix composite to produce an electrically conducting polymer and hybrid fillers such as carbon black, GNP and CNT is proposed to be used as the conductive filler. Even though polypropylene is an inherently insulating polymer, the electrical properties such as electrical conductivity and shielding effectiveness is expected to be enhanced with the addition of these fillers. It also can enhance the physical, mechanical and thermal properties of polymer composite.

3.3.1. Polypropylene (PP)

Polypropylene is a linear hydrocarbon polymer expressed as CnH2n. It is also one of the most versatile polymers in the market with the usage as plastic and fibers. It is frequently used as automotive components and sailing dinghies in the industry. Its properties such as semi-rigid, translucent, good chemical and heat resistance and good fatigue resistance is very suitable for any kind of usage. In this research, we are proposing to use polypropylene is beads form making it easier to be moulded in spite of its semicrystalline nature. Its characteristics is as follows:

Table 3.1: Properties of Polypropylene

Polypropylene (PP)	
Density	905 kgm^{-3}
Tensile Strength	25 MPa
Tensile Modulus	1.0 GPa
Hardness	80 Rockwell Scale
Melt Temperature	210 - 290 ℃
Typical Mould Shrinkage	2%

(Figure 3.2: Polypropylene Beads)

3.3.2. Natural Rubber (NR)

Composed and loosely bound by long isoprene polymer chains. When pulled apart, they re-attach themselves, giving the rubber its elasticity and made from latex sap of rubber trees. Natural rubber has strength and flexibility but also has impurities and vulnerabilities to environment conditions and hydrocarbons. Natural rubber is one of the most flexible types compared to other rubbers. It is resistant to tearing, wear and abrasion. Applications of natural rubbers in industry which requires high wear and heat resistance, it is a very suitable material to be used in automotive, foam mattresses, and used as stabilization materials such as cement and new roads. Its characteristics is as follows:

Table 3.2: Properties of Natural Rubber.

Natural Rubber (NR)	
Density	0.95 kg/m^3
Hardness	30 – 95 Rockwell Scale
Tensile Strength	3.5- 24 MPa
Abrasion Resistance	Good
High Temperature Range	82 – 105 ℃
Low Temperature Range	-28 - -56 ℃

(Figure 3.3: Natural Rubber)

3.3.3. Carbon Black (CB)

Carbon black used for this study is N220 (Figure 3.5). It acted as reinforcing filler to improve the mechanical properties of the polypropylene. This reinforcing filler in Figure 3.4 shows particle size, structure, and surface chemistry are the three main properties of carbon black. When carbon black is mixed with resins or other vehicles, the spherical particle diameter is the fundamental property that significantly affects blackness and dispersibility. The greater the blackness of carbon black, the smaller the particle size. However, as the coagulation strength grows, dispersion becomes more difficult. Like particle sizes, the size of the structure also affects the blackness and the carbon black dispersibility. Increased structure size improves dispersibility while decreasing blackness. Carbon black with a larger structure, in particular, has excellent conducting properties. Carbon black has a variety of functional groups on its surface. The type and quantity of functional groups determine the affinity of black carbon with inks or paint varnishes. Carbon black with a large amount of hydroxyl group that has been oxidised (Figure 3.6) has a much better affinity for print inks or varnishes and has excellent dispersibility.

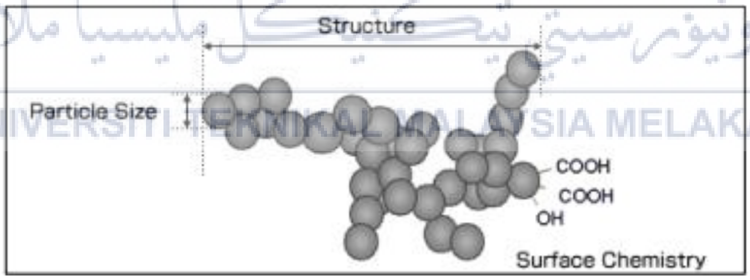


Figure 3.4: Structure of Carbon Black

Figure 3.5: Carbon black N220

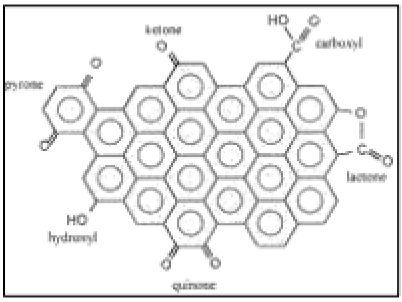


Figure 3.6: Chemical Structure of Carbon Black

3.3.4. Graphene Nanoplatelets (GNP)

Graphene nanoplatelets (GNP) or nanographene platelets (NGP) is proposed to be used as a conductive filler in order to shielding the ESD and EMI. The exfoliated graphene nanoplatelets is porposed to be used in this study were xGNP-C750-grade materials produced by XG Science, USA. This material was supplied by Terra Techno Engineering. By using the Mettler method (Metler-Teledo AG, Switzerland), the elementary analysis of graphene was classified as 88.68% carbon, 0.79% hydrogen, 1.11% nitrogen, and 7.65% oxygen. This type of nanographene particles typically consist of aggregates of sub-micron platelets which particles diameter <2µm, thickness of a few nanometres and surface area is approximately 750 m^2g^{-1}. The other properties of Terra Techno Engineering nanographene platelets is shown as in Table 3.2.

Table 3.3: Properties of Graphene Nanoplatelets (Terra Techno Engineering)

Terra Techno Engineering Nanographene	
Particle Size	5-25 µm
Density	2.2 g/m^3
Bulk Density	0.03 – 0.1 kg/m^3
Carbon Content	> 99.5 µm
Tensile Modulus	1000 GPa
Electrical conductivity	10^7 S/m
Thermal conductivity (at 300K)	3000 $W{\cdot}m^{-1}{\cdot}K^{-1}$

3.3.5. Carbon Nanotubes (CNT)

Carbon Nanotubes (CNT) are cylindrical molecules that can be single-walled (SWCNT) with a diameter less than 1 nanometer (nm) and multi-walled (MWCNT) which consists of several interlinked nanotubes with diameters more than 100 nm. CNT is chemically bonded with sp^2 bonds, an extremely strong form of molecular interaction. Their mechanical tensile strength is 400 times than steel, its density is one sixth of steel, thermal conductivity better than diamond and very high aspect ratio greater than 1000 is the characteristics that is suitable for the applications in the industry such as sporting goods, textiles and automotive. Its properties are as follows:

(Table 3.4: Carbon Nanotubes Properties)

Carbon Nanotubes (CNT)	
Size	0.6 – 1.8 nm in diameter
Density	1330 – 1400 kg/m^3
Tensile Strength	45 GPa
Tensile Modulus	1 TPa
Thermal Stability	> 3000℃

(Figure 3.7: Carbon Nanotubes Powder)

3.4. Sample Preparation

Since this is a critical review-based study, this would be the suggested sample preparation steps and formulation.

3.4.1. Formulation

The polypropylene (PP) will be mixed with natural rubber (NR) along with different types of hybrid fillers which is carbon black (CB), graphene nanoplatelets (GNP) and carbon nanotubes (CNT). Then, the mixture will be mixed using internal mixer based on the formulation of the materials. The machine is available either in UTeM or Saiko Rubber (M) Sdn Bhd located at Senawang, Negeri Sembilan. The mixture will be blend until both materials well-mixed together.

Table 3.5: Raw Material Formulations and Compositions

Formulation	**Composites**	**PP (wt%)**	**NR (wt%)**	**CB (phr)**	**CNT (phr)**	**GNP (phr)**
1	**PP**	100	0	0	0	0
2	**PP+NR**	75	25	0	0	0
3	**PP+NR**	50	50	0	0	0
4	**PP+NR+CB**	75	25	30	0	0
5	**PP+NR+CB+CNT**	75	25	29	1	0
6	**PP+NR+CB+GNP**	75	25	29	0	1

3.4.2. Sonication

For the preparation of graphene nanoplatelets and carbon nanotubes, it is proposed to be carried out in water/ethanol mixture where 70% ethanol and 30% distilled water. Firstly, graphene and carbon nanotubes were added into 600 mL ethanol-water and sonication process take place for 30 min by using Ultra Sonication Probe as shown in Figure 3.8. Then, the sonicated solvent was stirred at 80 ℃ for 2 hours. Afterward, the mixture was filtered with filters with pore size of 0.22 µm. After that, the product is then washed several times with methanol and distilled water sequentially and dried in a vacuum oven at 80 ℃ for 12 hours (Zhang et. al.,2016) and it becomes powder form. The process was repeated with other formulations too.

Figure 3.8: Ultra Sonication Probe

3.4.3. Melt Mixing

Melt mixing is one of the preferred methods for preparing polymer nanocomposites of thermoplastics. Usually, the polymer is melted and added with the fillers. This process is compatible with current industrial process such as extrusion and injection moulding. This process is done using internal mixer because there should be no vulcanization involved. Internal mixers consist of a chamber of two rotors that generate high shear forces, dispersing the fillers and other raw materials in the polymer which results in the production of a compound. After that, the compound is dropped to a mill or extruder when the mixing is completed for ease of handling. Different formulation would take different time to mix and size of internal mixer would be different too. We can control the temperature inside the mixer and mixing time by using the monitor. The samples are prepared according to the formulation.

(Figure 3.9: Internal Mixer)

3.4.4. Hot Compression

After the mixing process, the process continued with the rubber compound is molded in a press by using hydraulic press at high temperature.

(Figure 3.10: Hydraulic Press Machine)

3.4.5. Sample Shaping

Specimens are suggested to be shaped to 30 mm length, 20 width and 2 mm thickness mm with certain tolerance. Sample die for tensile and tear test is different.

3.4.5.1. Sample Shaping for Tensile Test

In order to make the test specimen, the blend between polypropylene and different type of filler are shaped by using hydraulic press (Figure 3.11) and dumb bell shape puncher (Figure 3.12). Sample for tensile test is shown in Figure 3.13.

Figure 3.11: Hydraulic Press

Figure 3.12: Dumb bell Shape Puncher

Figure 3.13: Dumb Bell Shape

3.5. Characterizations and Testing

In order to characterize the test specimen, several identification method and analysis have been done which is consist morphological analysis, characterize identification, thermal testing analysis, and mechanical testing analysis.

3.5.1. Particle Size Analysis

Used to characterize the size distribution of particles in a sample. The particle size of each fillers which is carbon black, graphene nanoplatelets and carbon nanotube is measured using Particle Size Analyzer (PSA) machine. The size of each filler is important for the result analysis.

(Figure 3.14: Particle Size Analyzer)

3.5.2. Mechanical Testing

The table shows the amount of specimen needed for each testing with different composition of fillers.

Table 3.6: Number of Test Run

Formulation	Tensile Test	Hardness Test	Impact Test
PP	2x	2x	2x
PP+NR	5x	5x	5x
PP+NR	5x	5x	5x
PP+NR+CB	5x	5x	5x
PP+NR+CB+CNT	5x	5x	5x
PP+NR+CB+GNP	5x	5x	5x

3.5.2.1. Tensile Test and Young’s Modulus

Tensile testing can be used to relate the ultimate state of cure as well as crudely relating to the cure rate. Standard applied for tensile test is ASTM D-412. Tensile testing at a standard rate is 500mm/min a distance of at least 750mm using special mechanical grips at each end of the dumbbell shape. Ultimate tensile strength and ultimate elongation result from pulling the dumbbell sample to rupture (failure). This is a destructive test, which relates to the intrinsic strength of the rubber compound. This test is suggested to be conducted for five times for each sample and average of tensile value is calculated. Figure 3.15 shown universal tensile machine. The sample is kept to observe fracture surface by using SEM.

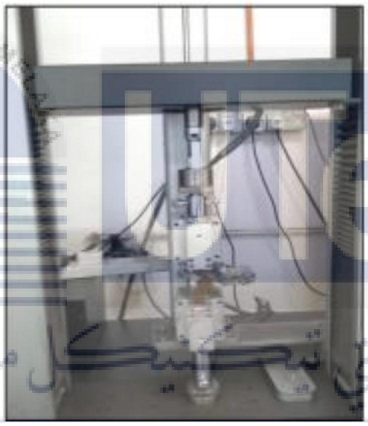


Figure 3.15: Universal Tensile Machine

3.5.2.2. Hardness Test

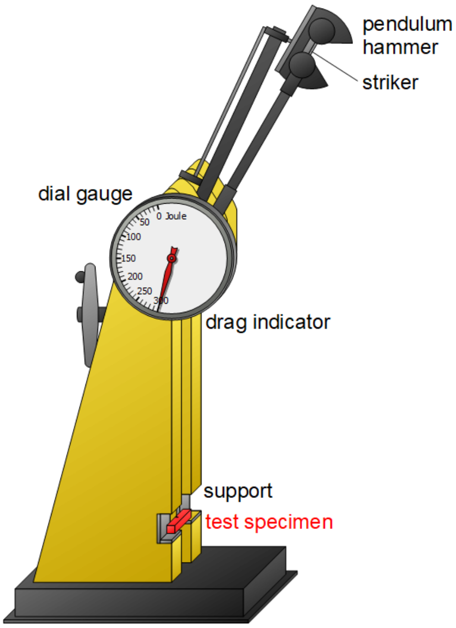
Hardness is defined by ASTM as the resistance to indentation as measured under specific condition. There are two different hardness test that claim nearly universal acceptance which are durometer and International Rubber Hardness tester (Alan N. Gent, 2001). For this test, Shore A Durometer (Figure 3.16) is proposed because type A scale is the most appropriate for rubber compounds such as used in engineering. Sample dimension was in circular shaped (Figure 3.17).

Figure 3.16: Shore A Durometer

Figure 3.17: Sample for Hardness Test

3.5.2.3. Impact Test

Directly related to the brittleness of a material, impact test is important to determine the impact strength, toughness of a material. These tests are to measure the total amount of energy a material can absorb without any damage occurred on the surface of the material. Thus, Charpy Impact Test is done to each sample to determine its strength and toughness. The specimen sized 55 x 10 x 10mm is placed and using a weighted pendulum, the pendulum is dropped from a specific height to make contact with the specimen. The result is determined by comparing the difference in the height of the pendulum before and after the fracture.



(Figure 3.18: Charpy Test)

3.5.3. X-Ray Diffraction

XRD (Figure 3.19) is applied in this study to investigate chemical composition of fillers which is carbon black, graphene nanoplatelets and carbon nanotubes.

Figure 3.19: X-ray Diffraction Machine

3.5.4. Swelling Test

Swelling test is proposed to be conducted under ISO 1817. The sample is shaped to 30 x 20 x 2 mm. Initial mass for each sample is recorded by using electric balance. Swelling test (Figure 3.20) is conducted by immersed swelling sample in petri dishes by pouring toluene organic solvent (Figure 3.21) until the sample drowned for 72 hours in dark environment at control temperature 25°C. After conditioning period, the swollen specimens were taken out and weighed again. The specimens were then dried in a drying oven at 70°C until constant weight was obtained.

Swollen percentage was measured by using Equation 3.1 and Q value (mass of toluene absorbed in each gram rubber compound) is calculated by using Equation 3.2. Swelling test is conducted for three times for each sample and average result is calculated.

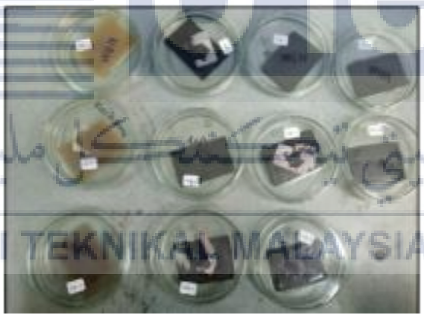


Figure 3.20: Dip Sample in Toluene

Figure 3.21: Toluene Solution

$$\text{Swollen (\%)} = \frac{W2-W1}{W1}\ X\ 100 \qquad \text{(Equation 3.1)}$$

Where W_1 was initial mass (gram) and W_2 was mass (gram) after sample was dip in toluene solvent. Mass of toluene absorb in each gram of rubber compound also calculated by using Equation 3.2 as stated below:

$$Q = \frac{Ws-Wd}{Wt-\frac{100}{Wt}} \qquad \text{(Equation 3.2)}$$

Where W_s swollen mass, W_d was final mass, W_i was initial mass and W_t was molecular weight of toluene which is 92.14 g/mol.

3.6. Morphological Analysis

In this research, observation of dispersion of CB or GNP or CNT in polypropylene matrix analysis is proposed to be done by Scanning Electron Microscopy (SEM) in order to get more accurate imaging of the CB, GNP and CNT. From the micrograph obtained, the relationship between morphology and PP composite properties can be interpreted.

3.6.1. Scanning Electron Microscopy

The scanning electron microscope (SEM) is the most common form of electron microscope. Electron scattering, also known as electron beam method, is used to examine the topography of the sample surface under inquiry. The cross-section surface of tensile fracture samples was examined using a SEM model ZEISS EVO 50 at magnifications of

200x, 1000x, and 3000x. Gold is applied to the samples (Figure 3.25) before proceed with SEM analysis. Figure 3.25 shown the SEM equipment to be used.

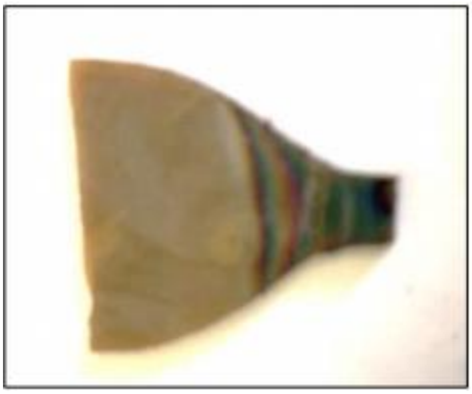


Figure 3. 22: Coated Sample

Figure 3.23: Scanning Electron Microscopy (SEM) Machine

CHAPTER 4

RESULT AND DISCUSSIONS

4.1. Introduction

This chapter intend to analyse and discuss both the experimental data and critical review for the results of several testing that has been conducted. The testing was conducted to verify that the project can achieve the objectives that have been mentioned. The particle size analyser (PSA) and scanning electron microscopy (SEM) of raw materials is based on experimental data. Meanwhile tensile test, Young's modulus, hardness test, impact test, X-Ray Diffraction (XRD), swelling test and scanning electron microscopy (SEM) of the composite is based on critical review.

4.2. Characterisation of Fillers

4.2.1. Particle Size Analysis

Characterisation of raw materials is important in order to understand the influence on properties of composites. Carbon Black (CB), Graphene Nanoplatelets (GNP) and Carbon Nanotubes (CNT) used in this study were characterized by using particle size analyser (PSA).

The goal of the particle size analysis is to determine the particle size range and average size for CB, GNP, and CNT. Particle size is significant because it influences composite processing abilities such as flow, mixing, and compaction. Besides, it will also affect the final formulation such as performance, appearance and stability of composites. There are 3 different fillers that is used in this project, all three fillers need to be around the same size particle to make the results comparable. Figure 4.1 to 4.3 summarize the data obtained for CB, CNT and GNP.

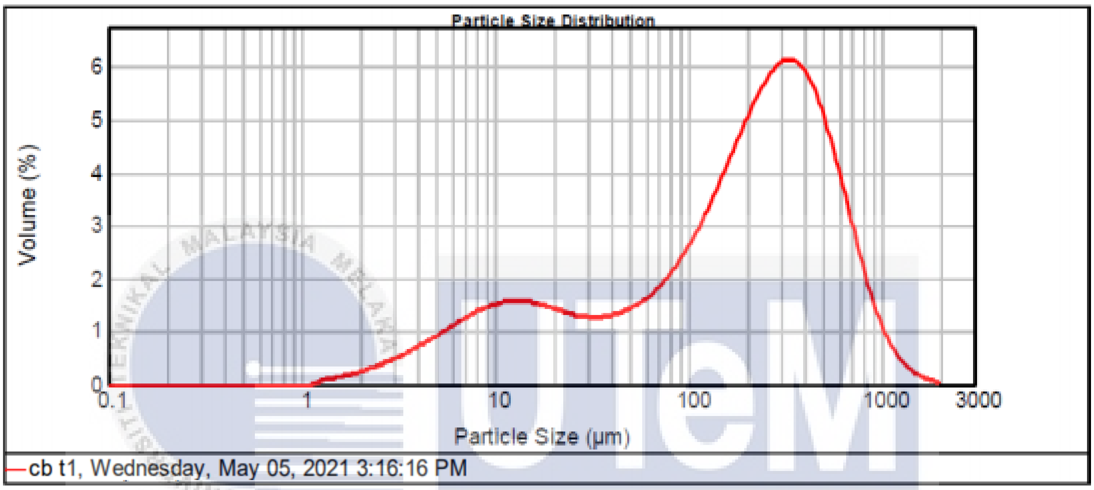


Figure 4.1: Particle Size Distribution for Carbon Black (CB)

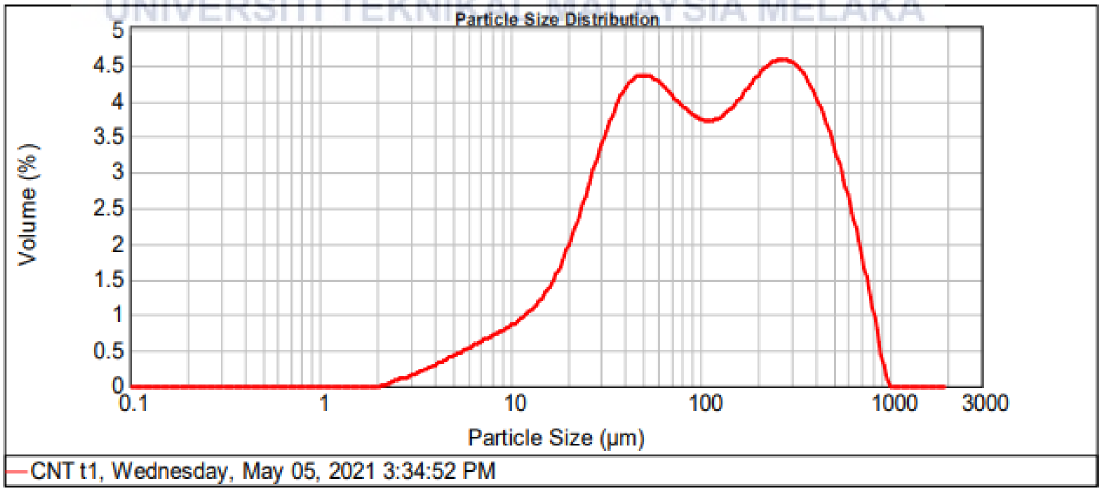


Figure 4.2: Particle Size Distribution for Carbon Nanotube (CNT)

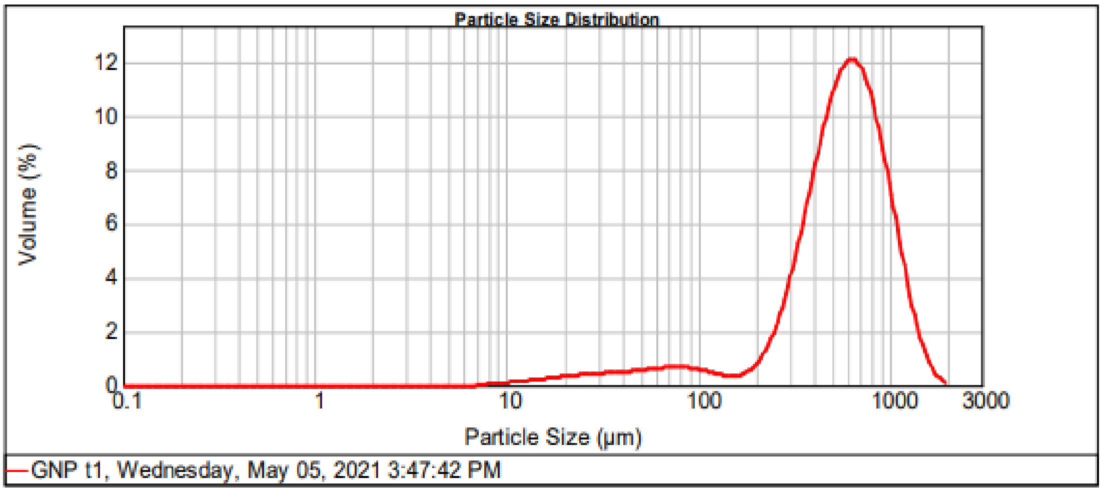


Figure 4.3: Particle Size Distribution for Graphene Nanoplatelets (GNP)

4.2.2. Scanning Electron Microscopy

Microscopic observation for CB, CNT and GNP was performed using SEM machine at 1000x and 3000x magnification in order to define the shape and size of the 3 raw materials. The scanning electron microscope (SEM) is a type of electron microscope that is used to provide information about the sample's surface topography. Figure 4.4, 4.5 and 4.6 shows SEM micrographs for CB, CNT and GNP respectively.

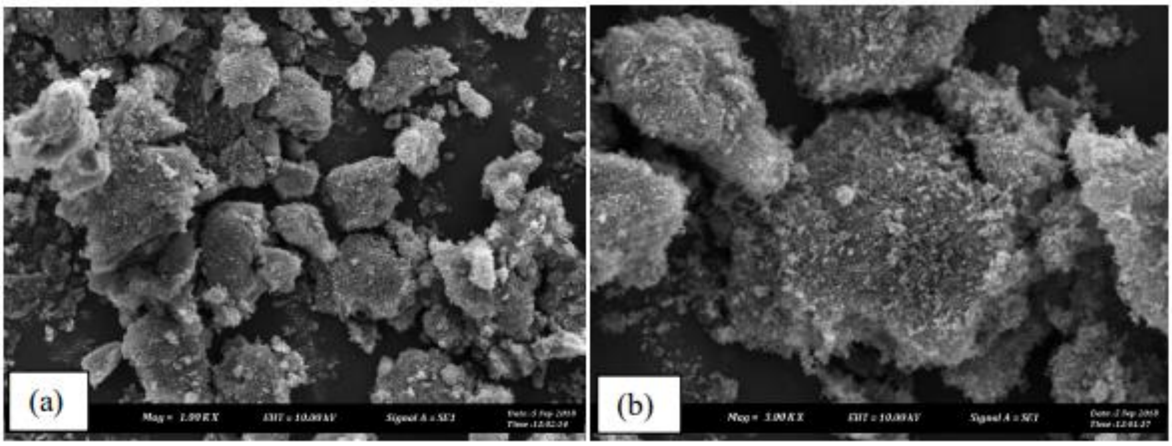


Figure 4.4: SEM for CB particle; (a) 1000x; (b) 3000x

SEM micrographs of CB particles as shown in both Figure 4.4. Through SEM shown, the particle shape is different from the shape of OPA particle. Unlike uneven an irregular shape, CB particles show it has had nearly a spherical shape. More uneven surface morphology and surface flaws resulted from carbon deposits on the surface of raw carbon black aggregates. This could explain why the specific surface area and micropore volume have increased.

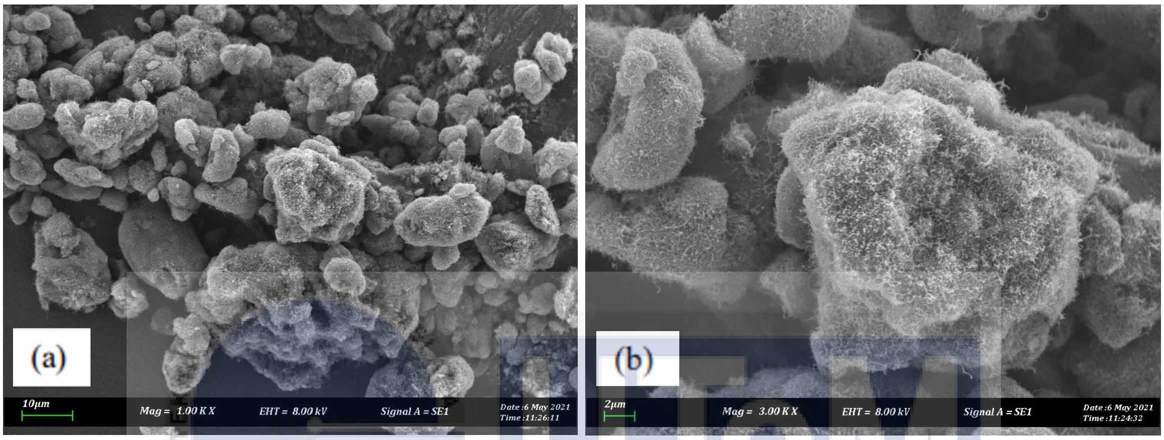


Figure 4.5: SEM for CNT particle; (a) 1000x; (b) 3000x

Carbon Nanotube is in close proximity self-assembled into very closely packed shells. It is very difficult to distinguish the individual tubes in the SEM images.

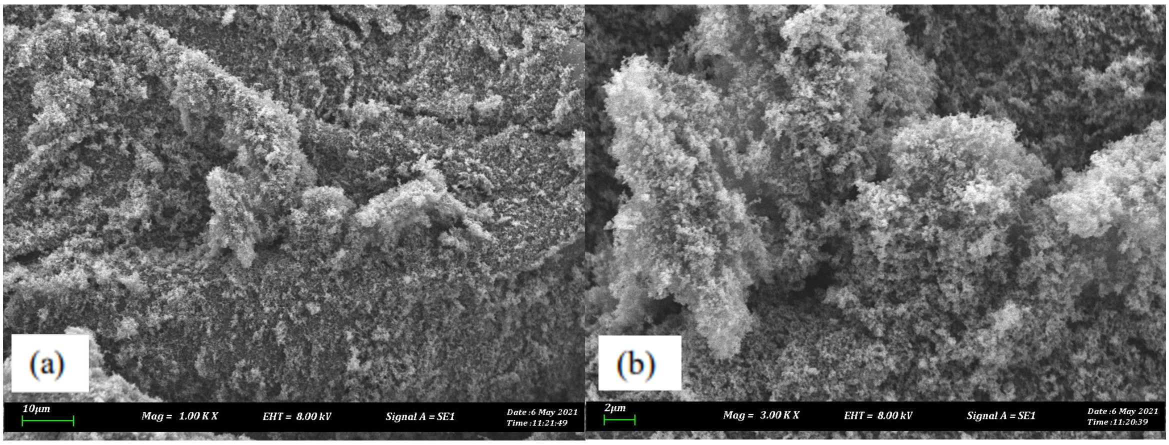


Figure 4.6: SEM for GNP particle; (a) 1000x; (b) 3000x

Meanwhile graphene nanoplatelet is experiencing agglomeration and need sonication process to agitate the GNP particles.

4.2.3. X-Ray Diffraction (XRD)

The presence of four peaks between 14° and 30° can be explained by the crystalline structure of PP phase. The peaks at 14.09°, 16.88°, 18.6° and 25.4° due to the (110), (040), (130) and (060) planes are characteristics of α-type monoclinic crystal structures of PP chains. The XRD spectrum of PP/NR blend shows sharp peaks associated with PP, as NR is fully amorphous (Chandran et al, 2015). Thus, in a well-blended PP/NR/CB, a similar XRD pattern is expected since the filler is fully exfoliated.

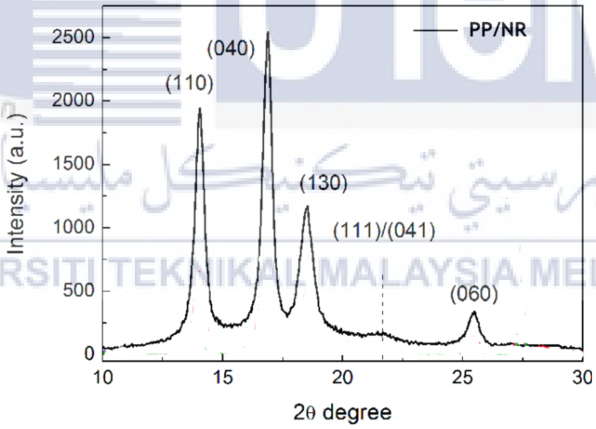


Figure 4.7: X-Ray Diffraction (XRD) of PP/NR (Chandran et al., 2015)

For all raw carbon black grades, the diffraction patterns are composed of three sharp peaks, which can be indexed as the (002), (10), and (004) graphite-type reflections.

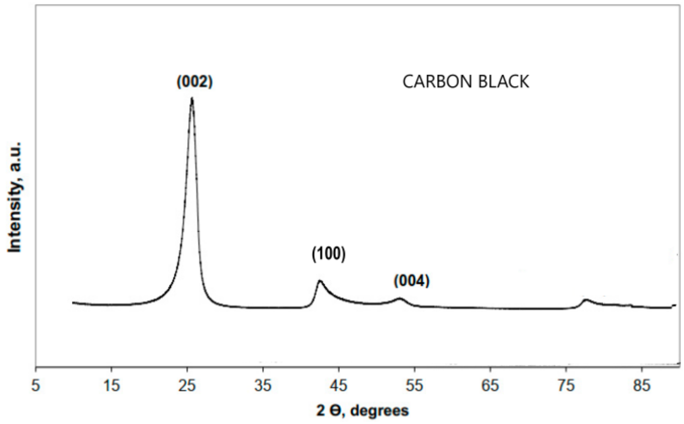


Figure 4.8: X-Ray Diffraction of Carbon Black (Jurkiewicz et al., 2018)

The sharp diffraction peaks in the XRD spectrum of CNT at 25.7° and 43.4° are attributed to (002) plane and (100) plane of graphite, respectively.

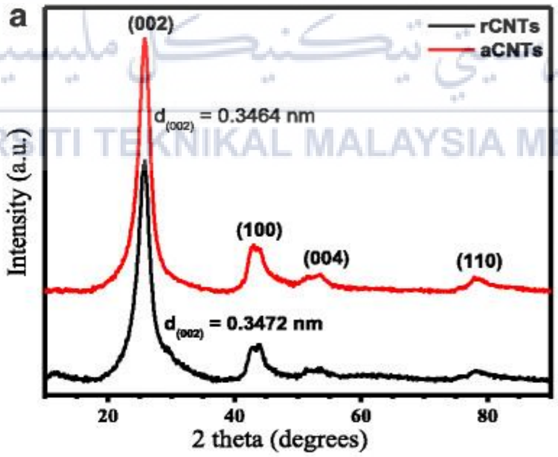


Figure 4.9: X-Ray Diffraction for CNT (Ramoraswi & Ndungu, 2015)

Figure 4.10 shows the XRD patterns of neat nylon 66 (control), pristine GNP and nylon 66/GNP nanocomposites The representative diffraction peaks of GNP can be clearly observed at 26.4°, 43.60°and 50.90°. These peaks can be assigned to the (002) (101) and (004) planes of graphitic carbon, respectively (Cunha et al., 2018). Meanwhile, the XRD pattern for nylon 66/GNP nanocomposite also shows exceptionally wide diffraction (Peak A and Peak B) from 21° to 23° which corresponds to reflection in α-form polyamide 6 crystal (Gong et al., 2015).

However, as 0.3 wt% GNP was added into the nylon 66 matrix, the diffraction peak of GNP observed around 26.4°, 43.6°and 50.9°disappeared. GNP was totally exfoliated into individual graphene sheets in the polymer matrix, and the regular and periodic structure of graphene had vanished, revealing the disordered and loose stacking of GNP, according to the XRD results in nylon 66/GNP composites (Linggawati, Mohammad and Ghazali, 2009).

Moreover, sharp albeit small diffraction peaks can be observed at 43.6° and 50.9° in the XRD patterns of the nylon 66/GNP containing 0.5 and 1.0 wt% GNP, which are associated to the presence of some GNP agglomeration in the composites with higher GNP concentration.

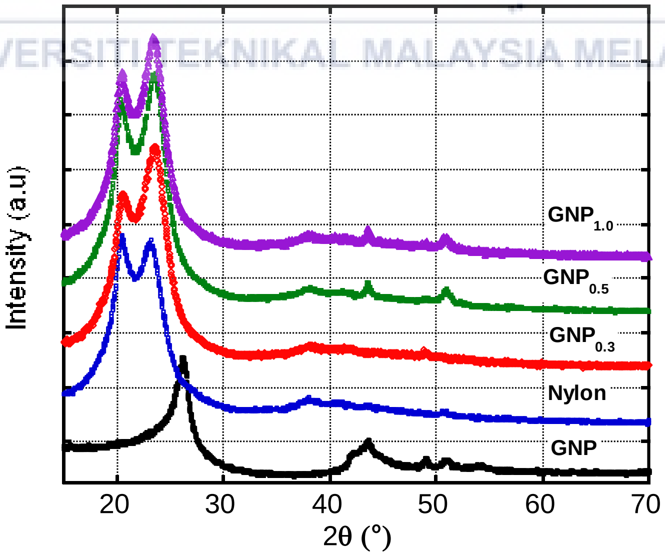


Figure 4.10: X-Ray Diffraction of GNP (Cunha et al., 2018)

4.3. Mechanical Properties of Composite

4.3.1. Tensile Test

As shown in Figure 4.11 by Suryadiansyah that the tensile test done on PP/NR. Stated that decrease of 43% of tensile strength from pure PP to 80/20 of PP/NR and decrease of 72% of tensile test from pure PP to 50/50 of PP/NR. The decrease in tensile strength could be attributed to agglomeration and particle-to-particle contact of rubber component. Based on studies by N. Mohamad et al., (2013), decrease in tensile strength is due to increase in rubber content imparts elastic behaviour of PP/ENR blends. In comparison to pure Polypropylene, the addition of rubber particles in the composite reduces crystallinity, resulting in reduced tensile strength of the PP/ENR blend. Therefore, it is predicted that the tensile strength will decrease by 46% (from 38 MPa to 20.35 MPa) at 75/25 compared to pure PP due to introduction of natural rubber to the blend which makes the blend become more elastic and decreases in crystallinity.

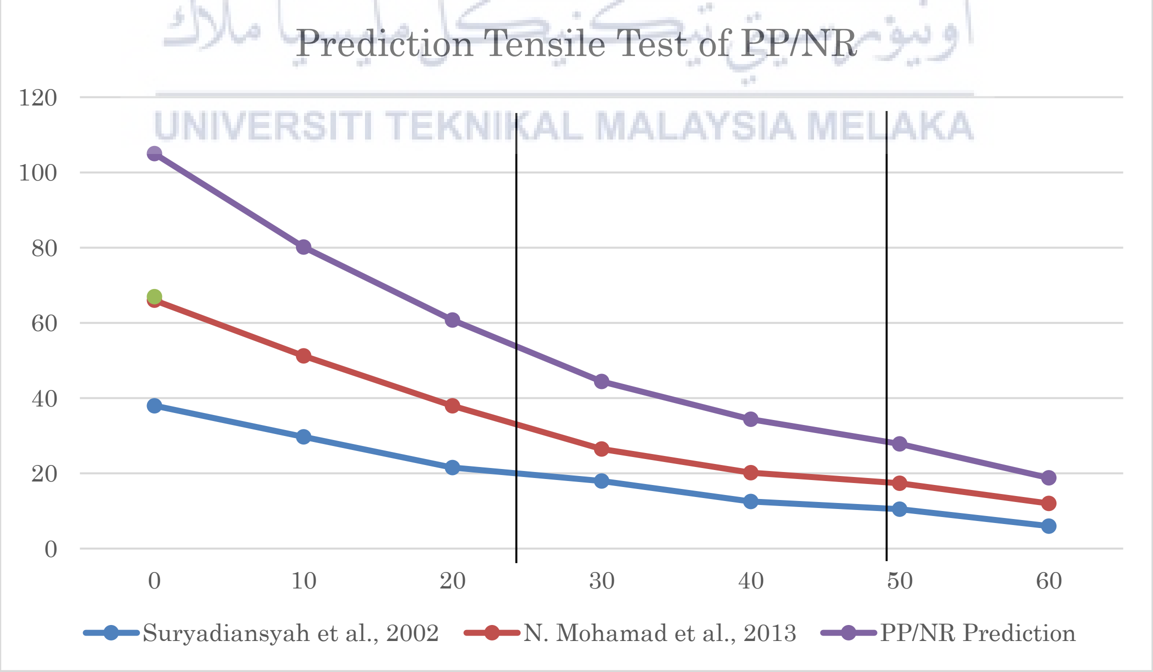


Figure 4.11: Predicted Tensile Test graph for PP/NR

Thongnuanchan et al., 2019 stated that increase of about 56% of tensile strength due to addition of 30 phr of CB into the blend. This is due to well dispersed CB in the rubber matrix which results in good rubber-filler interaction. Azura et al., stated with additional of 30 phr will give an increase of 44% to the tensile strength of the blend as the carbon black is evenly dispersed throughout the rubber matrix, interacting with it to generate high tensile strength. Taken from predicted 75/25 of PP/NR which is at 19.75 MPa. It is predicted that with additional of 30 phr of CB to 75/25 of PP/NR blend will gave boost in tensile strength from 20.35 MPa to 29.15 MPa (increase of 47%). This is due to good dispersion of CB in the blend.

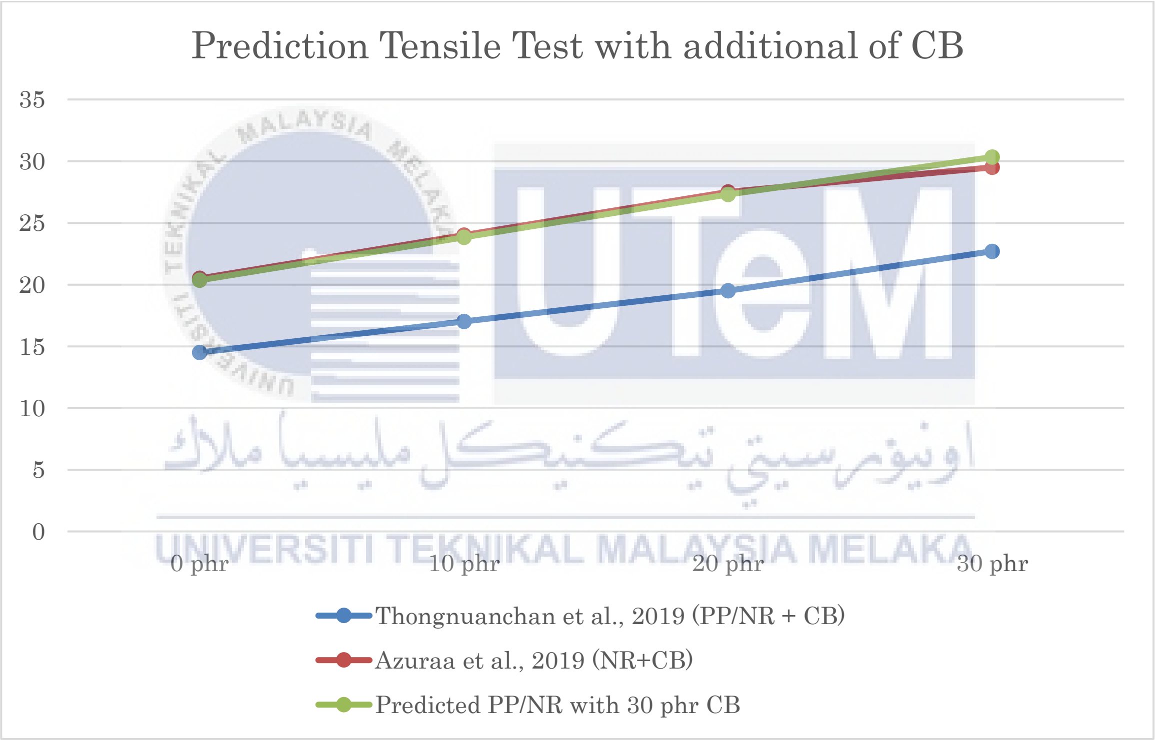


Figure 4.12: Predicted Tensile Test with additional of CB

Next, for the additional of CNT as fillers in the blend. A. Das et al., 2012 stated in Figure 4.13 that with the additional of CNT will give additional of 39.2% of tensile strength to the blend. MWCNT has a high aspect ratio, which allows it to build networks in polymer matrix with very low filler. (A Das et al., 2012) Meanwhile Sahrim et al. stated that with additional of 1 phr of CNT to the blend will give 29.2% of tensile strength to the blend caused by the strong interactions between PP/NR matrix and CNT, good dispersion of MWNTs in the nanocomposites which may have an effect of physical crosslinking points, thus increase the tensile strength. Additional of 1 phr of CNT to the blend will give increase of 27.6% to the blend caused by interfacial bonding between nanotubes and the rubber matrix which determines the efficiency of load transfer from the polymer matrix to the filler. (M. G. Maya et al., 2020). Therefore, will be predicting that with additional of GNP/CNT to the blend will give additional of 23.7% (from 29.15 MPa to 36.06 MPa) which is caused by the good dispersion of CNT to the blend.

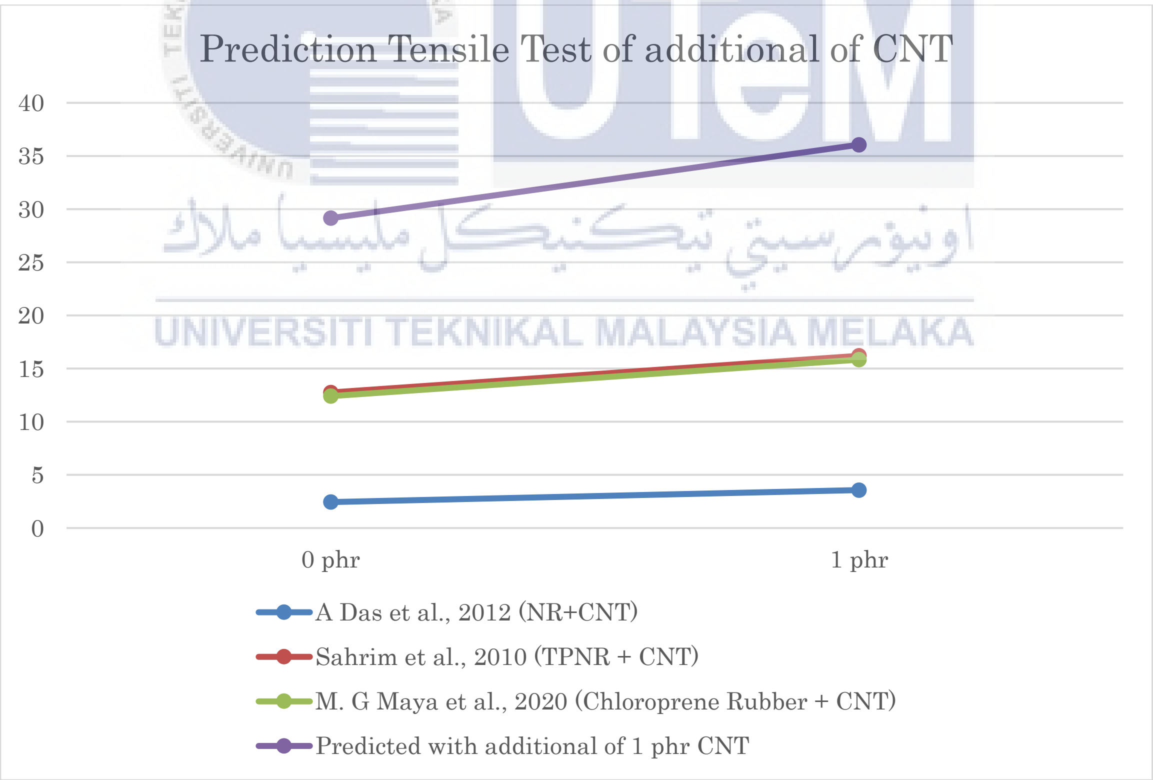


Figure 4.13: Predicted Tensile Test with additional of CNT

Thus, Chen et al., (2019), use TPNR with GNP and increase the tensile strength by 28%. Interfacial adhesion is high, allowing for efficient load transfer from the matrix to the GNP fillers. According to study by A Das et al., (2012), the tensile strength of NR with added GNP increases by 44% which is due to well dispersed of GNP in the polymer matrix. Meanwhile Siriyong et al., (2015) stated that an increase of 41% of tensile strength when adding 1 phr of GNP to the blend which caused by the fracture surface of TPNR nanocomposite is homogeneous and uniform. Good nanocomposites uniformity shows that the nanofiller is dispersed well, resulting in higher tensile strength. Thus, expecting the additional of 1 phr to PP/NR and CB will give a 30% increase in tensile strength (from 29.15 MPa to 37 MPa) which is due to good dispersion of nanofiller and effective load transfer from the matrix to the filler.

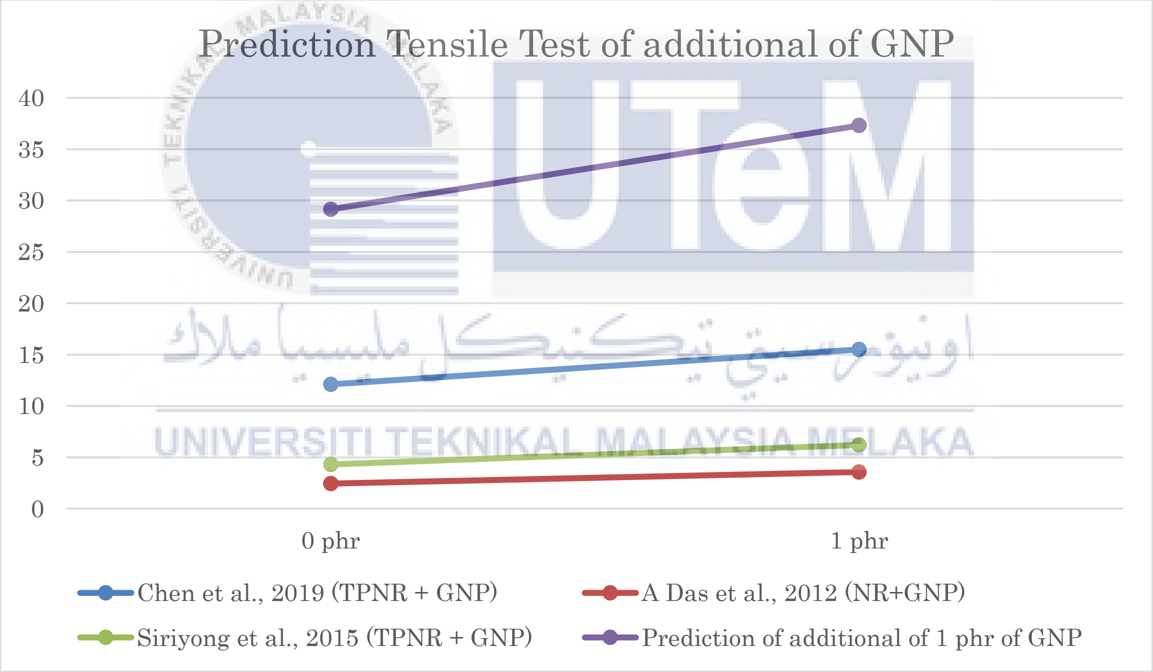


Figure 4.14: Predicted Tensile Test for additional of GNP

4.3.2. Young’s Modulus

N. Mohamad et al., 2013 stated that due to the rubber-like qualities imparted by the ENR, crosslinking in the rubber matrix of PP/ENR blends imparts elastic behaviour and decreases Young's modulus. Thus, resulting the decrease of Young’s modulus by 35% from pure PP to 75/25 PP/ENR. Meanwhile Suryadiansyah et al., (2002) reported a decrease of 28% of Young’s modulus from pure PP to 75/25 of PP/NR. The observed decrease in Young's modulus of PP/NR blends is due to particle–particle interaction of the rubber powder as the rubber percentage increases. Therefore, expecting the same trend for the comparison of pure PP and PP/NR blend for 75/25 of PP/NR which is the decrease of 35% of Young’s modulus compared to pure PP (from 1.01 MPa to 0.66 MPa). This is because of increasing elastic properties in the blend.

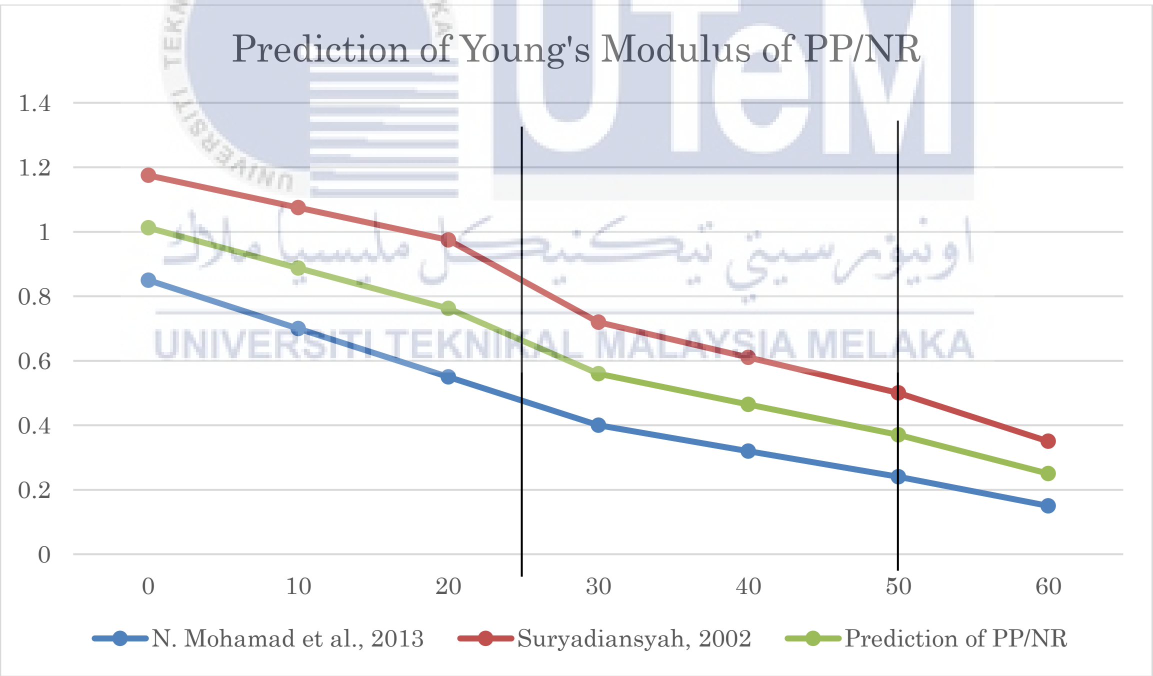


Figure 4.15: Predicted Young’s Modulus of PP/NR

Additional of carbon black by 30 phr will give additional of 75% of Young's modulus due to the strong interaction, which effectively constrained the motion of polymer chains. (Ginting et al., 2017). According to Abdelsalam et al., 2019, the improvement of 160% of Young's modulus is affected by several factors such as surface reactivity which determines the polymer–filler interaction, aggregates, size and shape of fillers, and structural and filler particle dispersion in rubber. Study by Maslowski et al., (2019) shown an increase of 75% of Young's modulus which is caused by well dispersed CB in the matrix. Therefore, it is predicted an increase in Young's modulus from 0.66 MPa to 1.23 MPa (increase by 86%) when adding 30 phr of CB into the blend. This is due to good dispersion of CB and good stress transfer from the matrix to CB.

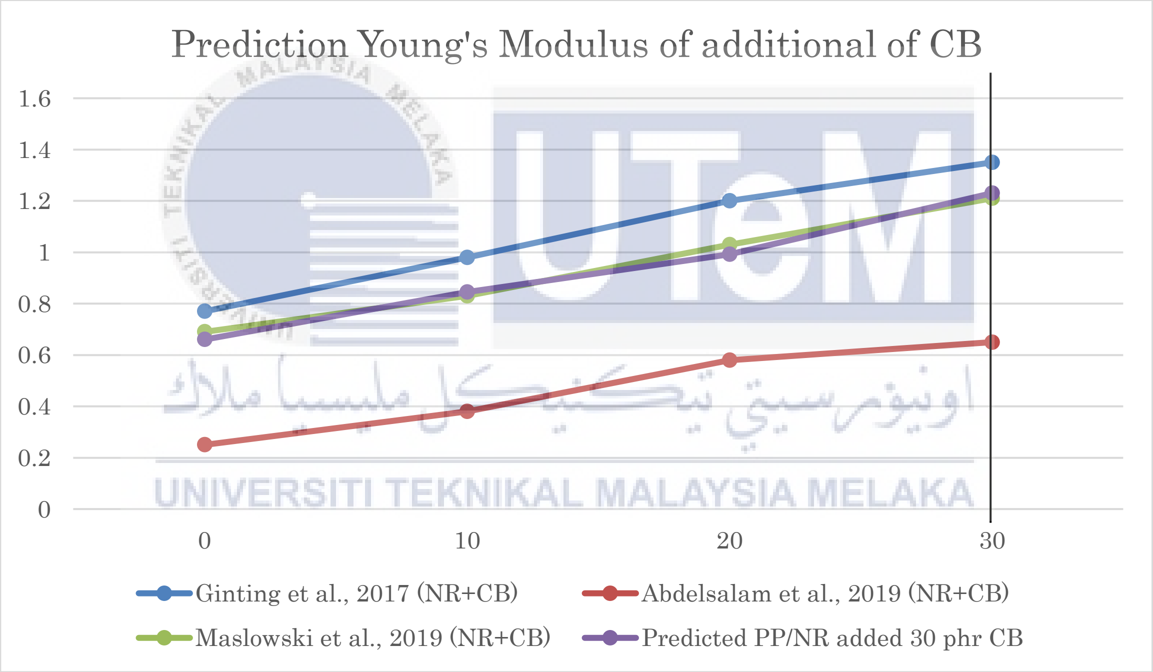


Figure 4.16: Predicted Young's Modulus with additional of CB

Study by A Das et al., (2012) stated that an increase of 9% of Young's modulus when adding 1 phr of CNT into the blend, This is due to the high aspect ratio of MWCNT enables the network formation in the polymer matrix at very low filler content. According to Sahrim et al., (2010), an increase of 18% of Young's modulus which is caused by the strong interactions between PP/NR matrix and CNT. M. G. Maya et al., (2020) stated that an increase of 21% of Young's modulus which is due to interfacial bonding between nanotubes and matrix. Thus, predicting an increase of 16% of Young's modulus (from 1.23 MPa to 1.43 MPa) which is caused by the good dispersion of CNT to the blend.

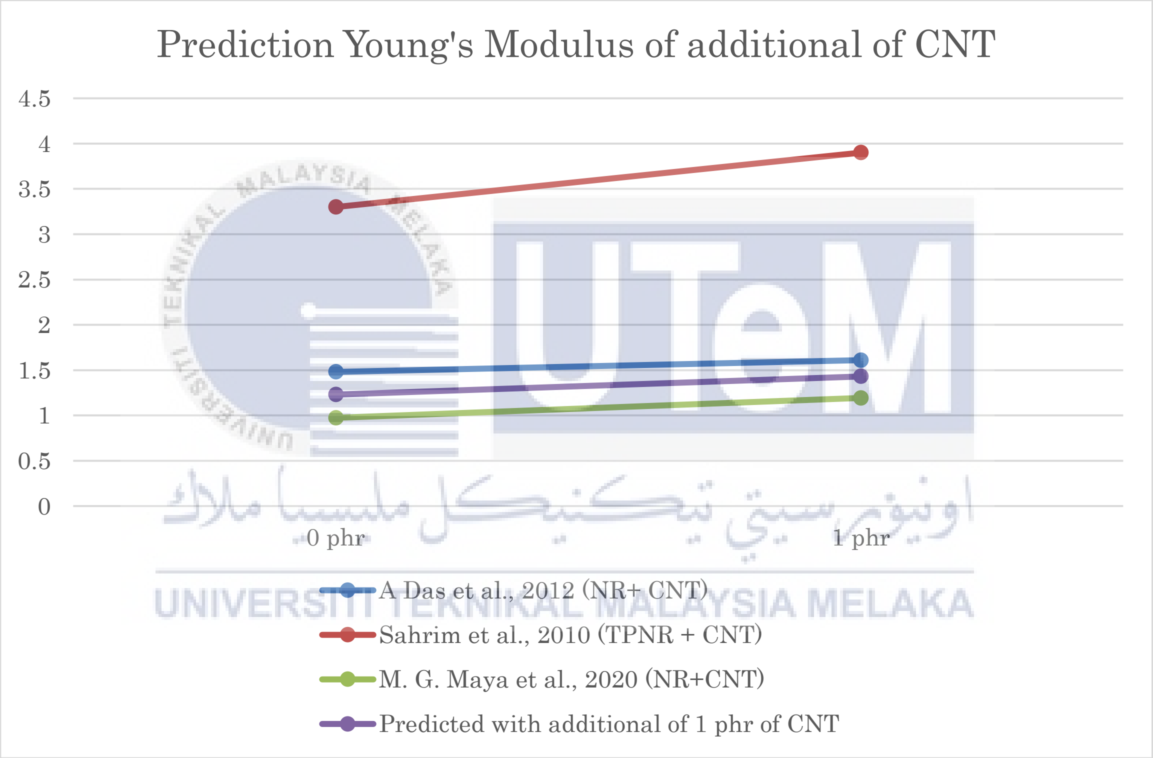


Figure 4.17: Predicted Young's Modulus with additional of CNT

According to Chen et al., (2019), an increase of 14.5% of Young’s modulus when adding 1 phr of GNP into the blend. This is due to strong interfacial adhesion between the filler and the matrix. An increase by 9% of Young’s modulus from 1.48 MPa to 1.61 MPa which is caused by good dispersion of nanofiller and effective load transfer from the matrix to the filler as reported by A Das et al., (2012). Therefore, a prediction increase by 12% in Young’s modulus with additional of 1 phr of GNP (from 1.23 MPa to 1.37 MPa) which is may be caused by well dispersed GNP in the polymer matrix.

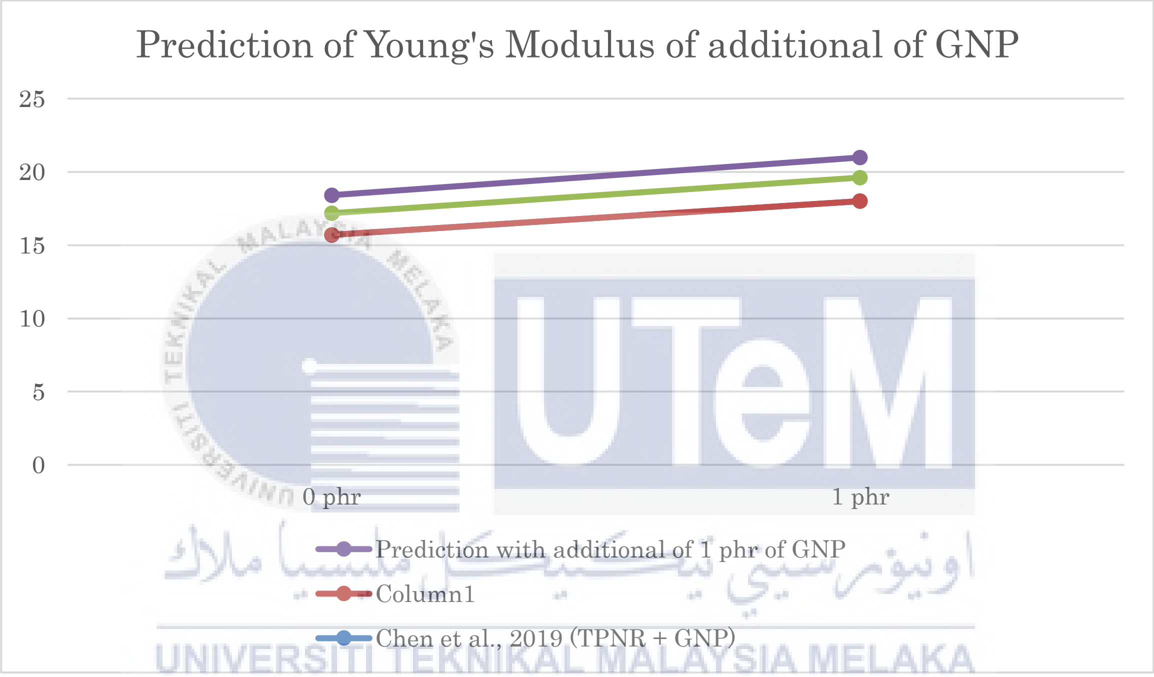


Figure 4.18: Predicted Young’s Modulus with additional of GNP

4.3.3. Hardness Test

N. Mohamad et al., 2013 stated that hardness decreases by 22% from pure PP to 75/25 of PP/ENR. This is due to the elastic properties contributed by the rubber content in the blends. According to study by Bendjaouahdou et al., (2018), decrease in hardness by 19% from pure PP to 75/25 of PP/NR which is caused by decrease in stiffness. Thus, prediction of hardness of PP/NR will also decrease by 20% (from 78 to 62.2 Shore A) from pure PP to 75/25 of PP/NR which caused by additional of rubber content into the blend which promote elastic properties to the blend.

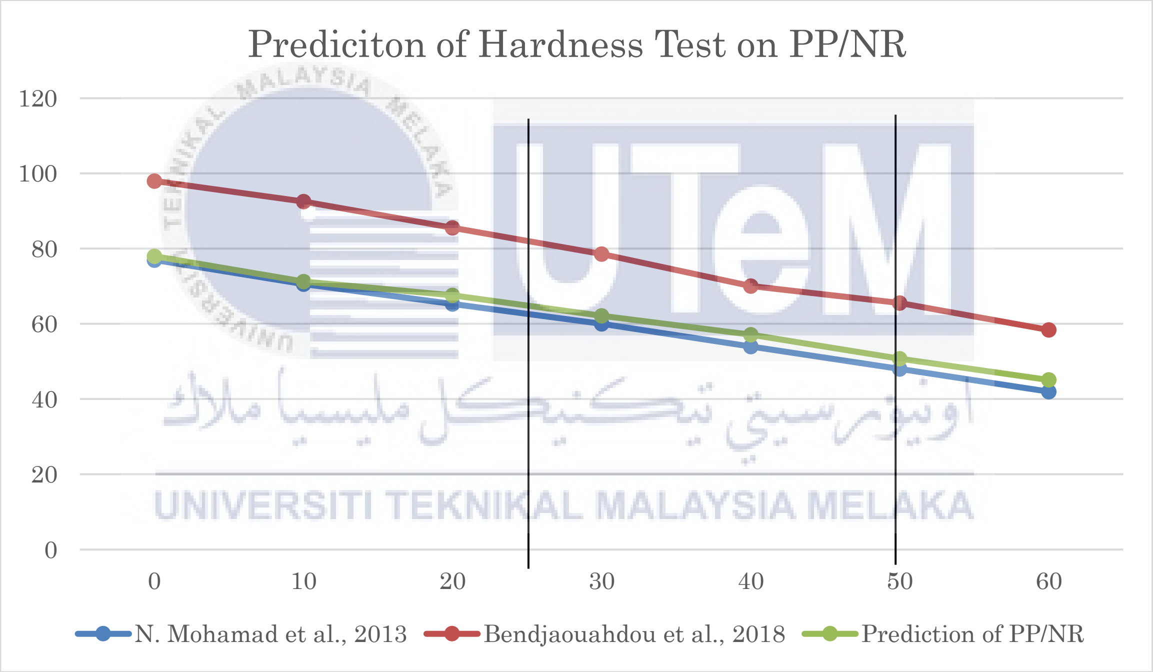


Figure 4.19: Prediction of Hardness of PP/NR

As shown in Figure 4.20, Varghese et al., (2013) stated increase of 37% of hardness when adding 30 phr of CB into the blend. This is because of well dispersed of CB in the matrix. According to Maslowski et al., (2019), an increase of 44% of hardness from 27 Shore A to 39 Shore A is caused by the agglomeration of fillers in the elastomeric matrix which influences the hardness value. Study by Ginting et al., (2017) stated that increase of 33% of hardness value which is due to increase in stiffness of the blend. Therefore, with additional of 30 phr of CB into PP/NR can increase the hardness value by 36% (from 62.2 to 85.1 Shore A) which is caused by crosslinking density and good dispersion of CB into the blend.

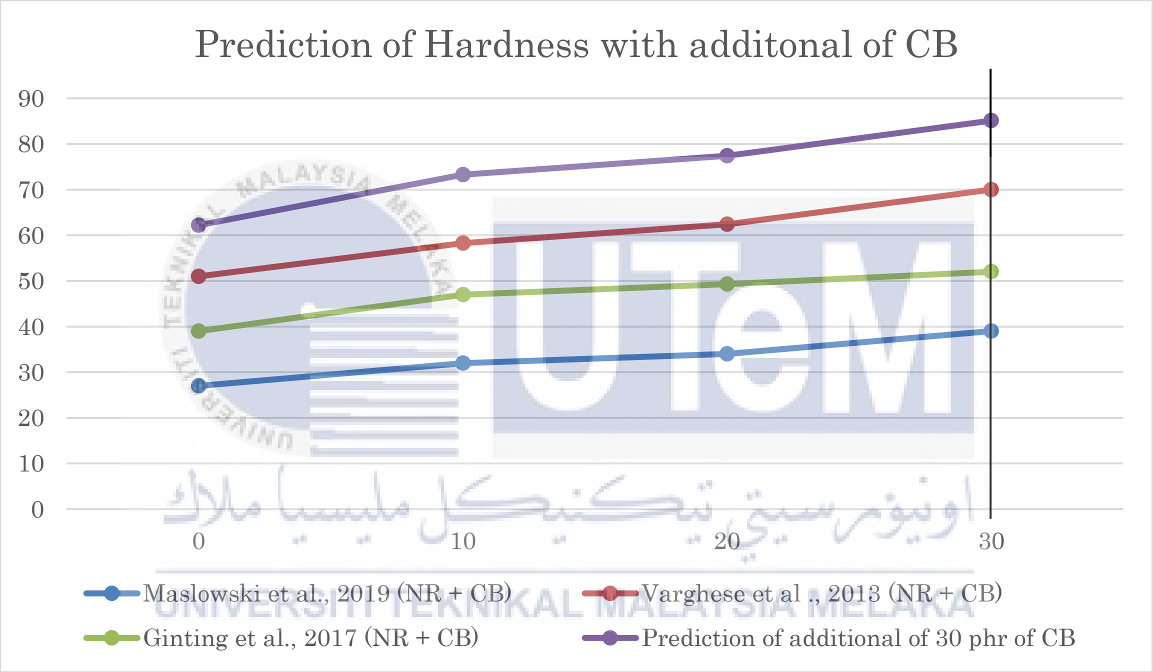


Figure 4.20: Prediction of Hardness with additional of Carbon Black

M.G. Maya et al, (2020) stated that with additional of 1 phr of CNT can increase the hardness value by 13% which is caused by concentration of the filler enhances the surface properties of the polymeric material. According to T Jose et al., (2017), increase of 19% of hardness value (from 34 Shore A to 41 Shore A) which is due to the addition of stiffer filler to the rubber matrix. Therefore, with additional of 1 phr of CNT to the blend will increase the hardness value by 14.6% (from 85.1 to 97.6 Shore A) which is caused by the additional of stiff filler into the blend.

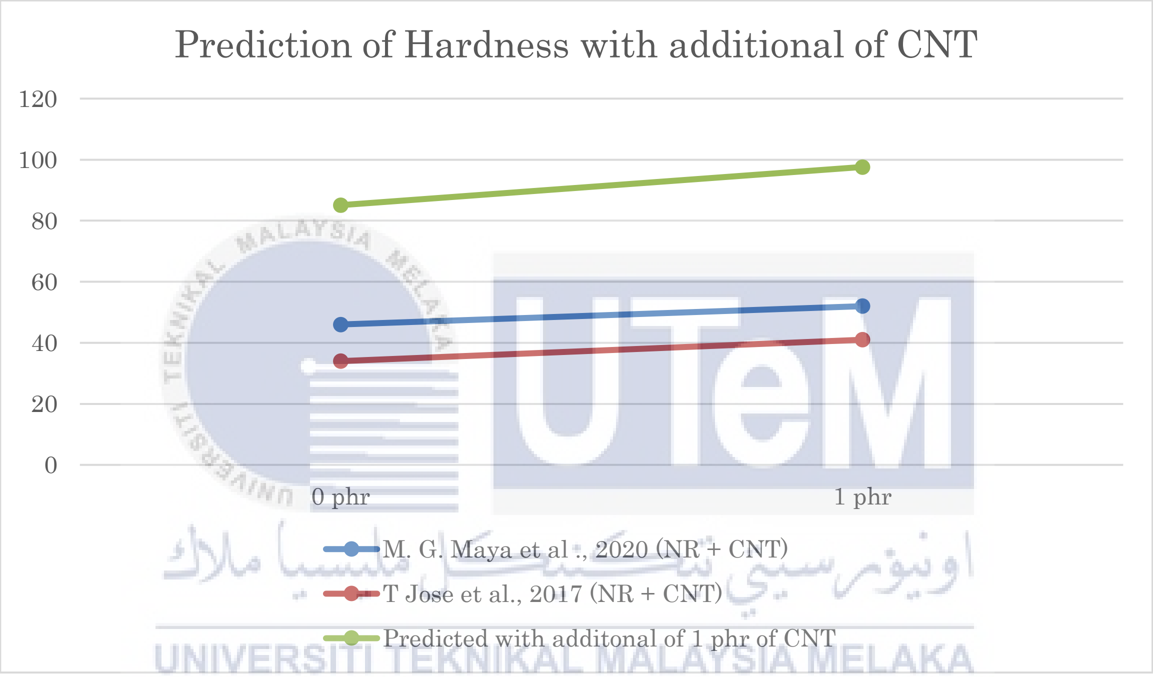


Figure 4.21: Prediction of Hardness with additional of CNT

With the additional of GNP to the blend can be a game changer. Such as stated by S.M.R. Paran et al. which increase about 13% of hardness value which is caused by increased elastic properties in the blend. According to Shojaie et al., (2021), an increase of 24% of the hardness value which is due to strong filler-rubber interation. Therefore, with additional of 1 phr of GNP to the blend could give an increase of 18% (from 85.1 to 100.4 Shore A) of hardness value to the blend which may be caused by the good dispersion of fillers in the blend thus increasing the value of hardness.

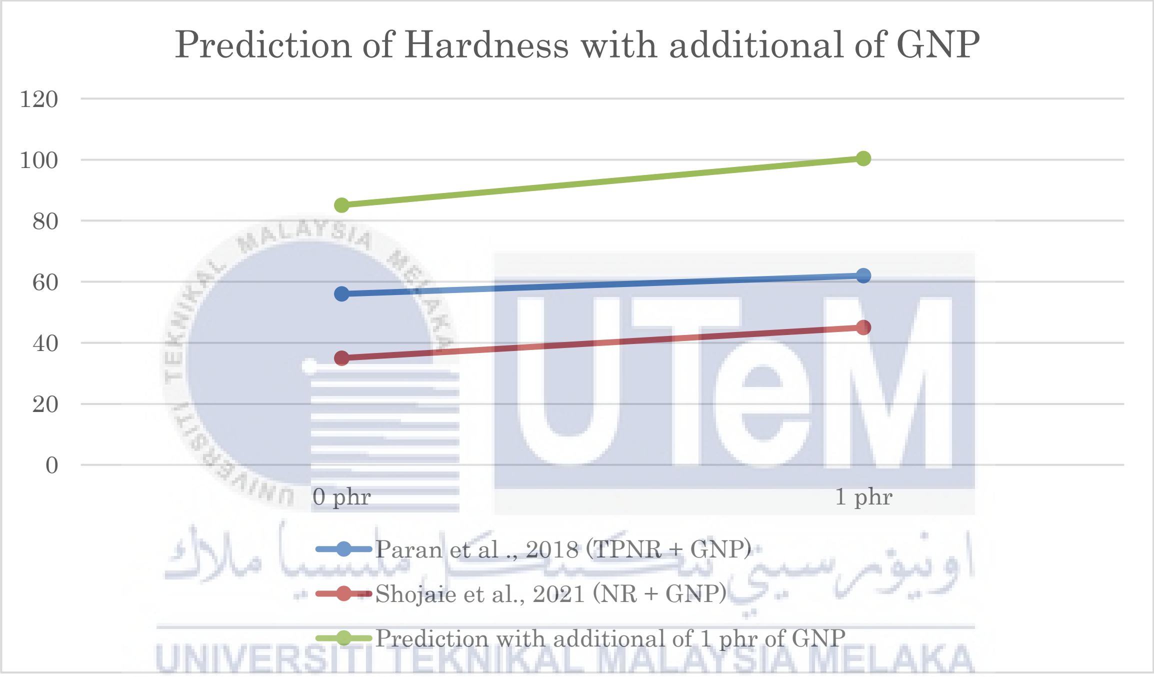


Figure 4.22: Prediction of Hardness with additional of GNP

4.3.4. Impact Test

N. Mohamad et al stated that the PP/ENR (40/60) shows the highest impact strength which is in the range of 2.1 to 2.7 kJ/m^2 which is 55% increase from pure PP. The results demonstrate that ENR is a good material for improving thermoplastic mix toughness and flexibility. PP/ENR (70/30), which has a weaker impact than pure PP, deviates from its correlation. This is due to the fact that deformation in impact tests reduces the ability of rubber particles in the intra-spherulitic structure of PP to absorb impact efficiently. The rubbers behave as frozen bodies, causing the combination to become brittle. R. Asaletha et al., (1999) stated that an improvement in impact strength of 51% from pure Polystyrene (PS) to 75/25 of PS/NR which is caused by increase in toughness of the blend. Therefore, the predicted PP/NR impact strength will be increase by almost 50% (from 1.8 kJ/m^2 to 2.7 kJ/m$^{2)}$ from pure PP to 75/25 of PP/NR which is due to the material's great resistance to fracture under impact loading, it has a higher impact strength, which is proportional to its toughness. It assesses a material's capacity to tolerate plastic and elastic deformation. It is concluded that the level of toughness at impact strain rate cannot be associated with energy absorption in a tensile test.

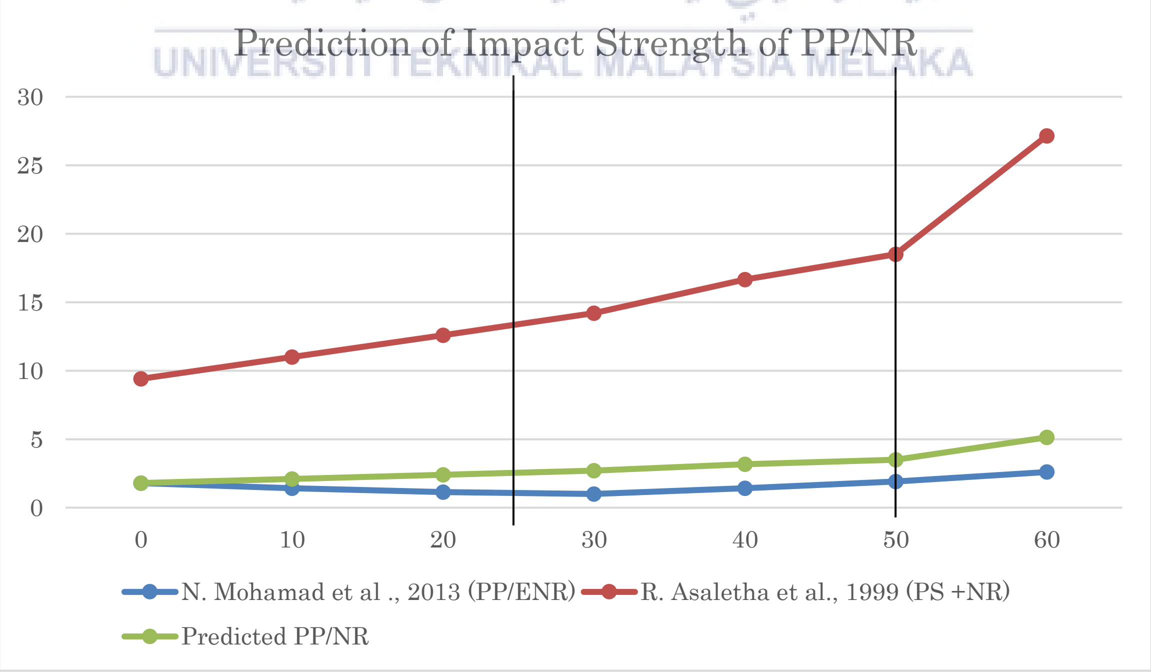


Figure 4.23: Prediction of Impact Strength of PP/NR

Stated by Sahu et al., (2020), with the mixture of High-Density Polyethylene (HDPE) and carbon black (CB), the impact strength of HDPE/CB composite decreases when the carbon black content increases. This is because the filler particle prevents macromolecule chain segments from wandering, limiting the composite's ability to accept contortion and rapid fracture distribution at the filler-matrix interface. According to Sombatsompop et al., (2006) stated that decreasing in impact strength by 59% is due to agglomeration of CB occurred in the blend. Thus, predicting the additional of 30 phr of CB into PP/NR blend will decrease the impact strength by 52% which is from 2.7 kJ/m^2 to 1.27 kJ/m^2. The main reason for the impact strength drop is the formation of fractures on the weaker interfacial areas due to an excess of filler content that increases the interfacial regions, as crack propagation is not as well resisted by interfacial regions as the polymer matrix.

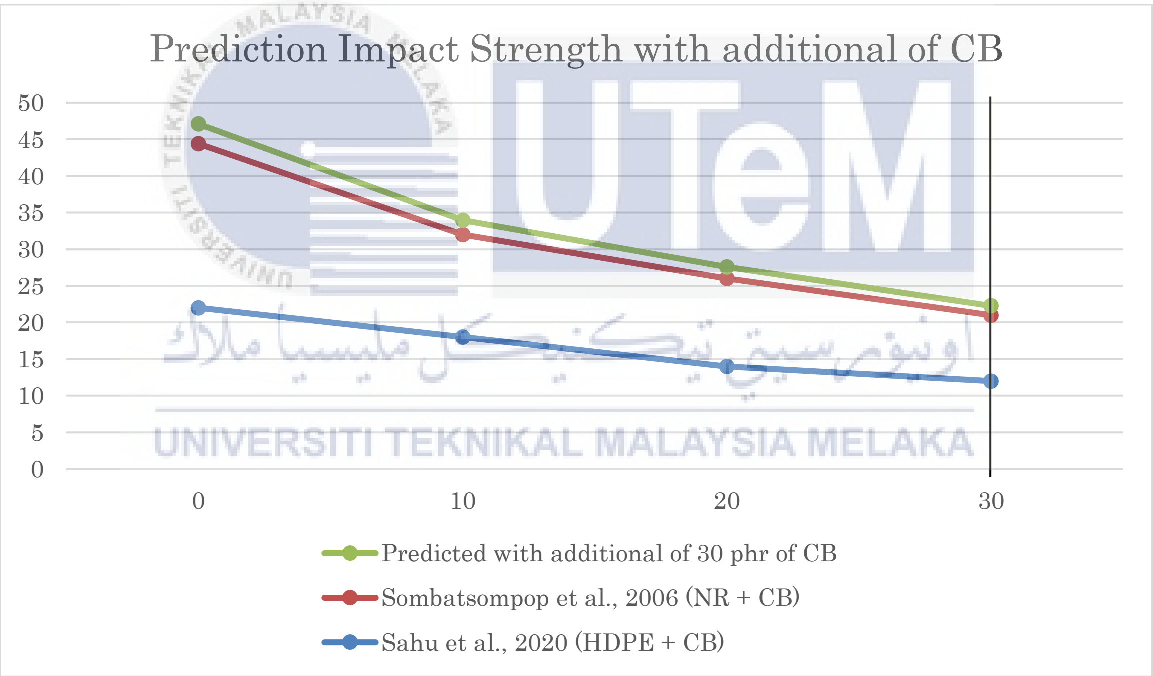


Figure 4.24: Predicted Impact Strength with additional of CB

The impact strength of TPNR/MWNTs has improved with inclusion of MWNTs. The results exhibited better impact strength and increased by 28% due to better dispersion of carbon nanotube in the matrix. When the load is transferred to the matrix-filler physical network, the debonding of the chain (disentanglement) segments from the filler surface allows the matrix entanglement structure to relax, resulting in increased impact toughness. (Sahrim et al., 2010). According to Tarawneh an increase of 46% of impact strength is due to good dispersion of CNT in the matrix which generated toughening effect on the blend. Meanwhile EhNoum et al., (2012) stated an increase of 32% of impact strength to the blend which is caused by good interaction between matrix-filler thus improving the impact strength. Therefore, with additional of 1 phr of CNT can increase the impact strength of PP/NR blend by 43% which is from 1.27 kJ/m^2 to 1.84 kJ/m^2. This is caused by good dispersion of filler in the matrix which leads to good load transfer from the matrix to the filler.

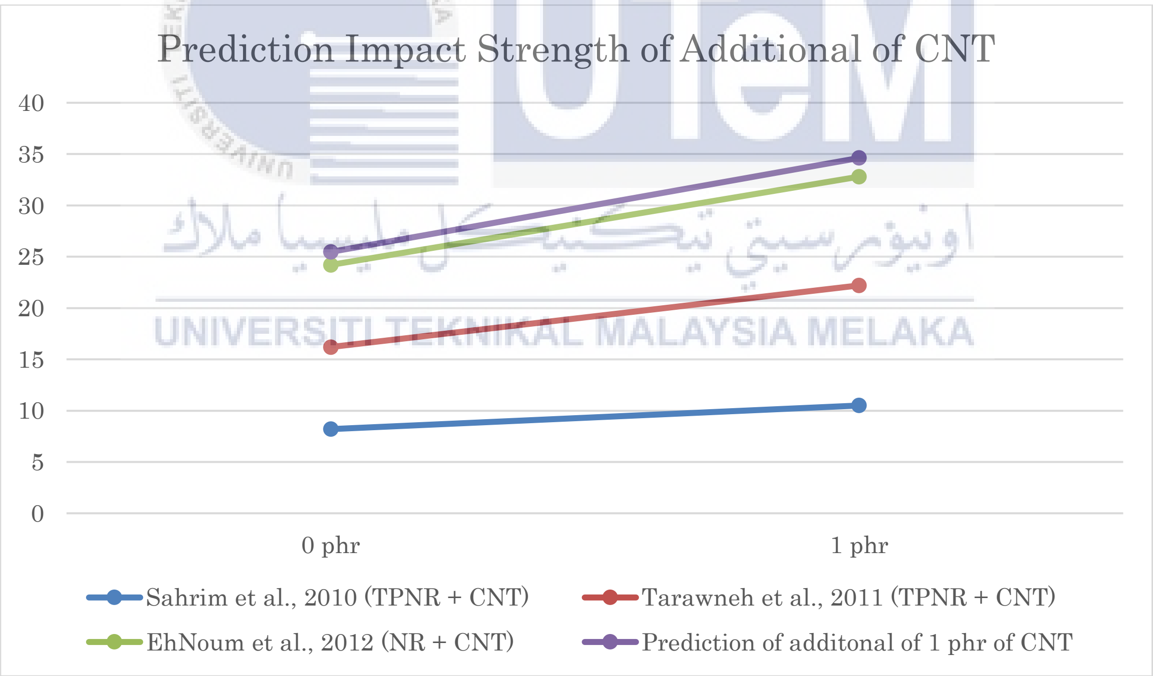


Figure 4.25: Predicted Impact Strength with additional of CNT

TPNR as shown in Figure 4.26 shows an improvement of 41% impact strength when adding 1% of GNP to the blend. This is due to increased plastic deformation of the matrix phase along the matrix-filler interface. (Chen et al.,2019). According to study by Saraireh et al., (2019) an increase of 23% of the impact strength is because of homogeneous dispersion of GNPs in the TPNR matrix, as well as their remarkable mechanical capabilities and flexible 2D architectural structure, contribute to impact strength. These factors may contribute to GNP reinforcement efficacy and a better interaction between GNPs and the TPNR matrix in the formation of a typical continuous structure, resulting in effective load distribution from the TPNR to the GNPs. Thus, prediction of additional of 1 phr of GNP to the PP/NR matrix will give an increase of 31% which is from 1.27 kJ/m^2 to 1.65 kJ/m^2. The results show that the matrix reinforcement is evenly distributed and provides a sufficient interface for load transfer from the matrix to the filler. In this situation, GNP improved the low stiffness and poor impact toughness of PP by having a positive reinforcing effect on the mechanical characteristics of the total weight fraction.

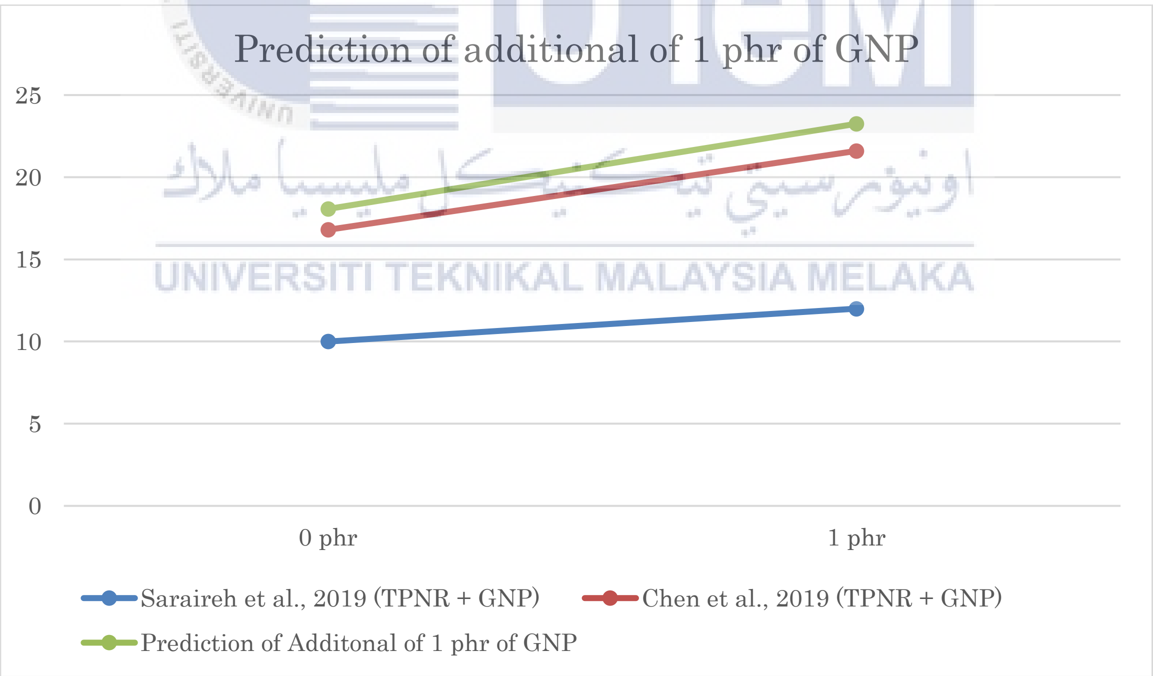


Figure 4.26: Predicted Impact Strength with additional of GNP

4.4. Swelling Test

In general, swelling test was performed to observe the swelling coefficient filler–rubber matrix interaction. As shown in Figure 4.27, Elamer et al., (2010) shows swelling ratio up to 2.6 at 75/25 from pure thermoplastic which is due to thermoplastic particles fill the porous portion between natural rubber chains. According to study by Ahmed et al., (2012), the swelling ratio increase to 2.75 at 75/25 compared to pure thermoplastic which shows the penetration of toluene into the composite increase when the rubber content increases. Therefore, the predicted swelling ratio of PP/NR is 2.7 at 75/25 of PP/NR and increasing as the rubber content increases. This is due to the fact that NR has a higher dispersion of smaller particles, allowing for improved filler-rubber matrix interaction in NR composites.

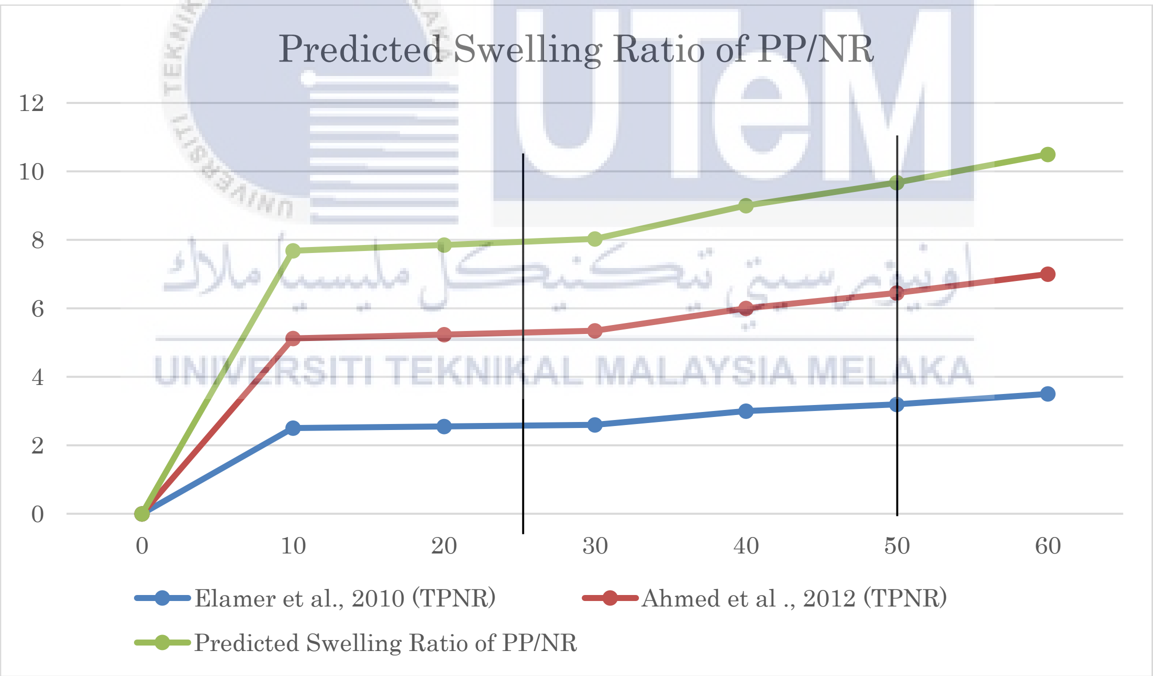


Figure 4.27: Predicted Swelling Ratio of PP/NR

According to Abdelsalam et al., (2019), with additional of 30 phr of CB into the blend will decrease the swelling ratio by 25% which is caused by the penetration of toluene into CB filled in rubber composites was reduced by increasing the filler. This means that a higher amount of CB loading restricted the penetration of toluene in filled rubber composites. Mostafa et al., (2009) stated that the swelling ratio decrease by 48% which is due to higher filler content which prevent the toluene absorption in the NR. Thus, the predicted swelling ratio with additional of 30 phr of CB will decrease from 2.7 to 1.66 which is 38% decrease. This is due to filler loading in the matrix which prevent the toluene from penetrating in the blend.

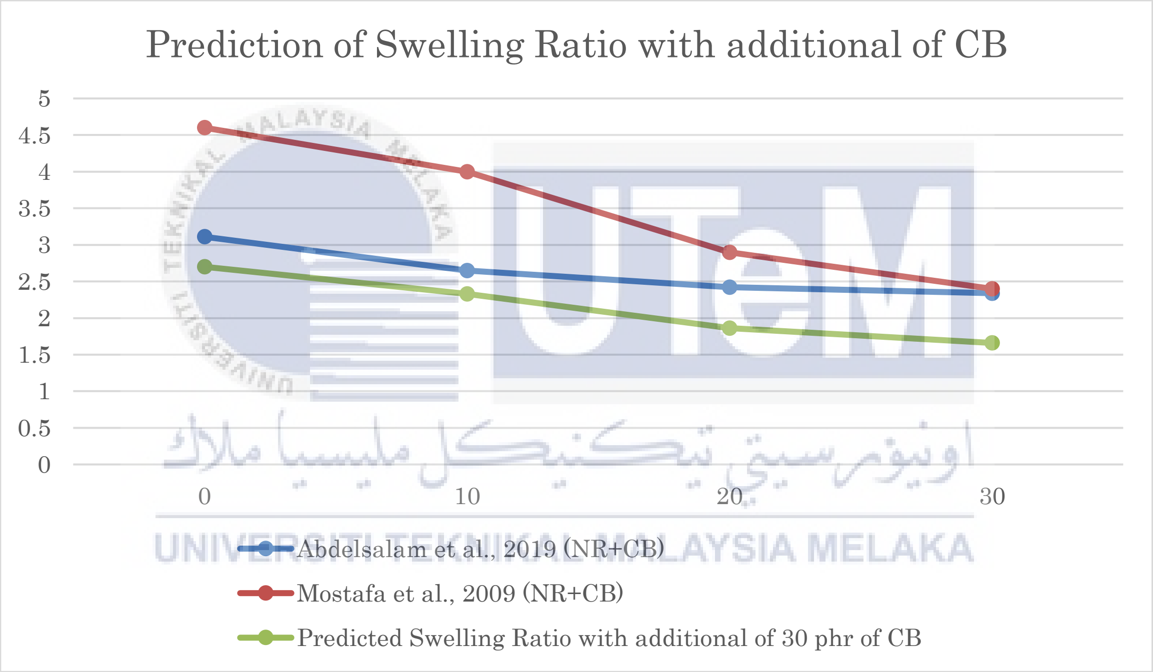


Figure 4.28: Prediction of Swelling Ratio with additional of CB

According to S.M. Lai et al., (2019), the swelling ratio decrease by 35% due to additional of 1 phr of CNT which increases the filler content in the blend. Thus, decreases the toluene penetration in the blend. Study by Thomas et al., (2019), as the free volumes increases and not filled with fillers, the swelling of the rubber composite increases the chain mobility which facilitates the transport of solvent molecules. As results, the swelling ratio decrease by 26% due to additional of fillers in the blend. Therefore, the prediction of swelling ratio of PP/NR added with 1 phr of CNT resulting in decrease of swelling ratio by 31% (from 1.66 to 1.16). This is because the presence of fillers in the intercalated structure of the nanocomposites limited the free space for solvent molecules. This demonstrates how the filler and matrix interact strongly, limiting solvent diffusivity within the entangled polymer matrix.

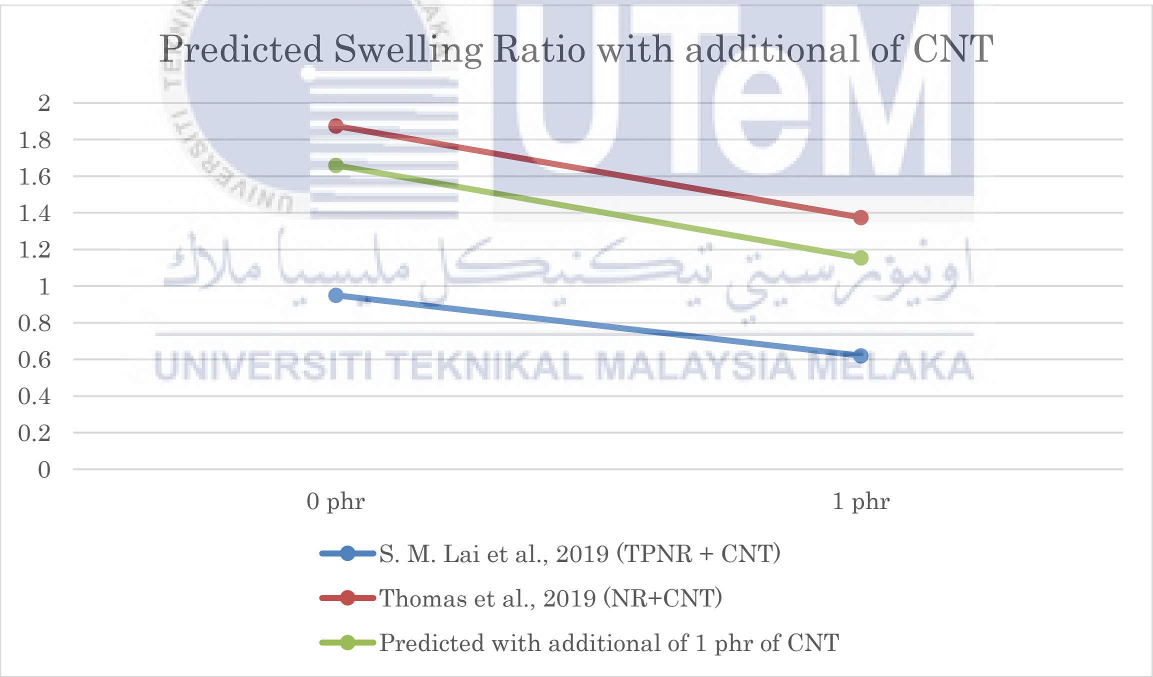


Figure 4.29: Prediction of Swelling Ratio with additional of CNT

According to Phetarporn et al., (2019), decrease of 4% in swelling ratio is due to increase in filler indicating there is increased crosslink density when the filler content increased. This might attribute to the physical crosslinking between GNP and the matrix, which immobilized the rubber chains and thus prevented the transportation of solvent, as was reported in rubber. Study by Asgarzadeh et al., (2019), which shows the swelling ratio is decreases as the GNP added to the blend. This shows the presence of GNP nanoplatelets also increase the material's resistance against solvent absorption. Therefore, it is expected that the swelling ratio of PP/NR added with 1 phr of GNP will decrease by 5.9% from 1.66 to 1.56. This is partly due to the nanocomposites' higher rigidity and stiffness. Furthermore, as the amount of GNP in the samples increases, the amount of free volume of material decreases. Thus, the same outcome for swelling test for PP/NR filled with hybrid fillers which results in as the filler loading increase, the swelling will decrease due to decrease in rubber content in the blend.

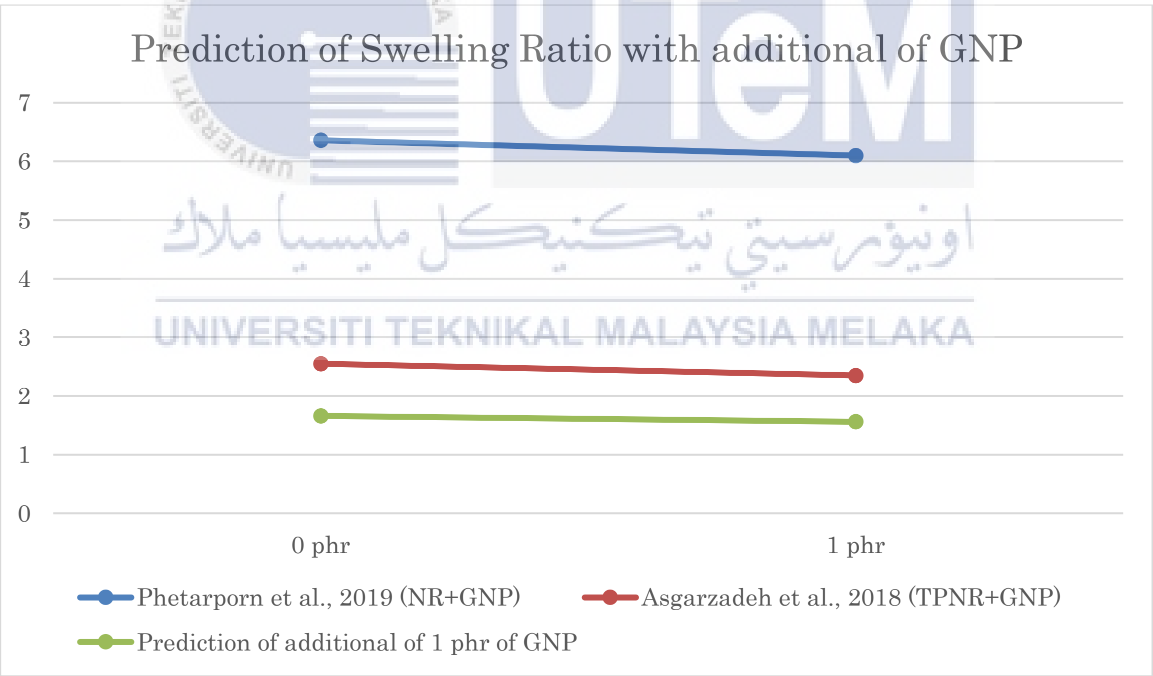


Figure 4.30: Prediction of Swelling Ratio with additional of GNP

4.5. Morphological Analysis

4.5.1. Scanning Electroscopic Machine

Figure 4.31 below shows the tensile fracture surface of PP, PP/ENR (70/30) and PP/ENR (40/60) blends respectively. The bright phase represents the PP and dark phase represents ENR. The fracture surfaces show spherical shaped dimples from pulled-out of PP domains or ENR domains except for unfilled PP. In figure 4.31 (b) shows fractured surface of PP/ENR (70/30) blends which reveals the ENR were dispersed as domains in a continuous PP phase which shows the stage ENR is present in the intra-spherulitic structure of PP. Meanwhile in figure 4.31 (c) shows that ENR phase has enlarge its size and formed bigger ENR domains in PP matrix. This is due to their higher composition of ENR compared to PP in the blend (40/60).

Thus, expecting quite the same SEM result for PP and PP/NR (75/25) but not quite the same for PP/NR (50/50) as they have a balance wt% of the composition in the blend. There should be balanced NR domains in the PP matrix.

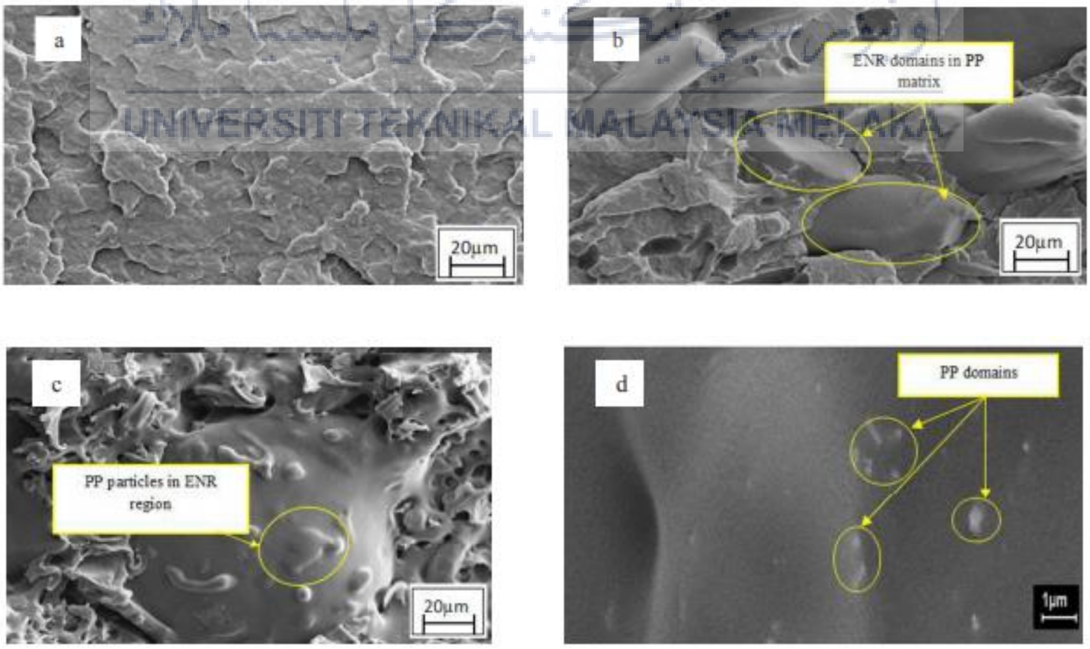


Figure 4.31: Scanning electron micrograph of (a) unfilled PP (b) 70/30 PP/ENR and (c) 40/60 PP/ENR at magnification of 500x (d) 40/60 PP/ENR at magnification of 5000x (N. Mohamad et al., 2013)

Figure 4.32 below shows the distribution of CB fillers in the composition of NR compound. Even spread of fillers occurs in the blend which increase the mechanical properties of the blend. Empty cavities emerge as a result of CB's inclination to agglomerate due to the presence of hydroxyl groups in silica in CB, which aid hydrogen bonding with silica molecules. The presence of CB in the blend which increases the agglomeration thus producing low tensile strength composite.

Therefore, expecting quite the same SEM image for PP/NR filled with CB which has the same agglomeration between NR and CB filled in PP matrix.

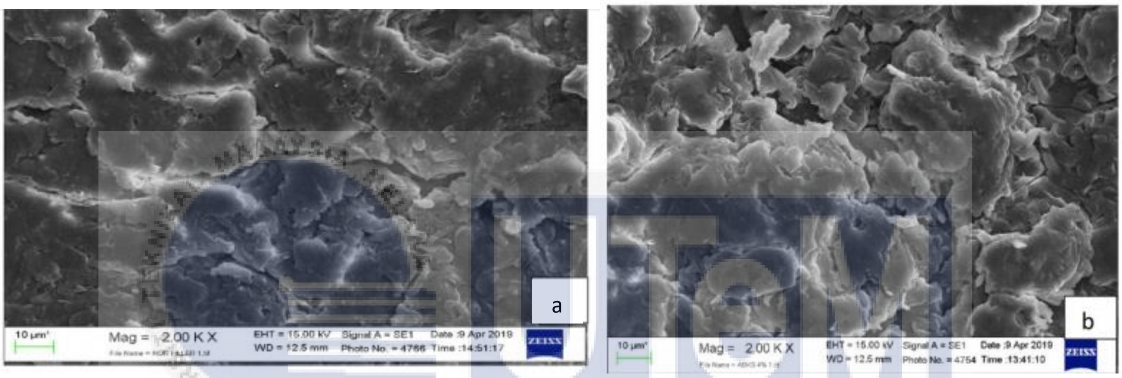


Figure 4.32: Morphology of natural rubber compound with filler CB (a) non filler, (b) filled CB (E. Farida et al., 2019)

As shown in figure 4.33 the 1% MWCNT is well dispersed as individual tubes in the matrix (bright dots in the SEM micrograph). The figure also showed the nanotubes that had pulled out from the matrix were still coated with polymer, suggestion a strong polymer nanotube interfacial. Efficient stress transfer from the matrix to the filler is essential due to strong interfacial adhesion which enhancing the tensile and impact properties of TPNR.

In PP/NR filled with CB and CNT should have the same dispersion of fillers in the blend as it has only 1 phr of CNT.

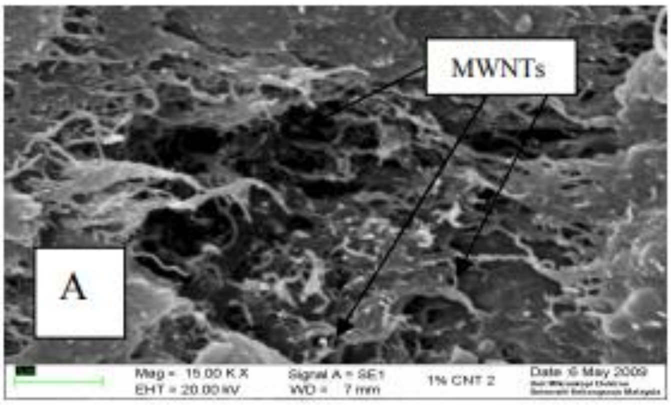


Figure 4.33: SEM micrograph of TPNR/MWNTs of 1% (Tarawneh et al., 2010)

Thermoplastic elastomer nanocomposites containing GNPs in Figure 4.34 which shows a matrix-disperse kind of morphology which the rubber phase could be identified with the dark hole in the SEM images. The results indicated that the GNPs could be successfully disseminated in a nanoscale in the polymer matrix using the melt mixing approach, resulting in the formation of LLDPE/RR/ GNPs nanocomposites.

Therefore, SEM image of PP/NR filled with CB and GNP should be well-dispersed too as the same melt-mixing method is used.

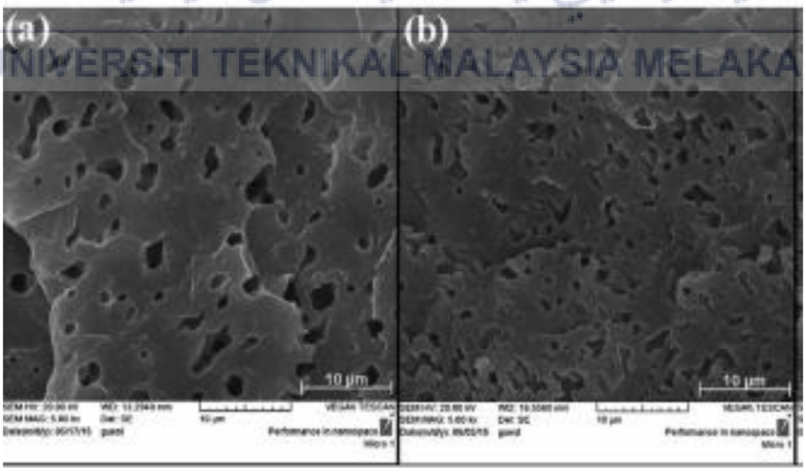


Figure 4.34: SEM micrograph of (a) LLDPE/RR (75/25) with no filler (b) 3 wt% of GNPs (S.M.R. Paran et al., 2018)

CHAPTER 5

CONCLUSION AND RECOMMENDATION

This chapter will provide a conclusion to overall characterizations and testing done in this studies. Besides that, the end of this research there are many unresolved issues, Thus, this chapter will provide a recommendation in for future works in order to ensure this study will gain a better result.

5.1. Conclusion

Returning to the first objective of this study which is to postulate the effect of natural rubber (NR) content to the physical and mechanical properties of Polypropylene/Natural Rubber thermoplastic elastomer based on the critical review based on the graph trend. There are only a few journals that had almost the same parameters and responses related to this research. This research set out to critically examine the graph pattern which is based on the past research data from Suryadiansyah et al., (2002), N. Mohamad et al., (2013), R. Asaletha et al., (1999) and Bendjaouahdou et al., (2018). The physical and mechanical properties is evaluated via tensile, Young's modulus, hardness, impact strength and swelling ratio. Then, the result is extracted based on the graph trend of the past studies. The tensile strength of PP/NR at 75/25 will decrease by 46%, Young's modulus decreases by 35%, hardness decreases by 20% and improvement of impact strength by 50%. Also, the swelling ratio is increased to 2.7.

The second objectives of this research were to predict the impact of filler hybridization on the physical and mechanical properties of the thermoplastic elastomer. Filler hybridization involved in this study is carbon black/carbon nanotube (CB/CNT) and carbon black/graphene nanoplatelet (CB/GNP). This is based on critical review graph trend. There are some journals that had almost the same parameters related to this objective. The result is evaluated once again via tensile, Young's modulus, hardness, impact strength and swelling ratio. The postulated result is based on the graph trend of the referred journal. PP/NR filled with CB/CNT and CB/GNP has both tensile strengths increased by 77%. For Young's modulus for PP/NR filled with CB/CNT increased by 116% meanwhile PP/NR filled with CB/GNP increased by 108%. Next, hardness of PP/NR filled with CB/CNT increased by 57% and PP/NR filled with CB/GNP increased by 61%. Impact strength of the blend PP/NR filled with CB/CNT has decreased by 32% and PP/NR filled with CB/GNP decrease by 38%.

Lastly, the third objective is to correlate the morphological properties of the nanofiller filled PP/NR composites with their mechanical behaviour. In this research, the particle size analysis is analysed by using particle size analyser which is used to determine the particle size range and average size for CB, GNP, and CNT. As it will influence the processability and also affect the final formulations such as performance and appearance. The crystallinity structure of the matrix and fillers is determined using X-Ray Diffraction (XRD) referred in the review data. Similar XRD pattern is expected if the filler is fully exfoliated and there is no agglomeration occurred in the blend. This can be supported by the morphological analysis by using scanning electron microscopy (SEM) which shows the surface morphology of the blend. SEM also helped in investigating the microscopic observation of CB, CNT and GNP in order to see the particle shape and make sure there is no agglomeration occurred. If there is agglomeration occurred in the filler particles, sonication process is done in order to agitate the particles. Hence, this is hypothesized that the XRD and SEM analysis will be aligned according to the review data.

5.2. Recommendations

For future work recommendation, there are still many rooms for improvement could be done in order to further enhance the deliverable and accuracy of the research work. The most important recommendation is to execute this study in a proper lab with all proper equipment. Other than that, are listed as the following:

1) Improving the particle size of the filler. In this study, the particle size of graphene nanoplatelet seems there is agglomeration occurred so sonication is needed in order to agitate the particles thus can produce a better blend sample with better morphology.

2) Keep the carbon black, carbon nanotube and graphene nanoplatelet properly in a proper care since those fillers are very sensitive and easily affected if not keep properly. This can influence the results obtained in the studies.

5.3. Sustainable Design and Development

The wise use of natural resources is encouraged in order to preserve the Earth that is getting worse day by day due to human's greedy which can affect the human itself, animals and environment. The usage of thermoplastic is recommended since it is recyclable compared to thermoset but there are still consequences in processing the thermoplastic as it is producing some bad fumes that is bad for the mother nature which is atmosphere. Other than that, it can also affect humans' daily life and gave sickness such as asthma and breathing difficulty. Usage of thermoplastic and natural rubber with conductive fillers is good in order to replace the old-school heavy and high density which is used as EMI shielding. This would make the EMI shielding product lighter and cheaper as it is using thermoplastic and natural rubber with conductive fillers.

5.4. Complexity

Throughout this study, there are difficulties and unexpected situations that come up at challenging and pressured periods. Increasingly case of the COVID-19 pandemic across the world had causes laboratory activities delayed and restricted laboratory use. This has made experimental works finished at a longer time. Moreover, the sudden Movement Control Order (MCO) announcement and only a few sectors are allowed at the MCO stage made the analysis that needs to be tested outside the lab are unavailable and need to be changed to critical review. The final year students should discuss with their supervisors the scope that aligned with the situation.

In order to overcome the problems, a critical review had been implemented. The lack and limited study involving this title has led to opportunities in novelty and originality of the study. The critical review has led to much complexity as knowledge on postulating results based on graph trend, science and engineering elements and fundamentals. In this study, only few results are based on experimental data. Other than that, the rest of this study is based on critical review. In the meantime, though it is hard, this study helps in enhancing self-research-based knowledge and creativity in applying engineering principles.

5.5. Life Long Learning and Basic Entrepreneurship

Thermoplastic industry can be a good platform since processing and manufacturing industry is booming in the world right now. There a variety of mix of materials can be obtained in order to achieve better material with better characteristics mechanically and physically. There are many companies competing in order to find a better material product at a cheaper price in order to get maximum profit with minimum capital. Furthermore, the usage of recycled product is better and cheaper compared to using raw materials which can save more money even though the processing cost is a bit higher. Therefore, usage of recyclable material is recommended in order to save the environment to give more green future for future generation. The knowledge of lifelong learning is reviewed by suggestions for further advancement as stated in the recommendations part.

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