DEVELOPMENT OF NITRILE BUTADIENE RUBBER – GRAPHENE OXIDE PARTICLES FILLED POLYVINYL CHLORIDE COMPOSITES

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Petrochemical Engineering

Faculty of Engineering and Green Technology
Universiti Tunku Abdul Rahman

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **“DEVELOPMENT OF NITRILE BUTADIENE RUBBER - GRAPHENE OXIDE PARTICLES FILLED POLYVINYL CHLORIDE COMPOSITES”** was prepared by **KUHANRAJ A/L VIJAYAN** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Petrochemical at Universiti Tunku Abdul Rahman.

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ABSTRACT

This research was intended to improvise the properties of PVC by blending with NBR-GO particles as blending compounds. In order to create high performance NBR/GO particle, it is vital to have a homogeneous dispersion of GO particle in NBR latex matrix. The dispersion of GO through latex compounding was performed in this study to determine the effectiveness of GO dispersion in NBR producing NBR/GO particle which may improve the impact and tensile properties of PVC. NBR latex with 1% wt% GO was compounded and cured to produce NBR/GO blend which are then crushed into small pieces. The NBR/GO particles are then mechanically mixed into PVC by mean of melt mixing/blending using Brabender Internal Mixer. Addition of NBR and NBR-GO increases the processing torque comparably. Presence of GO promotes better dispersion of NBR as seen by reducing the processing torque. However at high NBR loading contribute to a significant increase in processing torque due to over curing of NBR. The overall outcome of this research was positive since impact strength, swelling resistance, tensile properties and E-modulus was improved. Composite properties improved due to both good dispersion and good compatibility of NBR in PVC. In addition, SEM results provides further evidence on improvements of properties with NBR and NBR-GO loading by illustrating smooth surface and minor crack propagation on 10 wt% NBR showing high strength of composite. Presence of matrix tearing on 10 wt% NBR-GO composite shows increased strengths and E-modulus. AT 30 wt% NBR loading, presences of crack propagation are more frequent due to over curing thus lowering the strength of composite. Therefore the best loading of NBR or NBR-GO for optimum composite properties is 10 wt% NBR-GO.

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LIST OF SYMBOLS / ABBREVIATIONS

PVC	Polyvinyl chloride
NBR	Nitrile butadiene rubber
GO	Graphene oxide
ZDEC	Zinc diethyldithiocarbamate
ZMBT	Zinc 2-mercaptobenzothiazole
ZNO	Zinc oxide
KOH	Potassium hydroxide
DOP	Dioctyl phthalate
FTIR	Fourier transform infrared spectroscopy
SEM	Scanning electron microscope
XNBR	Carboxylated nitrile butadiene rubber
2-D	Two dimensional
3-D	Three dimensional
%	Percentage
wt%	Weight percentage

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Ever since the discovery of graphene oxide (GO), it has attracted significant interest among researchers worldwide in various field such as biology, medicines, membranes and utilization of GO as fillers in polymer composites. The main research that involves GO is on the preparation of GO allotropes as filler for enhancement of composites properties for various applications such as production of transparent conductive films, surfactant for dispersion and high thermal resistant composite. Graphene oxide is a pure carbon which is one atom thick and sheets of GO is highly oxygenated due to hydroxyl and epoxy groups in the core structure (Liu *et al*. 2013).

Despite its nano size, it is 200 times stronger than steel and also exhibits high thermo mechanical properties, excellent tensile properties and also an excellent electricity conductor (Jiang *et al.* 2011). Graphene and graphene oxide (GO) have since attracted a huge interest among researchers contributed by its high surface to volume ratio due to the 2-D single layered carbon structure and fully exfoliated GO sheets having large specific area (Mao *et al*. 2013). Graphene Oxide (GO) is oil-independent and can be readily produced from any types of graphene or graphite by Hummers method which is economical (Deshmukh *et al*. 2013).

Besides that, GO is also applied in biomedical and medicine field due to its feature which is fluorescent. Due to its fluorescent characteristic, applications such as bio-sensing, early disease detection and carrying cures for cancer is made possible. Besides, due to GO fluorescent biosensors, this property made detection of DNA possible, providing improved diagnostic on HIV, cancer and other terminal illness (Liu *et al*. 2013). GO is also incorporated as new carriers for drug delivery applications as an alternative to famously used carbon nanotubes (CNT), due to properties of GO which has high surface area, large layer number, lateral dimension, surface chemistry and purity. Surface area of GO is four magnitude higher than CNT or any other materials tested for drug delivery (Yang *et al.*2010). It is significantly excellent as compared to other drug carriers and anti-cancer drugs because of its specialized target cell which is the low toxicity tumorous cells (Xiaoying *et al*.2011).

In this study GO was incorporated into carboxylated acrylonitrile butadiene rubber (XNBR) latex which will further be used to prepare Nitrile Butadiene Rubber-Graphene Oxide particles filled Polyvinyl chloride (PVC/NBR-GO) composite. Usage of nanofiller to strengthen rubbers is important due to limited application of rubbers resulted from its poor mechanical properties (Lorenz *et al.* 2009). There are two forms of rubber latex being used commercially which are natural or synthetic latex. Known scientifically as *Caoutchouc* or more commonly as natural rubber, consist organic isoprene along with water and other impurities. Latex can be made synthetic simply by just polymerizing with a monomer through emulsion polymerization. For this study, carboxylated acrylonitrile butadiene rubber (XNBR) was used as supplied by Synthomer composes of carboxyl groups, nitrile groups and an alkane groups. The presence of the carboxylic group (-COOH) will significantly enhance the polymer matrix by increasing strength, better tear, increased tensile and improved abrasion resistance (Laskowska *et al*, 2014).

PVC was chosen as the host material in this study due to its commercial value as it is one of the most important and widely used commodity thermoplastic polymers. PVC exhibits valuable properties such as low cost, excellent processability, chemical stability and low flammability and it has vast applications in the development of rigid or flexible molds, pipes, tubes and fibers, automotive industries and laminates (Y.F.Luo *et al*, 2010). However, PVC requires the addition of thermal stabilizer and plasticizer due to its low thermal properties and high rigidity respectively.

Development of thermoplastic elastomer from PVC-NBR blends was studied previously by using PVC with nitrile butadiene rubber (NBR) (C.Lin *et al*.2011), results from that study toughness, strength, modulus of PVC increases but was not optimized. Thence, NBR-GO particle is used for this study to determine possibilities of blending with PVC to produce PVC/NBR-GO composite to improve PVC with high strength and impact properties at the same time with simple and low cost method using melt blending. The effects of NBR loading and addition of 1 wt% GO on the processing torque, tensile, impact strength, swelling resistance and morphological properties was studied.

1.2 Significance of Study

This research was intended to improvise the properties of PVC by blending with NBR-GO particles as blending compounds. In order to create high performance NBR/GO particle, it is vital to have a homogeneous dispersion of GO particle in NBR latex matrix. Based on studies conducted by other researchers (Deshmukh *et al*.2012), the method of conventional colloidal blending to produces PVC/GO composite, a non-uniform dispersion of GO into PVC matrix was observed resulting is no significant improvement on the new PVC/GO composite. Therefore, dispersion of GO through latex compounding was performed in this study to determine the effectiveness of GO dispersion in NBR producing NBR/GO particle which may improve the impact and tensile properties of PVC. NBR latex with 1% wt% GO was compounded and cured to produce NBR-GO blend which are then crushed into small pieces. The NBR-GO particles are then mechanically mixed into PVC by mean of melt mixing/blending using Brabender Internal Mixer. The potential of NBR-GO blend as blending component in PVC was determined by the processing torque value obtained from the mixer. PVC/NBR-GO composite produced was evaluated to determine the extent of properties improved by addition of NBR-GO into PVC as compared to PVC/NBR.

1.3 Problem Statements

1.3.1 Limitation of PVC application due to low mechanical and thermal properties

PVC is the current leading synthetic polymers in the world with global consumption of approximately 16 million tonnes per annum (Hassan.1996). Worldwide, PVC is the most widely used thermoplastic in a variety of field ranging from safety in electrical lines, medical apparatus, automotive component and domestic products such as furniture, toys and pipes. Although PVC are used in diverse application however the mechanical and thermal properties are limited and inhibits it's further development for high performance applications. At temperatures above 140 ℃ PVC starts degradation although it can sustain thermal up to 160 ℃ for a short period of time (Hassan.1996). Therefore, for this study NBR-GO is blended into PVC to improve its thermal stability due to presence of GO which poses excellent thermal stability. GO properties such as surface area, layer number, lateral dimension, surface chemistry and purity will significantly improve the mechanical and thermal properties of PVC for various applications requiring high thermal resistance such as fire extinguisher hose, automotive cables and conveyor belts (Khatake *et al*,2013).

1.3.2 The need of plasticizer as processing aid

PVC is difficult to be processed due to its high stiffness thus plasticizers are added as processing aids to subsequently increasing the market price and commercial value of PVC. Plasticizers functions to produce flexible and manageable plastic to provide easy processability. Besides plasticizers, there are several other processing aids or additives for enhancing PVC as shown in the Table 1.1 below (Hassan.1996). To increase the diversity of PVC applications to challenge imagination, incorporation of NBR-GO particle is an attempt to create a new type of thermoplastic elastomer PVC/NBR-GO with superior thermal properties, mechanical properties and electrical properties. Thus, significance of this study is to produce a new blend of PVC/NBR-GO composite with overall enhancement to its properties.

Table 1.1: Processing aids for PVC

Additives	Properties Achieved
Anti-oxidants & Stabilizers	Reduces rate of polymer degradation by oxygen, heat, UV radiation
Compatibilizers	Permits PVC to be compatible with other plastics and promotes plastic recycling
Flame Resistivity	Decreases flammability of plastics
Pigmentation	Coloring purpose
Impact modifiers	Increase shock resistance
Fillers	Add bulk to plastic

1.3.3 The drawback in conventional method of producing PVC/NBR composite

A blend of copolymers of NBR and PVC is significant in the rubber industry due to the good ozone and weathering resistance, high oil resistance and excellent flame resistance. Besides, NBR/PVC blends are favored because of their good processing properties as compared to pure PVC (Shokri *et al*.2006). The conventional method of producing NBR/PVC blends is called dry blend method and latex blend method.

In dry blending method, NBR is mixed with PVC powder in a Brabender Internal Mixer by batch loading of NBR. Mixture of NBR and PVC blend will be homogenized in the internal mixer at 170 ℃, the dispersion of PVC in NBR phase is found to be no discernible and no improvement on the properties or processing of PVC (George *et al*.1986). For the later blending method, NBR is blended with PVC before solidifying. The mixture will be coagulated by acid and gelled to obtain finished product of solidified NBR/PVC.

The drawbacks are non-homogenized mixing or dispersion of the blend and phase separation if the NBR/PVC is not thoroughly mixed before gelling. Thus in this research, NBR-GO are first produced through latex compounding method which are then shredded into smaller particles before being melt blended with PVC in Brabender internal mixer. Through this method, GO can be well dispersed onto NBR latex before being mixed into PVC, and melt mixing of NBR/GO using Brabender internal mixer can create high shear for homogeneous mixing of NBR or NBR/GO in PVC.

1.4 Objectives

This study was conducted for several purposes which are:

I. To prepare NBR and NBR-GO particles through latex compounding method.
II. To prepare PVC/NBR and PVC/NBR-GO composites through melt blending of NBR or NBR-GO and PVC using brabender internal mixer.
III. To study the effect of NBR and NBR-GO addition on the mixing torque, tensile properties, impact strength, swelling resistance and SEM morphological properties of produced PVC composite.

CHAPTER 2

LITERATURE REVIEW

2.1 Polyvinyl Chloride (PVC)

2.1.1 Introduction

In 1913, a German inventor named Friedrich Heinrich August Klatte patented PVC production method by polymerization of vinyl chloride under sunlight. Unfortunately, no useful purpose of PVC in 1913 until in 1920's when an American scientist Waldo Semon made PVC a functional material when he attempted to create a synthetic replacement for natural rubber. Thence, sales took off during World War 2 when the demand for PVC increases due to limited natural rubber supply (Kunststoffe. 1989). It was used for cable insulation for wiring on military ship due to its safety and high thermal stability properties due to presence of chloride group in molecular structure. Over the years, PVC volume increased dramatically around the world due to its necessity in construction industries. Its light weight, chemical and corrosion resistance made it the best option for building construction (Liu *et al*, 2010).

PVC is produced from vinyl chloride monomer by polymerization whereby linking of vinyl chloride monomer forming chains of PVC. The end product of polymerization produces PVC in form of white powder. The white powder PVC is not meant to be used as it is but to be blended with other ingredients to produce different formulations depending on applications purpose. (Azman, 1996)

Today polyvinyl chloride (PVC) is the most commonly and commercially used thermoplastics with global consumption of approximately 16 million tonnes per annum (Bos *et al.*1996). PVC fundamental repeat unit is as shown in Figure 2.1 where "n" represents the number of repeat units. Its molecular structure has amorphous structure containing polar chlorine atoms. Due to presence of chlorine in its molecular structure, fire retarding properties improved, higher durability, oil and chemical resistance. It is also widely used in industrial and domestic fields such as wiring, insulation and furniture. Due to the low cost as compared to other commodity plastics and good properties, it is the best choice of thermoplastics compounds. Besides, the intended physical properties of end products such as flexibility, impact strength, anti-fouling and fire retarding properties can be formulated by adding plasticizers or any processing aids. Thus the versatility of PVC combining with economical cost and excellent properties results in rapid growth of PVC polymer. (Vytenis, 2005)

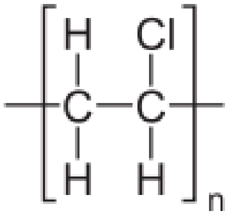

Figure 2.1: Monomer of PVC (Burke *et al*, 1978)

Although well known for compatibility with most other polymers such as nitrile butadiene rubber or styrene butadiene rubber, PVC bears low thermal stability causing processing to be difficult. However, with development of suitable heat stabilizers in early 1930's in Germany, thermal stability is no longer an issue and PVC development flourished. However the cost of PVC was higher than expected due to additional thermal stabilizers.. During the infamous World War 2, shortage of rubber for military purposes opened a path for plasticized PVC (Kunststoffe. 1989).

The morphology of PVC originates from manufacturing process where growth of PVC occurs through a series of steps. Terminology to describe the morphology is confusing thence a basis for the nomenclature of PVC relative to particle size as in Table 2.1 is formed by (Allsop, 1982).

Table 2.1: Polyvinyl chloride (PVC) nomenclature (Vytenis, 2005)

Term	**Approximate size**		**Description**
	Range (µm)	**Average (µm)**	
Grain	60-260	140	Visible constituents free flowing powders, more than 1 monometer droplet
Sub-grain	15-160	50	Polymerized monomer droplet
Agglomerate	3-11	6	Formed during beginning stage of polymerization by coalescence of primary particles.
Primary particle	0.5-0.7	0.6	Grows from domain. Formed at low conversion by coalescence of micro-domain.
Domain	0.2-0.3	0.3	Primary particle nucleus. Only observed after mechanical working.
Micro-domain	0.02-0.03	0.03	Smallest species.

2.1.2 Properties and applications of PVC

PVC is one of the most commercially used polymers for general purpose applications. Therefore, basic degradation chemistry of PVC is studied for some extend over the years. The molecular structure contains an amorphous structure along with polar chlorine atoms. Due to the presence of chlorine atom, this gives rise to the difference in performances and functions of PVC as compared to other plastic olefins. Due to chlorine in its molecular structure attributes to the chemically stable PVC. Thermal property is relatively higher due to the presence of chlorine in its molecular structure however PVC poses lower thermal stability due to the thermal history. Repetitive processing or exposure to high temperature may cause chain scissoring and PVC decomposition. PVC poses high ignition temperature of 455 ℃ which considerably lowers the risk of fire related incidents due to its high resistance towards ignition. Besides, heat released from burning PVC is much lower as compared to polyethylene, polypropylene and polystyrene. The comparison between the heat energy released for various polymers are as in Table 2.2 (Hirschler *et al*, 1989).

Table 2.2: Heat Released from burning polymers (Hirschler *et al*, 1989)

Material	Maximum heat release (kW/m^2)
PVC	91
Fire resistant ABS	250
Fire resistant PS	315
ABS	746
PS	859
Polyester	1216
PE	1325
PP	1335

The general properties of PVC are tabulated in Table 2.3. Maximum temperature before degradation is at 140 ℃ but PVC is capable of sustaining at 160 ℃ for a brief period of time. Its weathering stability is well known, resistance to extreme environmental factors makes it the perfect material for roofing. In addition, PVC is long lasting as it is able to last up to more than 100 years. For safety aspect, it plays a huge role in the electrical applications industry. PVC has good insulating properties, flexible in the presence of plasticizers and durable making it suitable for cable insulation and sheathing. Even in automotive industry, PVC increases safety by providing shock absorbing equipment like airbags and flame retardant. Being non-toxic and durable, most toys industry incorporates PVC as main material for making toys (Kalim *et al*, 2013).

Table 2.3: PVC properties (Allsop, 1982)

Parameters	Values
Maximum temperature	140 ℃
Minimum temperature	-25 ℃
Melting Point	160 ℃
Ignition temperature	455 ℃
Hardness	R105
UV Resistance	Excellent
Specific Gravity	1.34
Tensile Strength	6500 psi

2.1.3 Advantages and Disadvantages of PVC

PVC is the most widely used polymer in cables production in the world. It is dominant in the low voltage and specialized applications such as telecommunication. PVC has several benefits such as non-flammable, dimensionally stable, economical, good weathering resistance and recyclable. Therefore PVC can be reprocessed back into cable applications. On the other hand, the disadvantages of PVC include limited thermal capability, stained by sulfur and high density. PVC poses thermal history where the thermal effect accumulates over each reprocessing or thermal exposure which results in lower thermal stability of PVC.. The advantage and disadvantage of PVC is summarized in Table 2.4 (Hassan *et al*, 1996).

Table 2.4: Advantages and Disadvantages of PVC

Advantages	Disadvantages
Non- flammable	Limited thermal capability
Dimensional stability	Attacked by several solvent types
Economical	Stained by sulphur compounds
Good resistance to weathering	High density
Recyclable	Thermal decomposition evolves HCL

2.1.4 PVC blends and composites

PVC blending is done to further enhance the chemical and mechanical properties of PVC as well as for economic advantages. Due to the rigid nature of PVC, incorporation of NBR as plasticizer is performed for applications such as wire and cable insulators, containers and pond liners. Blending with PVC will improve ozone resistance, thermal aging and abrasion resistance. Presence of PVC in a blend will provide for a glossy finish upon processing (Wang *et al*, 2009).

There are numerous PVC blending studied previously such as PVC-vulcanized nitrile rubber waste powder on the year (2013) producing new polymer composite with lower hardness, increased flexibility, and higher elongation at break, better tensile strength and better ozone resistance suitable for irrigation pipes for agricultural field (Hassan *et al*, 1996). The new thermoplastic composite is processed by injection, extrusion and compression molding. Besides, PVC was also test blend with wood-plastic composite whereby it increases processability and poses much stiffer but brittle and less water resistant than composites made of PP or HDPE (Viviane *et* al, 2008).

2.2 Acrylonitrile Butadiene Rubber (NBR)

2.2.1 Introduction

Acrylonitrile butadiene rubber is the building block of the automotive rubber product industry and domestic industries. NBR is considered unsaturated copolymers of acrylonitrile and butadiene. During rubber compounding, selection of elastomer with particular acrylonitrile content can make NBR useful in various applications of oil, fuel and chemical resistance. NBR is manufactured by emulsion polymerization with the ratios of acrylonitrile (ACN) and butadiene (BD) are varied depending on the application requirements such as oil resistance, chemical resistance and low temperature requirements (Wang *et al*, 2014).

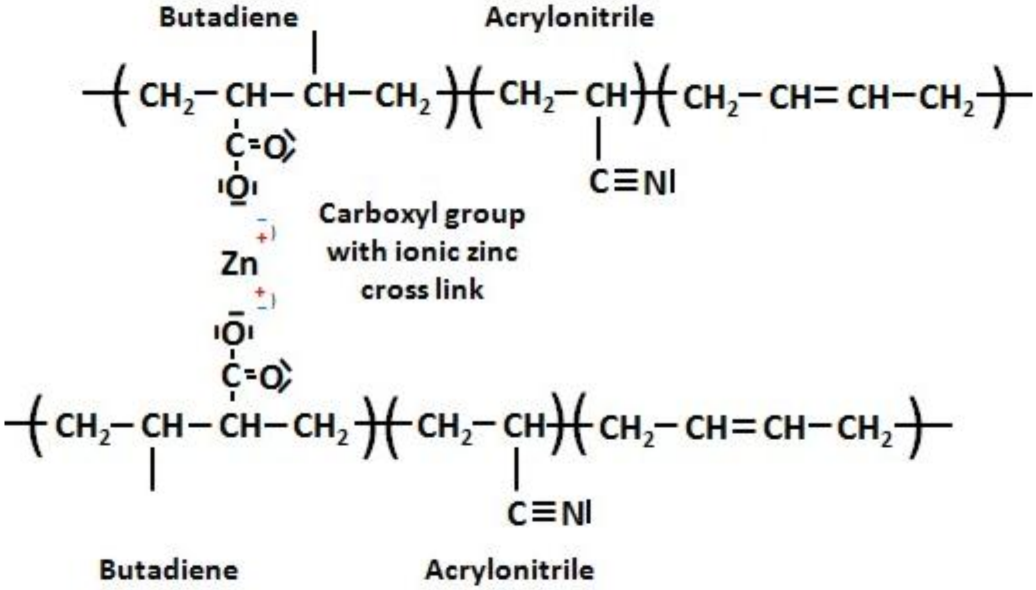

Figure 2.2: Molecular structure of NBR **(**Beurden, 2012)

In this study carboxylated acrylonitrile butadiene rubber (XNBR) was used. Presence of carboxylic group in XNBR molecular structure alters the processing and cured properties to that of non-carboxylated NBR (Horvath. 1990). XNBR have increased strength, increased tensile and abrasion resistance as compared to non-carboxylated NBR. The ACN content is the main factor defining NBR grade. Due to polarity of the ACN group, the basic properties such as oil and solvent resistance, glass transition temperature and abrasion resistance can be determined. Table 2.5 indicates the properties of NBR with respect to ACN content.

Table 2.5: Effect of Acrylonitrile loading in NBR (Worldwide Rubber Consumption,2001)

NBR with Low Acrylonitrile content	**Parameters**	**NBR with High Acrylonitrile content**
Poor	Processability	Excellent
Poor	Cure Rate with Sulfur Cure System	Excellent
Poor	Oil Resistance	Excellent
Poor	Compatibility with Polar Polymers	Excellent
Poor	Air/Gas Impermeability	Excellent
Poor	Tensile Strength	Excellent
Poor	Abrasion Resistance	Excellent
Poor	Heat Aging	Excellent
Good	Cure Rate with Peroxide Cure System	Excellent
Good	Compression Set	Excellent
Good	Resilience	Excellent
Good	Hysteresis	Excellent
Good	Low Temperature Flexibility	Excellent

2.2.2 Properties and applications of NBR

Similarly to all other unsaturated thermoset elastomers, NBR requires the addition of additives for enhanced processability and to produce useful inventions. The common additives that are added into NBR are usually reinforcement nanofillers to improve mechanical and thermal properties, protectants for anti-aging, plasticizers to increase flexibility to ease processing and vulcanization agents to improve strength and elasticity. Mixing and processing of NBR was generally carried out using an internal mixer and extruder or two roll mill mixing (Thakur *et al,* 2009).

In automotive industries, NBR is used for fuel and oil handling hose, seals and water handling application. Due to its wide range of thermal stabilities which is from -40 ℃ to 125 ℃, it could sustain most of the wear and tear of automotive applications. In industrial field, NBR applications include hydraulic hoses, conveying belts, oil field packers and seals of all sorts ranging from plumbing to oil column gaskets (Mackey *et al,*1999).

2.2.3 NBR blends

Polymer blending is an important process done for property enhancement and economic advantage particularly in polymer science field. One very important aspect for blending is the miscibility of the two constituents. Blending of NBR/PVC/CR was done to produce high performance oil resistance rubber for high performance applications (Khalaf *et al.* 2012). NBR/PVC blend requires processing aids, a study on NBR/PVC blend was conducted by George (1986). It was determined that the blend requires stabilizer comprising of MgO and ZnO with stearic acid which is very effective for PVC/NBR blend. Study was carried out using Brabender Plasticorder and blending using Brabender Internal Mixer.

For this study it is NBR/PVC, NBR acts as plasticizer for the rigid PVC for cable insulation applications, food containers and toys. Meanwhile, PVC at the same time compliments NBR in aspects of thermal aging and chemical resistance for applications such as gaskets, conveyor belt and water hose. PVC is responsible for the gloss of extruded stock of NBR/PVC blend. NBR/PVC blend can be easily processed, milled and extruded as compared to PVC. Over the years NBR was also blended with numerous materials such as hydrotalcite (Laskowska *et al.* 2013), carbon nanotubes nanocomposites (Zhu *et al*, 2009) and carbon black (Zhou *et al*, 2006).

2.3 PVC/NBR

2.3.1 Processing of PVC/NBR

There are certain grades of PVC and NBR which are highly miscible. The two blended constituents complement each other by improving overall properties while retaining their respective critical properties. These blends have excellent fuel resistance and ozone resistance. Stabilizers for high temperature stability are required for compounding. For the mixture of NBR/PVC usually stabilizers used are antioxidants, amine and phenol. Such examples of stabilizers are potassium oleate (KOL) and sodium hydroxide (KOH) (Christopher *et al.*1999).

Machine commonly used for the blending of thermoplastic elastomers are Brabender Internal Mixer, extruder or two roll mill mixer according to (Samira *et al*, 2013). The internal mixer was pre heated for 2 minutes then NBR is added first. After 1 minute the NBR will be heated up and homogenized in the mixer, then addition of PVC powder is done. The mixing of NBR/PVC takes 5 minute, product of mixing is obtained for testing. There steps are repeated with different blends ratio. If the content of PVC is higher than NBR, then the properties of thermoplastics are predominant. Else it would process similarly as rubbers if the PVC content is lower than that of NBR content (Ahmed *et al*, 2013).

A study on NBR/PVC/CR was done to produce high performance oil resistance rubber for high performance applications (Khalaf *et al.* 2012). The blend produced is designed for products in contact with oils. The result was identified that PVC in the blends induced to decrease in degree of swelling, penetration rate and the average diffusion rate making the blend oil resistant. In addition, another study by Shokri *et al*, 2006, investigates on the mechanical and rheological properties of NBR/PVC blends. The report states that, for better interfacial interaction, mechanical properties and increased processability of blending incorporation of compatibilizers is done. The reading in the torque rheometer for NBR/PVC blends shows that incorporation of compatibilizers will significantly improve mechanical properties and swelling behavior of PVC/NBR blend. Comparatively, by incorporating PVC powder as compared to PVC foam will produce a better effect on enhancing mechanical properties of the blend (Andreas *et al*, 1984).

2.3.2 Properties of PVC/NBR

NBR/PVC blend have great abrasion resistance and compression resistance thus making it good insulators for electrical applications. NBR/PVC blend is resistant towards water and oil making it suitable blend for applications in automotive and aeronautical industries. Due to the nature of the NBR/PVC blend which is soft it is considered as thermoplastic elastomer (TPE) and are suitable for most of the applications that requires high impact, toughness, deformation, fatigue life and strength (Wimolmala *et al*, 2012).

2.3.3 Advantages and disadvantages of PVC/NBR blend

The major advantages of NBR/PVC are the incorporation of good resistance towards oils and improved ozone resistance of NBR into PVC. NBR/PVC blends have excellent engine and hydraulic oil resistance (Omran *et al*.), thus making it the ideal material for engine gasket, seal and conveyor belt. Due to the chloride content in the PVC which compliments the blend thermal stability, NBR/PVC blends are essential in automotive industry and factory machinery components which requires high thermal resistant. Tensile strength, young's modulus, hardness and strain energy of NBR was significantly improved by addition of PVC. Processing of NBR is by adding processing aids as free flowing powders for easy blending with PVC powder. NBR is added to PVC dry blending cycle after PVC absorbs the liquid plasticizers. Die temperature is kept at 40 ℃ to prevent rubber agglomeration. The NBR/PVC blend processing is economical; it can be blended by conventional thermoplastic mixing equipment such as mixers, extruders and two roll mill. In addition, NBR/PVC blend can either undergo melt compounding and palletized or direct fabrication. Disadvantages of these blend is the poor weathering resistant contributed by the nature of NBR which low weathering resistance and poor steam resistant (Adams *et al*, 1993).

2.4 Graphene

2.4.1 Introduction

Graphene is an interesting material that has been tested and studied since 40 years ago. Molecular structure of graphene is showed in Figure 2.3. It is a major element in the field of nanocomposites among researchers. Graphene is widely used as nanofiller in nanocomposites due to its ability to be readily dispersed in most polymer matrices.

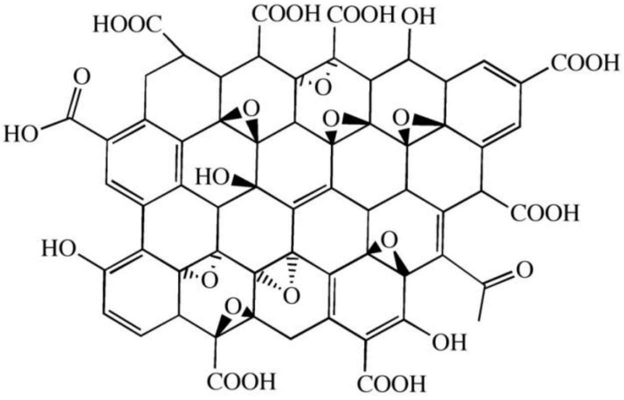

Figure 2.3: Graphene molecular structure (Hamilton, 2009)

Besides, it is well known that graphene poses superior chemical and mechanical properties such as high thermal conductivity (5000 $Wm^{-1}k^{-1}$), high surface area (2630 m^2g^{-1}) and high young's modulus (1.0 TPa) (Lee *et al.* 2008). Just a minute loading of graphene can significantly enhance the mechanical and chemical properties of the host polymer. Due to the nature of graphene which is one atom thick with honeycomb lattice of carbon, it can be rolled into various dimensions such as zero dimensional (0D), one dimensional (1D) and three dimensional (3D) graphite (Geim *et al*. 2007). Figure 2.4 shows the growth in interest in graphene studies over the years.

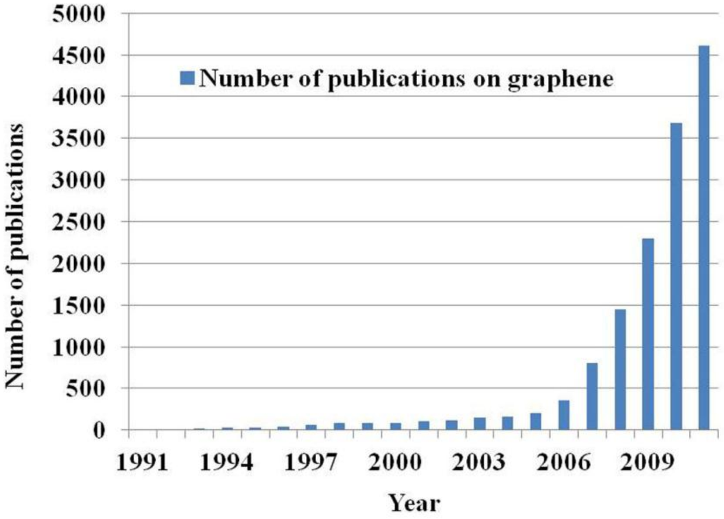

Figure 2.4: Growth in publications on graphene (Wang *et al.* 2012)

2.4.2 Properties and applications of graphene

Graphene structure is a honeycomb lattice with two equivalent carbon sub-lattice bonded together. This makes graphene stronger and stiffer than diamond by 200 times. Having Young’s modulus of 1TPa and ultimate strength of 130 GPa, it is the strongest material recorded. Graphene thermal conductivity is at 5000 W/(m.K), electrical conductivity of 6000 S/cm (Du *et al*. 2008). In addition to that, graphene large surface area of 2630 m^2/g and gas impermeability make it excellent for improving electrical, mechanical, thermal and gas barrier properties of any polymer. Graphene is applied as nanofiller for producing nanocomposites with improved properties for high performance applications (Hyunwoo *et al*,2010).

2.4.3 Oxidation of Graphene to Graphene Oxide (GO)

Graphene is oxidized to graphene oxide (GO) by modified Hummer's method. 5 g of graphite and 10 g of sodium nitrate ($NaNO_3$) were added to 100 mL of concentrated sulfuric acid (H_2SO_4) with continuous stirring with mechanical stirrer (500 rpm) for 30 min. Mixing was kept in ice bath to keep the temperature low and 10 g of potassium permanganate ($KMnO_4$) was added very slowly in it. It was carefully mixed with 200 mL de-ionized water to stop the reaction. 50 mL hydrogen peroxide (H_2O_2) was added to reduce the un-reacted $KMnO_4$. Then it was washed with de-ionized water and filtered to PH 5-7. The resulting GO was dried at 100 ℃ for 4 h (Wenge *et al*, 2013).

2.5 Graphene Oxide (GO)

2.5.1 Introduction

It was first prepared by chemist Benjamin C. Brodie in 1859 by using potassium chlorate and nitric acid to treat graphite. It was considered a dangerous process and in 1957, Hummers and Offeman developed The Hummer's Method which was much safer and efficient. Nowadays, graphene oxide (GO) is prepared by oxidizing graphite with strong oxidizing agents such as $KMnO_4$ which will introduce oxygenated functionalities to graphite. This makes graphite oxide hydrophilic enabling it to be exfoliated in water by sonication to produce Graphene Oxide (GO). (Deshmukh *at al*,2013)

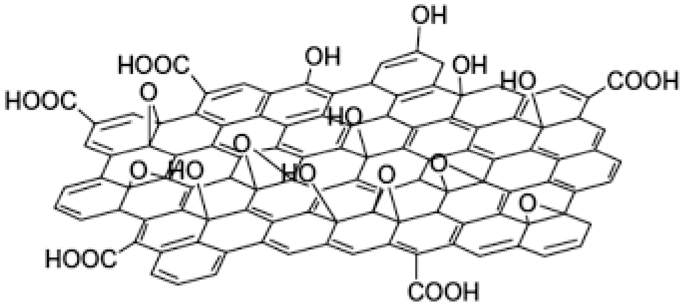

Figure 2.5: Graphene oxide molecular structure (Mahmoud, 2014)

2.5.2 Properties and applications

Graphene oxide is easily dispersed in water and organic solvents due to the presence on oxygenated group in its structure. It is an advantage because it can be mixed with any matrixes to improve their electrical, chemical and mechanical properties. Besides, due to disruption of the sp2 bonds it can insulate electricity excellently. This is why graphene oxide is incorporated as nanofiller in PVC to further enhance the already good electrical insulation of PVC for cable and wiring insulation application (Ban *et al*.2012).

Functionalization of graphene oxide will alter graphene oxide's properties. Thus the chemically modified graphene produced could become adaptable for various applications. There are many ways in which graphene oxide can be functionalized, depending on desired application. Nonetheless, graphene oxide is applicable is almost every applications and is considered the material of the future.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter covers on the raw materials used for the PVC/NBR and PVC/NBR-GO composite preparation, the supplier names, the physical properties of the raw materials, the composite preparation method and the processing conditions. In addition, the characterization of raw materials and testing of the composites were discussed.

3.2 Raw Materials

3.2.1 PVC

PVC resin with K value ranging from 60-67 and dioctylephthalate (DOP) with >99% purity was purchased from Chem Soln C6388. Stearic acid with AR grade, were obtained from Syntrtec Enterprise.

3.2.2 XNBR and additives

XNBR is obtained from Synthomer Sdn.Bhd. with Total Solid Content (TSC) of 44.8%, pH 8 and viscosity of 23 mPa.s. Latex compounding ingredients (sulphur: 50, antioxidant: 50, ZDEC: 50, ZMBT: 50, zinc oxide: 50, DPG and SSF) were all purchased from Zarm Scientific & Supplies Sdn.Bhd.Malaysia.

3.2.3 Graphene Oxide

GO was supplied by Platinium Senawang Sdn.Bhd in paste form which contains 15 wt% of GO. GO paste were further processed to produce GO particles.

3.3 Experimental Flow

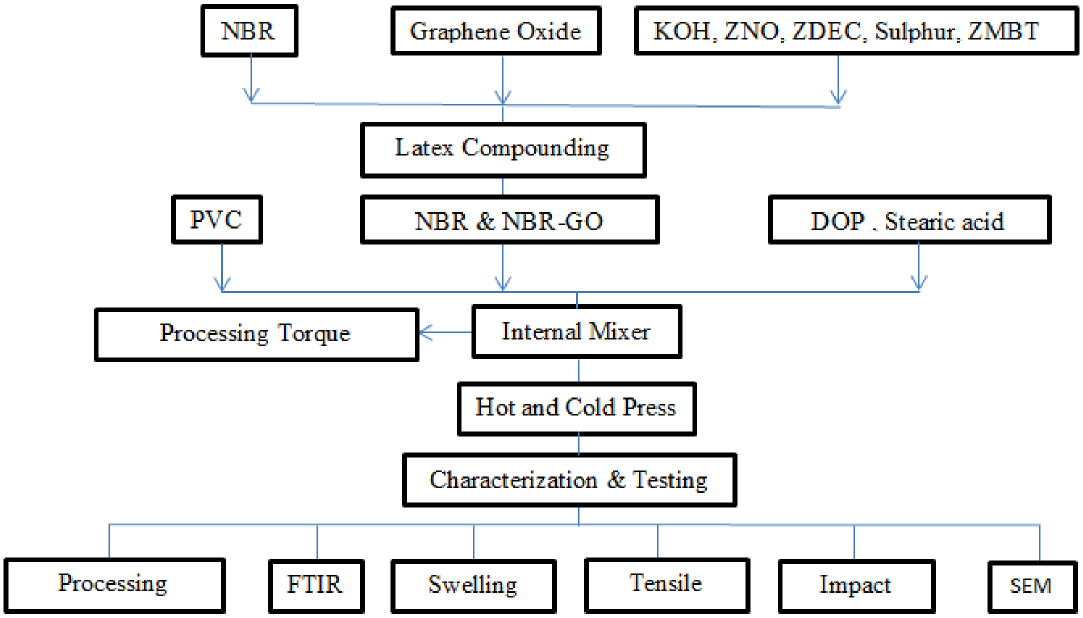

Figure 3.1: Experimental process flow

3.3.1 Graphene Oxide Preparation

Graphene Oxide paste supplied was filtered and washed several times with deionised water (DI) to remove the unwanted contaminant. Washing was carried out using decantation of supernatant with an ultra-centrifuge at 15,000 rpm for 30 minutes. Washing were done at least for 14 runs to achieve near neutral pH. As the pH of supernatant becomes 5~7, the product was re-dispersed with DI water and dried in an oven overnight at 80^{o}C**.** The dried GO powders are then used in NBR latex compounding.

3.3.2 NBR and NBR/GO compounding preparation

NBR latex used for this research is compounded with GO using a mechanical stirrer. Firstly, the NBR latex is stirred with KOH at 300 rpm. Then the scrapped GO powder was added into NBR followed respectively by the other compounding additives. As for compounding additives formulation is based on Table 3.1. Sulphur was added lastly to prevent incomplete mixing as sulphur promotes more cross-linking. Compounding is done for 30 minutes at 600 rpm. Then the compound was smeared in a container to be dried in oven at 100^{o}C for 24 hours. The dried and hardened NBR/GO is then crushed into small pieces to be used in PVC-NBR/GO composite preparation.

Table 3.1: NBR/GO Compounding Formulation

Ingredient	Total solid content (%)	Dry weight NBR (g)	Dry weight NBR-GO (g)
NBR	43.9	100	100
ZDEC	49.5	1.0	1.0
ZMBT	50.0	0.5	0.5
ZNO	45.6	1.0	1.0
KOH	10.0	1.0	1.0
Sulphur	44.0	1.0	1.0
GO	15.0	0.0	1.0

3.3.3 PVC and PVC/NBR Composite Preparation

The composites were produced by melt mixing using rheometer Brabender® Plastograph® EC 815652. Mixing was carried out at 180^{o}C for 8 minutes at 60 rpm. The processing formulation for PVC, PVC/NBR and PVC/NBR-GO composite are as in Table 3.2. The formulation recipe for PVC/NBR and PVC/NBR-GO composites is based on Table 3.3. The PVC/NBR-GO composite produced is scrapped of the internal mixer rotors ready to be pressed into films. The processing torque values were obtained from the mixer which is used as an indication of processability of the blends.

Table 3.2 : Compounding Formulation for PVC

Ingredient	Formulation (wt%)
PVC	100
DOP	30
Stearic acid	3.0

Table 3.3 : Compounding Formulation of PVC/NBR and PVC/NBR-GO Composites

Ingredient	PVC (wt%)	PVC/10NBR (wt%)	PVC/10NBR-GO (wt%)	PVC/30NBR (wt%)	PVC/30NBR-GO (wt%)
PVC	100	90	90	70	70
NBR	-	10	-	30	-
NBR-GO	-	-	10	-	30

3.4 Composite Characterization and Testing

3.4.1 Fourier Transform Infrared Analysis (FTIR)

Fourier transform infrared spectroscopy (FTIR) is carried out in this study to determine the functional group in each blending materials. The analysis is carried out using Perkin-Elmer FTIR spectrometer. The blend samples obtained from the hot press which is 0.5 mm thick film were placed on the sample holder. The spectra were recorded between 4000 and 400 cm^{-1} frequency range at four scanning number in transmittance.

3.4.2 Swelling resistance

Swelling test samples comprises of 5 samples of dumbbell shape from each composites according to ASTM D471-79 standard. Mass of each samples were weighed using an electronic balance before inserting into swelling bottle filled with toluene. Samples were left for 72 hours at room temperature in a dark environment. The composite samples were removed from swelling bottle and filter paper was used to remove excess toluene from surface. The samples were weighed to obtain final mass. High swelling percentage indicates that the composite have low solvent resistance. The percentage swelling ratio, Q is calculated by gravimetric method as given by equation 3.1

$$\mathbf{Q} = \frac{\boldsymbol{M_1 - M_0}}{\boldsymbol{M_0}}\ \boldsymbol{X}\ \mathbf{100\%} \qquad \text{(equation 3.1)}$$

Where $M_1$is the mass after immersion (g), M_0 is the mass before immersion (g) into toluene, Q percentage swelling ratio.

3.4.3 Tensile Test

Tensile test were determined by using dumbbell-shaped specimens. Tensile test was carried out according to ASTM D638 under ambient condition to measure the elastic modulus, ultimate tensile strength and elongation at break of PVC, PVC/NBR and PVC/NBR-GO at different NBR and NBR/GO loading. The test was conducted using Tinius Olsen H10KS-0748 with a load cell of 500N, at a crosshead speed of 50 mm/min. Total of 5 tensile tests were performed for each blending to obtain average values. The surface morphology of tensile blends fractured surfaces of were observed using Scanning Electron Microscopy (SEM).

3.4.4 Impact Test

Izod impact test was carried out according to ASTM D256 standard on notched samples of 64 mm X 12.7 mm X 3.2 mm in dimention. Zwick Impact tester was used to measure the total impact energy (Joule) required fracturing the standard test specimen. The samples were clamped to the holder and the pendulum is released, the impact energy on the scale is noted. The impact loads used are 7.5 J and 15 J. The impact strength of the specimens will be calculated based on equation 3.2.

Impact strength = Impact load / cross sectional area of the specimen (equation 3.2)

3.4.5 Scanning Electron Microscopy (SEM)

Morphology of PVC, PVC/NBR and PVC/NBR-GO at different NBR and NBR/GO loading were studied by JOEL JSM-6701F Field Emission Scanning Electron Microscopy (SEM). The test specimens were attached to an aluminium mounting with a double sided tape. The fractured surfaces are coated with thin layer of platinum to eliminate electron charging effect. The purpose of this study is to determine the dispersion of NBR and NBR/GO in PVC as well as to study the compatibility between the two phases. The surface morphology, dispersion of NBR or NBR/GO in PVC and the interfacial adhesion between PVC/NBR and PVC/NBR-GO was studied.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter covers on the results and discussion on the properties evaluation of PVC/NBR-GO as compared to PVC/NBR blends and neat PVC. Results for testing such as processing torque, FTIR, swelling test, tensile test, impact test and SEM were interpreted with regards to past research works done. All testing were conducted according to respective ASTM standards to ensure controlled testing condition as benchmark. Data obtained from each testing is tabulated and presented as support to solidify explanation beyond testing performed.

4.2 Processing Torque

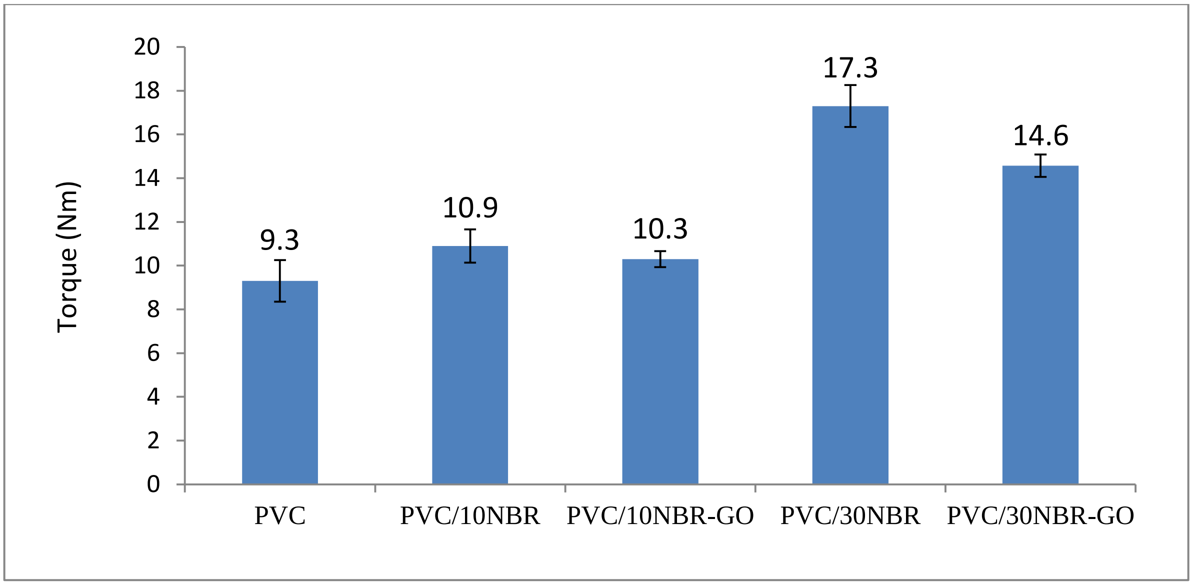

Figure 4.1: Effect of NBR and NBR-GO loading on PVC composites

Figure 4.1 shows the processing torque for melt mixing of PVC, PVC/NBR and PVC-NBR/GO composites. Torque indicates viscosity, stiffness and processability of the composites produced. Higher torque value indicates high viscosity and stiffness of composites and processing difficulties of the mixing. The processing torque of PVC/NBR and PVC/NBR-GO are comparably higher as compared to PVC. However with the addition 1 wt% of GO the torque value was slightly decreased as compared to the addition of NBR (10 wt% and 30 wt%) into PVC. GO promotes the processing and dispersion of NBR in PVC. High torque value might be due to the shearing of NBR chunks inside the mixing chamber.

The higher NBR loading requires more effort or torque for uniform mixing resulting in high shear and high temperature in mixing column. When at maximum torque which is the fusion point, most of the primary particles are likely to be fused together but are still distinguishable. Beyond the fusion point the melt temperature increases significantly causing a tremendous reduction in the melt viscosity and torque.

At this point the particulate structure starts to disappear. The temperature continues to rise and the viscosity of the blend decreases until it level out to relatively a constant value. At this equilibrium point all primary particles may have disappeared and a continuous melt is formed (Ku *et al*, 2004).

From Figure 4.1, as the NBR content in the composites increases, the torque value increases as well. This is due to a high NBR content in the composites which affects the torque required for mixing. Besides, the vulcanization of NBR having more cross-linking resulting is a need for a higher mixing torque to be blended with PVC. Besides, increasing NBR loading enhances the interaction between PVC/NBR blends making it hard to move. This results in higher shear requirement to achieve good dispersion of NBR and NBR/GO in PVC.

However from Figure 4.1, it also can be seen that the torque value of PVC/NBR-GO is lower than PVC/NBR composites. This is due to superior thermal properties of GO which upon mixed homogeneously into PVC/NBR blend, GO enhances thermal properties and reduce degradation caused by overcuring of NBR. An overcured composite will need more shear to be mixed uniformly because degraded composites are stiff and hard. When overcuring is overcome the mixing torque reduces, thus addition of GO reduces mixing torque (Ismail *et al*, 2011).

4.3 FTIR

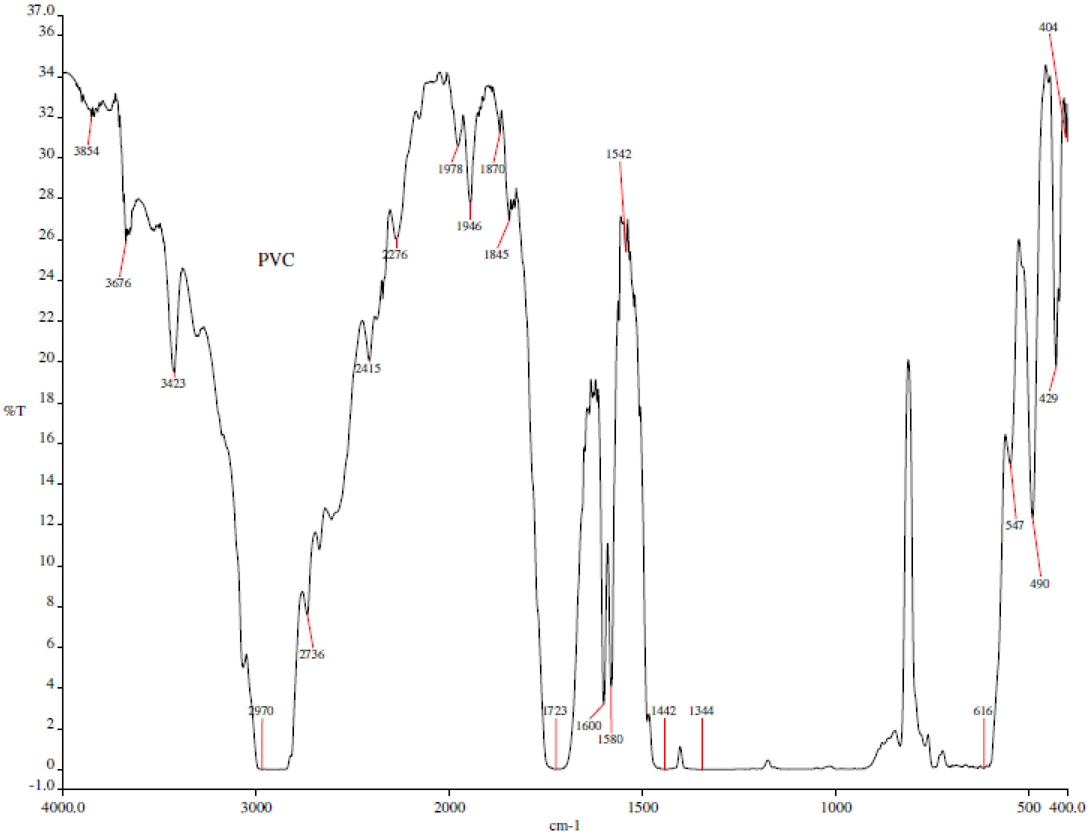

Figure 4.2: FTIR spectrum for raw PVC

FTIR is an essential method to determine structures of polymers by variation in compositions and interaction between components within a composition. Sample prepared by hot and cold press to thickness of 0.5mm and cut to small pieces for FTIR testing. For this research, FTIR was done to study the effect of NBR and NBR-GO loading on PVC through variation in compositions. Figure 4.2, 4.3, 4.4 and 4.5 shows the FTIR for raw PVC, GO, PVC/NBR and PVC/NBR-GO respectively. From figure 4.2, there are many peaks observed representing different functional group of compound. The Peak at 3720 cm^{-1} represent O-H stretching whereas 3515 cm^{-1} for NH_2 stretching. On the other hand peaks at 2970 cm^{-1} and 2415 cm^{-1} represent C-H stretching, 2276 cm^{-1}, 1580 cm^{-1} , 1542 cm^{-1} and 1442 cm^{-1} indicates C-H_2 stretching.

Furthermore, 1126 cm^{-1} and 1074 cm^{-1}represent C-C stretch, while at peak 616 cm^{-1} confirms PVC due to presence of chloride group C-Cl stretching. Table 4.1 summarizes all the peak values and the assigned functional groups in PVC, NBR and NBR-GO.

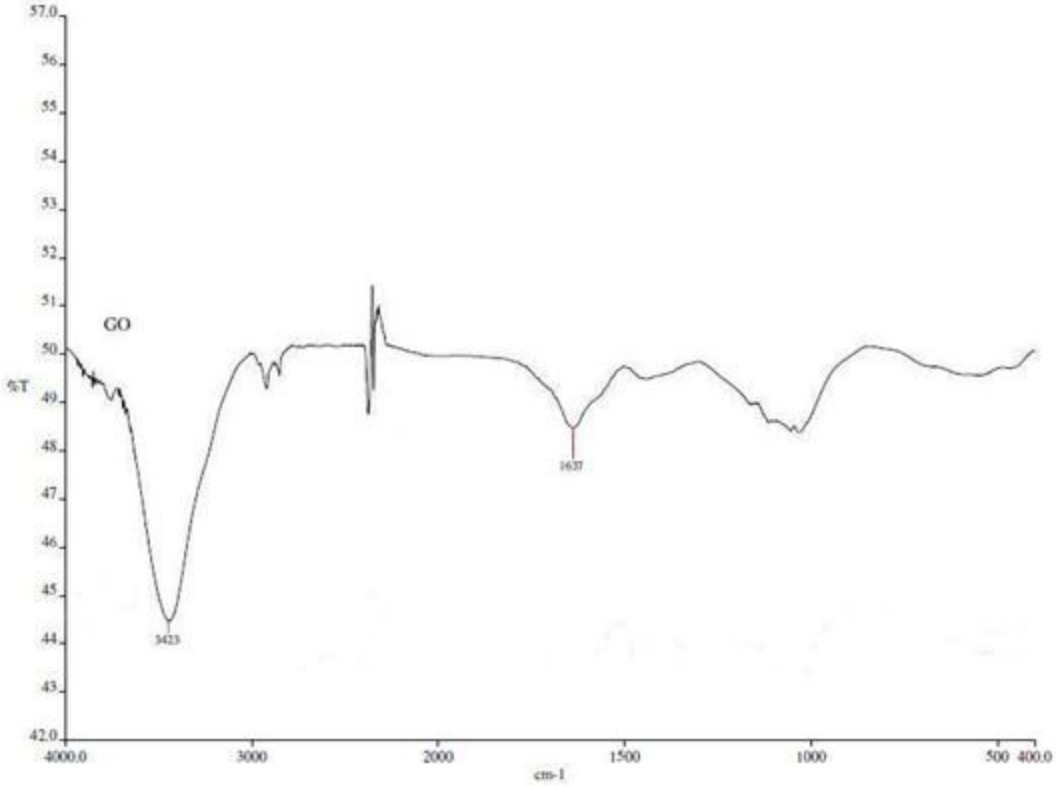

Figure 4.3: FTIR spectrum for graphene oxide

Table 4.1: FTIR analysis of PVC, GO, NBR and NBR-GO

Frequency (cm^{-1})	**Peak assignments**
3720	O-H stretch
3515	NH_2 stretch
2970	CH stretch
2415	CH stretch
2276	CH_2 stretch
1580	CH_2 stretch
1542	CH_2 stretch
1442	CH_2 stretch
1265	C-H stretch
1126	C-C stretch
1074	C-C stretch
860	C-Cl stretch
616	Si-O-Si stretch
547	Si-O-Si stretch
490	Si-O-Si stretch

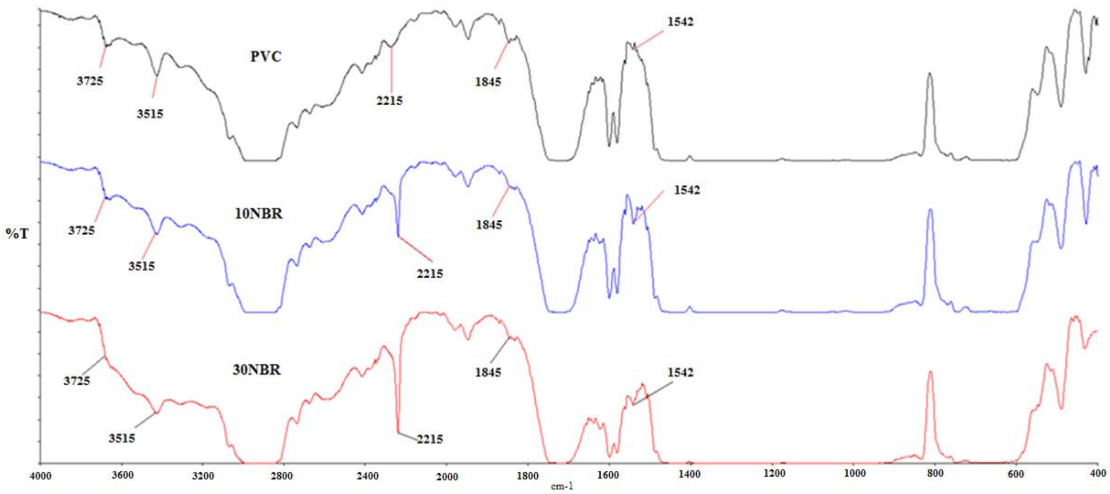

Figure 4.4: FTIR spectrum for PVC, PVC/10NBR and PVC/30NBR

As seen from Figure 4.4, peak ranging from 3515~3725 cm^{-1} increases in intensity as NBR was added into PVC. In addition, increasing to 30 wt% NBR further increases the intensity of peak due to presence of O-H bond from NBR which is carboxylated. In addition, at 2215 cm^{-1} peak increased tremendously when NBR was added at higher loading due to C-H_2 bonding increasing at intensity. However, peak at 1542 cm^{-1} are formed and increases in intensity might be due to the interaction between PVC and NBR.

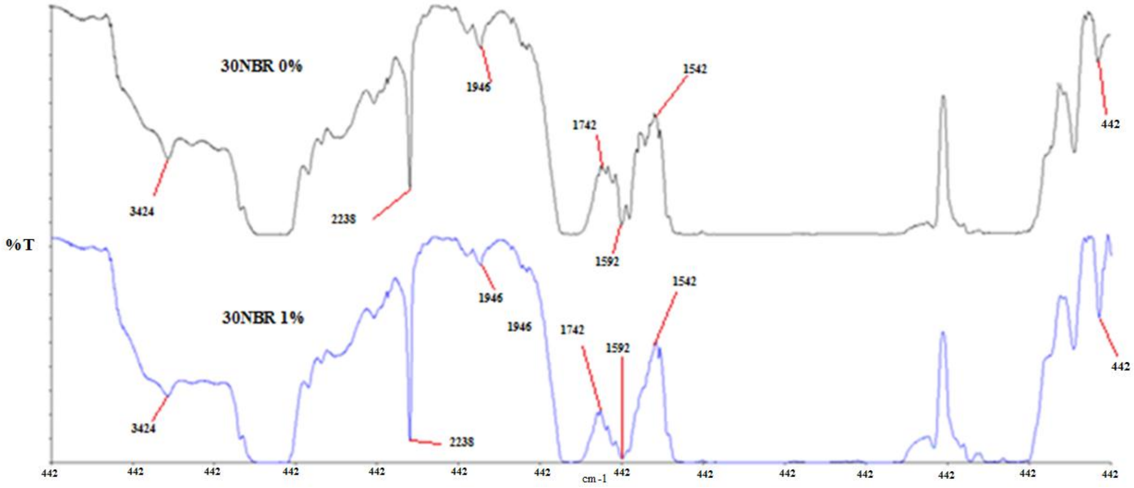

Figure 4.5: FTIR spectrum for PVC, PVC/10NBR-GO and PVC/30NBR-GO

On the other hand, incorporation of GO increases peak intensity at 2238 cm^{-1} where CH_2 bond appear indicating increased CH_2 in newly formed composite. Besides that, peak intensity for all other peaks increases overall after addition of NBR-GO into PVC as compared to PVC-NBR.

4.4 Swelling Test

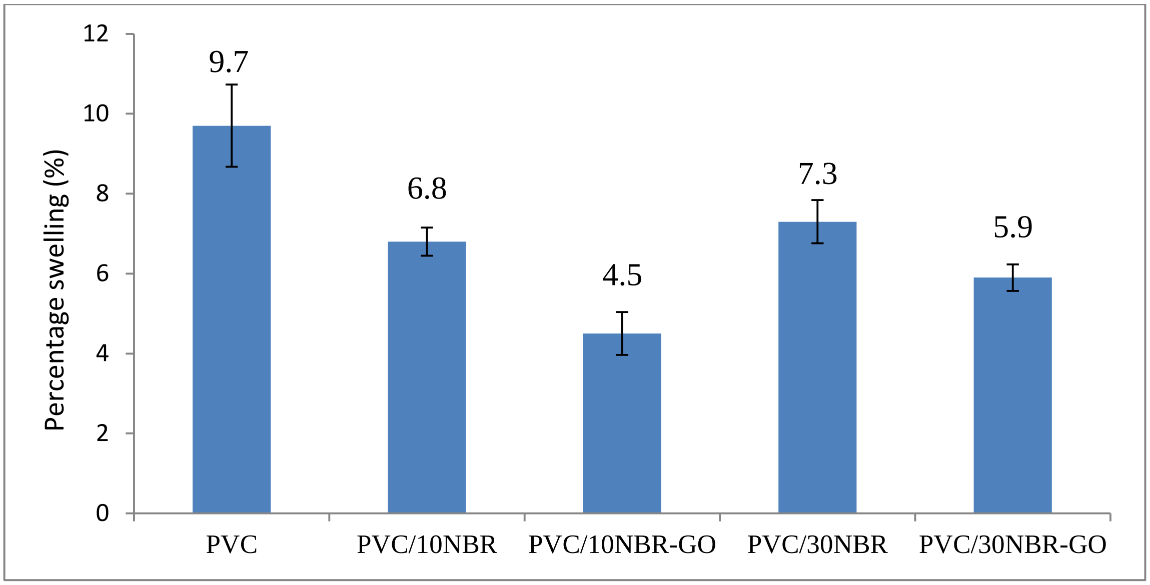

Figure 4.6: Swelling percentage of PVC, PVC/NBR and PVC-NBR/GO composites

Swelling test was performed to determine the solvent resistance of polymer composite. Higher swelling percentage indicate low swelling and chemical resistance and also indicate low crosslink density in NBR. Both NBR and PVC are capable of swelling in toluene, but the molded blend swells only to a limited extent showing the presence of chemical cross-links and good interfacial adhesion between PVC and NBR (George *et al*,1986*)* . The fact that the extent of swelling depends on the degree of cross-linking and interfacial adhesion is clear than the observation of the swelling index in Figure 4.6. This is expected since these blends show the higher rise in rheometric torque, which can be considered as proportional to the enhancement in interfacial adhesion and have a better mixing between NBR and PVC powder.

Swelling percentage can be related to the presence of interfacial adhesion due to the dispersion of PVC/NBR. The swelling percentage of each composites sample is given in Figure 4.6. It can be observed from the figure that the swelling percentage of composites prepared at mixing temperature (180 ℃) and the rotor speed (60 rpm) have the highest swelling resistance than pure PVC that can be related to the lower interfacial adhesion between the polymeric chains of PVC. Vice-versa when the NBR loading increases, amount of cross-linking increases. PVC and NBR being highly compatible will be mixed at high homogeneity resulting in a composite without phase separation, thus toluene absorption is limited (Demir *et al,*2006).

Besides, NBR naturally has high chemical stability which further attributes to being water and oil resistant (Khalaf *et al*, 2012). Figure 4.6 shows that when NBR loading increases, swelling decreases drastically. In addition, incorporation of GO further improves the swelling resistance of PVC/NBR. GO being nano sized, fills up remaining pores of the composites making it resistance to toluene at a higher degree (Mingchao *et al, 2012)*.

This can only be attributed to the morphology of the GO in this sample therefore, the dispersion of graphene oxide within polymeric matrix were examined by Scanning Electron Microscopy (SEM).

4.5 Tensile Test

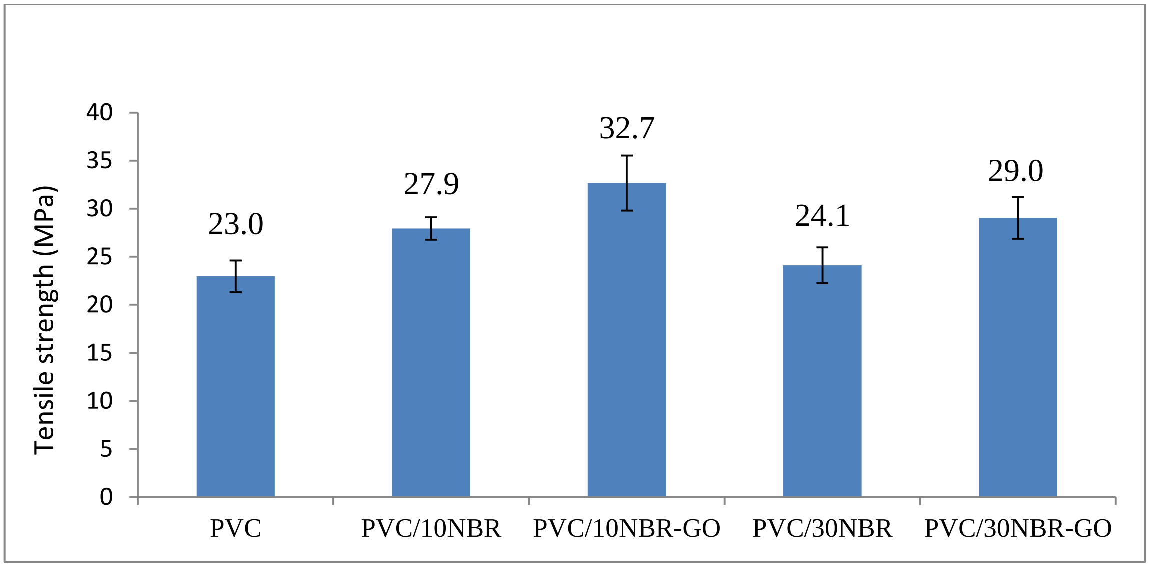

Figure 4.7: Ultimate Tensile Strength chart of PVC, PVC/NBR and PVC/NBR-GO composite

Tensile test was done to determine the ultimate strength, tensile modulus and elongation at break of the composite. Ultimate strength, E mod and Eb represents the strength, stiffness or rigidity and flexibility or deformability, of the composites respectively. Ultimate tensile strength (TS) increase with the 10 wt% NBR loading. Figure 4.7 shows that when 10 wt% NBR is added, the ultimate tensile strength increases as compared to PVC. This occurs because NBR inside PVC/NBR blend promotes rubbery behavior to the targeted PVC and introduces the tougher NBR phase which can resist more stress, thus increasing ultimate tensile strength. Additions of NBR containing 1 wt% GO into PVC further increases the ultimate tensile strength of the composite. This is due to nano sized GO contributing toward forming composite with little spaces in between PVC/NBR matrix, causing the composite to be high in stiffness thus increasing ultimate tensile strength. However, increasing NBR loading to 30 wt% causes the ultimate tensile strength to decrease slightly.

Theoretically, NBR loading increment would increase ultimate tensile strength of the composite but over-loading NBR causes overcuring. Overcuring occurs due to high shear exerted by internal mixer to ensure homogeneous mixing of the rubbery NBR in PVC. High shear results in heat buildup and the temperature of the mixing column exceeds the maximum processing temperature, resulting in overcuring of NBR and decomposition of PVC phase. Based on studies done by past researchers, degraded composite poses high stiffness resulting in a low ultimate tensile strength (Basfar *et al*, 2003). This report is also in line with this research finding by which increase NBR loading above 10 wt% decreases tensile strength but increased the stiffness / E mod of the composites as can be seen from Figure 4.8.

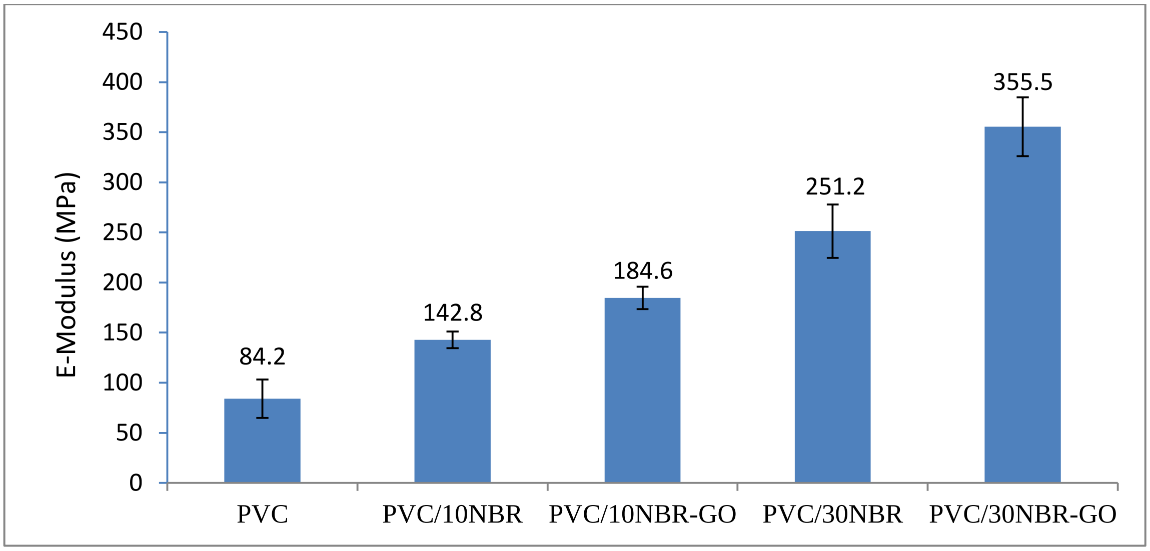

Figure 4.8: E-Modulus chart of PVC, PVC/NBR and PVC/NBR-GO

Figure 4.8 shows the trend for E-Modulus after addition of NBR and GO forming composites. PVC is in powdered form and has a very low E-Modulus followed by PVC/10NBR, PVC/10NBR-GO, PVC/30NBR and PVC/30NBR-GO respectively. Addition of NBR loading enhances E-modulus of composites, which is reasoned due to the increased NBR loading increases shear of internal mixer. Besides, good dispersion of

NBR and NBR-GO in PVC matrix as well as good interfacial adhesion between the phases resulted in higher interaction and improved stiffness of the composites. At higher loading however, the over curing of NBR attributes to the formation of brittle and stiffer phase in PVC which further increase the E-modulus value. On the other hand, incorporation of GO into composites shows an increasing trend because GO reduces the chain mobility of PVC/NBR blend. Decreased chain mobility is due to nano sized GO dispersed homogenously into PVC/NBR matrix blend. Low chain mobility indicates high stiffness composites produced (Mingwang *et al*, 2009).

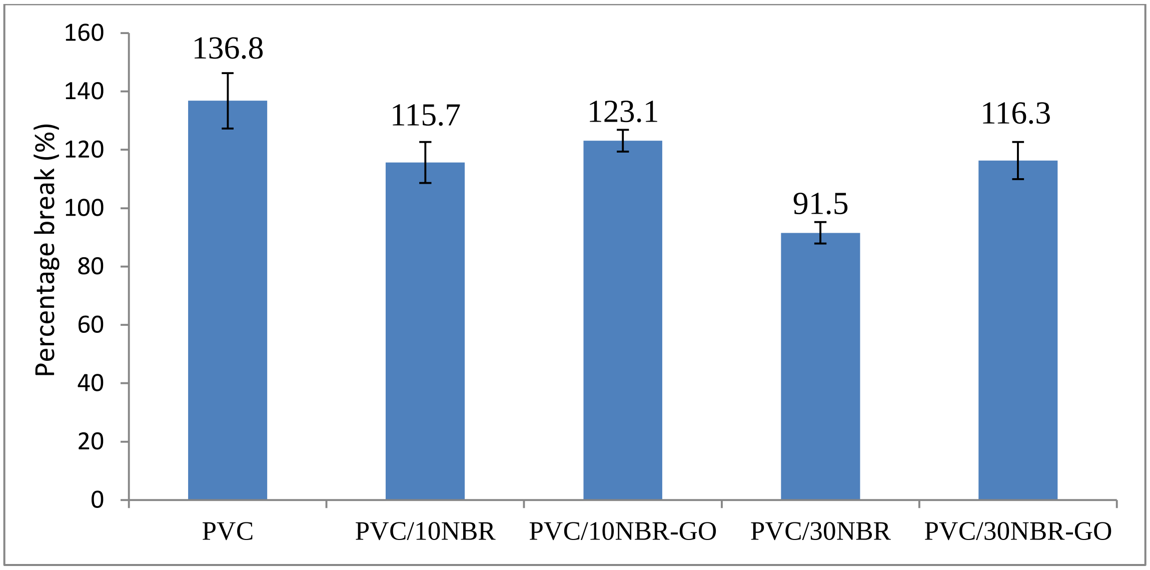

Figure 4.9: Elongation at Break percentage of samples

Figure 4.9 shows effect of NBR and NBR/GO loading on the elongation at break of PVC/NBR and PVC/NBR-GO composites. The increasing of NBR and GO loading in the composites decreases the elongation-at break, due to the increasing stiffness of the composite upon addition of NBR and GO loading. As chain mobility reduces, composites tend to become stiff and rigid thus lower elongation at break. These results are in line with the increasing E-Modulus and torque value which indicates the high stiffness of PVC/NBR as compared to PVC and the further improvement on the composite stiffness in the presence of 1 wt% GO.

4.6 Impact test

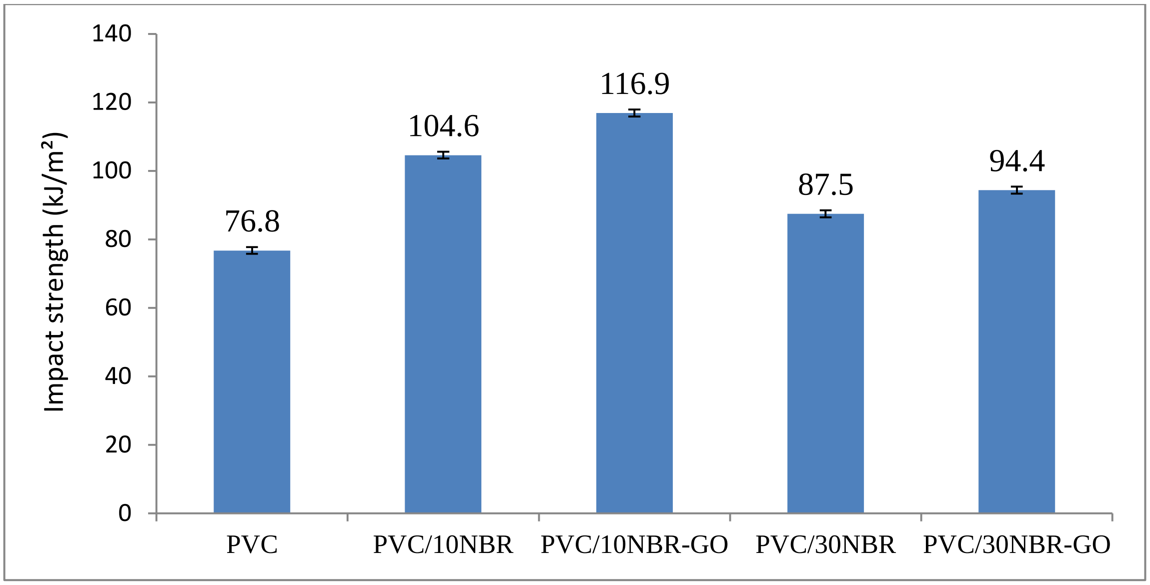

Figure 4.10: Impact Strength of PVC, PVC/NBR and PVC/NBR-GO composites

Impact test is carried out to determine the mechanical properties of samples by imposing destructive force on the sample. Izod impact test was done according to ASTM D256 standard on notched samples. For the first run of impact test, load of 7.5 J was used on the samples which resulted in the notched samples to not break due to insufficient load applied. Then load was increased to 15 J for second run causing the notched samples to break. Figure 4.9 depicts the average impact strength of 5 samples tested at load of 15J.

From Figure 4.10, it can be concluded that the composites are enhanced by two factors which are NBR loading and GO addition. PVC alone is very rigid, thus having low impact strengths compared to other composites studied. Addition of 10 wt% NBR shows slight increase in impact strength due to rubbery property courtesy of elastic nature of NBR. Further addition of 30 wt% NBR showed a slight decrease on the impact strength of the composites. This is due to the over curing of NBR at high loading and are in good agreement with the tensile properties obtained. Thus providing that deterioration of properties at 30 wt% NBR is due to over curing of the NBR.

On the other hand, addition of NBR-GO showed further improvement on the impact strength of PVC/NBR composites, both at 10 wt% NBR-GO and 30 wt% NBR-GO. In the presence of high thermally stable GO, the effect of over curing was reduced and NBR-GO shows better interfacial adhesion with PVC as compared NBR alone. Thus allows the PVC/NBR-GO composite to withstand higher impact load as compared to PVC/NBR. Besides, addition of GO further enhances impact strength of composites by uniform dispersion into PVC/NBR matrix producing high toughness and high impact strength composites.

4.7 Scanning Electron Microscopy (SEM)

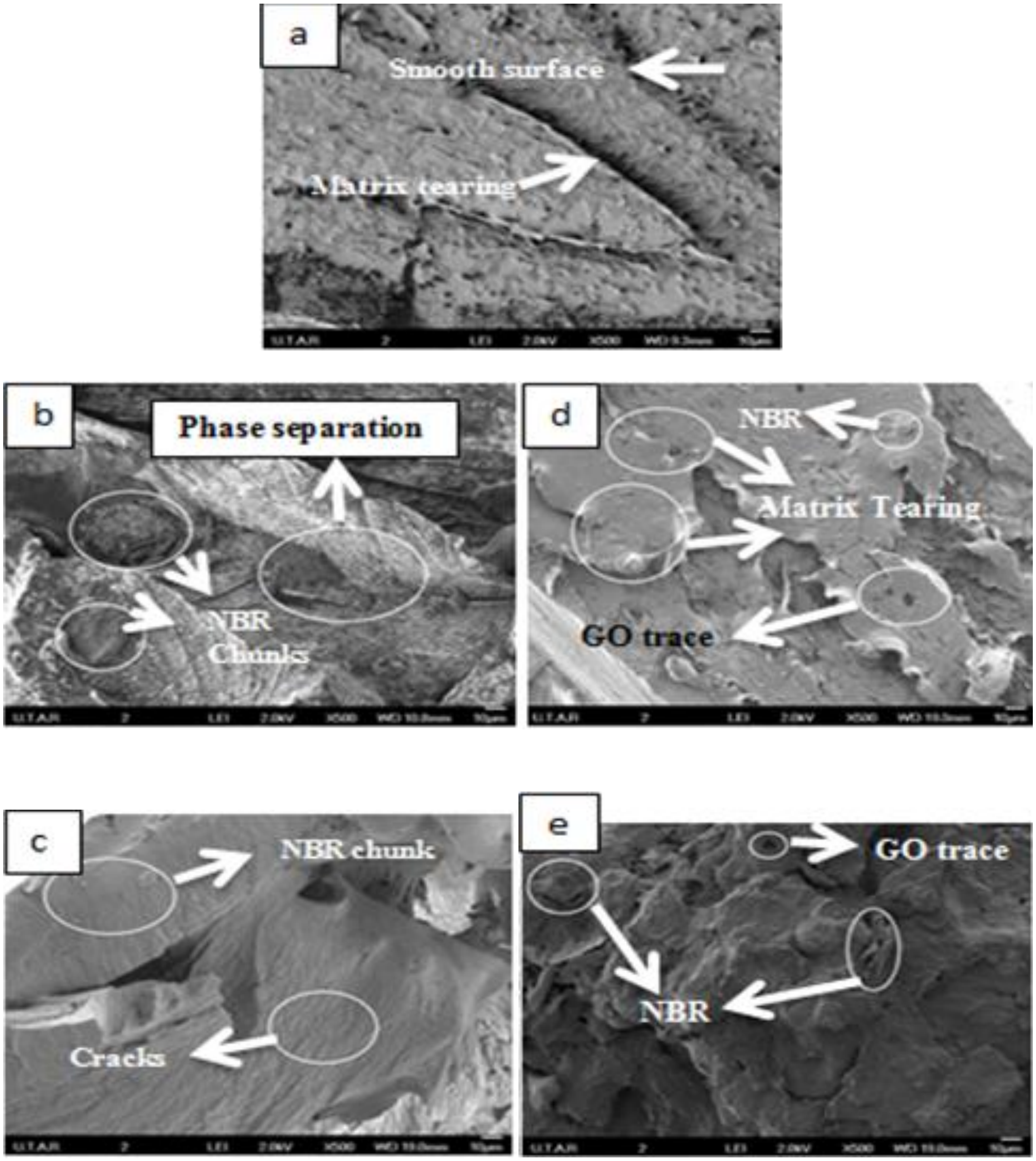

Figure 4.11: SEM images of (a)PVC, (b)PVC/10NBR, (c)PVC/30NBR, (d)PVC/10NBR-GO and (e) PVC/30NBR-GO at X500 magnification

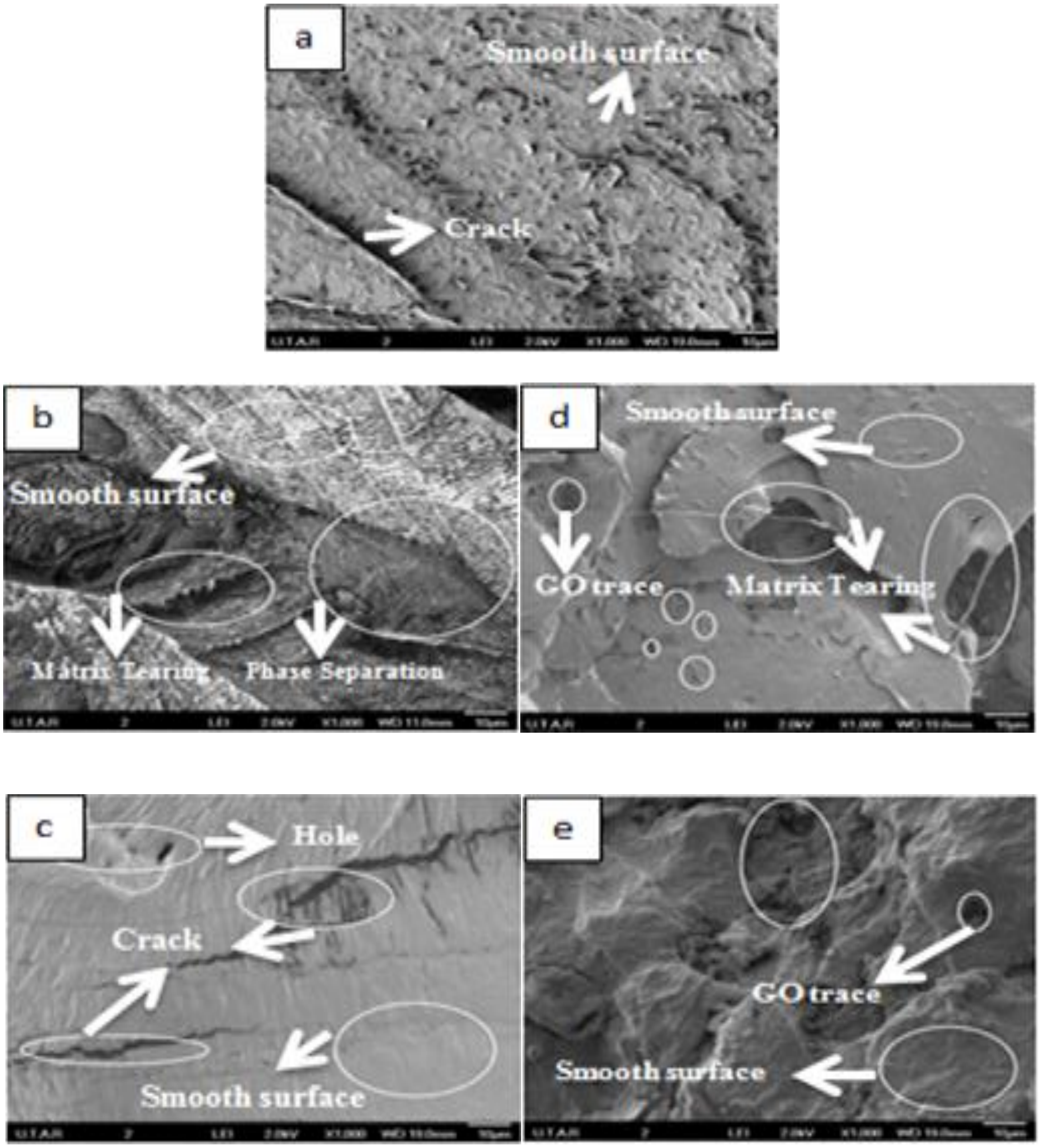

Figure 4.12: SEM images of (a) PVC, (b) PVC/10NBR, (c) PVC/30NBR, (d) PVC/10NBR-GO and (e) PVC/30NBR-GO at X1000 magnification

From Figure 4.11 (a), PVC showed a smooth fracture surface with slight matrix tearing. The higher surface roughness and matrix tearing indicates the resistance to crack propagation can be used to prove the strength of the material. With the addition of 10 NBR into PVC, the surface roughness of the composite was increased and traces of NBR can be seen clearly in Figure 4.11 (b) which shows high resistance of the matrix to applied load which are responsible for the higher strength of PVC/NBR as compared to PVC. However addition of 30 wt% NBR shows slight decrease in tensile strength and impact strength. Morphological observation of PVC/30NBR proves the deterioration of the composite properties are due to the over curing of NBR as can be seen from the small cracks on the composite phase as can be seen from Figure 4.11 (c) and 4.12 (b). The cracks are resulted from over curing of NBR phase which are very rigid and decomposed PVC at high processing temperature.

On the other hand, with the addition of 1 wt% GO, it can be seen that the surface roughness and matrix tearing of both PVC/10NBR and PVC/30NBR was increased as can be seen from Figure 4.11 (d and e) and 4.12 (c and d). High matrix tearing with smooth fracture surface is a clear evidence of improved strength and modulus of PVC/NBR-GO composites as compared to PVC and PVC/NBR composites. Besides that, chunks of NBR particles can be observed in Figure 4.11 (b) and 4.12 (a) which proves the poor dispersion of NBR in PVC. This however was overcome with addition of 1 wt% GO which also helped on the dispersion of NBR in PVC. This can be proven from Figure 4.12 (d) and 4.12 (c) which shows no phase separation or the presence of NBR chunk with the addition of GO.

CHAPTER 5

CONCLUSION AND RECCOMENDATIONS

5.1 Conclusion

NBR and NBR-GO compoundings were successfully prepared through latex compounding method using sulphur as curing agents. NBR and NBR/GO was melt blended together with PVC to produce PVC/NBR and PVC/NBR-GO composites using Brabender internal mixer at 180 ^oC for 8 minutes at 60 rpm.

NBR showed good compatibility with PVC has been proved from the improved tensile strength, E-modulus, impact strength and swelling resistance of PVC/NBR composites as compared to neat PVC.

However slight phase separation of NBR at low loading (10 wt%) and over curing of NBR at high loading (30 wt%) was revealed from the SEM observation. This problems were overcome with the incorporation of 1 wt% GO into PVC/NBR composites through NBR-GO particles which are blended with PVC. PVC/NBR-GO showed tremendous improvement on the tensile strength, E-modulus, impact strength and swelling resistance at both low and high NBR-GO loading as compared to PVC/NBR and neat PVC composites.

Furthermore addition of 1 wt% GO have reduced the processing torque which indicate better processing of PVC/NBR-GO as compared to PVC/NBR and also slightly improved the elongation at break. However the drawback of NBR addition on PVC are the reduction of elongation at break and higher processing torque which indicates difficulty on processing of PVC/NBR as compared to PVC.

5.2 Recommendations

Throughout this research, there were several problems encountered which affected the outcome of this research. Therefore some recommendations are made such as:

- Spray drier machine would provide for a better dispersion of the NBR into PVC. This would greatly have contributed to a homogenize mixture with better enhancement in chemical and physical properties.
- Thermal curing agent should be available, this would prevent higher loading of NBR to be over cured hence producing a much improved composites.

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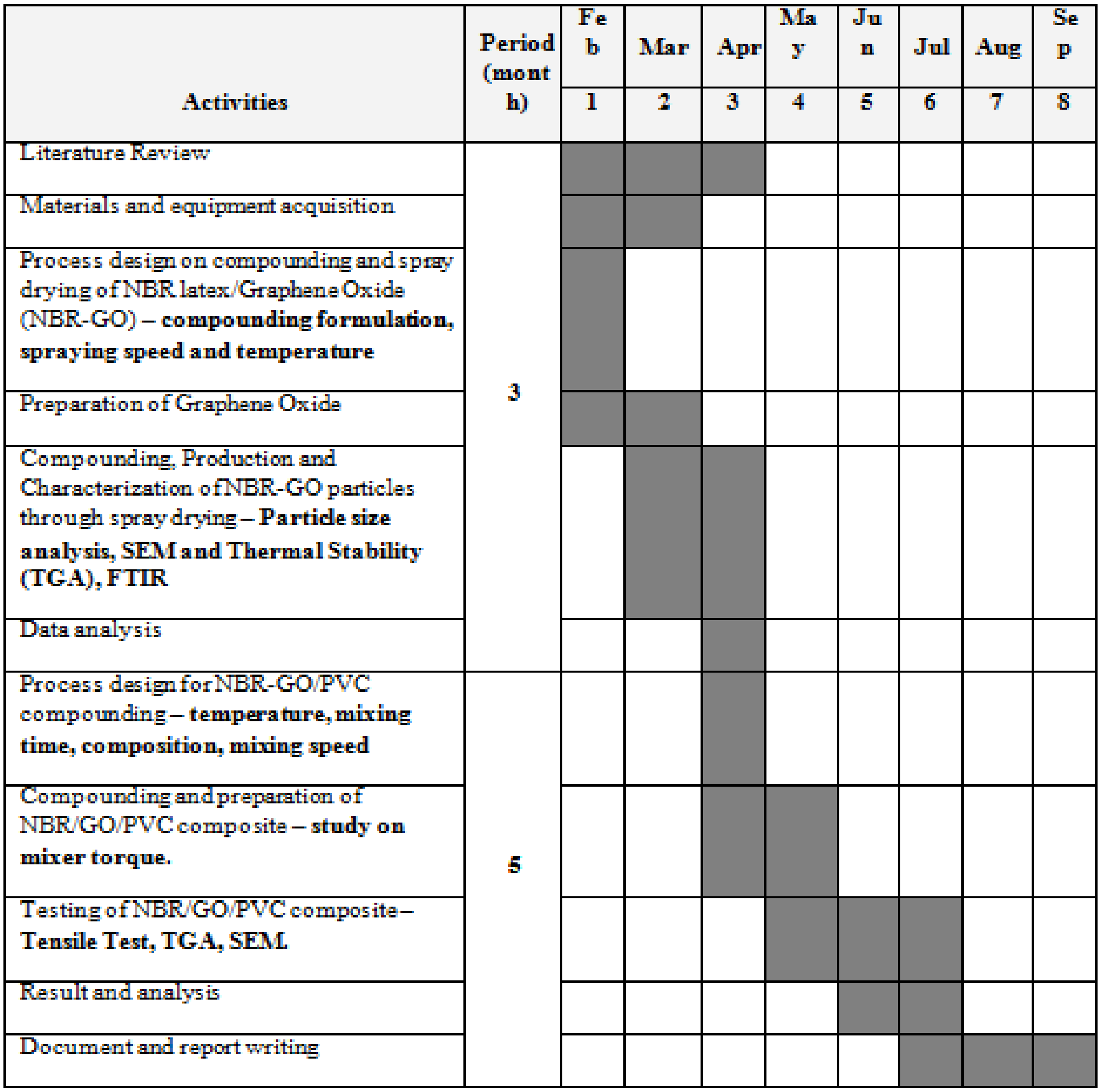
APPENDICES

APPENDIX A: Gantt Chart



Activities	Period (month)	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep
		1	2	3	4	5	6	7	8
Literature Review	3	■	■	■					
Materials and equipment acquisition		■	■						
Process design on compounding and spray drying of NBR latex/Graphene Oxide (NBR-GO) – **compounding formulation, spraying speed and temperature**		■							
Preparation of Graphene Oxide		■	■						
Compounding, Production and Characterization of NBR-GO particles through spray drying – **Particle size analysis, SEM and Thermal Stability (TGA), FTIR**			■	■					
Data analysis				■					
Process design for NBR-GO/PVC compounding – **temperature, mixing time, composition, mixing speed**	5			■					
Compounding and preparation of NBR/GO/PVC composite – **study on mixer torque.**				■	■				
Testing of NBR/GO/PVC composite – **Tensile Test, TGA, SEM.**					■	■	■		
Result and analysis						■	■		
Document and report writing							■	■	■