

**ASSESSMENT OF CHANGES IN PLASTICITY AND MECHANICAL PROPERTIES  
OF POLYSTYRENE FATTY ACID BASED NEEM OIL BLENDS**

**BY**

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NIGERIA**

**FEBUARY, 2018**

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OF POLYSTYRENE FATTY ACID BASED NEEM OIL BLENDS**

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**A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES,  
AHMADU BELLO UNIVERSITY, ZARIA,  
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD  
OF MASTER DEGREE IN POLYMER SCIENCE AND TECHNOLOGY**

**DEPARTMENT OF CHEMISTRY,  
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AHMADU BELLO UNIVERSITY,  
ZARIA, NIGERIA**

**FEBUARY, 2018**

### **DECLARATION**

I declare that this dissertation entitled “ASSESSMENT OF CHANGES PLASTICITY AND MECHANICAL PROPERTIES OF POLYSTYRENE FATTY ACID BASED NEEM OIL BLENDS” has been carried out by me in the Department of Chemistry. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other institution.

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TAKUMA, Salihu

.....

Date

## CERTIFICATION

This dissertation entitled “ASSESSMENT OF CHANGES IN PLASTICITY AND MECHANICAL PROPERTIES OF POLYSTYRENE FATTY ACID BASED NEEM OIL BLENDS” BY SALIHU TAKUMA meets the requirements governing the award of degree Master of Science (M.Sc.) in Polymer Science and Technology of Ahmadu Bello University, Zaria, and is approved for its contribution to knowledge and literary presentation.

**Prof. Paul A. P. Mamza**

(Chairman, Supervisory Committee)

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**Date**

## ACKNOWLEDGEMENTS

I wish to begin by thanking Almighty Allah (SWT) for giving me good health, opportunity and sparing my life out of His infinite mercy, blessing and wisdom to witness this day of my final defence.

My sincere and unreserved appreciation goes to my supervisors, Prof. Paul. A. P. Mamza and Prof C. E. Gimba for their efforts, time and contributions; constructive and instructive criticisms without which this dissertation would not have been a success. To all academic and non academic staff of Chemistry Department, Ahmadu Bello University, Zaria, I thank them once again for their contributions.

My sincere appreciation also goes to Dr. A. Ejila and all the staff of Research Division of National Institute of Leather Science and Technology (NILEST), Zaria, for their understanding and support, during the course of my bench work. My gratitude also goes to Metallurgical and Materials Engineering, Chemical Engineering and Mechanical Engineering Departments for their various contributions to this research.

My sincere gratitude to my dear wife and two children, for their kindness, understanding, patience, moral support, contributions and above all for assuring me always that am not alone and will never be alone.

I wish to also thank Dr. Halliru Ibrahim and Dr. Siaka Abdulfatai Adabara for their kind supports and contributions offered in this work. Thanks are due to my friends and colleagues, whose help and encouragement led to success of this work. Though words cannot express my gratitude and well wishes to all of them. May we all find success in our future endeavours, ameen.

## **DEDICATION**

I dedicate this work to Allah (S. W. A.) who created me as a human being. I also dedicate this research to my beloved parents, late Alhaji Mohammad and Hajiya Aishatu Mohammad, for their immeasurable love.

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## ABBREVIATIONS AND SYMBOL

ASTM = American Society for Testing and Materials

DSC = Differential Scanning Calorimetry

DEHP = Di(2-ethylhexyl)phthalate

DOP = Dioctylphthalate

E = Young`s modulus or tensile modulus

E<sup>+</sup> = Storage modulus

ELO = Epoxidised Linseed Oil

ENO = Epoxidised Neem Oil

EPO = Epoxidised Palm Oil

ESO = Epoxidised Soybean Oil

EVO = Epoxidised Vegetable Oil

FAEs = Fatty Acid Esters

FTIR = Fourier Transform Infrared

HIPS = High impact polystyrene

IUPAC = International Union of Pure and Applied Chemistry

IR = Infrared spectroscopy

LOE = Linseed Oil Epoxy

MEK = Methylene ketone

MFR = Melt flow rate

PE = Polyethylene

PMMA = Poly(methyl methacrylate)

PP = Polypropylene

PS = Polystyrene

PVAc = Poly(vinyl acetate)

PVC = Poly(vinyl chloride)

RNO = Raw Neem Oil

RTW = Rubber Tyre Waste

SEM = Scanning Electron Microscope

$T_c$  = Crystallisation Temperature

$T_g$  = Glass-Transition Temperature

THF = Tetrahydrofuran

$T_m$  = Melting Temperature

## ABSTRACT

The aim of this research is to develop a value-added product from a renewable resource, investigate the effect of its loadings on the mechanical and thermal properties of PS, as well as, to investigate the interaction between PS and plasticiser (ENO). Neem oil has high contents of unsaturated fatty acids which can be converted to epoxy fatty acids. The vegetable oil-based epoxy materials are sustainable, renewable and biodegradable materials replacing petrochemical-based epoxy materials in some applications. Neem oil was epoxidised at 60<sup>0</sup>C and one atmospheric pressure for 5 hours. Fourier transform infrared (FTIR) spectroscopy was used to identify the unsaturation and epoxy group in the neem oil (NO) and epoxidised neem oil (ENO). Disappearance of the absorption band around 3011.7 cm<sup>-1</sup> shows that the C=C has been used up and the appearance of a band around 943 cm<sup>-1</sup> which is not seen in the spectrum of the raw neem oil confirm the success of epoxidation. ENO was used as a green plasticiser and added to PS. ENO was added to PS at different contents using solution casting method. Different compositions of PS/ENO blends; (95/5, 85/15, 75/25, 65/35, 45/55, and 35/65) were tested for mechanical performance, thermal behaviour, morphological arrangement and miscibility. Comparison of mechanical properties such as elongation at break, tensile strength and tensile modulus revealed apparent compatibility domain for 95/5 PS/ENO (8.70±0.08, 24.40±0.02 and 37.0±1.0). The miscibility of the two components (PS/ENO) in solution phase was investigated by reduced viscosity as well as relative viscosities. The viscosity measurements revealed that miscibility occurs between the compositions 95/5, 85/15, 45/55 and 35/65 wt% PS/ENO while phase inversion and phase separation occur at compositions 65/35 and 75/25 wt% showing immiscibility and incompatibility. Morphological arrangements of the blends were examined by scanning electron microscopy (SEM). The SEM micrographs of the blends showed a two-phase system appearing bright (epoxy phase) and the other appearing black (PS phase) in virtually all the micrographs, even though the heterogeneity due to phase inversions (phase changes) was relevant for some compositions. For other compositions, a domain distribution showed considerable miscibility within the range of compositions. But blends composition of 95/5, 85/15, 65/35 wt% show better morphology. However, blend composition of 35/65 forms another region within the morphology leading to phase separation. The thermal study reported that plasticisation of the PS with ENO at certain compositions lowers the glass-transition temperature (T<sub>g</sub>), crystallisation temperature (T<sub>c</sub>) as well as melting temperature (T<sub>m</sub>) revealing the level of miscibility of PS with ENO. From the results obtained, this value added product which is potentially biodegradable has great potentials as alternative to the conventional use plasticisers such as phthalates, which can be used to enhance structure-property relationship in polymers.

## **CHAPTER ONE**

### **1.0 INTRODUCTION**

#### **1.1 Background of the Study**

Polymers are widely used due to their ease of production, light weight, design flexibility and processability. However, polymers are of lower modulus and strength compared to metals and ceramics. One way to modify their properties is to reinforce them with additives; most common of which being embedding of inclusions in the polymer. The resulting material will contain desirable properties not achieved by either phase alone. Hence, polymer properties can be improved while maintaining their light weight and ductile nature and such modifications could be done at relatively low filler content.

Plasticisation, in general, refers to a change in the thermal and mechanical properties of a given polymer which involves lowering of its rigidity at room temperature, lowering of temperature, at which substantial deformations can be effected with not too large forces, increase in the elongation to break at room temperature and increase in the toughness (impact strength) down to the lowest temperature of serviceability. These effects can be achieved through compounding the given polymer with a low molecular weight compound or with another polymer and also by introducing into the original polymer a comonomer which reduces crystallisability and increases chain flexibility.

The formulation of polymer blends has been an area of research interest for the past three decades owing to the enhancement in physical and mechanical properties of blends achieved via

synergism (Coleman *et al.*, 1991; Utracki, 1998; Ashraf *et al.*, 2007). The physical as well as chemical properties of the blends depend on the degree of miscibility of the components in the blends. Although even immiscible or partially miscible blends have found commercial applications, complete miscibility of the components in the blend is desirable because mixing on molecular scale results in superior physical as well as mechanical properties with change in composition (Zaccaria and Utrack, 2003).

Modification of the composition of the structural units represents one of the main approaches to the modification of polymer behaviour. In addition to the chemical nature and composition of the structural units that constitute the polymer backbone, molecular architecture also contributes to the ultimate properties of the polymeric products (Ebewele, 2000). The improvement in the toughness, flexibility and tensile strength of a polymer of high molar mass can also be achieved by blending it with an additive of low molar mass. Low molar mass from vegetable resource like lactose (Fan *et al.*, 2001) and starch cinnamate (Thakore *et al.*, 2001; Thakore *et al.*, 1999) have been used to modify the properties of poly(methyl-methacrylate) and other polymers. Development of consumer products from renewable agricultural raw materials is an area of great interest for researchers in academia, industry and government (Kaplan, 1998). The materials provide renewable and low cost source of raw material for various applications. In addition, these materials can be used and disposed without negatively impacting the environment or the health of people associated with their use, and disposal. These properties make agricultural products the preferred raw materials over the petroleum resource for the manufacture of consumer products. Nearly all agricultural raw materials have the potential to be used in the manufacture of consumer products ranging from automobile to utensils. Some of the agricultural-based raw materials being pursued for various applications include vegetable oils

(Biresaw *et al.*, 2002) (e.g. lubricants), fibre (Mohanty *et al.*, 2000) (e.g. composite for automobile), starches (Doane *et al.*, 1992) (e.g. biodegradable polymers), and cellulose (Edgar *et al.*, 2001) (e.g. bio-plastics).

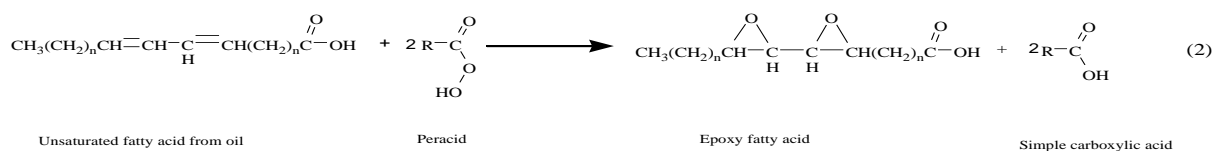
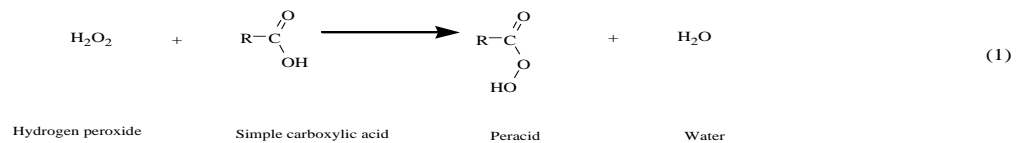
## **1.2 Vegetable Oils**

Vegetable or plant oils are the fats and lipids containing triglyceride molecules and represent a renewable resource that can be used as starting material to access new products with a wide array of structural and functional variations. For a long time, plant oils and their derivatives have been used by polymer chemist due to their renewability nature and relatively low prices, and their wide application possibilities. In recent years, there has been a great demand for plant oils as an alternative resource for production of additive for various applications such as polymer, coating, adhesive and nanocomposite (Wool and Sun, 2005). The necessity of releasing the polymer industry from its dependence on depleting resources represent a major concern, and consequently deemed necessary the search for industrially applicable renewable alternatives. Fortunately, plant oils offer many advantages which make them industrially attractive and feasible, as daily demonstrated by oleo chemistry. Their availability and relatively low prices make them industrially attractive and feasible, as daily demonstrated by oleo chemistry. The largest sources of vegetable oils are annual plants such as soybean, corn, linseed, cottonseed or peanuts. However, other sources are oil-bearing perennial plants such as the palm, olive, coconut or neem (Hui, 1995). The application of modified natural fats and oils in the chemical industries is becoming more and more interesting because of their availability from renewable resources (Ikhuoria and Dadson, 2007). Naturally occurring plant oils and fatty acids are mostly considered to be the most important renewable feedstock processed in the chemical industry and in the preparation of bio-based functional polymers and polymeric materials (Guner *et al.*, 2006).

At low temperature (below  $-10^{\circ}\text{C}$ ), vegetable oils undergo various physical changes like cloudiness, precipitation, poor flow and solidification (Schuster *et al.*, 2008) in sharp contrast to mineral oil-based fluids. Thus successful conversion of vegetable oils into viable and consumer products require overcoming these and other shortcomings. The unsaturation present in vegetable oils can be chemically modified to a value added product by epoxidation.

### 1.3 Epoxidation of Vegetable Oil (EVO)

Epoxidation increases the polarity and the stability of vegetable oil by improving their compatibility with polymers. Hence, epoxidised vegetable oils can be used as plasticizers, stabilisers, lubricants, composite, etc, in the polymer industry (Padmasiri *et al.*, 2009). The reason why vegetable oils are widely used as plasticisers is because the high numbers of carbon-carbon double bonds present in the vegetable oils make them a good target for manipulation into some other useful products e.g. soybean oil into epoxidised soybean oil (Hosler, 2008). Usually, a peroxide or per acid is used to add an atom of oxygen and convert the  $-\text{C}=\text{C}-$  bond to an oxirane group which is more reactive than double bond. An example of the conventional method of preparing epoxidised vegetable oils (Hill, 2000) is displayed in the scheme below.



### **Scheme 1.1: Conventional method of producing epoxidised vegetable oil.**

These EVO from biological origin substrates could bring along numerous advantages and new beneficial properties, which may not be derived from petroleum-based epoxy resins. EVO have been evaluated as ecological and environment friendly alternative for petroleum-based epoxy resins since they are neutral in carbon (IV) oxide cycle and are readily biodegradable. Other advantages of the EVO include cost effectiveness, renewability and availability. EVO or polymerisable monomers (Ikhuoria and Dadson, 2007) possesses epoxy ring in their backbone chain and produces flexibility and elasticity when it is treated with thermoplastic or thermosetting polymer along with suitable curing agents (Tayde *et al.*, 2011). Because of these special kinds of properties, EVO can easily replace phthalates which are petroleum base. Many plants oils such as soybean oil, rubber seed oil, Karajan seed oil, linseed oil, castor oil, African bean seed oil, e.t.c., (Ikhuoria and Dadson, 2007; Okiemen *et al.*, 2005; Vaibhav *et al.*, 2007; Akpan *et al.*, 2006) have been modified in various forms to improve their industrial potentials.

The epoxidised soybean oils are used as plasticisers for poly(vinyl chloride) resins to improve its quality in terms of flexibility, elasticity and toughness and to impart stability to the polymer towards heat and UV radiation (Vaibhav *et al.*, 2007). Due to high reactivity of the oxirane ring, epoxides can also be used as starting materials for a variety of chemicals such as alcohols, glycols, alkanol-amines, carbonyl compounds, olefin compounds and polymers like polyesters, polyurethanes and epoxy resins (Carlson and Chang, 1985). Today, one of the most important epoxidised vegetable oils is the epoxidised soybean oil (ESO) and its worldwide production is about 200,000 tonnes per year (Rusch *et al.*, 1999). Epoxidation of vegetable oil on an industrial

scale is most frequently carried out with per-oxo-acetic acid and per-oxo-formic acid due to low cost. Those per-acids are generated in the reaction mixture *in situ* reacting the relevant acid with hydrogen peroxide, under pre-selected conditions. In general, olefins can be epoxidised with various per-acids, of which *m*-chloro-per-benzoic acid has been most often used (March, 1992). Other per acids especially per-acetic acid and per-benzoic acid have also been used (trifluoroperacetic acid and 3, 5-dinitroperoxybenzoic acid) as reported by Vijayagopalan and Gopalakrishnan, (1971).

#### **1.4 Polystyrene**

Polystyrene is brittle, rigid, transparent, easy to process (shrinkage is low), free from odour and taste polymer. It is thermally stable, with excellent electrical properties. All these properties are responsible for its commercial success. Polystyrene is sometimes referred to as crystal polystyrene, which refers to the clarity of the finished product and does not imply that the molecular structure responsible for many of the good properties of polystyrene such as clarity of products, the low energy input required for processing and eases of processing with low shrinkage.

Polystyrene is used in a wide range of products due to its versatile properties. Some of these properties are listed below.

##### **i. General**

Polystyrene is an amorphous thermoplastic with a density of  $1.05 \text{ g/cm}^3$  with extremely low moisture absorption (0.05%). Styrene polymers have some unique properties which make them useful in a wide range of products. The single most important characteristic of general purpose

polystyrene is that it is a glass-like solid below 100°C. Above this temperature, commonly called the glass-transition temperature, the polymer chain (on a molecular level) has rotational freedom which allows large-chain-segment mobility. The polymer is thus fluid enough to be easily shaped into useful forms. Below the glass-transition temperature, polystyrene possesses considerable mechanical strength, allowing it to be used in load-bearing tasks in many applications.

Rubber-modified polystyrene is a two-phase system consisting of a dispersed rubber phase and a continuous polystyrene phase. The dispersed rubber particles initiated large numbers of crazes without crack formation, thus contributing to the development of very tough products. In addition to toughening, the rubber particles also increase the environmental stress-crack resistance because the microscopic rubber particles are placed in tension as they are cooled after fabrication, compressing the rigid phase. The particles try to shrink more than the rigid phase because rubber has a greater coefficient of expansion than polystyrene. Modern micrographic and analytical tools have been developed to measure and predict the complex interactions of these two-phase systems. Styrene readily copolymerises with a variety of other monomers. The first well known copolymer was styrene-butadiene synthetic rubber. Other significant copolymers include tough, solvent-resistant copolymers with acrylonitrile; heat resistant polymers with maleic anhydride; and rubber-modified, transparent systems with methyl methacrylate. Although there have been many studies concerning multiple (more than two) comonomers, few significant commercial products exist.

Since styrene polymers are non-polar, chemically inert, resistant to water, and easy to fabricate, they are the products of choice for electronic, medical, food packaging, appliance and

automotive applications. Recent manufacturing trends provide improved processability and further decrease trace impurities. High-speed, efficient fabrication equipment is both reducing the cost of manufacturing and increasing the strength of the fabricated parts.

Polystyrene molecules can be oriented during fabrication. Modern processing equipment uses controlled orientation to produce tougher fabricated parts. Tensile strengths may double and elongation may increase by up to two orders of magnitude, resulting in tremendous increase in toughness. Toughening by orientation contributes to the success of polystyrene foam, now widely used in both insulation and as foam sheet in food packaging, and to the success of clear, thermoformed, biaxially oriented polystyrene. Pure polystyrene does not absorb ultra violet light in the terrestrial sunlight spectrum and would apparently have better ultraviolet stability if it were not for the presence of ultraviolet absorbing trace impurities. The presence of rubber tends to decrease the outdoor stability; this is countered by incorporating special rubbers and stabilisers. Anionic polymerisation produces a more thermally stable polymer which can be made even more stable by proper selection of the end group, because most degradation begins at chain ends. Because of the commercial interest in polystyrene, its polymerisation ease, and its relatively simple linear structure, polystyrene is one of the most thoroughly investigated polymer systems in the world (Wool and Sun, 2005).

Several attempts have been made to enhance the mechanical properties and stability of polystyrene during loading conditions in recent years. Unmodified, unblended or virgin polystyrene is a brittle, inflexible material with limited commercial possibilities and usefulness. Its utilisation is based on the compounding of the base polymer with additives. With the addition

of additive such as plasticisers, heat stabilisers, lubricants, fillers and copolymerisation with other monomers; the poor properties of polystyrene can be improved (Xiea *et al.*, 2004). Fracture resistance of polystyrene can be enhanced by blending it with elastomers like natural rubber (Shaws and Singh, 1989), polyurethane (Siddaramaiah and Somashekar, 1998), ethylene polypropylene rubber (Shaws and Singh, 1989), polybutadiene (Ivankova *et al.*, 2003), polyethylene (Gao *et al.*, 2003), poly(acrylic acid) (Zhang and Eisenberg, 1999). The morphology, miscibility and mechanical properties of these blends are well documented. In these blends, however, the problem of immiscibility and phase separation is overwhelmingly encountered that ultimately hamper the synergism in the physico-mechanical properties of the blend (Gao *et al.*, 2003).

#### **ii. Mechanical properties**

Mechanical properties of any material is essentially defined as those properties that determine the response of the material to applied stresses or strain during service (Bello, 2001). Polystyrene is hard, stiff and dimensionally stable but relatively inextensible material with high tensile strength (55 – 80 NM/m<sup>2</sup>) and low elongation at break (<10%). The mechanical strength is affected to a large degree by the processing conditions. The highest value can be obtained with free flowing materials at a low processing temperature.

#### **iii. Chemical resistance**

Polystyrene has good chemical resistance. It is resistant to alkalis, dilute mineral acids, water and aqueous solution at room temperature.

#### **iv. Resistance to stress-cracking**

Polystyrene is susceptible to stress-cracking with internal stresses which can form stress cracks even in the resistance. It is therefore advisable to produce injection-moulded parts with a few internal stresses as possible.

#### **v. Advantages and limitations**

Polystyrene has good chemical properties, low cost, easy to process, low shrinkage, however, it has limitations, which include negligible mechanical properties above 70°C, brittle at room temperature and degrade rapidly in outdoor use due to ultraviolet light.

### **1.5 Neem Seed (*Azadirachta indica*) Oil**

Neem (*Azadirachta indica*) belongs to *Meliceae* family and grows rapidly in the tropics and semi-tropic climates. It is also observed that this tree could survive in very dry and arid conditions. Neem tree is an evergreen related to mahogany, growing in almost every part of the world like India, Saudi Arabia, East Asia and West Africa, etc (Muthu *et al.*, 2010). In Nigeria, neem forms about 90% of the trees in the forestry plantations established in the 12 states within the savannah zone under the afforestation programme (Ogbuewe *et al.*, 2011).

The importance of the neem tree has been recognized by U S National Academy of Sciences, which published a report in 1992 entitled 'Neem a tree for solving global problems' (Biswas *et al.*, 2002). Neem has been in a global context today because it offers answers to the major concerns facing mankind. Neem (*Azadirachta indica*) is considered harmless to human, animals, birds, beneficial insects and earthworms and has been approved by the U S Environmental Protection Agency for use on food crops (Debjit *et al.*, 2010; Sharma *et al.*, 2011). A matured neem tree produces 30 to 50 kg of fruits every year and has a productive life span of 150 to 200

years (Ragit *et al.*, 2011). Neem oil comprises mainly of triglycerides and large amount of triterpenoid compounds. It contains four significant saturated fatty acids, of which two are palmitic acid and two are stearic acid. It also contains polyunsaturated fatty acids such as oleic acid and linoleic acid (Muthu *et al.*, 2010). The quality of oil in terms of its fatty acids composition is very important. All parts of neem plant such as leaves, bark, flower, fruit, seed and root have advantages in medical treatment and industrial products. Its leaves can be used as drug for diabetes, eczema and reduce fever. Bark of neem tree can be used to make toothbrush. Neem root has an ability to heal diseases and is used against insect bites (Puri, 1999; Ragasa *et al.*, 1997). Neem seed is a part of neem tree which has high concentration of oil. Neem oil is widely used as insecticides, lubricant, drugs for variety of diseases such as diabetes and tuberculosis (Puri, 1999; Ragasa *et al.*, 1997 and Johnson *et al.*, 1996). There are several methods to obtain neem oil from the seed like mechanical pressing, supercritical fluid extraction and solvent extraction (Puri, 1999). Mechanical extraction is the most widely used method to extract neem oil from its seed. However, the oil produced with this method usually has low price, since it turbid and contains a significant amount of water and metal contents. In extraction using supercritical fluid, the oil produced has very high purity; however, the operating and investment cost is high. Extraction using solvent has several advantages. It gives higher yield and less turbid oil than mechanical extraction and relatively low operating cost compared with supercritical fluid extraction (Maria *et al.*, 2008). In order to increase the application potential of neem oil, the side-chain olefinic groups are converted to epoxide.

The table below shows the physicochemical properties and fatty acid composition (%) of NO.

**Table 1.1: Physico-chemical Properties and Fatty acid composition (%) of NO**

| Physico-chemical property /Fatty acid<br>(g / 100 g) | Neem oil                          |
|--|-----------------------------------|
| Specific gravity                                     | 0.915 – 0.920 / 30 <sup>0</sup> C |
| Saponification value (mg / g KOH)                    | 175 – 200                         |
| Iodine value (mg / g I <sub>2</sub> )                | 65 – 80                           |
| Palmitic acid (C <sub>16</sub> )                     | 13.6 – 16.2                       |
| Stearic acid (C <sub>18</sub> )                      | 14.4 – 24.0                       |
| Oleic acid (C <sub>18:1</sub> )                      | 49 – 62                           |
| Linoleic acid (C <sub>18:2</sub> )                   | 2.3 – 15.8                        |
| Linolenic acid (C <sub>18:3</sub> )                  | —                                 |
| Total unsaturated acid                               | 64.55                             |
| Total saturated acid                                 | 34.10                             |

Source: Uko *et al.*, 2008, — = not determined.

### 1.6 Plasticiser as Additive to Polymers

Polymer additives are substances compounded into a resin to enhance or improve specific resin characteristics. They function by contributing to the quality, life and usefulness of the resin. Based on chemical profiles and overall functions, additives are commonly divided into categories. In order to improve the processing, performance and elasticity of plastic materials, the polar and non-polar additives (plasticisers) are added. In 1951, the International Union of Pure and Applied Chemistry (IUPAC) developed a universally accepted definition of a plasticiser as a substance or a material incorporated in a material (usually a plastic or elastomers) to increase its flexibility, workability, or extensibility (Krauskopf and Godwin, 2005).

Plasticiser is typically present in between 1% to 10% by weight of polymeric material. Below 1%, the plasticiser may not effectively plasticise the polymeric material and above, it tends to leach out of the material (Hu *et al.*, 2013). The interactions of plasticiser molecules with polymer chains cause disruption of secondary valence bond or van der Waals force between polymer

molecules. As a consequence, a decrease in molecular interactions and thus an increase in mobility of the polymer chains are observed. As a result, the materials are characterised by lower moduli, stiffness, glass-transition temperature ( $T_g$ ) and hardness. The elongation of material and chain flexibility significantly also increases (Adelia *et al.*, 2013). The most generally applied plasticisers are low molecular mass organic compounds characterised by low volatility in order to prevent their rapid evaporation from manufactured products. Among commercial applied plasticisers for polystyrene are phthalate esters such as dimethyl, diethyl, dipropyl, dibutyl, diheptyl, dioctyl, diisodecyl or dibenzylbutylphthalate commonly used (Etchenique and Weisz, 1999; Mills *et al.*, 1998). In addition, the application of adipate and glutarate esters as plasticisers for expanded polystyrene and the liquid paraffin and zinc stearate as internal plasticisers is reported (Garder *et al.*, 1999; Usui *et al.*, 2002). In the last decade, the worldwide production of plasticisers was around 5 million tonnes per year. These were applied to around 60 polymers and more than 30 groups of products (Bialecka-Florjanczyk and Floranczyk, 2007). The use of plasticisers for plastic products manufacture is well known. Its application to modify polymer characteristics began in the 1800s. In these early days, manufacturers of colloid or colloid lacquers used camphor and castor oil for plasticisation purposes, but these were unsatisfactory for many end uses. Later, in 1912, triphenyl phosphate was tested to substitute camphor oil, representing the beginning of the ester plasticisers' era. Phthalic acid esters found applications as plasticisers for the first time in 1920 and continue to be the largest class of plasticisers in the 21<sup>st</sup> century (Rahman and Brazel, 2004). Di(2-ethylhexyl)phthalate (DEHP), also known as dioctylphthalate (DOP), was introduced in 1930 and has been the most widely used plasticiser since 1930s. However, most of the phthalates have toxic properties for human. Due to this, the intensive studies on the new, non-toxic and biodegradable materials that could replace harmful

plasticisers are developed (Hendorf *et al.*, 2007; Yang *et al.*, 2006). Nowadays, there is increasing interest in the use of natural- based plasticisers that are characterised by low toxicity and low migration. This group includes epoxidised triglycerides vegetable oils from soybean oil, linseed oil, castor oil, sunflower oil and fatty acid esters (FAEs) (Baltacioglu and Balkose, 1999).

Several theories have been proposed to explain the mechanism and action of plasticisers on polymers. Among those theories, lubricity theory and gel theory have been widely accepted to describe the effect of plasticisers on polymeric networks. Lubricity theory proposes that the plasticiser acts as a lubricant to reduce friction and facilitates polymer chain mobility past one another and consequently lowering deformation. Gel theory extends the lubricity theory and suggests that plasticiser disrupts and replaces polymer-polymer interactions (hydrogen bonds, van der Waals or ionic forces etc) that hold polymer chains together resulting in reduction of the polymer gel structure and increase flexibility.

### **1.7 Fourier Transform Infrared (FTIR) Spectroscopy**

FTIR spectroscopy is a technique that is sensitive to intermolecular interactions. Infrared spectrum helps to reveal the structure of a new compound by telling us what groups are present or absent from the molecule. A particular group of atoms give rise to characteristic absorption bands; that is a particular group absorbs light of certain frequencies that are much the same from compound to compound. In this research, FTIR spectroscopy is used to monitor the absorption peak shift in specific region to determine the functional groups in raw neem oil and epoxidised neem oil.

## 1.8 Tensile Properties

Tensile testing instruments are widely used to study mechanical properties of the plastic material. These properties which include, tensile stress, % elongation and Young's modulus all depend on the basic properties of the polymer chain molecule and other factors such as processing and environmental conditions. Mechanical properties of polymer blends normally determine its applicability. Tensile measurement is employed to investigate the influence of EVO on the mechanical properties of the sample at different compositions. The response of a polymer to applied stresses would depend upon its gross morphology and molecular behaviour (Bello, 2001). One of the most accessible ways of determining mechanical properties of polymeric materials is by the stress-strain curve experiment and Instron tensile tester is the most common instrument being used. The results from the tensile test are commonly used to select a material for an application, for quality control, and to predict how a material will react under other types of forces. Properties that can be measured from tensile test are tensile stress, percentage elongation, tensile modulus, e.t.c. (Czichos, 2006). Tensile strength is the stressed state caused by an applied load that tends to elongate the material in the axis of the applied load, in other words, the stress caused by pulling the material. Tensile strength is the most often specified property of plastic materials used to indicate the inherent strength of the material. Tensile strength is dependent on molecular structure and the orientation of the polymer within a particular sample, as well as any filler or reinforcements that may be incorporated in the polymer (Shah, 1984). The strength of any material relies on three different types of analytical methods: strength, stiffness and stability, where strength means load carrying capacity, stiffness means deformation and stability means ability to maintain the initial configuration of the material.

Stress ( $\delta$ ) is expressed by:

$\delta = \frac{F}{A}$ ..... (1.1); where  $F$  is the force (N) acting on  $A$  ( $m^2$ ) (Beer and John, 2006).

Tensile stress ( $N/m^2$ ) =  $\frac{\text{Breakind load (N)}}{\text{Cross sectional area (m}^2\text{)}} \dots\dots$  (1.2); (Beer and John, 2006).

Elongation is a measure of the permanent extension of a length of the polymer specimen after failure and it can be obtained by the expression shown below:

% Elongation =  $\frac{\text{Extension} \times 100}{\text{Initial length}}$  ... .. (1.3) dimensionless. (Beer and John, 2006)

It is sometimes referred to as the 'strain percent'. It's a measure of ductility and can be related to toughness in plastic materials.

Modulus of elasticity (E), also called tensile modulus or Young's modulus, is the ratio of stress to the strain, below the elastic limit. It is a measure of material's stiffness. The modulus is calculated using the equation below. The value is recorded as the E value.

$E = \frac{\text{Tensile stress}}{\text{Tensile strain}} = \frac{F/A}{e/l} \dots\dots\dots$  (1.4); Pa.

where  $F$  is the force,  $A$  is the cross sectional area,  $e$  is the extension and  $l$  is the initial length of the polymer film. Materials with high E values are rigid stiff materials while materials with low E values are rubber-like. Plastics that behave like rubbers have high elongation (change in length to low stress or force applied).

### 1.9 Thermal Properties

Differential scanning calorimetry (DSC) measures the amount of heat energy absorbed or released when a material is heated or cooled. For polymeric materials that undergo important property changes near thermal transition, DSC is a very useful technique to study glass-transition

temperature ( $T_g$ ), crystallisation temperature ( $T_c$ ) and melting behaviour ( $T_m$ ), in addition to the associated enthalpy ( $\Delta H$ ) for each process.

### **1.10 Morphological Study**

Scanning electron microscopy (SEM) is normally employed to study the surface morphology of the fractured tensile specimens of polymeric material and qualitatively illustrate the state of dispersion of the additives in the polymer matrix. SEM is used to study the morphologies of the plasticised polymeric films and examine the contrast difference between phases of varying composition in the blends.

### **1.11 Viscosity Measurement**

Viscometry is a simple and effective technique for monitoring the interactions in solutions of polymer blends. The miscibility studies of polyblends in solution phase could be determined by viscometric measurements. The viscosity method is found to be more sensitive and accurately reflects the changes in compatibility of the polyblends. Low viscous polymeric fluids are more miscible than higher viscous ones.

### **1.12 Research Problem Statement**

The existing plasticiser (phthalate) obtained from non-renewable resource (petroleum) is highly toxic and expensive. Polystyrene is highly brittle and have limited mechanical applications. Hence the need to modify its structure for enhanced mechanical properties. This study is to see the viability of applications of the oil sample (ENO) towards improving the structure-property

relationships in the polyblends. It is in this vein that various researches like this are embarked upon to produce polystyrene system that has enhanced and stabilised mechanical and thermal properties under a variety of loading conditions when blended with a value-added product derived from a renewable resource (EVO).

### **1.13 Aim of the Study**

The study is aimed at investigating the effect of ENO (plasticiser) loading on the mechanical and thermal properties of polystyrene, as well as the interaction between polystyrene and (epoxidised neem oil).

### **1.14 Objectives of the Study**

The aim will be achieved through the following objectives:

- I. To improve industrial potential of the neem oil sample via epoxidation.
- II. To establish the effectiveness of ENO loading in enhancing the mechanical property of polystyrene under a variety of loading conditions.
- III. To establish the effectiveness of ENO loading on the thermal behaviour of polystyrene.
- IV. To investigate the molecular interaction between PS and ENO at different wt % compositions.

### **1.15 Scope and Limitation**

This research is focused on the chemical modification of virgin oil sample (raw neem oil) via conventional epoxidation method and analysis of the modified neem oil through FTIR spectroscopy. Investigating the effect of ENO loading on the mechanical properties of the PS.

Investigation of the thermal behaviour of PS and PS/ENO blends samples at different compositions. Examination of the morphologies of the cross-section of the film samples of different compositions by scanning electron microscope (SEM).

### **1.16 Significance of the Study**

The unique high biodegradability, low toxicity, renewability and excellent lubricating performance of vegetable oils make them a viable alternative to petroleum based oils. Owing to these properties and potentials, environmentalists and engineers have made attempts to explore the possibilities of using vegetable oils as environmental friendly lubricants for range of applications. In this vein, significance of this research is to develop a value-added product (ENO) from locally available and economically viable vegetable oil (neem oil) and establish whether the epoxidised oil sample can be used to enhance the mechanical and thermal properties of polystyrene and its stability under a variety of loading conditions which can serve as substitute for phthalates used as plasticisers in polymer industry.

The analysis derived from this research will reveal the quality and sustainability of this epoxidised oil for many industrial applications. Finally, this study will serve as a means to create awareness on the economic potentials and industrial applications of vegetable oils especially the non-edible vegetable oils.

## CHAPTER TWO

### 2.0

### LITERATURE REVIEW

#### 2.1 Review of the Past Related Works

For a polymer to be useful, it must be able to function properly in a given application. The performance of a polymer is determined primarily by the composition and the structure of the polymer molecule. Polymers are tailored to suit the most demanding applications on earth, in space and even in the human body. The engineering of material properties is accomplished primarily through mixing of chemistry and manipulation of structure.

Sharif *et al.*, (2001) reported that linseed oil epoxy-polystyrene (LOE-PS) and linseed oil epoxy-methylmethacrylate (LOE-PMMA) made miscible homogeneous blends as shown by the presence of single glass transition temperature ( $T_g$ ) in these blends and shifting of infrared (IR) peaks of OH groups, oxirane ring and ester groups in these blends. They also observed that only amount of PMMA and PS (16.6%  $w/w$ ) in LOE turned into a rigid mass and the polyblends are not transparent like pure PS and PMMA but are faintly white with a colour value of 1. Sharif *et al.*, (2001) established that the information obtained can be used in making high performance coatings and paints.

Orathai *et al.*, (2013) studied the mechanical properties of the natural rubber latex (NRL)/polystyrene (PS) blend and treated waste natural rubber latex (TWL)/PS blends prepared from solution casting and reported that the tensile strength of TWL is higher due to the cross linked molecules. It is well known that cross links can improve the material strength. Orathai *et al.* also reported that when NRL was blended with PS it showed a slight increase in tensile

strength with the addition of 30% PS (70/30 NR/PS). This indicates that PS behaves as reinforcement in the NRL matrix phase due to its rigidity. Orthai *et al.*, (2013) observed that tensile strength decreased when the blend contained 70% PS (30/70 NRL/PS) which could be attributed to phase inversion that took place between 50% PS (50/50 NRL / PS) to 70% PS (30/70 NRL/PS). They asserted that for the TWL/PS blends, tensile strength also increased with the addition of 30% PS into TWL due to the reinforcement. The morphological investigation of solution casted NRL/PS and TWL/PS blends showed that the rubber particles around are round shaped and PS are flake shaped and the amount of rubber particles increases as the rubber proportion increased. Orathai *et al.* also observed how the morphology of the 30/70 and 50/50 TWL/PS, the PS region formed a wall structure which was attributed to the fact that TWL contains crosslinked molecules, which high surface tension in their own network molecules and other polymers can be distinguished. It was revealed that the TWL/PS phases are clearly separated at composition of 30/70 and 50/50 TWL/PS, which causes poor interfacial interaction between the phases and give lower tensile and tear strength compared to NRL/PS at similar compositions. However, 70/30 TWL/PS showed better morphology without the phase separation which may be due to PS which dispersed in TWL at this composition. It was also concluded in this study that based on the results, the 70/30 TWL/PS blend showed better tensile, tear strength and morphological properties compared to other compositions and recommended for further research.

Mamza and Folaranmi (1996) carried out compatibility studies on solution of PS and poly(vinyl acetate) (PVAc) blends by viscometric and density methods. The studies revealed that experimental (observed) densities of the blends were found to be lower than the calculated values

assuming additivity of volumes of polymers and solvent, while the plots of relative viscosity with compositions are S-type, indicating two-phase formation with phase separations at the intermediate compositions and the comparison of the calculated and observed intrinsic viscosities shows higher calculated values, thereby suggesting that PS and PVAc are incompatible.

Larissa *et al.*, (2013) evaluated the effect of the incorporation of rubber tire waste (RT) particles on the properties of polypropylene (PP), high impact polystyrene (HIPS) and PP/HIPS matrices. The studies revealed that the rubber tire particles have density higher than those of the PP and HIPS matrices; however incorporation of tires scraps into the polymer matrix causes a reduction in density when compared with the neat polymer while the tire scraps have a greater density than the PP and HIPS mixtures, which may be due to the voids and poor homogenization. It was also observed that an increase in the RT particles size led to a reduction in the density due to an increase in the void content of the polymer blends. The morphological investigation revealed that the presence of small cavities were observed on the fractured surface of the PP/RT composite due to the removal of RT particles during the tensile test indicating poor interfacial interaction between the RT filler and PP matrix. On the other hand, the HIPS/RT showed that some of the tire rubber particles in the HIPS matrix, indicating that the RT has a large surface area and therefore greater dispersion in the polymer matrix resulting in smaller cavities. These results may reflect a better interfacial interaction between these phases, possibly due to the presence of polybutadiene in HIPS. In the case of the blend matrix (PP/HIPS) filled with RT, an increase in the roughness can be observed due to the heterogeneity of the surface morphology. The rheological studies revealed that the presence of smaller RT particles led to a lower melt flow rate (MFR) for

the PP/RT composites (increased viscosity) and higher MFR for the HIPS/RT composites as confirmed by capillary rheometry. The mechanical properties investigation also revealed that the presence of RT with larger particles in the mixtures of PP/RT and HIPS/RT led to a decrease in the mechanical performance i.e. the tensile, flexural, and impact strength.

Ashraf *et al.*, (2007) studied and highlighted the utilisation of linseed oil epoxy (LOE) (a product from a sustainable resource), to obtain blends of LOE with polystyrene (PS) forming tough and flexible free-standing films. The mechanical properties of LOE/PS blend films were found to match with those of LDPE at composition LOE/PS, 65/35. The potential applications for such sustainable resource-based blend included packaging films and production of biodegradable plastic sheets which can be formed into products such as bio-bags. It was observed in this study that the blends of LOE with PS were miscible in solution phase in the composition range of LOE/PS, 85/15 to 45/55 as confirmed by viscosity and density measurements. At 35/65 LOE/PS composition, phase separation takes place which indicates the onset of immiscibility. The morphological investigation revealed a two-phase system in the case of LOE/PS, 85/15. The toughness of the films was found to increase with increasing content of PS in the blend. The mechanical properties of LOE/PS blend films were found to match with LDPE at composition LOE/PS, 65/35. The study concluded that the linseed oil epoxy (a product from sustainable resource) can be substituted up to 65% or even higher with polystyrene to obtain tough and flexible films.

Mamza and Nwifo (2009) investigated the density and morphological properties of some reinforced polymers blends of PS and PVAc and revealed that the trend is similar in both the

blends except that the filler increases the density of the blends and that in 30/70%, 20/80% and 10/90% PS/PVAc the densities are higher than the other compositions. The densities increase slightly for 90/10% and 80/20% PS/PVAc and decreases sharply for 70/30%, 60/40%, 50/50% PS/PVAc blends; increasing again for 40/60% PS/PVAc and more pronounced in the case of 30/70%, 20/80% and 10/90% PS/PVAc blends, the rise in density was attributed to the fillings of the inherent voids within polymer matrix by the filler particles. The morphological studies revealed a two-phase system; bright PVAc phase and black PS phase. It was observed that PVAc phase engulfed PS phase and for compositions 70/30, 60/40, 50/50, 40/60, and 30/70 PS/PVAc, (with and without filler) there was apparent heterogeneity of phases which reveal the level of immiscibility of PVAc with PS at these compositions which is an indicative of phase inversion. However, blends of compositions 80/20 and 90/10 PS/PVAc showed a considerable miscibility due to a domain distribution in these ranges of compositions. The study concluded that the density and morphological studies carried out on the blends had established the level of micro-structural arrangement in the polymer-polymer matrices, under the effect of  $\alpha$ -cellulose filler and had shown that structure-property relationships are essential aspect of polymer blend technology through proper end-use application in the industries.

Perez-Guerrero *et al.*, (2011) carried out studies on the influence of silica nanoparticles on the thermo-mechanical properties of recycled PS (rPS). The results of this study revealed that rPS from expanded polystyrene is a material with glass transition temperature ( $T_g$ ), storage modulus ( $E^+$ ) and impact strength of rPS higher than those of virgin PS. It was also asserted that incorporation of nano-silica in small percentage (1, 3 and 5%) to rPS no significant influence on the  $T_g$ ,  $E^+$  and impact strength values was observed, but increases the thermal stability of rPS to

similar values to those of virgin PS. The low influence of nano-silica in rPS may be associated with a poor adhesion of nano-particles in the polymer matrix as confirmed by the morphological studies, indicative of insufficient polymer melt mixing process.

Mamza *et al.*, (2008) carried out modification studies on the mechanical properties of blends of polystyrene (PS) and poly(methyl methacrylate) (PMMA) and results obtained revealed that both pure PS (100%) and pure PMMA (100%) showed high tensile strength than those containing varying proportions. PMMA showed a higher tensile stress than PS, so blends containing a higher composition of PMMA showed better mechanical properties. Mamza *et al.*, (2008) also established that PS/PMMA 20/80% showed the best mechanical stress at 10 tons, with a high modulus of extension at 11.70 GN/M<sup>2</sup>.

Worzakowska (2015) carried out investigation on the thermal and mechanical properties of pure PS and observed that the T<sub>g</sub> for the pure PS is 96°C, but the addition in the amount of ester to the PS from 0.5 to 10 mass %, the T<sub>g</sub> values of the materials obtained slightly decrease. However, when the amount of ester is higher than 10%, the changes in T<sub>g</sub> values become more significant. The T<sub>g</sub> value are 65°C for the PS/20% mass CBE (ester of 3-phenylprop-2-en-1-ol and succinic anhydride) and 60°C for the PS/20% mass CSE (ester of 3-phenylprop-2-en-1-ol and sebacic acid). The tensile properties of the materials studied revealed that the addition of esters to PS has significant influence on the mechanical properties of prepared compositions that the PS/esters composition are characterised by smaller Young`s modulus and tensile strength than the pure PS. With increase in the amount of ester derivatives in the compositions, the strain at break ultimately increases as well. The presented results confirmed that the addition of esters of

derivatives of 3-phenylprop-2-en-1-ol to PS allowed obtaining softer and more flexible material due to the weakness of secondary valence bonds between polymer molecules. As a consequence, PS/ester compositions were characterised by lower values of  $T_g$ , storage modulus, Young's modulus, stress at break, hardness and thermal stability compared to pure PS. In addition, it was found that CSE had higher influence on decreasing the intermolecular interactions and thus increasing the mobility of the polymer chain of PS than CBE. The studies proved that esters derivatives of 3-phenylprop-2-en-1-ol can be utilised as external, environment friendly plasticisers for commercially used thermoplastic polymers such as PS. They can be suitable alternative to widely, industrially applied compounds such as toxic phthalates.

Folaranmi and Zayyan (2002) studied some properties of polystyrene (PS)-polyisobutylene (PIB) rubber blends and observed that as the percentage of PIB in the blend is increased, the transparency of the film diminished. At much higher concentration of the PIB, the transparency was impaired and phase separation was observed indicating that there was greater tendency towards demixing as the rubber content of the blend increases. Results of the mechanical properties of some selected films showed higher value of yield and ultimate strains than for pure PS and increased appreciably with increasing rubber content of the blend. Large area under the stress-strain curve for the blends with increasing rubber contents in the blends, suggesting that PS was toughened by blending with the PIB rubber. The highest value of Young's modulus for 95/5 blend with subsequent decrease for blends with higher PIB content was observed. From the results, it was concluded that PS was semi compatible with PIB at low percentage concentration of rubber in the blend at low solid content of solution. The morphological study also revealed the

tendency of the blend demixing at higher PIB content in the blend. Toughening of PS with PIB rubber must therefore, be at fairly low concentration preferably < 10% of the total weight.

Boung *et al.*, (2017) carried out an investigation on epoxidised jatropha oil (EJO) as a sustainable plasticiser to poly(lactic acid) (PLA). They reported that the FTIR spectra of PLA, EJO and EJO-plasticised PLA revealed that the characteristic peaks of PLA stretching vibrations of  $-\text{CH}_2$  around  $2995\text{ cm}^{-1}$  and  $2964\text{ cm}^{-1}$  and  $\text{C}=\text{O}$  ( $1746\text{ cm}^{-1}$ ), EJO showed the  $\text{C}=\text{O}$  at  $1741\text{ cm}^{-1}$ . In addition, two strong peaks at around  $2900 - 3000\text{ cm}^{-1}$  were derived from the  $-\text{CH}_2$  stretching vibrations. The presence of the epoxide group in EJO was proven by the stretching band at around  $832\text{ cm}^{-1}$ . The disappearance of this epoxide stretching vibration peak in EJO-plasticised PLA indicated the possibility of interaction between EJO plasticiser and PLA. The tensile results of EJO-plasticised PLA obtained revealed that pristine PLA has a very low flexibility or elongation at break of 5.37% and the elongation at break of PLA was significantly increased after being plasticised by EJO plasticiser. The elongation attained the highest value of 388.08% when 3 wt% of EJO plasticiser was incorporated into the PLA matrix. It showed around 7000% improvement compared to pristine PLA. However, a higher amount of EJO content led to a decrease in elongation at break because PLA was saturated with plasticiser and phase separation occurred, leading to the formation of PLA-rich and EJO-rich phases, within the EJO-plasticised PLA. On the other hand, the tensile modulus of EJO-plasticised PLA decreases at 1 wt% EJO, it remain stable at 3 wt% and 5 wt% and a second slight drop occurs at 7 and 10 wt% EJO. A gradual decrease in tensile strength of EJO-plasticised PLA from 57, 98 to 28.6 MPa was observed as the content of EJO increased from 0 to 10 wt%. An increase in elongation at break means that the brittleness of the samples decrease since elongation at break and

brittleness are inversely proportional. The thermogravimetric behaviour of EJO-plasticised PLA is similar to PLA, revealed only one major degradation step at around 300 – 400°C. Thermal characteristic factors such as initial decomposition temperature ( $T_{\text{onset}}$ ), temperature of maximum rate of degradation ( $T_{\text{max}}$ ), and decomposition temperature at 50% weight loss ( $T_{50}$ ) were determined from the TG and DTG thermograms. Neat PLA has a  $T_{\text{onset}}$ ,  $T_{\text{max}}$ , and  $T_{50}$  of 274.26, 345.12 and 339.16°C, respectively. The addition of 3 wt% EJO into PLA improved the thermal stability of PLA, as seen from the increased  $T_{\text{onset}}$  (303.17°C),  $T_{\text{max}}$  (362.81°C), and  $T_{50}$  (362.33°C), compared to those of neat PLA. It was established that the homogeneously and well dispersed EJO could act as a protective layer, which deterred the release of volatile degradation products out from the composites and therefore delayed the thermal degradation. The DSC thermogram of PLA showed a sharp  $T_g$  at 62.85°C and  $T_m$  at 149.79°C but no obvious crystallisation exothermic peak ( $T_c$ ) was observed. The addition of EJO plasticiser to PLA induces a shift of  $T_g$  to a lower temperature, e.g., from 62.85 to 59.92°C, which is due to an enhanced chain mobility of PLA. Enhanced PLA chain mobility further promotes  $T_c$  and thus the  $T_m$  of around 111.79 and 146.69°C, respectively, as revealed by EJO-plasticised PLA thermogram. The morphological investigation also revealed that the incorporation of EJO as a plasticiser into the PLA matrix showed remarkable changes on the morphology due to enhanced interfacial adhesion and EJO dispersion. This study concludes that the potential of non-edible EJO as a plasticiser for PLA that can replace the current dependence on edible oil resources. The use of EJO plasticiser as a modifier of PLA meets multiple criteria, such as biodegradability and non-toxicity. EJO plasticisers could constitute attractive alternatives for petroleum based plasticiser such as phthalates.

AlMamun and Norimasa (2014) carried out miscibility and thermal studies of isotactic polystyrene (iPS) and poly(cyclohexylmethacrylate) (PCHMA) blends. They found that neat iPS has greater thermal stability than the PCHMA, shown by the mean displacement of the weight loss curve to much higher temperature. Three regions of temperature may be considered in investigating the thermal stability of iPS and PCHMA. The initial degradation of iPS starts at about 340°C. No significant change of mass loss was observed at this temperature and found solid iPS as stable. In the temperature ranges 340 – 370°C, only negligible amount of mass loss; about 2% loss can be seen at 370°C, while between 393 and 423°C volatilisation becomes very rapid and almost complete distillation occurs at 440°C, about 97% mass losses at this temperature ranges. On the other hand, the PCHMA degrades with three degradation steps, an initial degradation of PCHMA starts at about 212°C, more mass losses at 298°C (~25%) and again it losses 65% at 347°C and finally complete distillation occurs at 465°C that is few degree higher than that of distillation temperature of iPS. The miscibility of iPS and PCHMA was investigated using differential scanning calorimetry (DSC), the results showed increase first with PCHMA composition in iPS/PCHMA blends, showing a level off and again increase with composition. The  $T_g$  composition relationship apparently suggests that the blend system is miscible whose intermolecular interactions leading miscibility depending on the composition. They concluded that all the experimental results suggest that iPS and PCHMA are mixed at the molecular level within the blends at all compositions, confirming the miscibility of the blends. The addition of iPS into the blend improves the thermal stability of PCHMA for all composition and temperature ranges.

Silverajah *et al.*, (2012) carried out a comparative study on the mechanical, thermal and morphological characterisation of poly(lactic acid) (PLA)/epoxidised palm oil (EPO) blend and found that the tensile strength, elongation at break and tensile modulus were determined at room temperature (25°C) to ascertain the films quality in a packaging use for instance. They reported that addition of 1 wt% EPO significantly improved the tensile strength of PLA/EPO (1) and PLA/EPO (3) blends by approximately 5% and 13%, respectively. This suggests that EPO acts as plasticiser, which increases the interaction at the phase boundaries and improves the flexibility of blends. Generally, the compounded EPO is dispersed in the interphase between the PLA chains leading to strong interphase interaction, which reduces the stress concentration point when tensile load is applied on the blends and consequently produces higher mechanical strength. However, a decrease by 2.6% in the tensile strength of PLA/1 wt% EPO(2) was observed. The tensile strength of blends decreased with the addition of EPO above 1 wt% in all the three types of EPO blends, indicating that there was no improvement in interaction between PLA and EPO. The drop in the tensile strength may be contributed by the plasticiser-plasticiser interaction which dominates at higher EPO content. In addition, when the amount of EPO is above 1 wt%, only part of the EPO is located in the interfacial area, and the excess is dispersed in the matrix, affecting its homogeneity and consequently reducing the tensile strength of the blends. Thus, only 1 wt% EPO is sufficient to enhance the tensile strength and PLA/1 wt% EPO(3) displayed the highest tensile strength of 65.8 MPa compared to neat PLA, 58.2 MPa. Neat PLA exhibited a tensile modulus value of 1054 MPa, and attained the highest modulus with 1 wt% EPO for PLA/EPO(1) (1119 MPa), PLA/EPO(2) (1175 MPa) and PLA/EPO(3) (1214 MPa). A high tensile modulus signifies that the material is rigid, thus more stress is required to produce a given amount of strain, which means it resists deformation or stretch. EPO has been found to be

efficient in stiffening PLA polymers as the tensile modulus increases by 6.2%, 11.5% and 15.2% for PLA/1 wt% EPO blend of EPO(1), EPO(2) and EPO(3) respectively. The increase in tensile modulus was attributed to blends having the stiffness of PLA and the polymer-plasticiser interaction which made the blends more rigid. Above 1 wt%, the tensile modulus decreased and plateaued. This could be considered the critical interfacial concentration, which is the minimum value of interfacial saturation for EPO in the interphase. Moreover, the elongation of PLA/EPO blends increases with the addition of plasticiser. The elongation at break of PLA/1 wt% EPO blends of EPO(1), EPO(2) and EPO(3) were 8.6%, 6.6% and 11.1% respectively, while neat PLA exhibited 6.3%. It has been observed that elongation at break of blends increases significantly with increasing EPO loading. As expected, PLA blends with 5 wt% EPO loading bear maximum elongation. With 5 wt% EPO loadings, PLA/EPO(1), PLA/EPO(2) and PLA/EPO(3) displayed elongation of 114%, 42% and 130% respectively. In general, plasticiser is introduced to a polymer matrix to overcome the film brittleness caused by extensive intermolecular interactions. Thus, the presence of plasticiser, EPO, reduces these intermolecular forces and increases the mobility of PLA chains, thereby enhancing the flexibility and extensibility of the PLA/EPO films. Consequently, higher EPO loading produces film with lower tensile strength but higher elongation. The flexural strength of PLA enhanced significantly upon adding 1 wt% EPO into the matrix, from 64.2 MPa (neat PLA) to 77.0, 73.6 and 80.3 MPa, for PLA/EPO(1), PLA/EPO(2) and PLA/EPO(3). The trend of flexural strength for PLA/EPO(1) and PLA/EPO(2) blends are quite constant. Conversely, the trend of flexural modulus for PLA/EPO(3) exhibited a maximum with 1 wt% and eventually a decrease. The high flexural strength was contributed by the improved adhesion between the PLA matrix and EPO, which provides an increase in stress transfer from the matrix to the plasticiser. Thus, this increased the

stress at failure and contributes to the higher values for flexural strength. However, further increase in the EPO loadings decreases the flexural strength indicating that presence of excess EPO reduces the stiffness of the PLA molecular chain. Moreover, increasing EPO content above 1 wt% adds to the occurrence of voids in the blends, which influence the local stress acting on the blends. Impact test reflects the ability of material absorbing energy at fracture, when exposed to sudden impact. The impact strength of PLA is improved by 10% (PLA/1 wt% EPO(1)) and 24% (PLA/1 wt% EPO(3)) from 254.8 J/m (neat PLA), with the presence of 1 wt% of EPO. These results indicate that reactions might occur between epoxy groups of EPO and hydroxyl groups at the terminals of the PLA matrix, improving the interfacial adhesion and leads to an increase in the impact strength. However, further addition of EPO in these blends beyond optimum amount (1 wt% EPO), the impact strength gradually decreased. In this case, excess epoxy groups from EPO contribute to higher plasticiser-plasticiser interaction, along with poor interaction between PLA and EPO. This triggers the formation of voids as observed in SEM analysis and eventually decreases the impact strength. Conversely, the impact strength of PLA/EPO(2) blends decreased by approximately 20% and plateaued. This indicates poor interfacial adhesion in the blends, thus decreasing the toughness with increasing plasticiser content and finally remains constant at a particular point. The morphological study revealed that the addition of 1 wt% EPO significantly influences the morphological structural deformation of PLA phase which creates neither a brittle fracture, as observed in the neat PLA blend, nor defect cavities, as observed in the PLA/5 wt% EPO blends. However, the dispersion of EPO(2) in the PLA matrix is not homogenous which may be contributed to by the incompatibility of the materials. The SEM micrograph of PLA/1 wt% EPO(1) and PLA/1 wt% EPO(3) displays a good adhesion between the components with a diffused polymer-plasticiser interface, producing single

phase morphology. This is indirectly reflected in more efficient load transfer under stress conditions, which was consistent with the improved tensile and impact properties of the blends. Comparatively, SEM analysis of fracture surfaces of PLA/5 wt% EPO blends for EPO(1), EPO(2) and EPO(3) displayed similar micrographs. These micrographs revealed poor interfacial adhesion properties, and the cavitations caused by debonding can be clearly identified. Presence of empty micro-voids was observed in the blends indicating a formation of EPO-rich phase in PLA matrix. EPO was located inside of the empty voids of PLA continuous phase. In addition, the stretched PLA phase in the blend may indicate ductile fracture of the PLA in the presence of EPO. Therefore, the degree of dispersion of the plasticiser in the PLA matrix is better at lower EPO loading, and the tendency to form empty voids and phase separation increases when the EPO content rises. These results are in good accordance with the mechanical property data, where the good interfacial adhesion results in higher mechanical strength of PLA/1 wt% EPO compared to PLA/5 wt% EPO blends. They used dynamic mechanical analysis (DMA) to investigate the thermomechanical properties of PLA/EPO blends to obtain measurements of the storage and loss modulus ( $E'$  and  $E''$ ) and the loss factor ( $\tan \delta$ ). They reported that the  $E'$  values of neat PLA were slightly higher, suggesting high brittleness of the PLA than the blends. The lower storage modulus of the PLA/1 wt% EPO blends compared to neat PLA, indicating an increase in the flexibility of PLA imparted by the EPO. Further, there was a large drop on the storage modulus around 50 – 70°C corresponding to the glass-transition region, followed by a horizontal plane. EPO provides moderate toughening and elastomeric effect, which brings about a small decrease in the modulus values. Reduction in storage modulus with respect to temperature is related to softening of the matrix at higher temperature. As the temperature exceeds the softening point, mobility of matrix chains increase leading to sharp decrease of

modulus at temperature between 50 – 70°C. The peak intensity of loss modulus represents the melt viscosity of a polymer. As observed, the PLA/1 wt% EPO(3) blend showed enhancement in loss modulus compared to neat PLA. This suggests an increase in the melt viscosity of the corresponding blend. However, a decrease in the loss modulus is observed for PLA/1 wt% EPO(1) and PLA/1 wt% EPO(2) blends signifies that the incorporation of EPO into PLA matrix decreases the melt viscosity of the corresponding blends. This is attributable to the addition of 1 wt% EPO(2) which decreases the flow-ability due to poor interaction and compatibility, leading to a less rigid polymeric material. Besides, the fall in the modulus is attributed to an energy dissipation phenomenon involving cooperative motions of the polymer chains. The major relaxation process is associated with the glass-rubber transition ( $T_g$ ) of PLA. The height of the  $\tan \delta$  peak point out to the degree of crystallinity. Furthermore, the height of the  $\tan \delta$  peak is associated with the mobility of the amorphous region in the polymer blend. As presented, PLA/1 wt% EPO(1) and PLA/1 wt% EPO(2) blends display a reduction in the sharpness and height of  $\tan \delta$  peak, as the dispersed crystalline regions hinder the chain mobility in the amorphous regions. In addition, the restriction force increases directly with increase in crystallinity of the polymer. With the presence of 1 wt% EPO(1) and EPO(2), the molecular mobility of the materials decreases and the mechanical loss to reduce the intermolecular chain friction. Comparatively, PLA/1 wt% EPO(3) blend exhibits a sharp and intense  $\tan \delta$  peak as there is no restriction to the motion of the main chain. This denotes that this blend contains a more amorphous region. This indicates that the blend has a good structural damping property; therefore, there is improved capacity to absorb mechanical energy by this blend compared to neat PLA, resulting in higher impact strength. The  $T_g$  were obtained from the peak values of the  $\tan \delta$  curves. The  $T_g$  of PLA/1 wt% EPO blends of EPO(1), EPO(2), EPO(3) and neat PLA are 67.3,

65.8, 68.1 and 67.9°C, respectively. The slight shift in the  $T_g$  is a result of the plasticisation effect. Furthermore, the molecular mobility of the PLA/EPO blend material is affected slightly with the addition of 1 wt% EPO. The thermo-gravimetric study revealed that the incorporation of EPO in PLA matrix has significantly affected the thermal degradation temperature by improving the thermal stability of the blends. It can be observed that the PLA/1 wt% EPO blends appear to be thermally stable at temperatures lower than 270°C. These materials lose about 10% of their weight at temperature between 270 and 330°C, followed by an abrupt weight loss after 330°C. Greater than 98% weight loss is observed for the three PLA/EPO blends, which were due to the thermal decomposition of the PLA polymer chains. Neat PLA exhibits an onset temperature of 211.9°C, which increased to 272.3, 270.4 and 279.3°C when 1 wt% of EPO(1), EPO(2) and EPO(3), respectively, incorporated into the blend. For PLA/1 wt% EPO(2) and PLA/1 wt% EPO(3), the difference in the curves can be hardly distinguished. However, a delay of the degradation is observed for PLA/1 wt% EPO(3) from the onset temperature. The blends showed a higher degradation temperature by approximately 27%, than neat PLA. The maximum degradation temperature ( $T_{max}$ ) also increased by compounding the PLA matrix with EPO. The  $T_{max}$  of the blends is higher, that is 358.6, 361.5, and 361.3°C, for PLA containing 1 wt% of EPO(1), EPO(2) and EPO(3), respectively, compared to the PLA blend (324.8°C). These higher degradation temperatures may be attributed to increase in molecular weight due to interaction between PLA matrix and EPO, or molecular chain-extension of the PLA matrix itself. Besides that, the presence of EPO dispersed homogeneously in the PLA polymer acts as a barrier sheet to prevent oxidation, as well as, hinders the permeability of volatile degradation products out from the blend materials and helps delay the thermal degradation process. In the thermal study, Silverajah *et al.*, (2012) reported that the addition of EPO into PLA matrix decreased the  $T_g$  of

neat PLA from 63.6°C to 59.9°C, 62.9°C and 60.4°C by adding 1 wt% of EPO(1), EPO(2) and EPO(3), respectively. The  $T_g$  of all three PLA/1 wt% EPO blends was lower than neat PLA due to the plasticisation effect of EPO. In addition, the downward shift of  $T_g$  suggests some mixing of the EPO soft segments into the hard segment phase. This decrease in  $T_g$  can be explained on the basis of increased mobility of the soft segments because of the penetration of EPO units into the PLA hard segments. With increasing EPO content to 5 wt%,  $T_g$  of PLA blends decreased slightly to 56.8°C, 60.2°C and 60.2°C for PLA blends with 5 wt% of EPO(1), EPO(2) and EPO(3), respectively. As expected, increasing the EPO, soft segment content led to a slight decrease in the  $T_g$  of the blends due to the hard segments motion imposed by the EPO soft segments. This also indicates that the PLA blends are partially compatible. However, the  $T_g$  with 5 wt% EPO was not considered, as the compatibility of blends became poor due to phase separation which can be evident from the SEM micrographs. Thus, the  $T_g$  at 1 wt% EPO was considered as the minimum  $T_g$  as the PLA blends have greatly enhanced properties in terms of tensile strength and impact strength. However the  $T_g$  obtained from DSC and DMA does not correlate. The  $T_g$  of PLA/1 wt% EPO blend of EPO(1), EPO(2) and EPO(3) obtained from DMA analysis are 67.3°C, 65.8°C and 68.1°C, respectively. While  $T_g$  of neat PLA from DMA measurements were 67.9°C. The difference in the  $T_g$  values based on DSC and DMA can be explained by the different measuring principles and heating rates selected. The neat PLA indicated a melting endothermic peak at 151°C. It was also observed that the DSC thermogram of PLA/1 wt% EPO(1) and PLA/1 wt% EPO(2) exhibits two distinct peaks of melting temperature at 149.8°C and 153.1°C, as well as, 148.5°C and 155.1°C respectively. Silverajah *et al.*, (2012) also reported that the lower melting endotherm corresponds to the crystalline phase of PLA/EPO soft segments and the higher one to the crystalline phase of hard segments. However,

there is possibility that these blend systems are not completely miscible. Conversely, in the heating scan of PLA/1 wt% EPO(3) only one  $T_m$  peak appeared at 150.1°C resembling to the crystalline phase of soft segments. The downward shift in  $T_m$  of this blended film indicates the increased miscibility of the components in the blends. Furthermore,  $T_c$  was detected for neat PLA and PLA/1 wt% EPO blends of EPO(1), EPO(2) and EPO(3) at 117.9°C, 110.8°C, 105.9°C and 111.1°C. The incorporation of EPO dispersed in PLA leads to a significant shift of the crystallisation peak towards lower temperatures. The  $T_c$  decreased because PLA chains possessed higher mobility after the addition of EPO, which made it easier for them to fold into a crystalline lattice. When we discuss the mechanical properties of PLA blends in connection with the degree of incorporation, the influence of degree of crystallinity should also be considered because it may change with the addition of EPO. In this investigation, the neat PLA showed  $X_c$  of 69.0%, which means that PLA is semi-crystalline. The  $X_c$  of PLA/1 wt% EPO(1) and PLA/1 wt% EPO(2) increased to 72.3 % and 71.8%, respectively. These results clearly indicate that PLA/1 wt% EPO(1) and PLA/1 wt% EPO(2) are identical in terms of crystallinity, suggesting that these two polymers were previously subjected to the identical processing conditions (thermal history). PLA/1 wt% EPO(3), on the other hand, has a sharper melt and lower crystallinity of 58.3% indicating different processing conditions and different end-use properties. Besides that, high plasticiser content contributes to a decrease in the crystallisation peak as a result of phase separation. X-ray diffraction (XRD) study revealed that the PLA did not show any characteristic peak, which indicates that the structure is amorphous. The neat PLA employed in this research has 5.49 Å of interlayer spacing at  $2\theta = 16.22^\circ$ . The XRD pattern of PLA/1 wt% EPO(1) and PLA/1 wt% EPO(2) blends has a very strong crystalline peak at  $2\theta$  of  $17.09^\circ$  and  $16.85^\circ$ , which correspond to the basal spacing 5.18 Å and 5.26 Å, respectively. The shift to a higher angle

indicates a decrease in the corresponding interlayer spacing, which is contributed to by the fact that the blend components have an ordered structure. As the PLA chain was the main component of the blend, the position of crystalline peak was almost similar to that of the PLA. Unlike PLA/1 wt% EPO(1) and PLA/1 wt% EPO(2) blends, PLA/1 wt% EPO(3) blend shows absence of crystalline peak, indicating an amorphous structure. This blend showed an increment of interlayer spacing, where the  $d$ -spacing increased from 5.49 Å (neat PLA) to 5.79 Å at diffraction peak centred at 15.28°. The increment in the interlayer spacing of PLA evidences that this blend has more amorphous region and the addition of 1 wt% EPO(3) creates a less-ordered structure, thus crystallisation becomes more difficult. Interestingly, these results contradict the percent crystallinity calculated from DSC data, which revealed that PLA and PLA/1 wt% EPO(3) are semi-crystalline instead of amorphous observed from the XRD analysis. This may be due to the different conditions of instrumental analysis and the distribution of amorphous and crystalline region in the semi-crystalline blends, which affects the crystallinity data obtained. From the results obtained, Silverajah *et al.*, (2012) concluded that the optimum EPO loading with enhanced mechanical and thermal properties of PLA is 1 wt%. PLA/1 wt% EPO(3) blend showed excellent properties compared to PLA/1 wt% EPO(1), PLA/1 wt% EPO(2) and neat PLA. The tensile strength, flexural strength, impact strength and elongation at break of PLA/1 wt% EPO(3) were improved by 13%, 25%, 23% and 77%, respectively compared to neat PLA. This reveals good stress transfer of the material and addition of 1 wt% EPO(3) also significantly decreased the storage modulus while increased the loss modulus and loss factor. From XRD patterns, it can be inferred that the amorphous phase of the PLA/1 wt% EPO(3) blend was increased, whereas the crystalline phase increased for PLA/1 wt% EPO(1) and PLA/1 wt% EPO(2), compared to neat PLA. From the TGA results, there is a significant improvement about

27% on the thermal stability of blends with the addition of EPO. Furthermore, the DSC results illustrate a decrease in the glass-transition temperature due to the plasticising effect of EPO. The entanglement and aggregation, indicating good interaction between PLA and EPO(3). This is in agreement with the significant improvement of mechanical properties. Thus, this blend can be considered as an alternative to the conventional plastics used. Additionally, EPO can be seen as a potential useful plasticiser.

Kouroosh *et al.*, (2012) carried out epoxidation reaction of soybean oil (SBO) and reported that the highest epoxy content of epoxidised soybean oil (ESO) was 6.1%. The full epoxidised figure was not achieved because there might be some side reaction such as epoxy ring opening. The Fourier transform infrared investigation revealed that the presence of peak in the spectrum of ESO at  $826.4\text{ cm}^{-1}$ , attributed to epoxy group, corroborated the conclusion that the success of epoxidation reaction of SBO. The broad hydroxyl O-H stretching vibration peak ( $3459.8\text{ cm}^{-1}$ ) in the spectrum ESO indicates that the epoxy group might be opened. They concluded that the possible side reaction was the epoxy ring opening that produced hydroxyl functional groups found by FTIR spectroscopy.

Prerna and Chhibber (2013) studied the epoxidation of karanja oil for bio-lubricant applications and reported that the structures of the synthesised compounds as confirmed by FTIR spectroscopy showed characteristic signals at  $830$  and  $845\text{ cm}^{-1}$  that correspond to quaternary carbons of the oxirane ring the signals at  $2987$  and  $2865\text{ cm}^{-1}$  correspond to aliphatic carbons in the molecules. In monoester product the bands at  $1738$  and  $1710\text{ cm}^{-1}$  due to C=O stretching. Furthermore, the most characteristic evidence confirms trimer formation was the

disappearance of OH stretching vibration around  $3400\text{ cm}^{-1}$ . In NMR spectroscopy the signal around  $9.40 - 9.65\text{ ppm}$  confirmed the disappearance of OH group. Furthermore, at about  $2.15 - 3.57\text{ ppm}$  resonance the protons signals of the aliphatic  $-\text{CH}_2-$  appeared for the prepared compounds. The prepared compounds were screened for low temperature behaviour through determination of both flash point (cp) and pour point (pp) and reported that modified trimer exhibited a pp of  $-36^\circ\text{C}$  which is an improvement over that other compounds. As expected, as the chain length of the ester increased, a corresponding improvement in pp is observed, which may be due to more effectively disrupt macro-crystalline formation at reduced temperatures. Conclusively, in this study several basic trends were observed. The prepared compounds exhibited the favourable cold-flow characteristic as determined by pp. The presence of branching group at the head of the molecule will make it more effectively in disruption of crystalline formation at reduced temperatures. These products can be effectively utilised for bio-based industrial materials such as bio-lubricants.

Padmisiri *et al.*, (2009) carried out epoxidation of some vegetable oils and their hydrolysed products with peroxyformic acid. In the characterisation of the vegetable oils (i.e. rubber seed oil (RSO), neem oil (NO) and mee oil (MO)), they reported that the fatty acid compositions determined by GC-MS; palmitic acid (16:1) for RSO, NO and MO is traces, 11 and 18, respectively. Stearic acid (18:0) is traces, 14 and 25 for RSO, NO and MO, respectively. Oleic acid (18:1) is 33, 42 and 40 for RSO, NO and MO, respectively. Linoleic acid (18:2) is 48, 32 and 17 for RSO, NO and MO, respectively. Linolenic acid (18:3) is 19 and traces for RSO, NO and MO, respectively. The FTIR spectroscopy revealed the main peaks and their corresponding functional groups of the oils C-H stretching of alkanes ( $2850 - 2860\text{ cm}^{-1}$ ), C-H stretching of

non-conjugated unsaturation ( $3010\text{ cm}^{-1}$ ), C=O stretching of esters ( $1745 - 1750\text{ cm}^{-1}$ ), C-H bending of unsaturated alkanes ( $1460 - 1465\text{ cm}^{-1}$ ), C-O stretching of esters ( $1115 - 1170\text{ cm}^{-1}$ ) and C-C bending of saturated carbon atoms ( $720 - 725\text{ cm}^{-1}$ ). The disappearance of the band at  $3010\text{ cm}^{-1}$  in the FTIR spectra of epoxidised oils shows C=C has been used up and the appearance of a band around  $820 - 950\text{ cm}^{-1}$  which not seen in pure oils spectra is characteristics of the epoxide and can be assigned to ring vibrations of epoxy ring *cis* epoxide. They reported that the hydrolysed products are characterised by the reduction of carbonyl stretching frequency due to the hydrolysis and the peaks around  $940$  and  $1300\text{ cm}^{-1}$  for C-O in ester and carboxylic acid, respectively. In general, the stretching frequency of the carbonyl group is reduced when ester is hydrolysed to form carboxylic acid. In MNR analysis, it was reported that the epoxy protons were observed at  $2.8 - 3.0$  ppm in all spectra of epoxidised oils, whereas olefinic protons observed (due to traces of unreacted groups left) in spectra of epoxidised oils. Both peaks have appeared as a quartet due to the coupling of adjacent two protons of the  $\text{CH}_2$  group and the *cis* coupling of the proton attached to the next  $\text{sp}^2$  hybridised carbon atom. The terminal methyl group appeared as triplet in the range of  $0.7 - 1.0$  ppm in all the spectra. The methyl proton of the CH backbone of the glycerol carbon is observed at  $5.1$  ppm as a triplet in both cases, whereas the adjacent methyl proton give a characteristic double doublet pattern between  $4.1 - 4.35$  ppm which is common for both epoxidised and virgin oils. On the other hand,  $\text{sp}^2$  hybridised carbon in olefinic group has appeared in the range  $125 - 130$  ppm in  $^{13}\text{C-NMR}$  spectra of virgin neem oil which is not observed in epoxidised neem oil. In the solubility study, it was reported that the thermodynamic concept for miscibility and the compatibility is that the smaller the difference between solubility parameters, the higher the miscibility of the components. The solubility parameter values obtained for oils and epoxidised oils are in good agreement with that of

conventional plasticisers such as di-2-(ethyl) hexylphthalate used in PVC formulations. Padmisiri *et al.*, (2009) concluded that rubber seed oil, madhuca oil (mee oil) and neem oil and their hydrolysed products were epoxidised successfully by peroxyformic acid generated 'insitu' by reacting formic acid (methanoic acid) with hydrogen peroxide at the temperature range 50 – 60°C. The epoxidation was confirmed by FTIR analysis and NMR analysis. Solubility parameters of oils and epoxidised oils were determined and values obtained were found to be in the range of those conventional plasticisers used in the PVC industry. This will lead to a more convenient and economically viable method for large-scale epoxidation of vegetable oils, which could be useful especially in plasticiser/stabiliser industry.

Buong *et al.*, (2014) investigated the effect of epoxidised palm oil and epoxidised soybean oil (EPO and EPSO) on plasticised poly(lactic acid) bio-composites: mechanical, thermal and morphological properties. They reported that the FTIR spectra of PLA/EPO and PLA/EPSO show 4 main regions: -CH stretching at 3000 – 2850  $\text{cm}^{-1}$ , C=O stretching at 1750 – 1745  $\text{cm}^{-1}$ , C-H bending at 1500 – 1400  $\text{cm}^{-1}$  and -C-O stretching at 1100 – 1000  $\text{cm}^{-1}$ . The FTIR spectra of EPO and EPSO exhibited unique characteristic peaks that corresponded to the C-O-C stretching from oxirane vibrations at 950 – 850  $\text{cm}^{-1}$  and around 1250  $\text{cm}^{-1}$ . Buong *et al.*, (2014) reported that the signal at 1250  $\text{cm}^{-1}$  usually overlays with others, mainly -C-O which is present in oils. For the plasticised PLAs, the peaks at about 3500  $\text{cm}^{-1}$  indicates the presence of the free O-H stretching vibration from the production of EPO via acid catalysed with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). During the epoxidation with per-acids, the acid produced simultaneously proceeds along with the reversible reaction with hydrogen peroxide to generate per-acid again and free water group. A small amount of hydroxyl group (O-H) in the bio-composite could be attributed to the

possible terminal hydroxyl groups in the PLA main chain which was released during the interaction between PLA and EPO. A small shift of C-O stretching peak from  $1080\text{ cm}^{-1}$  (neat PLA) to  $1085\text{ cm}^{-1}$  in both PLA/EPO and PLA/EPSO were observed. This shift in the absorption peak indicates the miscibility and interaction of PLA and EVO. The upward shift may possibly due to an interaction between the hydroxyl group of PLA and the epoxy group of EVO through hydrogen bonding. In the investigation of mechanical properties, Buong *et al.*, (2014) reported that addition of 1 wt% EVO plasticisers into PLA matrix significantly improves the tensile strength of PLA. PLA/1 wt% EPO and PLA/1 wt% EPSO show increments of approximately 5% and 11%, respectively, compared to neat PLA after which the tensile strength of PLA decreases with the addition of plasticisers above 1 wt%. The drop in tensile strength may be caused by the formation of plasticiser-plasticiser interaction which dominates at higher EPO or EPSO contents, resulting in a phase separated structure. In addition, at higher plasticiser loading, only a part of the plasticiser was located in the interfacial area, while the remaining is spread in the matrix, influencing the homogeneity and causing the drop in the tensile strength of the plasticised PLA. Neat PLA exhibits an elongation at break of 5.3%. Buong *et al.*, (2014) observed that elongation at break of PLA increases significantly with increasing plasticisers (EPO and EPSO) loading until an optimum point. Addition after this point causes decrease in elongation at break, making the bio-composite more brittle. With 5 wt% plasticiser`s loadings, PLA/EPO and PLA/EPSO displayed elongation at break of 114.4% and 220.5%, respectively. In general, plasticiser is introduced to a polymer matrix to overcome the brittleness caused by extensive intermolecular interactions. Thus, the presence of plasticisers EPO and EPSO decreases these intermolecular forces and enhances the mobility of PLA polymer chains, causing an increase in flexibility and extensibility of the PLA. Neat PLA exhibited a tensile modulus value of 1209 MPa; addition of

10 wt% EPO and 10 wt% EPSO reduces the stiffness of PLA to 757 MPa and 841 MPa, respectively. This was attributed to the toughening and elastomeric effect of EPO and EPSO. EPO and EPSO, which contain the epoxy group, could form favourable interactions with PLA, presumably via hydrogen bonding. Based on the result of elongation at break of plasticised PLAs, the PLA plasticised with 5 wt% EPO, 5 wt% EPSO showed the best results and were selected for further study and compared to pristine PLA. In dynamic mechanical analysis (DMA), Buong *et al.*, (2014) reported PLA is a semi-crystalline material, and its storage modulus begins to decrease rapidly at 50°C as the material enters its glass-transition. Because of its crystalline properties, it displays a region of relative stability before its modulus plummets rapidly as its structure approaches the melting point. The lower storage modulus of the plasticised PLA compared to neat PLA indicates increase in the flexibility of PLA imparted by the plasticisers. The storage modulus of the plasticised PLAs decreased with presence of plasticiser below 50°C. Further, there was a large drop on the storage modulus around 50 – 60°C corresponding to the glass-transition region. The storage modulus of the plasticised PLAs decreased, indicating that plasticisers increase the mobility of the PLA molecular chain. The storage modulus value measurements were in agreement with the measurements of tensile modulus values from tensile test. Besides, the plasticiser provides moderate toughening and elastomeric effect, which brings about a decrease in the modulus values. Reduction in storage modulus with respect to temperature is related to softening of the matrix at higher temperature. As the temperature exceeds the softening point, the mobility of the matrix chains increases, leading to the sharp decrease of modulus at the temperature range 50 – 60°C. They reported that the peak intensity of loss modulus curve signifies the melt viscosity of a polymer. As observed, the enhancement of loss modulus is higher in plasticised PLAs compared to neat PLA. This

indicates that incorporation of plasticiser increases the melt viscosity of PLA by acting as a good solvent or plasticiser. This is attributable to the addition of EVO which increases the flow-ability by triggering the PLA polymer chains to align in the direction of flow, owing to a less rigid polymeric material. PLA/EPSO shows higher melt viscosity due to improved interphase interaction between PLA and EPSO through hydrogen bonding, compared to PLA/EPO, and have higher ability to dissipate mechanical energy through molecular motion. The  $\tan \delta$  peak has been used to investigate the glass-transition of semi-crystalline polymer or polymeric networks. The  $\tan \delta$  curves show two dynamic relaxation peaks at 80 – 90°C and 50 – 60°C, which are referred to as  $\alpha$  and  $\beta$ -relaxation peaks, respectively. It is assumed that the  $\beta$ -relaxation peak is linked to the breakage of the hydrogen bonding between polymer chains, inducing long-range segmental chain movement in the PLA matrix. Therefore, the  $\beta$ -relaxation peak at 50 – 60°C was assigned to the glass-transition temperature,  $T_g$ . The  $T_g$  of PLA is about 55°C and the plasticised PLAs have slight shifts to lower  $T_g$  temperature. Differential scanning calorimetry (DSC) was used to measure the amount of heat energy absorbed or released when the material is heated or cooled and reported that Pristine PLA showed an endothermic peak of melting,  $T_m = 149.79^\circ\text{C}$ . A minor decrease in the melting temperature of 3 to 4°C was observed, indicating that the melting temperature of PLA was not greatly affected by the addition of EVO plasticiser. The pristine PLA showed a sharp  $T_g$  and its value decreased gradually with addition of EVO.  $T_g$  decreased from 62.85°C for pristine PLA to 60.12°C and 60.79 °C when 5 wt % of EPO and EPSO respectively was added due to enhanced segmental mobility of PLA chains caused by the presence of EVO plasticisers. No trace of separate melting or crystallisation of EVO was found confirming that the phase separation of EVO did not occur. Cold crystallisation was chosen as a crystallisation method because it leads to a more intense spherulite nucleation resulting in shorter

crystallisation time and smaller spherulite sizes. Pristine PLA showed cold-crystallisation temperature at about 124.11°C, the cold-crystallisation temperature of PLA decreased with EVO addition, in parallel with the shift in  $T_g$  as shown in Figure 6. The cold-crystallisation decreased to 114.16°C and 108.97°C for the bio-composite containing 5 wt % EPO and EPSO, respectively. The depression of  $T_{cc}$  and the decrease in  $T_g$  indicated that the EVO was compatible with PLA. Enhanced chain mobility increased the rate of crystallisation, which allowed PLA to crystallise at lower temperature. Furthermore, the crystallisation peak of the bio-composites was narrowed due to increased ability of PLA to crystallise. In the morphological investigation scanning electron microscopy (SEM) was employed to discern the surface morphology of the fractured tensile specimens and qualitatively illustrate the state of dispersion of the EVO in the polymer matrix and they reported that addition of EVO as plasticiser to PLA matrix determined a marked change in the morphology with improved interfacial adhesion and dispersion. SEM micrographs of PLA/5 wt % EPSO shows very good compatible morphologies without edge, cavity, and holes compared to PLA/5 wt % EPO. This incidentally means more transfer of loads under stress conditions, consistent with the enhanced tensile properties of the bio-composites. This phenomenon shows a good adhesion between the components with a diffused polymer-plasticiser interface, which is attributed to formation chemical interactions between PLA and EVO. Thus, the EVO was well-dispersed to form a homogeneous matrix with evident signs of plasticisation in the PLA matrix, without separation at the interface producing single phase morphology. Based on the results obtained it was concluded that the EVO can be used as an excellent plasticiser, which increases the interaction at the phase boundaries and overall properties. Further, PLA/EVO bio-composites can be used as biodegradable or green composite alternatives to the conventionally used polymers, such as polypropylene.



## CHAPTER THREE

### 3.0

### MATERIALS AND METHODS

#### 3.1 Materials

The materials used in this study, their models, source and their manufacturers are outlined in the table below.

**Table 3.1: Names of the equipment used, model, source and manufacturing countries**

| Name of Equipment          | Model                              | Source   | Country                                   |
|----------------------------|------------------------------------|--|---|
| <b>FTIR Spectrometer</b>   | Agilent Technologies Cary 630 FTIR | Chemistry Dept, A. B. U. Zaria                 | Germany                                   |
| <b>Monsanto Tensometer</b> | Type (`w`) S/No. 9875              | Mech. Eng. Dept, Zaria                         | A. B. U. Germany                          |
| <b>D.S.C.</b>              | DSC 1 METTLER TOLEDO               | Metall. and Material Eng. Dept, A. B. U. Zaria | Germany                                   |
| <b>SEM</b>                 | Phenom Prox MVE9I6477830           | Chem. Eng. Dept, Zaria                         | A. B. U. Phenom world Eind, Nertherlands. |
| <b>Viscometer</b>          | NDJ – 5S                           | Chem. Dept, F.C.E. (T), Gusau                  | Germany                                   |

Neem seed oil was obtained from National Research Institute for Chemical Technology (NARICT) Basawa, Zaria. Polystyrene (BDH Ltd) (M. Wt. = 280,000 approximately, (PDI = 2.2) BP chemicals, Onitsha. The entire chemicals used in this research were of analytical grade and used without further purification.

## **3.2 Methods**

### **3.2.1 Modification of oil sample via epoxidation**

Epoxidation of neem oil was carried out in a one-litre three-necked conical-round bottomed flask equipped with a thermometer, separatory funnel and a magnetic stirrer. Neem oil (100 g), formic acid (98%, 6 ml) and 2% concentrated hydrogen tetraoxosulphate (VI) acid (1 ml) were first added into the flask. The contents in the flask were mixed through vigorous stirring for five (5) minutes prior to dropwise addition of the aqueous solution of hydrogen peroxide (40%, 44 ml) to the flask. Thereafter, the temperature of the reaction mixture was raised to 60<sup>0</sup>C and kept for five (5) hours at this temperature with constant stirring. The molar ratio between moles of double bond in the neem oil to formic acid (HCOOH) to hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was kept as 2: 1: 4. The same procedure was reported by Padmasiri *et al.*, (2009).

### **3.2.2 Characterisation of raw and epoxidised neem oil samples via FTIR spectroscopy**

The FTIR spectra of raw and epoxidised neem oils were recorded using Fourier transform infrared spectrometer (table 3.1) equipped with a universal attenuated total reflectance (UATR) accessory. The spectra were recorded between 4000 cm<sup>-1</sup> and 1000 cm<sup>-1</sup> frequency range.

### **3.2.3 Preparation of PS/ ENO blends**

The method employed for the preparation of polystyrene/modified oil blends was that described by Ashraf, *et al.*, (2007) with some modifications.

#### **Procedure:**

The samples were prepared by mixing the polymer solution (PS) with oil in the following weight ratios: 100/0, 95/5, 85/15, 75/25, 65/35, 45/55, 35/65, by taking the requisite amount of

the two components to obtain 100 ml of 10wt% solutions of the blend in chloroform (A.R Grade). The samples were weighed on a digital Mettler balance, AT400, with precision + 0.1 mg.

### **3.2.4 Casting of PS/ENO films**

This was done following the method described by Folaranmi *et al.*, (2002).

#### **Procedure:**

Solutions (10 wt %) of selected composition of the blend in chloroform were cast in clean dry 8.5 cm petri dishes. The dishes were kept on a flat surface of the fume cupboard and were allowed to dry under ambient conditions. After 15 days, the free-standing films were obtained. The films were further dried in vacuum oven kept at 60<sup>0</sup>C for 10 h. After which the films were taken for tensile t measurements, thermal and morphological studies.

## **3.3 Determination of Mechanical Properties**

### **3.3.1 Sample preparation**

The sample preparation was done according to the method described by Kotiba *et al.*, (2012).

**Procedure:** The tensile samples were prepared according to American Society for Testing and Materials (ASTM D638). The solution casted samples were dog bone-shaped with a thickness and width of 4 mm and 10 mm respectively. The gauge lengths of the samples were 10 mm. The obtained products were immediately packed in plastics bags and taken for tensile test.

### **3.3.2 Tensile properties measurement**

The tensile properties were tested using Monsanto Tensometer 9875 (type `w`) series. The samples were cut in dumbbell shapes following ASTM D638 standard as described by Imran *et al.*, (2010). The tensile strength, tensile modulus, and elongation at break were evaluated from the stress-strain data. Each sample was tested three times and the replicates were used to obtain a reliable mean. The gauge length was set at 10 mm, a maximum force of 300 N was used with chart to cross-head ratio 1:1 and a cross-head speed of 200 mm/min; the chart obtained was interpreted. All tests were prepared at 25°C and 17% relative humidity (R.H.).

## **3.4. Determination of Thermal Properties**

### **3.4.1. Differential scanning calorimetry (DSC)**

The melting and crystallisation behaviours of the PS/ENO blends were investigated using DSC analyzer machine (Model DSC 1, Mettler Toledo, Germany). The DSC procedure consists of three steps. At the first step, the films were heated from 30 to 180°C with a heating rate of 10°C/min. Then, they were held at 180°C for 5 min to eliminate the thermal history, and they were cooled to 30°C at a cooling rate of 10°C/min and held at 30°C for 5 min. In the last step, they were reheated to 180°C at a heating rate of 10°C/min.

## **3.5. Determination of Morphological Properties**

### **3.5.1. Scanning electron microscopy (SEM)**

The morphology of tensile fractures on the surface of the PS/ENO blends were studied using a Phenom Prox, scanning electron microscopy (SEM) instrument MVE016477830 (Netherlands) with accelerated voltage of 20 KV. In order to avoid electrostatic discharge during electron

irradiation, the samples were sputter coated with gold of 5 nm thickness using sputter coater model Quorum, Q150RES, in vacuum conditions prior to each examination.

### 3.6 Viscosity Measurements

1 g each of PS/ENO films of different composition were dissolved in 100 ml of chloroform and the solutions subjected to viscometric runs at 30<sup>0</sup>C for different dilutions. A digital viscometer (model NDJ – 5S) using rotor 1 at 60rpm was used for this measurement. The viscosity of the pure chloroform was also determined using this instrument. The relative and reduced viscosities were calculated for each film using the following equations.

$$\text{Relative viscosity } (\eta_r) = \frac{\eta}{\eta_0} \dots\dots\dots (3.1)$$

$$\text{Specific viscosity } \eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1 \dots\dots\dots (3.2)$$

$$\text{Reduced viscosity } \eta_{red} = \frac{\eta_{sp}}{c}; (dl/g) \dots\dots\dots (3.3)$$

where;  $\eta$  = viscosity of polymer solution,  $\eta_0$  = viscosity of the solvent (chloroform) and  $c$  = concentration of the polymer solution.

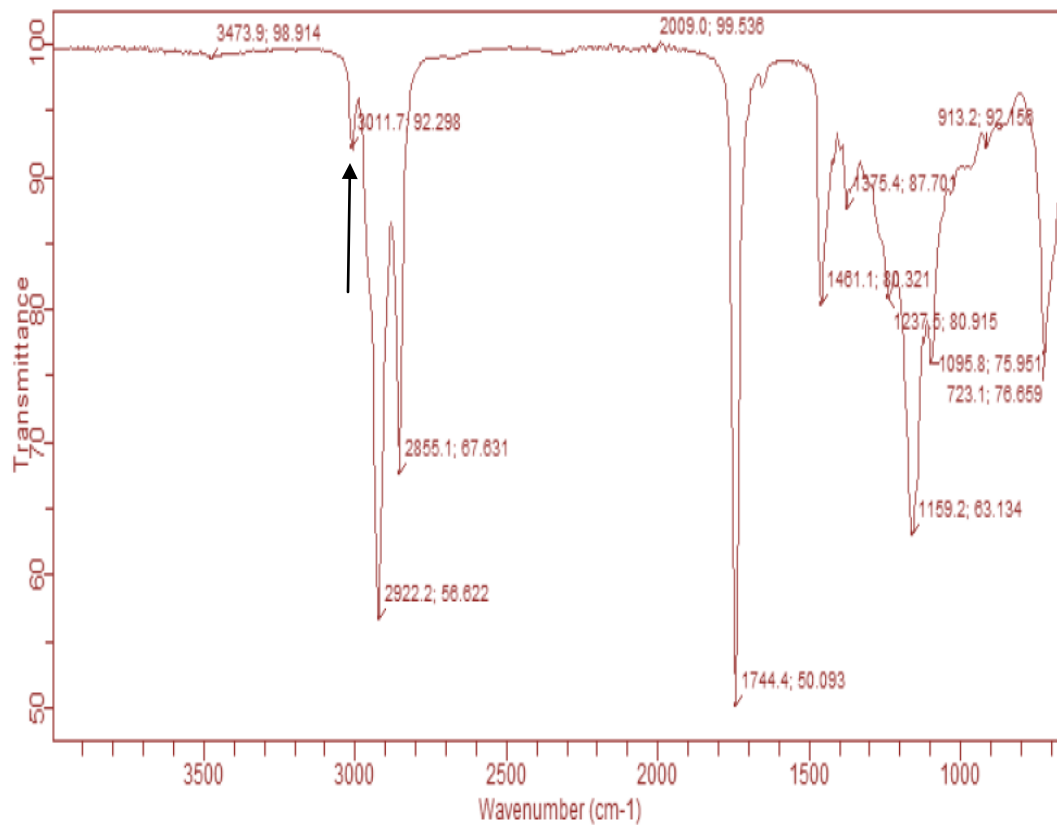
## CHAPTER FOUR

### 4.0 RESULTS AND DISCUSSION

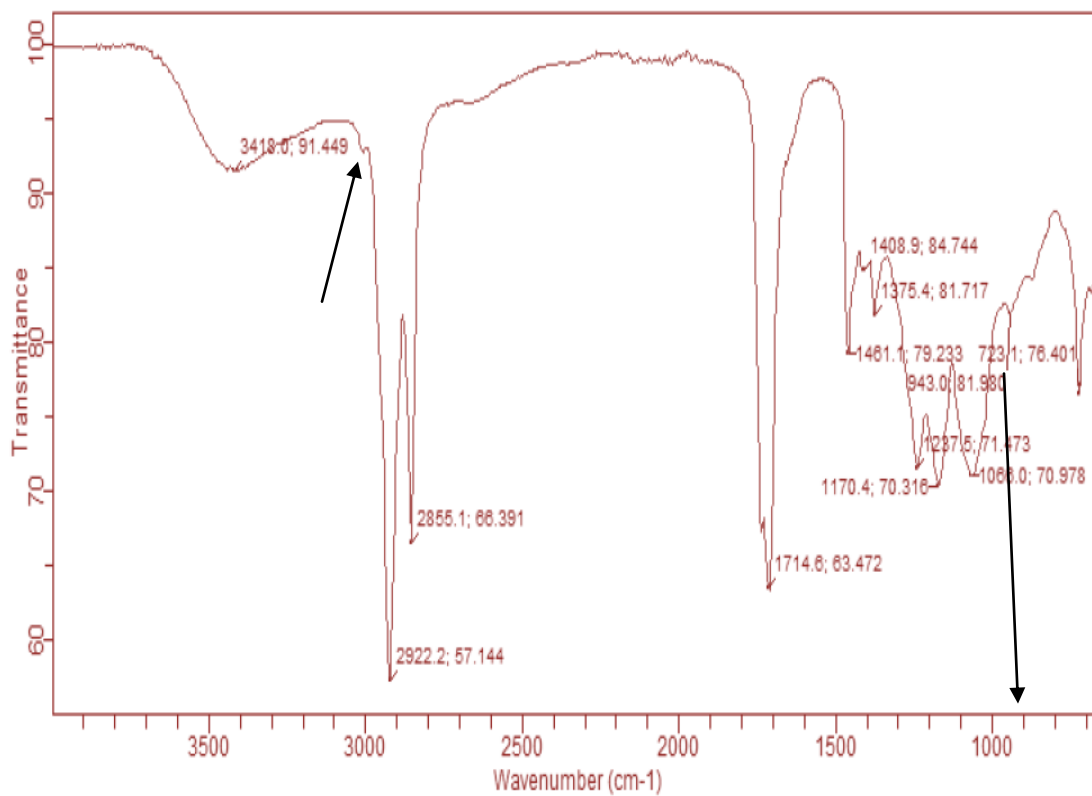
Epoxidation reaction, which adds an oxygen atom to a carbon-carbon double bond, has been established as an important method for the formation of carbon-oxygen bonds (Chua *et al.*, 2012). Unsaturated fatty acids were the components of interest in the epoxidation of vegetable oils due to the presence of carbon-carbon double bond required in the reaction. Neem oil (NO) contains high unsaturated fatty acid content, including oleic (C<sub>18:1</sub>) and linoleic (C<sub>18:2</sub>) acids and was suitably converted to an epoxy group via epoxidation to produce epoxidised neem oil (ENO).



#### 4.1 Fourier Transform Infrared Analysis of the Neem and Epoxidised Neem Oil samples.



**Fig. 4.1: FTIR spectrum of Raw Neem Oil**



**Fig. 4.2: FTIR spectrum of Epoxidized Neem Oil**

The FTIR spectra of raw neem oil and epoxidised neem oil are depicted in Figures 4.1 and 4.2, respectively. The two spectra have C=O stretching vibration of the carboxylic acid functional group and esters around  $1714.6 - 1744.4 \text{ cm}^{-1}$ , and C-H stretching vibration of alkane around  $2855.1 - 2922.2 \text{ cm}^{-1}$ , C-H bending of unsaturated alkane around  $1461.1 \text{ cm}^{-1}$ , C-H stretching of esters around  $1159.2 - 1170 \text{ cm}^{-1}$  and C-C bending of saturated carbon atoms around  $723 \text{ cm}^{-1}$ . But the remarkable difference between the two spectra is the C=C stretching peak around  $3011.7 \text{ cm}^{-1}$  (Figure 4.1) which is completely absent in the spectrum of epoxidised neem oil (Figure 4.2) indicating that epoxidation has taken place with the disappearance of C=C (Espinoza *et al.*, 2009; Kouroosh *et al.*, 2012). To complement this claim, the broad hydroxyl group absorption band observed around  $3418.0 \text{ cm}^{-1}$  in Figure 4.2 was due to epoxy ring opening as a result of the available moisture in the system (Pin-pahn *et al.*, 2008); Kouroosh *et al.*, 2012). In the same vein, the epoxidised spectrum displayed a unique characteristic peak that corresponds to the C-O-C stretching from oxirane vibration at  $943.0 \text{ cm}^{-1}$  which is within the range of  $850 - 950 \text{ cm}^{-1}$  reported by similar literatures (Ahmad *et al.*, 2001; Silveraja *et al.*, 2012; Prerna and Chhibber, 2013; Buong *et al.*, 2014). The relative instability of concentrated hydrogen peroxide in air necessitates its use in varying concentration in aqueous solution. This could be attributed to the inability of obtaining 100% conversion as reported in similar literatures (Pin-pahn *et al.*, 2008; Silveraja *et al.*, 2012; Buong *et al.*, 2014).

#### 4.2 Effect of ENO loading on the Tensile Properties of PS.

**Table 4.1: Tensile properties and wt% composition of PS/ENO blends**

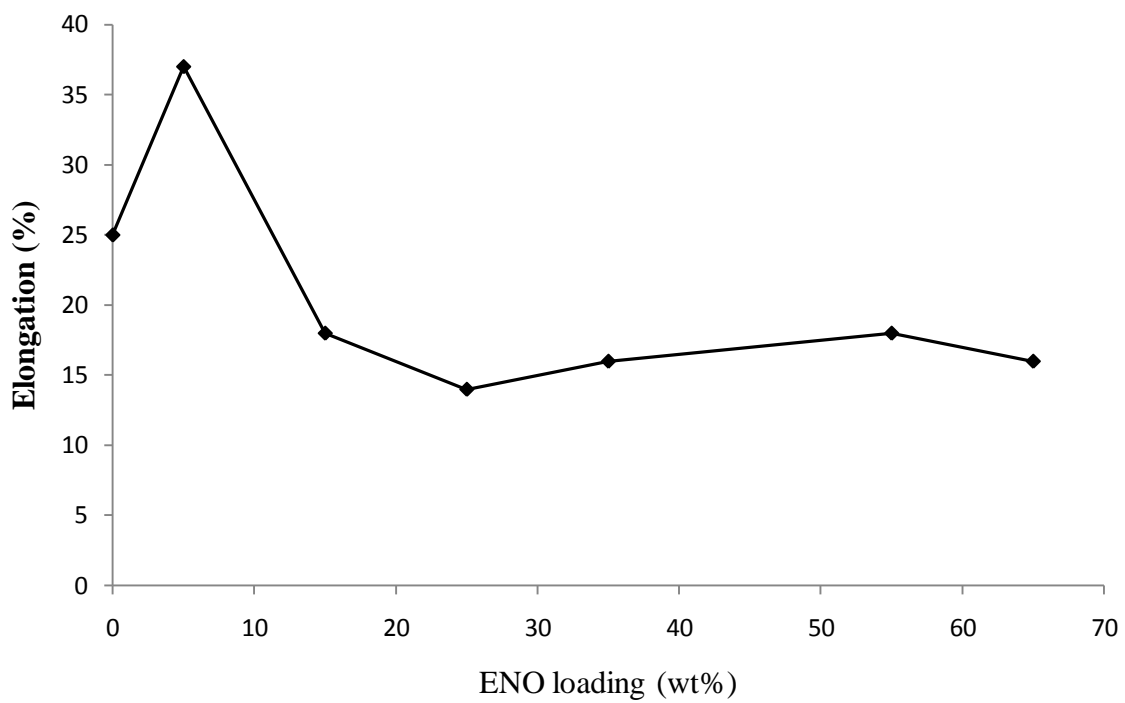
| % composition of PS/ENO (10 % wt solution) | Force (N) | Area (mm <sup>2</sup> ) | Lo (mm) | $\Delta L$ (mm) | Tensile Stress (MPa) | Strain | Tensile Modulus (MPa) | Elongation (%) |
|--|-----------|-------------------------|---------|-----------------|----------------------|--------|-----------------------|----------------|
| <b>35/65</b>                               | 25.5      | 11.62                   | 10      | 1.60±0.03       | 2.2                  | 0.16   | 10.38                 | 16             |
| <b>45/55</b>                               | 21        | 11.62                   | 10      | 1.80±0.03       | 1.8                  | 0.18   | 9.7                   | 18             |
| <b>65/35</b>                               | 49        | 11.62                   | 10      | 1.60±0.03       | 4.2                  | 0.16   | 33.8                  | 16             |
| <b>75/25</b>                               | 39.2      | 11.62                   | 10      | 1.40±0.03       | 3.4                  | 0.14   | 34.3                  | 14             |
| <b>85/15</b>                               | 70.5      | 11.62                   | 10      | 1.80±0.03       | 6.1                  | 0.18   | 27.2                  | 18             |
| <b>95/5</b>                                | 101       | 11.62                   | 10      | 3.70±0.03       | 8.7                  | 0.37   | 24.4                  | 37             |
| <b>100/0</b>                               | 118.17    | 11.62                   | 10      | 2.50±0.03       | 10.2                 | 0.25   | 38.6                  | 25             |

| % composition of PS/ENO (10 %wt solution) | Force (N) | Area (mm <sup>2</sup> ) | Lo (mm) | $\Delta L$ (mm) | Tensile Stress (MPa) | Strain    | Tensile Modulus (MPa) | Elongation (%) |
|---|-----------|-------------------------|---------|-----------------|----------------------|-----------|-----------------------|----------------|
| <b>35/65</b>                              | 25.5      | 11.62                   | 10      | 1.60±0.03       | 2.20±0.08            | 0.16±0.01 | 10.38±0.02            | 16             |
| <b>45/55</b>                              | 21        | 11.62                   | 10      | 1.80±0.03       | 1.80±0.08            | 0.18±0.01 | 9.70±0.02             | 18             |
| <b>65/35</b>                              | 49        | 11.62                   | 10      | 1.60±0.03       | 4.20±0.08            | 0.16±0.01 | 33.80±0.02            | 16             |
| <b>75/25</b>                              | 39.2      | 11.62                   | 10      | 1.40±0.03       | 3.40±0.08            | 0.14±0.01 | 34.30±0.02            | 14             |
| <b>85/15</b>                              | 70.5      | 11.62                   | 10      | 1.80±0.03       | 6.10±0.08            | 0.18±0.01 | 27.20±0.02            | 18             |
| <b>95/5</b>                               | 101       | 11.62                   | 10      | 3.70±0.03       | 8.70±0.08            | 0.37±0.01 | 24.40±0.02            | 37             |
| <b>100/0</b>                              | 118.17    | 11.62                   | 10      | 2.50±0.03       | 10.20±0.08           | 0.25±0.01 | 38.60±0.02            | 25             |

Table 4.1 summarises the values of the tensile properties of PS/ENO blends.

#### 4.2.1 Percentage elongation

Figure 4.3 illustrates the effect of ENO loading on the elongation at break of PS/ENO blends. The elongation at break of PS/ENO blends with 5, 15, 25, 35, 55 and 65 wt% ENO are 37, 18, 14, 16, 18, 16 percent, respectively. Pure (neat) PS exhibited an elongation at break of 25%. It can be observed that elongation at break of the blend increases with 5 wt% ENO loading and began to decrease with increase in wt% ENO loading. The increase in elongation at break with the addition of 5 wt% ENO loading indicates that ENO at this composition reduces the intermolecular forces and increase the mobility of the PS chain, thus enhancing the flexibility and extensibility of the blend at this weight percent composition (Diez-Pascual *et al.*, 2009; Mohammed *et al.*, 2015; Bounq *et al.*, 2017). However, the percentage elongation of the blends decrease from 37% to 18% and 14% respectively, when ENO content increased from 15 wt% to 25 wt%, and this agrees with literature reports by Sahari *et al.*, (2013) and Mohammed *et al.*, (2015). This occurrence can be explained by the anti-plasticisation behaviour or phase separation of highly plasticised PS films. The addition of 35 wt% and 55 wt% ENO to PS led to a slight increase in elongation at break of these blends indicating that some molecular interaction between PS and ENO thereby reducing the intermolecular forces and increase the chain mobility of the PS. This could be attributed to the plasticisation behaviour of the plasticised films. Also the addition of 65 wt% of ENO to PS led to a decrease in percentage elongation of the blend which may be due to anti-plasticisation behaviour. Zavareze *et al.*, (2012) reported that elongation of polymeric materials depends on the mobility of their molecular chains.

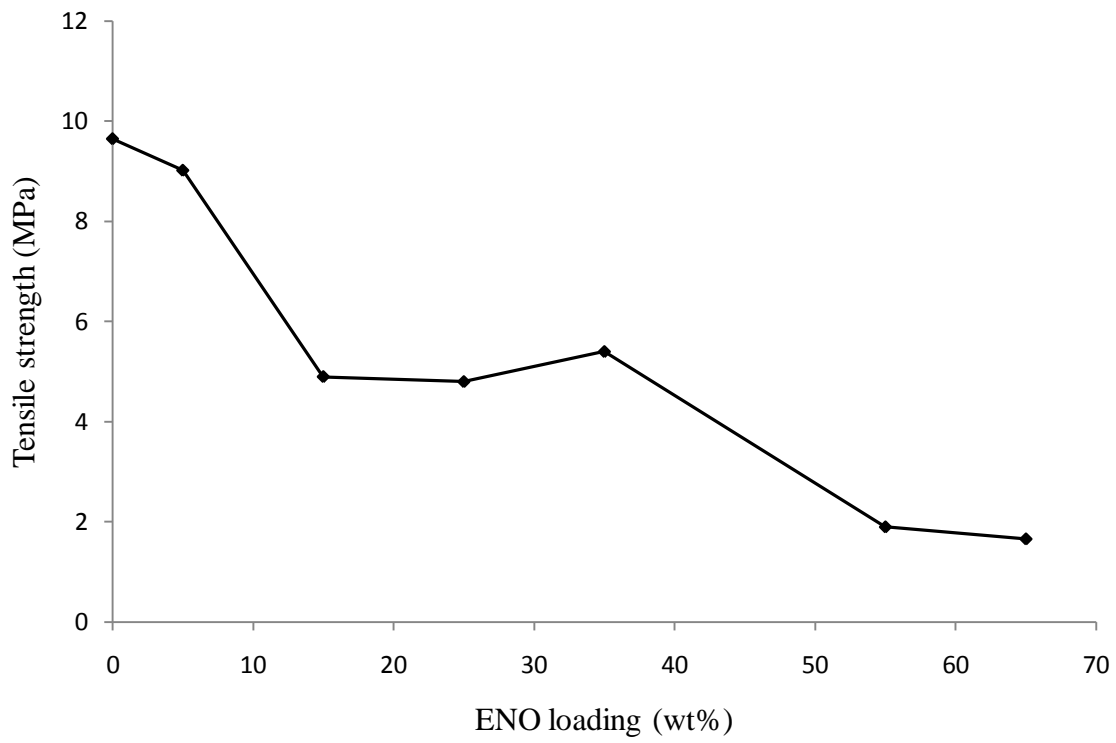


**Fig. 4.3: Elongation (%) versus ENO loading (wt %)**

#### 4.2.2 Tensile strength

Figure 4.4 illustrates the effect of ENO loading on the tensile strength of PS/ENO blends.

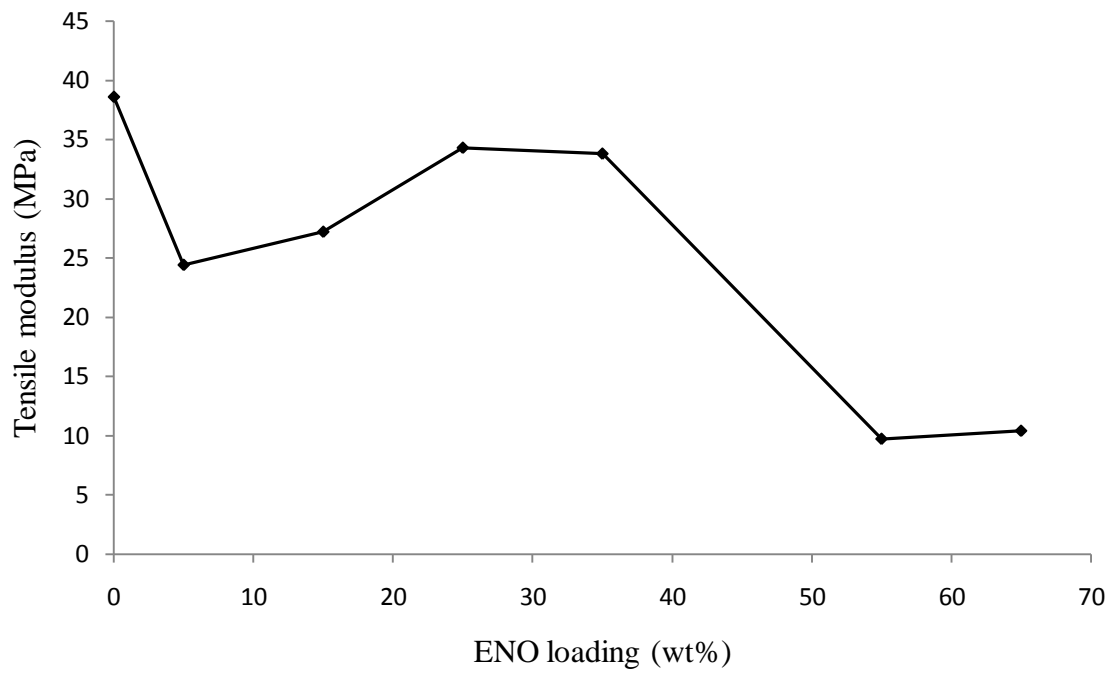
The influence on the values of the tensile strength of PS/ENO blends was observed due to the addition of different contents of ENO in the blends. The tensile strength was observed to decrease with increasing amount of ENO. There is a loss of about 14% of its strength (8.7 MPa) with 5 wt% ENO (910.2 MPa) and almost 97.8% (2.2 MPa) with 65 wt% ENO (figure 4.4). This is in accordance with the common rule that the plasticiser can decrease the tensile strength of the polymer. In general, on plasticisation a polymer solid undergoes a change from hard to soft. The drop in tensile strength may be caused by the formation of plasticiser-plasticiser interaction which dominates at higher ENO contents resulting in a phase separated structure. In addition, at higher plasticiser (ENO) loading, only part of the plasticiser was located in the interfacial area, while the remaining is dispersed in the PS matrix. This influenced the homogeneity and caused the drop in tensile strength of the blends (Silveraja *et al.*, 2012; Buong *et al.*, 2014; Puyou *et al.*, 2016). The reduction in tensile strength above 5 wt% ENO content may also be due to agglomeration of the ENO which leads to poor interaction at the interphase (Diez-Pascual *et al.*, 2009; Silveraja *et al.*, 2012). The rise in the tensile strength at 65/35 wt% PS/ENO blend may be due to phase inversion. Asaletha *et al.*, in (Orathai *et al.*, 2013) established that every solution casting blend (based on chloroform, benzene and carbon tetrachloride) showed a tensile strength drop and then rose again at the point at which phase inversion is possible.



**Fig 4.4: Tensile strength (MPa) versus ENO Loading (wt %)**

### 4.2.3 Tensile modulus

Tensile modulus (E) also called modulus of elasticity or Young`s modulus is a measure of material`s stiffness and rigidity. Figure 4.5 illustrates the effect of ENO loading on the tensile modulus of the PS/ENO blends. The addition n of ENO to pure PS decreases the tensile modulus of the blend losing up to 58% with 5 wt% ENO (24.4 MPa) followed by rise in tensile modulus with increase in ENO loading (15, 25 and 35 wt%) as depicted in figure 4.5 below. Beyond 35 wt% ENO loading, the tensile modulus values dropped (9.7 and 10.38 MPa for 55 and 65 wt% ENO loading). The drop in tensile modulus may be due to the presence of excess ENO in the polyblends which reduced the stiffness and rigidity of the of the PS molecular chain. Moreover, increasing ENO content above 5 wt% adds to the occurrence of empty voids in the blends and influences the local stress acting on the material (Park *et al.*, 2010; Silveraja *et al.*, 2012).



**Fig 4.5: Tensile modulus versus ENO loading**

### **4.3 Thermal Property Study of PS/ENO Films**

The table 4.2 shows the various values of glass-transition temperature ( $T_g$ ), crystallisation temperature ( $T_c$ ), melting temperature ( $T_m$ ) and the heat of fusion associated with each transition obtained from the DSC curves for the blend samples.

**Table 4.2: Values of  $T_g$ ,  $T_c$ ,  $T_m$  and associated heat of fusion for PS/ENO blends**

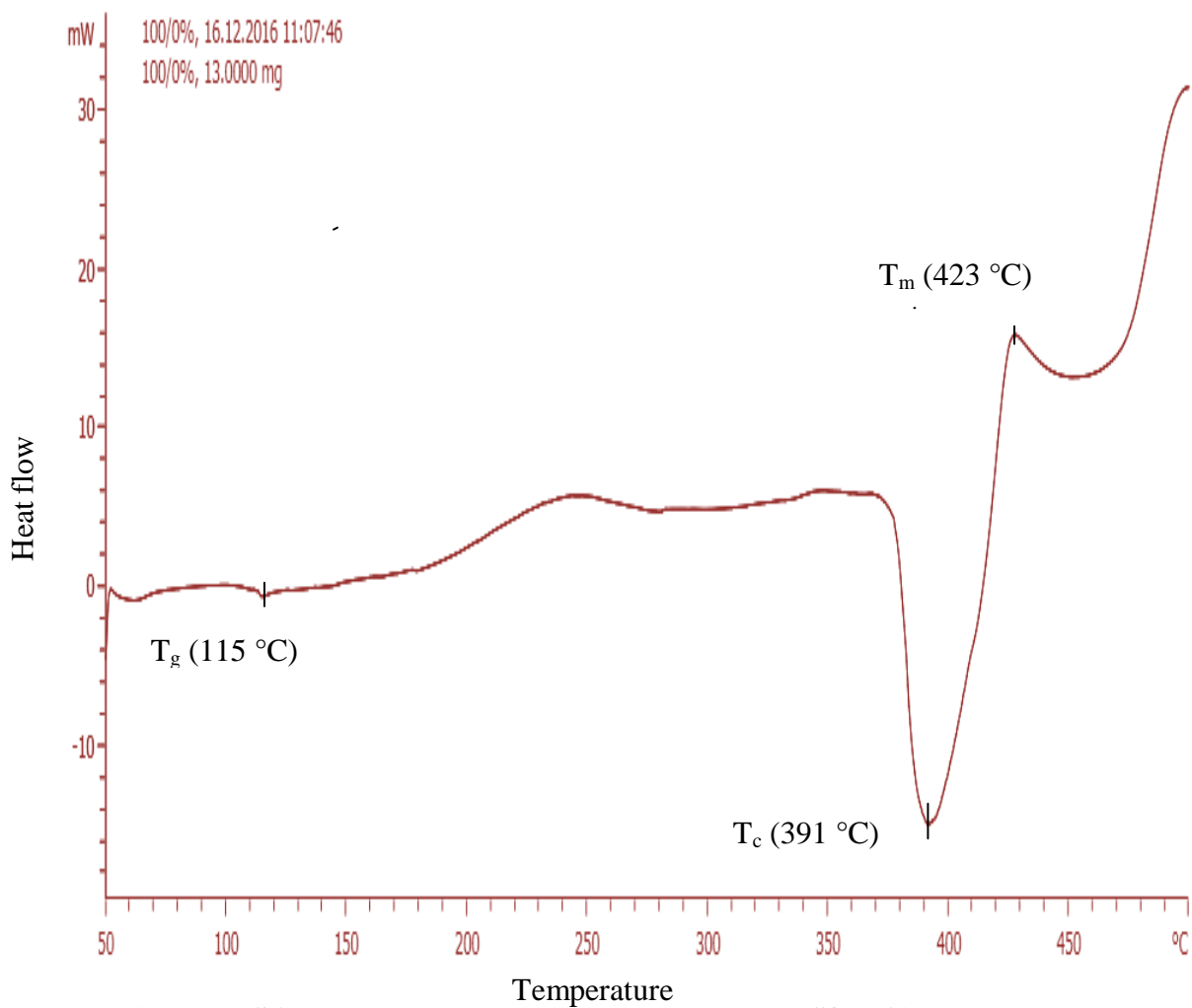
| PS/ENO (Wt %) | $T_g$ ( $^{\circ}\text{C}$ ) | $\Delta H_g$ (J/g) | $T_c$ ( $^{\circ}\text{C}$ ) | $\Delta H_c$ (J/g) | $T_m$ ( $^{\circ}\text{C}$ ) | $\Delta H_m$ (J/g) |
|---------------|------------------------------|--------------------|------------------------------|--------------------|------------------------------|--------------------|
| 100/0         | 115                          | -2                 | 391                          | -8                 | 423                          | 16.0               |
| 95/5          | 105                          | 2                  | 390                          | 3                  | 420                          | 15.9               |
| 85/15         | 110                          | 2.9                | 382                          | 9.2                | 421                          | 14.5               |
| 75/25         | 110                          | 7                  | 400                          | 9                  | 430                          | 20                 |
| 65/35         | 110                          | 1.4                | 385                          | 0.4                | 430                          | 13.1               |
| 45/55         | 110                          | 1.1                | 398                          | 0.6                | 438                          | 16.0               |
| 35/65         | nd                           | nd                 | 388                          | 8                  | 445                          | 18.0               |

nd = not detected

The DSC thermograms of pure PS and PS/ENO blends in the temperature range 50 – 450°C are shown in Figures 4.6 to 4.12. The curves exhibited three thermal transitions, i.e., glass-transition ( $T_g$ ), crystallisation ( $T_c$ ) and melting ( $T_m$ ) temperatures. The thermogram of pure PS shows a sharp  $T_g$  at 115°C with an enthalpy of 2 J/g. With the onset of the molecular chain mobility above the  $T_g$ , obvious crystallisation exothermic peak ( $T_c$ ) was observed indicated by the sharp drop in the specific heat curve located around 391°C with enthalpy 8 J/g. At still higher temperature, the crystals melted with a corresponding rise in the specific heat curve around 423°C with enthalpy 16 J/g which is the  $T_m$  as depicted in Figure 3a. Addition of 5, 15, 25, 35, 55 wt% of ENO to the PS induces a shift of  $T_g$  to a lower temperatures i.e. from 115°C to 105°C with enthalpy 2 J/g, 110°C with enthalpy 2.9 J/g, 110°C with enthalpy 7 J/g, 110°C with enthalpy 1.4 J/g and 110°C with enthalpy 1.1 J/g, respectively, which were due to enhanced chain mobility of PS as shown in Figures 4.7, 4.8, 4.9, 4.9, and 4.9. The  $T_g$  of the blend with 5 wt% ENO loading decreases after which the  $T_g$  of the blends increases with increase in ENO loading in the blends showing a level off compared to the  $T_g$  of the pure PS. This could be attributed to the level of miscibility of the PS with ENO as the content of the ENO is increased. The decrease in  $T_g$ , as expected, was enhanced with ENO content due to reduction in cohesive forces of attraction between polymer chains. ENO molecules (being relatively small in size compared to PS molecules) penetrate into the polymer matrix and established polar attractive

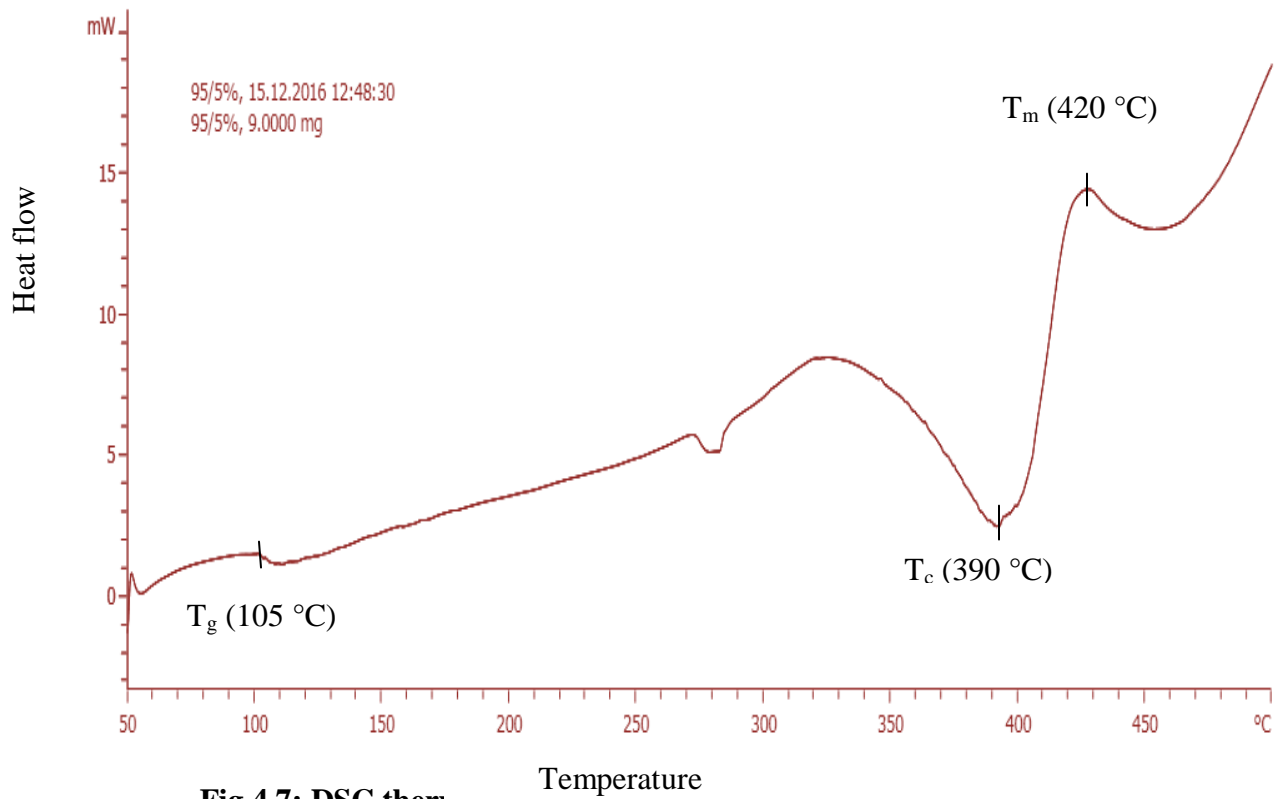
forces between it and the chain segments. These attractive forces reduce the cohesive forces between the polymer chains and increase the segment mobility, thereby reducing  $T_g$  values which is an indication of partial miscibility of PS with ENO. The addition of 65 wt % ENO in the blend shows no obvious  $T_g$  peak which may be due to traces of separate melting of the heat curve as a result of phase separation as indicated in Figure 4.12 (Silveraja *et al.*, 2012; Boungh *et al.*, 2014; AlMamum and Norimasa, 2014). Addition of ENO enhanced PS chain mobility which made it easier to fold in to crystalline lattice (Boonfaung *et al.*, 2011; Silveraja *et al.*, 2014). In addition, the  $T_g$  width for the blends except for 35/65 wt % PS/ENO are almost identical to that of pure PS which support single phase behaviour in the blends, indicating the level of miscibility (Osiris and Manal, 2012). Furthermore, the crystallisation temperature ( $T_c$ ) of PS also decreases with the addition of ENO. Addition of 5, 15, 35, and 65 wt% of ENO decreased the  $T_c$  of the pure PS from 391°C to 390°C with enthalpy 3 J/g, 382°C with enthalpy 9.2 J/g, 385°C with enthalpy 0.4 J/g and 388°C with enthalpy 8 J/g, respectively. It can be observed that as the content of ENO is increased, the polymer chain mobility is enhanced with the rate of crystallisation and allowed the PS/ENO blends to crystallise at lower temperature. The  $T_c$  of PS gradually decreased by the addition of ENO suggesting that the ENO enhances the ability to cold crystallisation of PS. It is evident that the  $T_c$  of PS decreases in parallel with the shift in  $T_g$  of PS. Such a decrease in  $T_g$  and an enhancement in crystallisation process are common for plasticised polymer systems and are due to the increase in segmental mobility of the polymer chains by plasticisation (Fathilah *et al.*, 2009; Silveraja *et al.*, 2012). The variations in the  $T_c$  of the blend samples were influenced by the rates of cooling (Shankar *et al.*, 2016). Thus the 75/25 wt% of PS/ENO blend showed the highest  $T_c$  which implies that the blend cooled slowly (Shankar *et al.*, 2016).

Differences in shape and area of the melting endotherm are also noticed. The melting point is a physical parameter used to identify the nature of the substance and its degree of purity. The variations in shape and area of the melting endotherm were attributed to the different degree of crystallinity found in the blends as opined by Gireeo *et al.*, 1985; Ciemmieeki and Glasser, 1988 in Osiris and Manal, 2012. Pure PS showed endothermic peak of melting ( $T_m$ ) at 423°C, but with addition of 5 and 15 wt% ENO, the  $T_m$  decreases from 423°C to 420°C with enthalpy 15.9 J/g and 421°C with enthalpy 14.5 J/g, respectively, as can be seen from figure 4.7, and 4.8. From Figures 4.9, 4.10, 4.11 and 4.12, the  $T_m$  increases (430°C with enthalpy 20 J/g, 430°C with enthalpy 13.1 J/g, 438°C with enthalpy 16.0 J/g and 445°C with enthalpy 18.0 J/g) for 25, 35, 55, and 65 wt% ENO, respectively. The increase in  $T_m$  and decrease in heat of fusion suggested that the crystallinity and perfection of the crystal structure are reduced with increasing degree of crosslinking (Osiris and Manal, 2012). As well known by the previous reported work, change in the crystalline structure may results from polymer-polymer interactions in the amorphous phase; therefore, disorder in the crystals is created, reducing the enthalpy of the phase change (Hammel *et al.*, 1975 and Wenig *et al.*, 1975). Halal *et al.*, (2011) and Silveraja *et al.*, (2012) established that the lower melting endothermic (temperature) corresponds to the crystalline phase of plasticised polymer soft segments and the higher one to the crystalline phase of hard segments. Traces of separate melting of ENO was found with 35/65 wt% PS/ENO blend confirming phase separation due to poor compatibility (figure 4.12). This is not similar to what was established by authors of similar literatures (Silveraja *et al.*, 2012; Bounig *et al.*, 2014). The  $T_g$ ,  $T_c$  and  $T_m$  with their respective heat of fusion ( $\Delta H$ , J/g) values associated with each transition obtained through analysis of DSC curves for blend samples are summarised in Table 4.2.

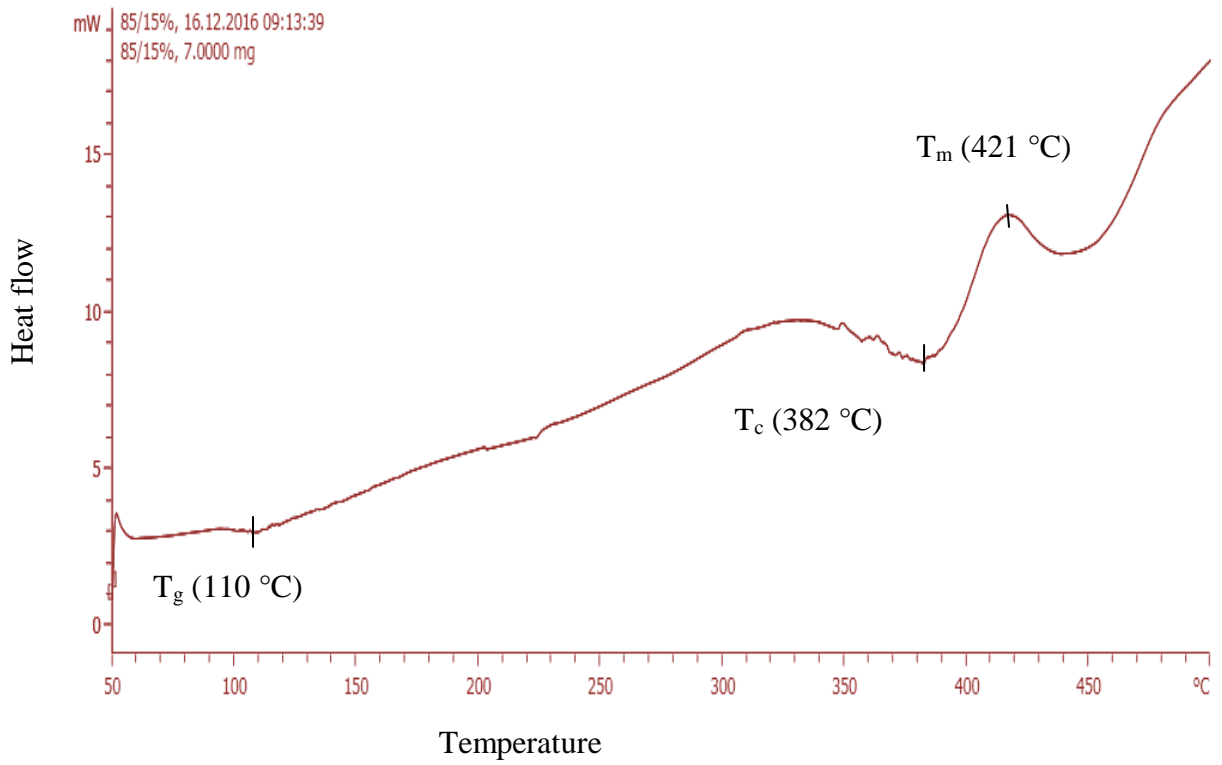


**Fig 4.6: DSC thermogram of pure PS (100/0 wt% PS/ENO)**

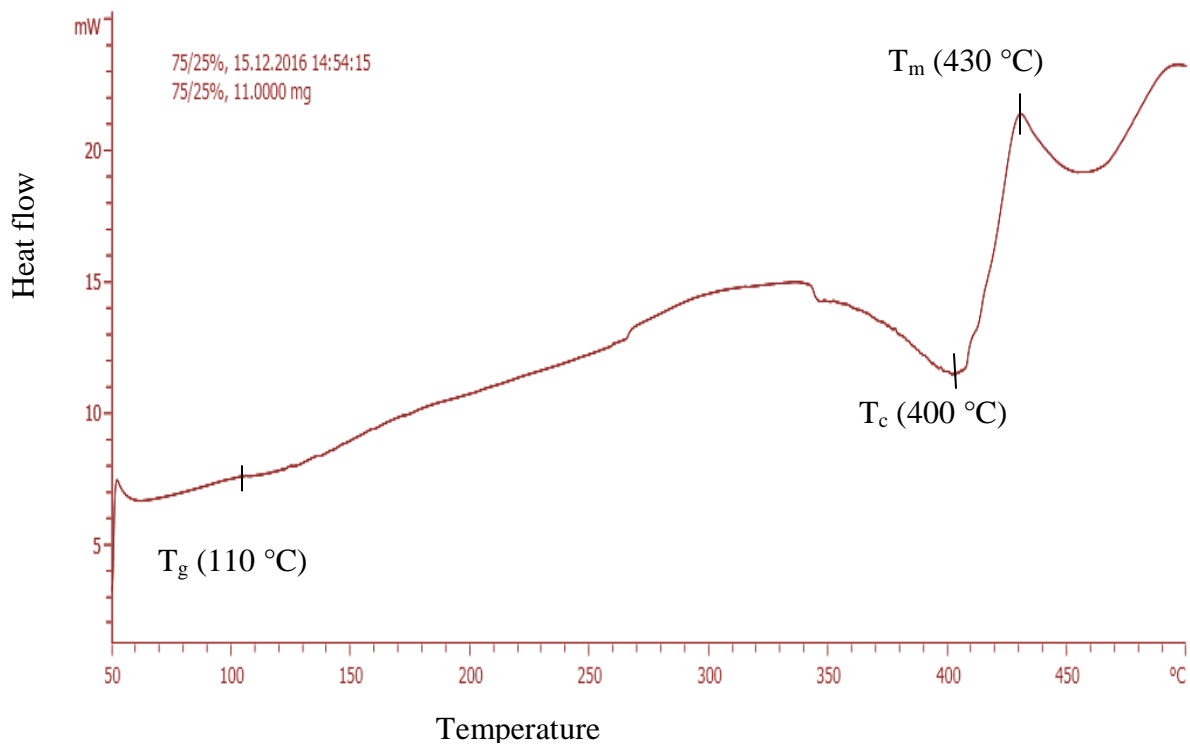




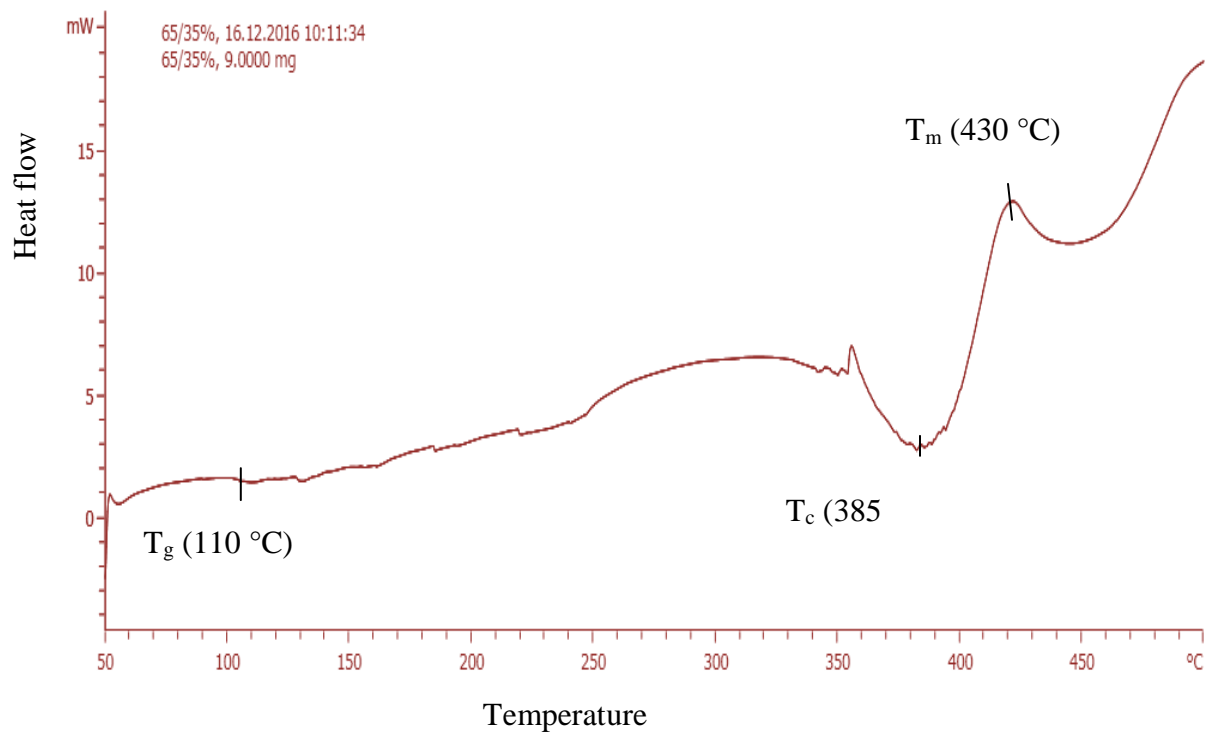
**Fig 4.7: DSC thermogram**



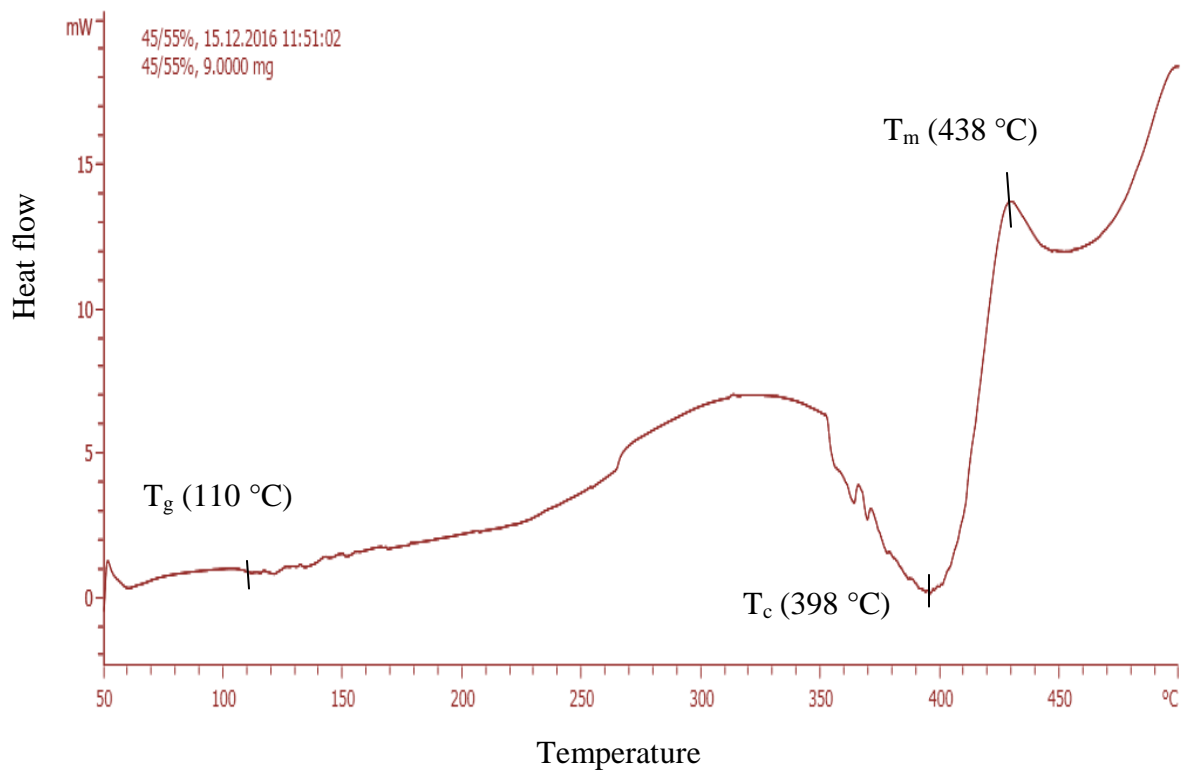
**Fig 4.8: DSC thermogram of 85/15 wt% PS/ENO**



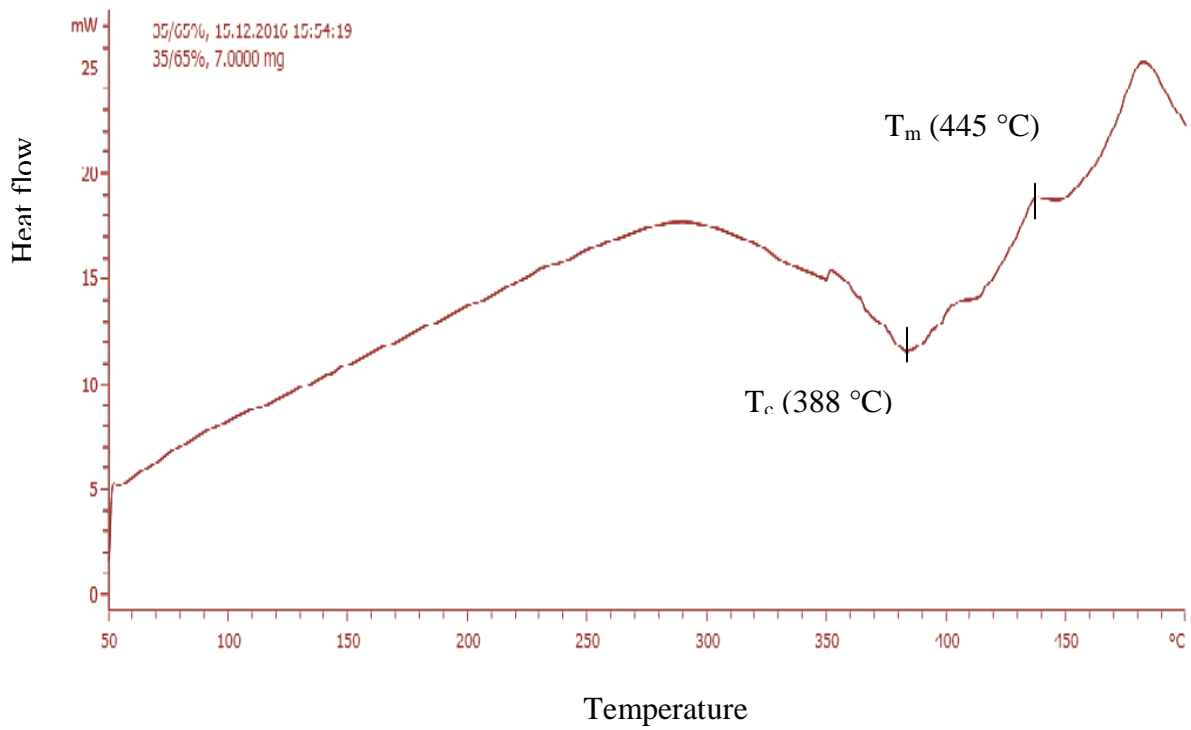
**Fig 4.9: DSC thermogram of 75/25 wt% PS/ENO**



**Fig 4.10: DSC thermogram of 65/35 wt% PS/ENO**



**Fig 4.11: DSC thermogram of 45/55 wt% PS/ENO**



**Fig 4.12: DSC thermogram of 35/65 wt% PS/ENO**

#### 4.4 Morphological Property Study of PS/ENO Films

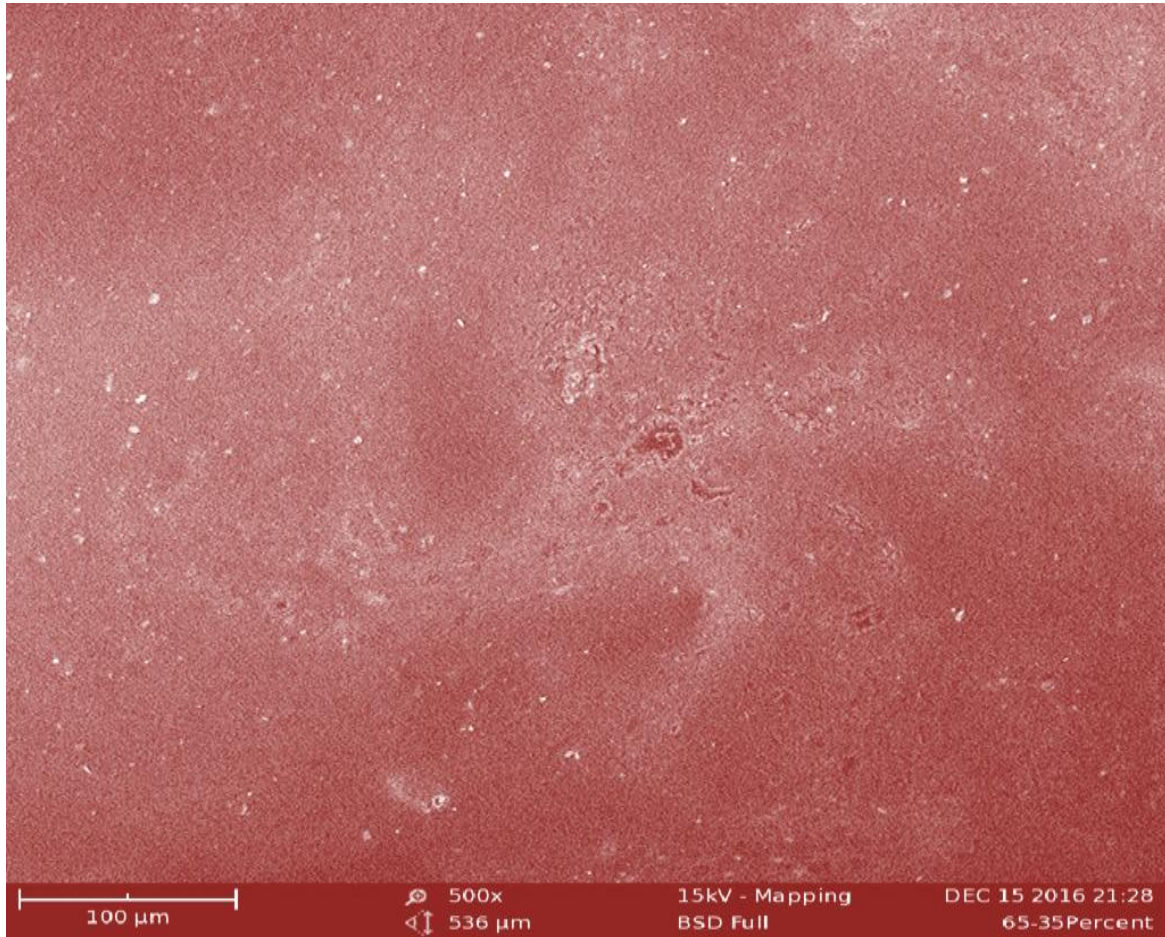
Scanning electron microscopy was employed to study the surface morphology of the fractured tensile specimens and qualitatively illustrate the state of dispersion of ENO in the polymer matrix. SEM was used to study the morphologies of the plasticised PS films and examine the difference between phases of varying composition in the blends. As it can be seen from all of them, ENO distribution into the PS matrix is reasonable with voids in the blends. It seems that the ENO has a profound effect in creating interaction between the components in some compositions, as confirmed by the mechanical studies; the bonding is not very strong and perfect because some debonding can also be seen on the interface of ENO and the PS matrix.

The tensile fractured surface micrographs of the PS/ENO blends (35/65, 65/35, 75/25, 85/15, 95/5,) wt% of magnification 500× are displayed in plates 4a to 4e, respectively. The SEM micrographs show a two-phase system, one appearing bright (epoxy phase) and the other appearing dark (polystyrene phase) in the micrographs. Large microdomains of ENO appeared to be dispersed in the dark phase of the PS which shows the heterogeneity of the phases and immiscibility of the ENO with PS at these compositions, Ashaf *et al.*, (2007). Likewise, ENO phase engulfs polystyrene phase. These SEM micrographs show poor compatible morphologies with edges, cavities and holes (voids) (Mamza and Nwufu 2009). For compositions 35/65, and 75/25 depicted in plates 4a and 4c, there is apparent show of heterogeneity of phases which indicates poor interfacial adhesion (miscibility) between the components with no proper diffused polymer-plasticiser interface revealing the level of immiscibility of ENO with PS at these

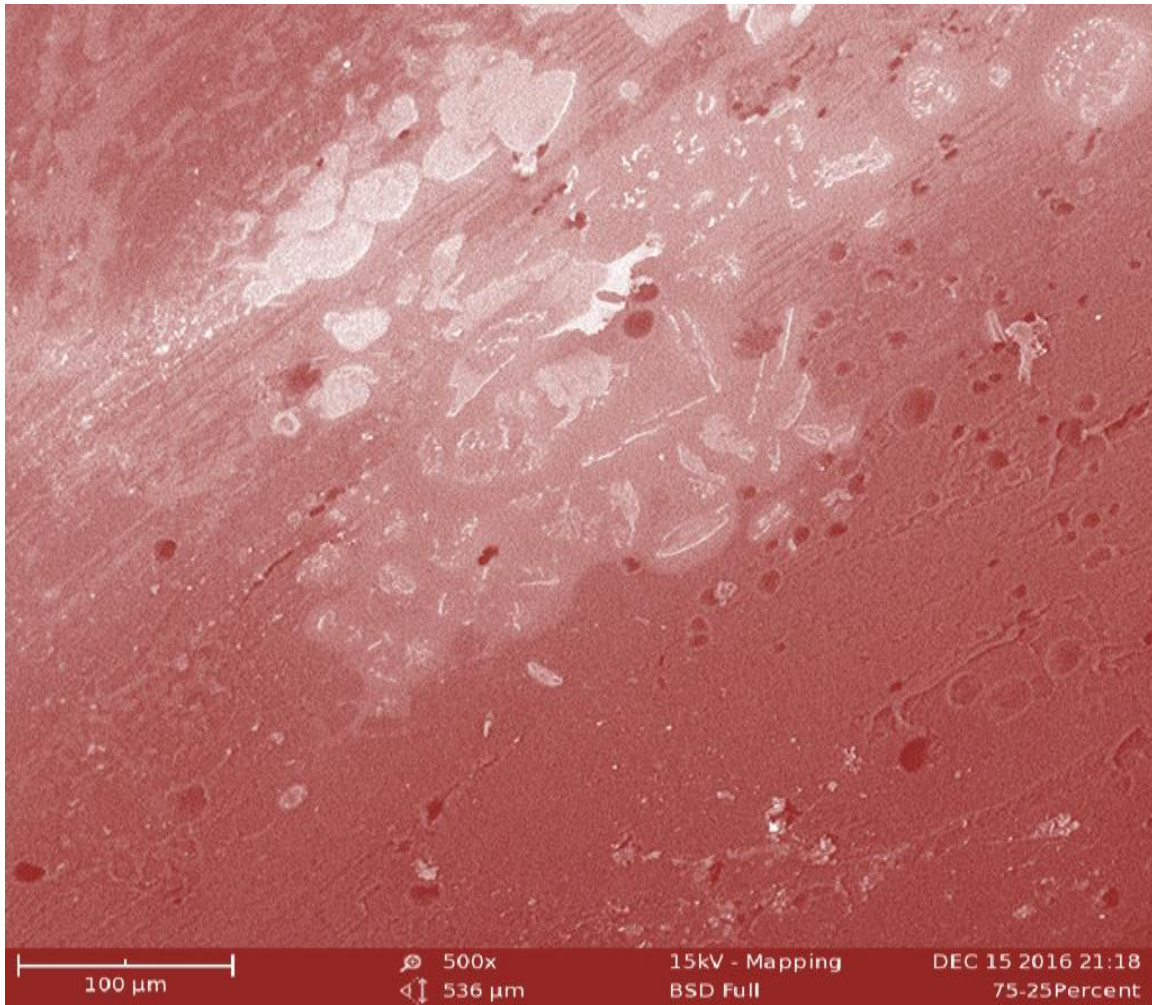
compositions which may be attributed to weak intermolecular interaction between the PS and ENO due to the presence of the bulky (aromatic) group in the backbone of the polystyrene chain and also due to the hydrophilic nature of ENO which is not compatible with hydrophobic polymers (Shaharuddin *et al.*, 2015). However, blend compositions 65/35, 85/15 and 95/5 depicted in plates 4b, 4d and 4e, showed better morphology without phase separation. It may be due to ENO which is dispersed into PS matrix at these compositions revealing a considerable miscibility due to domain distribution. There is a possible limit in the dispersed amount of ENO in the PS matrix; in case the amount of ENO is higher, then it would form another region (ENO wall in case of 35/65 PS/ENO). Based on the results, the 95/5 PS/ENO blend shows better elongation at break, tensile strength, tensile modulus, thermal and morphological properties compare to other compositions; thus, it will be selected for further studies.



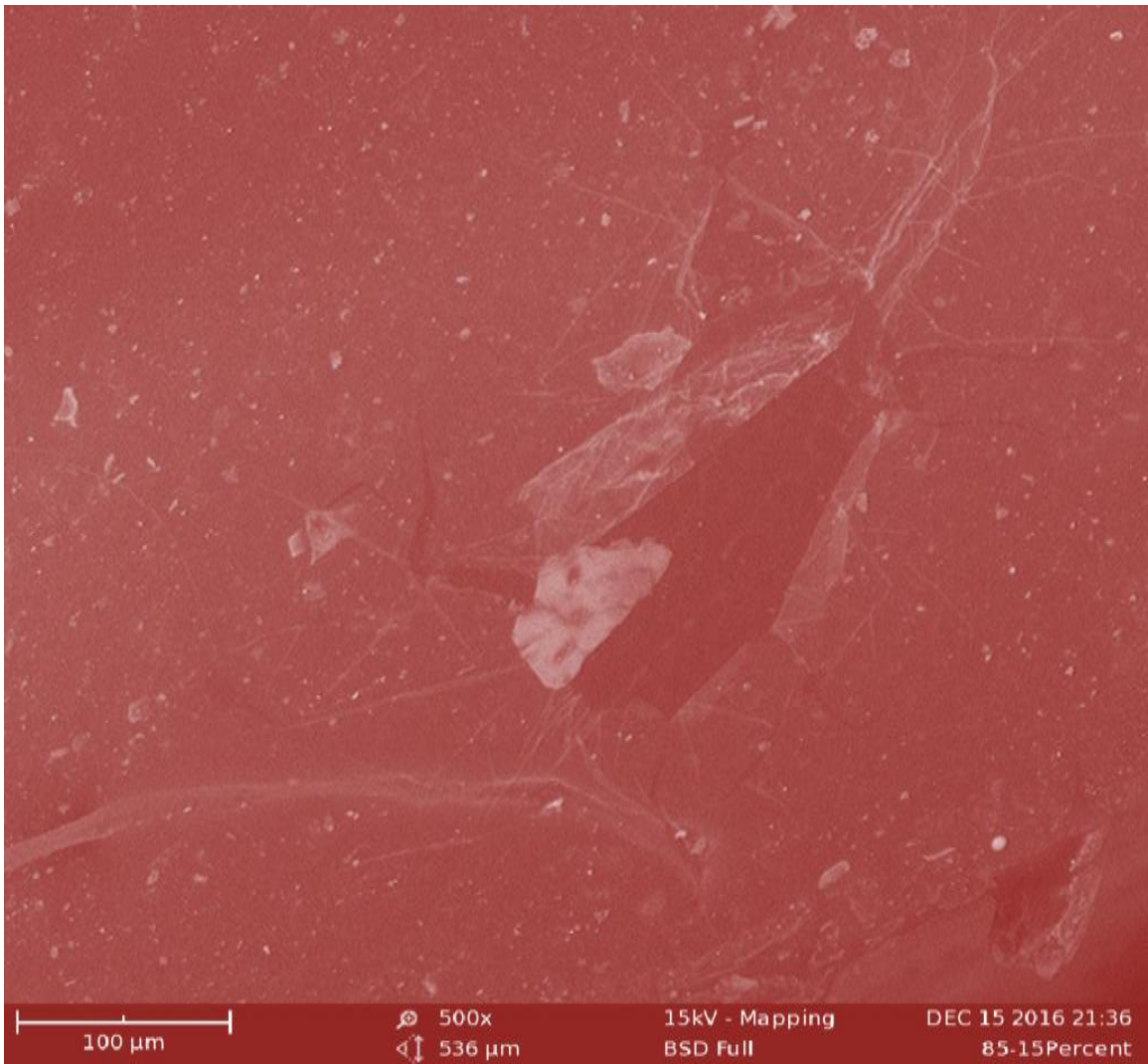
**Plate 4a: SEM micrograph of 35/65 wt% PS/ENO**



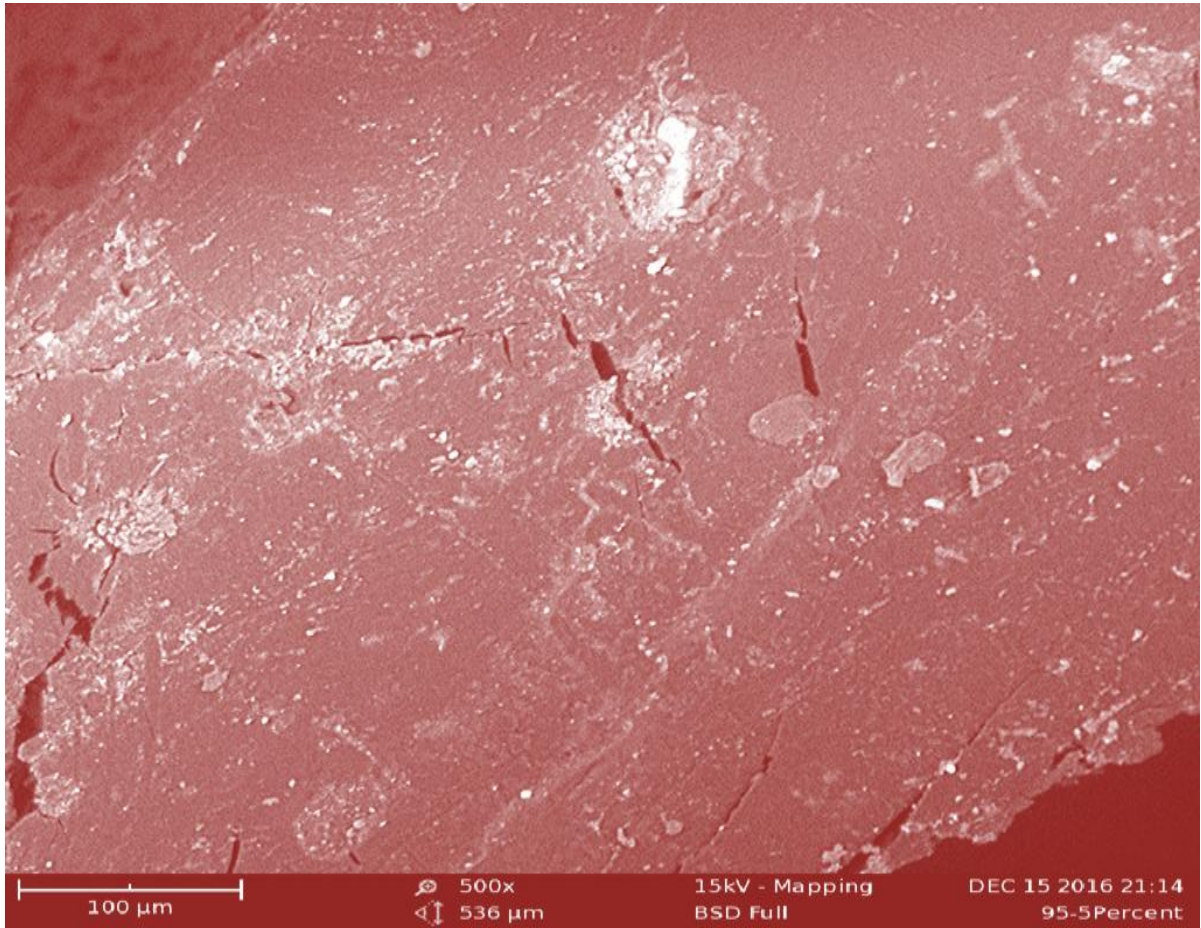
**Plate 4b: SEM micrograph of 65/35 wt% PS/ENO**



**Plate 4c: SEM micrograph of 75/25 wt% PS/ENO**



**Plate 4d: SEM micrograph of 85/15 wt% PS/ENO**



**Plate 4e: SEM micrograph of 95/5 wt% PS/ENO**

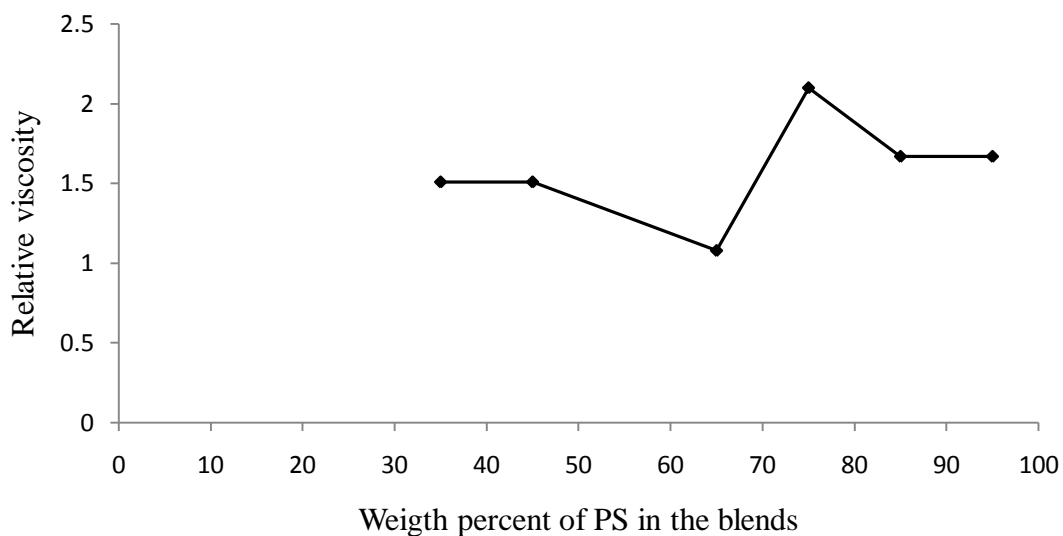
**Table 4.3: Relative viscosity, reduced viscosity and wt% of PS/ENO composition in solution**

| <b>Wt % of PS in blend</b> | <b>Relative viscosity</b> | <b>Reduced viscosity (dl/g)</b> |
|----------------------------|---------------------------|---------------------------------|
| <b>95/5</b>                | 1.67                      | 335                             |
| <b>85/15</b>               | 1.67                      | 335                             |
| <b>75/25</b>               | 2.10                      | 500                             |
| <b>65/35</b>               | 1.08                      | 48                              |
| <b>45/55</b>               | 1.51                      | 250                             |
| <b>35/65</b>               | 1.51                      | 250                             |

#### 4.5 Miscibility Study of PS/ENO Films

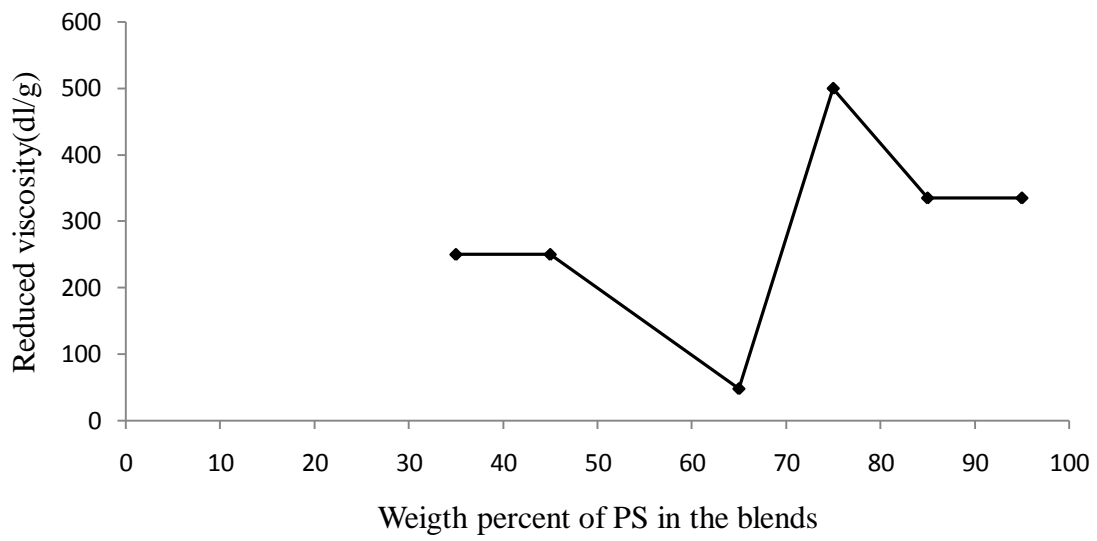
The miscibility studies of PS/ENO in solution phase (chloroform as a solvent) were by viscometric measurements. Mamza and Folaranmi, (1996) adopted viscometric methods for the compatibility studies of polystyrene and poly(vinyl alcohol) in toluene, tetrahydrofuran (THF) and methylethylketone (MEK). They found that the choice of the solvent did not affect the miscibility of the blend. Likewise, Kulshreshta *et al.*, (1988) also concluded that miscibility of the two polymers in solution were unaffected by the choice solvent. The effect of varying composition compositions on the relative viscosity of PS/ENO at 30<sup>0</sup>C is shown in figure 4.13. The plots are non-linear with inflexion at 65 and 75 wt% PS in the blends. The nature of variation of the relative viscosity at these compositions indicates phase inversion due to poor compatibility of PS and ENO (Ashraf *et al.*, (2007); Orathai *et al.*, (2013)). The overall non-linearity of the plots with phase inversions indicates immiscibility of ENO with PS in solution especially at compositions 65/35 and 75/25 wt% of PS/ENO blends. This agrees with the findings of Ashraf *et al.*, (2007); Kulshreshta *et al.*, (1988) and Mamza and Folaranmi, (1996) who established that the plots of the relative viscosity of the polymer blends versus wt% composition is linear when the components are compatible or completely miscible and when the plots are non-linear or S-type, indicating two phase formation with reversal of phases at

intermediate compositions. The plots for the PS/ENO blends are non-linear (figure 4.13) suggesting that the PS and ENO are incompatible. The issue of incompatibility in polyblends is a consequence of repulsive forces as established by similar literatures (Mamza and Folaranmi, (1996) and Mohammad *et al.*, (2008)). The relative and reduced viscosities were obtained using equations 3.1 and 3.3.



**Fig. 4.13: Effect of varying compositions on the relative viscosity of PS/ENO Blends**

The variation of reduced viscosity ( $\eta_{sp}/C$ ) with increasing wt% composition of PS in solution is non-linear as shown in Figure 4.14. From the shape of the plot, one can account for the compatibility or miscibility of the components in the blend (Chimankar *et al.*, 2011). The variation of  $\eta_{sp}/C$  is observed to be non-linear or S-shaped type indicating non-compatibility or immiscibility between PS/ENO at some compositions. At 35/65, 45/55, 85/15 and 95/5 wt% of PS/ENO compositions, the plots are linear indicating considerable miscibility as confirmed by viscosity measurements, but at 65/35 wt% PS/ENO there is phase inversion indicating ENO-rich region which agrees with finding of Ashraf *et al.*, 2007 and the peak at composition 75/25 wt% PS/ENO suggest PS-rich region an indication of non-homogeneity as a result of double phase formation in the system. It may also suggest heterogeneity as indicated by double phase separation in the blend and thus suggests non-compatibility of the components at this composition.



**Fig 4.14: Variation of reduced viscosity with composition of PS in the blends**

## CHAPTER FIVE

### 5.0 CONCLUSION AND RECOMMENDATIONS

#### 5.1 Conclusion

The epoxidation of neem oil was performed using a conventional method. The successful development of value-added products from sustainable resources has been demonstrated as confirmed by FTIR analysis. A possible side reaction was the epoxy ring opening that produced hydroxyl functional groups found by FTIR analysis. The presented results confirmed that the addition of epoxidised neem oil to PS allowed obtaining softer and more flexible material due to the disruption or weakness of secondary valence bonds. As a consequence, PS/ENO compositions were characterised by higher values of percentage elongation, lower values of tensile strength and tensile modulus compared to pure PS.

From the DSC results, the shift to lower glass transition temperature ( $T_g$ ), crystallisation temperature ( $T_c$ ) and melting temperature ( $T_m$ ) were observed due to an increase in the mobility of the polymer chains by the addition of ENO. These compositions also displayed lower crystallinity, indicating that they are amorphous. In addition, SEM results of PS/ENO wt% compositions showed a two-phase system, one appearing bright and the other appearing dark virtually in all the micrographs, even though the heterogeneity due to phase inversion is relevant for some compositions. For some compositions, a domain distribution shows considerable miscibility with the range of composition. Morphological study carried out on the blends had established the value(s) of micro-structural arrangement in the polymer matrixes, under the effect of ENO as plasticiser. The existence of relative good dispersion and adhesion between the components were also found from the examination of SEM micrographs. Furthermore, PS/ENO blends were found to be miscible in solution phase in some composition ranges (95/5, 85/15 and

65/35) wt% as confirmed by viscosity measurement. At composition 75/25 PS/ENO wt% phase inversion takes place which indicates the onset of immiscibility. Considering all the analyses performed, it can be concluded that some blends enhanced the overall structure-property relationships of pure PS. Consequently, the main goal to improve the flexibility of PS was achieved. These findings agree that the epoxidised neem oil (ENO) can be used as a plausible plasticiser, which increases interaction at the phase boundaries and overall properties of the polymer. Therefore, ENO (a product from sustainable resource) can be an interesting material for possible industrial applications.

## **5.2 Recommendations**

### **5.2.1 Recommendations on Application of Vegetable Oils**

The development and utilisation of vegetable oils for polymeric materials are currently in the spotlight of the polymer and chemical industry, as they are the largest renewable platform due to their universal availability, ingrained biodegradability, low cost and excellent environmental aspects (low eco-toxicity and low toxicity towards humans). These excellent natural characteristics are now being taken advantage of in research and development, with vegetable oil derived polymers/polymeric materials/composites being used in numerous applications including paints and coatings, adhesives and nanocomposites. Therefore, it is recommended that government, plastic and chemical industries should encourage and support research institutes, academia and other relevant bodies to come up with a blue print on how to develop and produce epoxidised vegetable oil-based materials at sufficient commercial conversion, so that dependence on the non-renewable and non environment friendly petroleum resource by polymer industries would be reduced.

### **5.2.2 Recommendation for Future Studies**

Based on the results obtained for the 95/5 wt% PS/ENO blend, it is recommended that other blends (80/20 and 90/10) be studied for their performance.

Melt-mixing method should be encouraged over the use of solution casting method to minimise phase inversion that may occur in some of the blends. This may also reduce cost.

The following vegetable oils that have not been to epoxidation are recommended for future studies to explore their industrial potentials. The vegetable oils include Baobab seed oil (*Adansonia digitata L.*), Duam palm nut oil (*Hyphenia thabeaca*), Orange seed oil (*Citrus cyniansis*), e.t.c

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