An-Najah National University

Faculty of Graduate Studies

Formulation of Bio-Based Composites from Renewable Products: Poultry Feathers and Palm Oil

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This Thesis was defended successfully on 23/9/2018 and approved by

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Dedication

This thesis work is dedicated to the sake of ALLAH, my Creator and my Master,

My great teacher and messenger, Prophet Mohammed (May Allah bless and grant him), who taught us the purpose of life,

To the soul of my beloved late father, Ezzat, who had always loved me unconditionally and whose good examples had taught me to work hard for the things that I aspire to achieve; may GOD let him rest in mercy and peace.

To my beloved mother; Aliah, who has been a constant source of support and encouragement during the challenges of graduate school and life. I am truly thankful for having you in my life.

This work is also dedicated to my darling wife, Duha

To my cherished daughter; Aliah

To my precious son; Ezzat

To my professors and all who supported me in completing this work

To everyone who cares about the environment and works to save it.

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Thank you GOD for the opportunity to learn…

To complete a research like this, several minds are essentials. But God sent people who have been very helpful and instrumental in the accomplishment of this study. I am forever grateful to those people who have supported and encouraged me along the way.

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

Formulation of Bio-Based Composites from Renewable Products: Poultry Feathers and Palm Oil

أقر بأن ما اشتملت عليه الرسالة إنما هو نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل أو أي جزء منها لم يقدم من قبل لنيل أي درجة أو لقب علمي أو بحثي لدى أي مؤسسة علمية أو بحثية.

Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degrees or qualifications.

Student's	إسم الطالب:
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List of Abbreviations

Symbol	**Abbreviation**
AESO	acrylated epoxidized soybean oil
AV	Acid value
BPA	Bisphenol A
DETA	Diethylenetriamine
DGEBA	diglycidyl ether of bisphenol A
DPP	Diphenylpropane
DSC	Differential scanning calorimetry
ECH	Epichlorohydrin
EMS	Epoxy methyl soyate
EPO	Epoxidized Palm Oil
ER	Epoxy Resin
ESO	Epoxidized soybean oil
ESR	Epoxidized soybean rubber
EVO	Epoxidized Vegetable Oil
FFA	Free Fatty Acids
FRC	Fiber reinforced composites
FTIR	Fourier transform infrared
GC-MS	Gas Chromatography Mass Spectrometry
I.V	Iodine Value
KFS	Keratin Feather Fibers
M Pa	Mega pascal
MWCNTs	multi-wall carbon nano tubes
m-XDA	*m*-xylylenediamine
PBMs	Polymer-based materials
PCFF	pyrolyzed chicken feather fibers
PLA	Polylactic acid
SEM	Scanning electron microscopy
TGA	Thermal gravimetric
TTT	time-temperature-transformations
VO	Vegetable oil

Chemical Compounds

CH_3CO_3H	Peracetic acid
CH_3COOH	glacial acetic acid
DW	distilled water
H_2O_2	hydrogen peroxide
HCl	Hydrogen chloride
KOH	Potassium hydroxide
$Na_2S_2O_3$	Sodium thiosulfate
NaOH	Sodium hydroxide
Latin abbreviation:	
*T*g	glass transition temperature °C

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Abstract

Plant or vegetables oils exemplify a renewable resource that can be used as reliable preliminary material to access new products with a widespread array of structural and functional variations. In the recent years, epoxidized vegetable oils (EVO) are considered new resource materials, more environmental friendly than other materials such as fossil-fuel and low cost material. Advanced materials from palm oil and chicken feathers are a great feedstock for the synthesis of advanced materials due to the colossal amounts of feathers that are wasted and affect environment.

The aim of this study was to characterize the fundamental functional properties and their palm-based bio-composites, as well as carrying out epoxidation of palm oil to enhance epoxy resin and the properties of epoxidized palm oil (EPO), and then explore the possible applications for enhancing properties of epoxy resin through the addition of (EPO) and chicken feathers. Moreover, clear the environment of chicken feathers.

In this study, FTIR spectrum was used to indicate the presence of the double bond group in palm oil (PO) and epoxy group in epoxidized palm oil (EPO), as well as Gas Chromatography-Mass Spectrometry (GC-MS) that was used to determine fatty acid composition of PO, and the percentage for each category. Moreover, a compression machine was used to determine toughness of epoxy, and an instron to determine tensile strength of epoxy was used. In this study, PO was first epoxidized to form epoxidation of palm oil (EPO). Epoxidation reaction of palm oil was carried out for four (4) days with six (6) samples for each day, and with miscellaneous temperatures (30°C, 40°C, 50°C and 60°C). Trials have been carried out to explore the effect of addition of EPO/chicken feathers on the toughness and tensile strength of epoxy(10 wt%, 20 wt% and 30 wt%) individually/ collectively .

Results have shown that FTIR spectrum of PO bonding peak of HC=CH (cis) was at wave number 1647.49 cm^{-1}, and a stretching vibration peak of =CH 3008.97 cm^{1}, whereas for the FTIR spectrum of EPO, the unsaturation bonding peak HC=CH (cis) and stretching vibration peak of =CH for PO have been disappeared. Nonetheless, the oxirane ring peak was detected at wave number 1104.76 cm^{-1}. Epoxidized palm oil (EPO) has been used to measure the toughen of epoxy resin cured at ambient temperature hardener. Optimum percent of conversion double bond by epoxidation reaction was 86.45% at temperature 50°C at 5 hours from the beginning of the reaction, while the toughness of epoxy increased when adding 10% and 20% EPO of the weight of epoxy, but decreased when adding 30% EPO of weight of epoxy. However, the tensile strength of the epoxy increased when adding 10% and 20% EPO blend with chicken feathers of the weight of epoxy, but decreased when adding 30% EPO blend chicken feathers of weight of epoxy. Solely, chicken feathers did not give positive results, but, when blend with epoxy, chicken feathers lessened the tensile and toughness of the epoxy. Nevertheless, the addition of EPO enhanced the tensile and toughness properties of the epoxy resin.

Chapter One

General Introduction

1.1 Overview

Bio-mass materials have involved a considerable care as raw material because the existing petroleum concerns such as the cost rising and running down of remnant assets. Diverse bio-based composites such as polysaccharides and vegetable oils may be customized for the clarification of smart polymers (Raquez et al., 2010). Vegetable oils (VOs) comprise the nonpoisonous, largest, simply-obtainable, soft price, and non-exhaustible group producing materials proficient of vying with products developed from petrol fossil fuel. Its exclusive chemical organization is the exceptional aspect of VOs with epoxies, esters and other useful groupings by the side of intrinsic fluidity characteristics (Alam et al., 2014). Consequently, lipids are broadly demoralized to polymerize the bio-based materials, (Xia and Larock, 2010; Sharma and Kundu, 2006) like polyamide 11, (Hill, 2000) as well as thermoset resources, like polyurethanes (Desroches et al., 2011) and epoxy resins (Pascault and Williams, 2010).

The employment of vegetable oils is the foremost substitute for the petroleum based lubricants, but has intrinsic limitations that have to be taken into account when devising lubricants such as engine oils, hydraulic fluids, machining fluids and gear oils. The drawbacks can be lessened by chemical adjustment and suitable selection of additives (Erhan, 2005).

However, the plant oil-based epoxy resins magnetized manufacturing concern owing the need of bisphenol-A or aromatic amine that are cancer-causing or poisonous. By means of polyol, polyacid, anhydride in the existence of catalyst or polyamine hardener, polyaddition produces resins (Girard-Reydet et al, 1995).

1.2 History of Epoxy Resin Development

The discovery of epoxy resin has been a long time ago. In the early 1891, the German Lindmann developed hydroquinone and epichlorohydrin through the reaction of intensification into the resin and take advantage of anhydride curing. Nevertheless, its importance has not been exposed. The first creation of epoxy resins took place concurrently in Europe as well as in the United States in the late 1930s and early 1940s. In 1933, Schlack informed the first liquid diepoxide from bisphenol-A, and an access of epichlorohydrin. Greenlee (1948) revealed the procedures to prepare the high molecular weight solid epoxy resins by two techniques:

(a) Direct reaction of bisphenol-A with epichlorohydrin and caustic employing appropriate mole ratios to create the resinous products in line with salt and water, attributed to later as the “taffy” procedure.

(b) Utilization of a liquid diepoxide resin as an initial material for reaction with bisphenol-A, herby eradicating the necessity for exclusion of salt and water (the so-called advancement of fusion technique) (Gannon, 1986).

While the German researcher Paul Schlack achieved an obvious invention in the year 1934; for generating a new innovative product, rave review is utmost indorsed by Pierre Castan from Switzerland and Greenlee from the United States. They had investigated the reaction of bisphenol-A with epichlorohydrin. The group of epoxy resins that they traded were first used as casting combinations and coatings. Nowadays, similar resins are product materials that supply the origin for most epoxy constructions (Lee and Neville, 1967). However, the primary marketable potentials for epoxy resins were recognized in Switzerland by Pierre Castan of De Trey Freres and in the US by Greenlee of Devoe and Raynolds (Gannon, 1986).

Nevertheless, in 1936, Castan created a bisphenol-A based epoxy resin by means of reaction with epichlorohydrin and consequently primed a thermoset composition following reaction of the resin with phthalic anhydride[1]. Employment of the toughened resin was projected in dental inventions, other than preliminary endeavors to promote the resins had failed. The patents and franchises were accredited to CIBA AG of Basel, Switzerland (now CIBA-GEIGY) and, in 1946; the first epoxy adhesive was publicized at the Swiss Industries Fair. For the duration of 1939, Greenlee bent a high molecular weight resin from bisphenol-A, and epichlorohydrin which was later esterified with unsaturated fatty acids to afford an air-drying coating. Greenlee's first patent was issued in 1948. Immediately post World War II, Greenlee and colleagues patented for De

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[1] Phthalic anhydride: "the organic compound with the formula $C_6H_4(CO)_2O$. It is theanhydride of phthalic acid. Phthalic anhydride is a principal commercial form of phthalic acid. It was the first anhydride of a dicarboxylic acid to be used commercially" (Lorz et al., 2007).

Voe and Raynolds (later Celanese Chemical Company) a chain of epoxy resin composites encompassing resins and resin esters. For the meantime, CIBA AG, supplementary advanced epoxy resins for casting, laminating and adhesive applications and CIBA Products Company was founded in the United States (Gannon, 1986).

In 1940's, the Shell Chemical Company, the solitary provider of epichlorohydrin, and Union Carbide (then Bakelite) joined the area of epoxy resin. In 1955, there were four elementary epoxy resin constructers came into a cross-licensing agreement. Afterward, both the Dow Chemical Company and Reichold attained the patent pool and announced marketable lines of epoxy resins. The maximum significant transitional in the development of epoxy resins was the viscous liquid product derived from epoxidation of bisphenol-A (Gannon, 1986).

In 1960, both Nils Malmgren and Curt Augustsson have started to devise and construct products established on epoxy with hardener. Nevertheless, in 1967, the capacity became broad that Nils Malmgren AB was founded, focusing on epoxy-based products. The firm was licensed in excellence (Augustsson, 2004).

From the time when it was discovered, more than eight decades ago, the epoxy resin expanded rapidly to be fundamentally used in daily activities around the world. They also confirmed effectively the researches in this field. No one suspected that only a few decades soon after, the epoxy resins will be an integrant part of the daily life, fitting a crucial element of the modern civilization (Goodman, 1986; Brydson, 1966).

For the time being, epoxy has the reputation in aerospace, automotive industry and the electronics, over and above in foodstuff, pharmaceuticals, and the nautical industry. Nowadays, the majority of people are accustomed with the epoxy term (Goodman, 1986; Brydson, 1966).

1.3 History of Palm Oil

Nations used oil palms ten thousand years ago; in the late 1800s, archaeologists revealed an element that they determined was initially palm oil in a grave at Egypt, antedate back to 3,000 BCE (Kiple and Ornelas, 2000). It is whispered that buyers and sellers transported the oil palm for Egypt (Obahiagbon, 2012).

Palm oil from *(Elaeis guineensis)* (also known as dendê oil) has been recognized as a cooking oil in Central and West African countries, and is widely used. Dealers of Europe trading with West Africa intermittently bought palm oil to utilize as a cooking oil in Europe. Palm oil became a much desirable product by British merchants, for use as an industrial grease to machinery through Britain Industrial Revolution (Aghalino, 2000).

Palm oil designed the basis of soap production, like Lever Brothers' (now Unilever) "Sunlight" soap, and the American Palmolive trademark (Bellis, 2010).

About 1870, palm oil systematized the chief export of several West African countries, such as Nigeria and Ghana , although this was overhauled by cocoa at the 1880_s (Aghalino, 2000).

In the beginning of the 1800, worldwide trade of P.O initiated while that of palm kernel oil developed only after 1832. Later abolition of the slave trade, P.O became the primary shipment for slave ships. The launch of trade in palm oil from West Africa was chiefly the effect of the Industrial Revolution in Europe. As people in Europe started to take hygiene and sanitization industriously, request for soap improved, causing in the mandate for vegetable oil appropriate for soap manufacture and another technical utilizes. Palm oil was found suitable for tinplating. In the early 1870s, exports of palm oil from the Niger were 20 000 to 25 000 tonnes per year (Poku, 2002).

Palm kernel oil exportation start in 1832, and by 1912 West Africa alone exported 157 000 tonnes about 75 % of them came from Nigeria which was the largest exporter until 1934 when was exceeded by Malaysia. Africa (Nigeria and Zaire) was the first one in the world in manufacture and export of palm oil during the foremost half of the 20th century. By 1966, however, Indonesia and Malaysia had exceed all Africa’s palm oil production. Along with *Oil Palm Review*, the Tropical Research and Development Association in the United Kingdom published that over 3 million tonnes of palm oil were produced by Malaysia alone in 1984, contrasted with a total of about 1.3 million tonnes of African production (Poku, 2002).

1.4 Composition and Characterization of Chicken Feathers

Chicken feathers are waste products of the poultry industry generating a dangerous solid waste problem in many countries (Menandro, 2010). It’s projected that 400 million chickens are killed every week. As every bird has up to 125 grams of feather the world production about 3000 tons of feather waste per week. A bout 24 billion chickens, per year, are killed around the world which is throwing away 4 billion pounds (18, 14,369 tones) of poultry feather (Parkinson 1998, McGovern, 2000).

The chicken feathers corrupt the soil, or when burnt out, pollution the air. In the two the cases, the presence of sulphur dioxide in feathers cause the danger behind heavy pollution. This massive mass of discarded feather also reason many human diseases involve mycoplasms, chlorsis, and fowl cholera view on the magnitude of pollution arising from feathery waste. Tradition disposal method of chicken feather are difficult and costly. They are more often buried in landfills, burned in ignition plants, or recycled to animal feed but the quality low. The disposal of this bulk waste is a worldwide environmental dilemma resulting in the pollution of the land and underground water resources. Nonetheless, this disposal process are restricted or make greenhouse gases that pose risk to the environment (Prasanthi et al., 2016).

However, feathers are naturally resistant to deterioration and persevere in the environment for decades. Consequently, they take up large space in landfills and the bad odor from residual fertilizer, blood and other extraneous materials cause pollution in the area (Menandro, 2010).

Chicken feathers vary in form and function. They are generally classified as either contour, down, semiplume, filoplume and bristle. However, regardless of type, chicken feathers are about half feather fiber (barbs) and half quill (rachis) by weight. The quill is the stiff central core with hollow tube structure and the barbs are the fine fibrous materials that branch out of the quill. The quill and feather fiber are both made from keratin (about 90% by weight), which is an impossible to solve and very strong protein found in hair, horns and hoofs of animals (Schmidt, 2002).

Despite the need for additional research on the utilize of waste poultry feather, it offers an environmentally friendly process for removal a dangerous waste product and encourage competitiveness of both the chicken (Menandro, 2010). In our study, an innovative way to utilize poultry feathers in eco-friendly way into a novel composite material is to join them with epoxy resin and palm oil. This present research designates a primary methodology to decrease the feather to avert the pollution caused by feather in ground water and soil. However, future studies can result in the generation of a proper methodology for industrial level disposal.

1.5 Significance and Justification of the Study

Vegetable oils are possibility bio-resources that are renewable and profusely obtainable. The employment of renewable resources for the groundwork of new materials is a marginal route for dipping the rise demand of fossil feedstocks. Triglyceride-based vegetable oils, such as palm oil, are being considered as precursors in the production of polymers.

This effort focuses on modifications of epoxy resin. There are several motivations of this research; First: to minimize the amount of epoxy resin used, which has a lot of damage to health and the environment, by adding palm oil and chicken feathers. Second: to reduce the cost of producing the resin. Third: to improve the mechanical properties of epoxy resin.

Finally, to get rid of large amounts of chicken feathers by blending them with the epoxy resin.

In many applications, the epoxy resins are, the first choice, especially in applications where the development of high performance is required.

1.6 Goal/Objectives

The goal of this research is to investigate the fundamentals of the development of high performance, low cost of chemical structure of natural palm oil and it use in bio-composites.

The steps to achieve this goal are as follows:

1. Characterize the fundamental functional properties and their palm-based bio-composites.
2. Epoxidation of palm oil to enhance epoxy resin and the properties of epoxidized palm oil (EPO).
3. Then explore the possible applications for enhancing properties of epoxy resin through the addition of (EPO) and chicken feathers.
4. Clearance the environment of chicken feathers.

Chapter Two

Background and Literature Review

2.1Vegetable Oils (VOs)

Nature granted a profuse amounts of plant oils that are ester compounds and involved a glycerol molecule related with three saturated or/and unsaturated fatty acids. Furthermore, oils can be categorized as nondrying, drying and semidrying, depending on the unsaturation present on them. Moreover, after a period of time by exposing to air, drying oil develops a stiff film-like material due to the interlace between strings of fatty acid over the atmospheric oxygen molecule. Besides, drying oils are being used in oil paints. Properties of oil could be calculated by diverse factors, including the iodine value, acid value, saponification value, and peroxide value, while the iodine value can control the degree of unsaturation in oil (Hendl et al., 2001).

Epoxidized vegetable oil (EVO) is considered a predominant industrial application of wide vegetable oils (VOs), and extensively used as a plasticizer and as an artificial transitional for polyol or unsaturated polyester (Wang, 2014).

Since epoxidized vegetable oils (EVOs) are a structure of epoxy monomer derived from raw VOs, they are extensively used as plasticizers and intermediates for polyols of bio-based polyurethane or unsaturated polyesters (Wang and Schuman, 2014). Vegetable oils (VOs) are natural resource for the creation of biobased polymers due to their low and constant price, organized availability in large amount, and potential biodegradability[1] (Montero and Meier, 2011).

Generally, biological vegetable oils are exceptional renewable raw materials for evolving new monomers and polymers. In the main, most vegetable oils are triglycerides (Chen, 2014).

VOs are primarily used in food and feed applications, whereas only about 20% are used as industrial feedstocks for biofuels, coatings, paints, lubricants, plasticizers, surfactants (http://lipidlibrary.aocs.org/mark).

VO is domestically abundant, non-depletable, non-toxic, non-volatile and biodegradable resource, used as the principal constitutive in coatings and paints, even in ancient times during the days of paintings. Currently, as a result of numerous environmental and health menaces from remnant fuel products, and the concern of exhaustion of petroleum resources in the end of twenty-one centuries, expert in chemistry have regressed to the widespread exploitation of VO derived materials in paints and coatings. A number of VO developed and tailored to various applications. Widespread literature surveys disclose that VOs have massive prospective, significance and applications in coating (Alam et al., 2014).

Notwithstanding oil palm considers the smallest percentage (5.5-7%) of the refined land for oils and fats, but harvests the major percentage (32%) of the entire output in the midst of major oilseed yields. However, below than half the land is needed by other yields (such as soybean, sunflower, or rapeseed oil) to supply the equivalent quantity of oil. Harvest and use of

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[1] Biodegradation: is "the disintegration of materials by bacteria, fungi, or other biological means. The term is often used in relation to: biomedicine, waste management, ecology, and the bioremediation of the natural environment. It is now commonly associated with environmentally-friendly products, capable of decomposing back into natural elements" (Ikada and Tsuji, 2000).

viable palm oil can benefit to sustain or improve ecological, biological and social values in the homelands (Alam et al., 2014).

While the oil palm tree is considered the greatest resourceful oil crop from side land use, the uppermost vintage matched to additional oil harvests per hectare of land. Fruits are picked when the oil palm trees amount to three to four years old. Worldwide palm oil production has risen greater than before from 15.2 million tons in 1995 to 62.6 million tons in 2015. Surpassing the 2nd largest oilseed crop by more than 10 million tons, oil palm is the utmost manufacturing size of all vegetable oils (Figure 2.1.). This volume is mainly produced by Indonesia (53 per cent) and Malaysia (32 per cent) (Figure 2.2.). A noticeable rise in the production of palm oil has also been in other parts of the world; most of the additional volume is produced in South and Central America (3.4 million tons), Thailand (1.8 million tons) and Western Africa (2.4 million tons) (Alam et al., 2014).

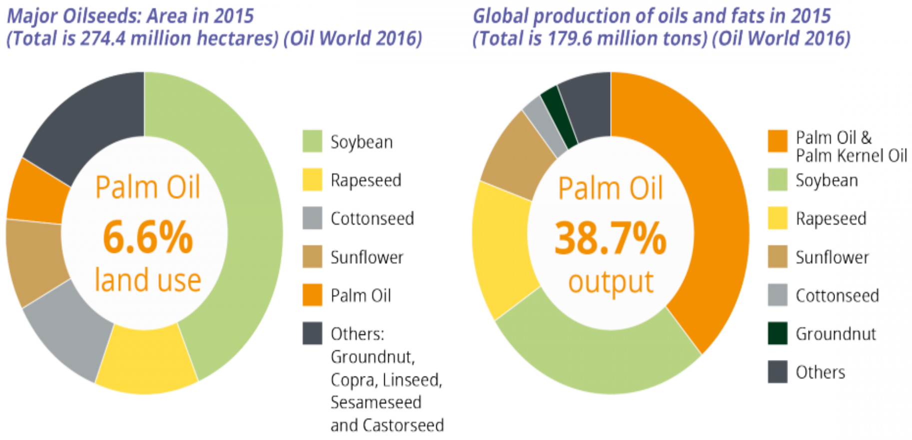

Figure 2.1.: The global total vegetable oil production and that of major oilseed crops.

Source: (Alam et al., 2014).

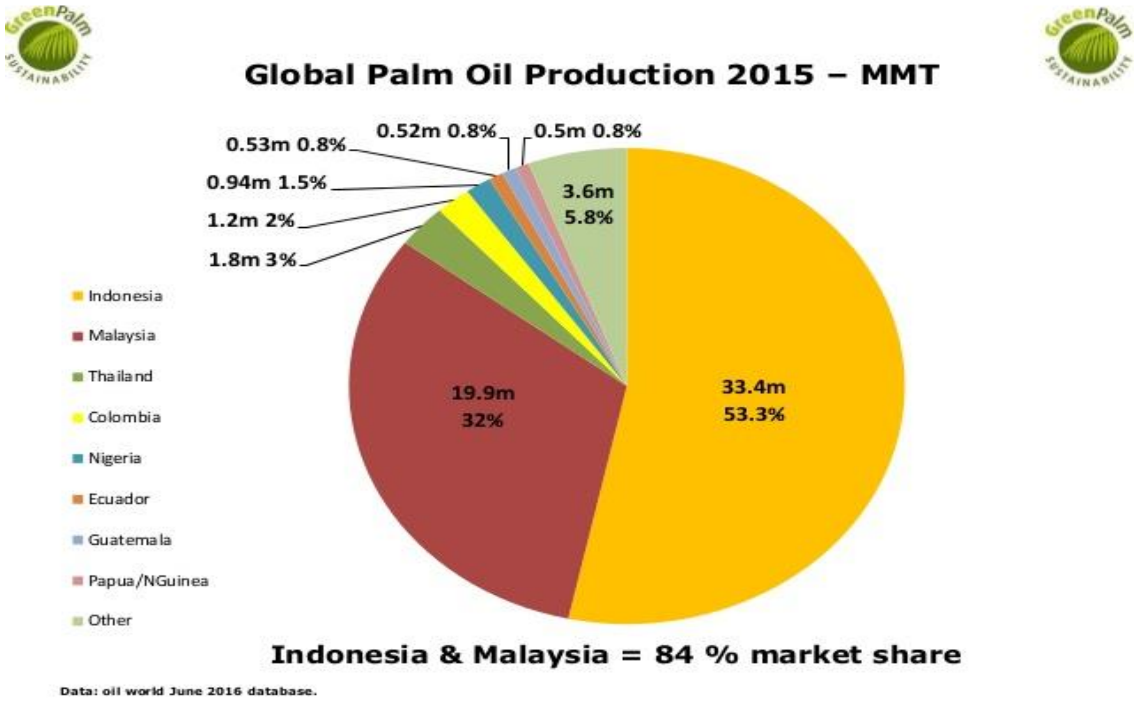

Figure 2.2.: 2015 Global Palm Oil Production by Country (Note: percentages may not add to 100% due to rounding). Source: (Alam et al., 2014).

2.2 Composition and Characterization of Palm Oil

Palm oil *(Elaeis guineensis)* is an edible vegetable oil, glutinous semi-solid, grown at hot surroundings, and a compacted fat in temperate climates. The oil palm is currently grown as a farmstead harvest in most countries with high rainfall (minimum 1 600 mm/yr) in tropical climates within 10° of the equator. As a result of its commercial significance as a high-yielding source of palatable oil, palm oil is plentiful in carotenoids, (pigments found in plants and animals) from which it originates its ruddy color, and the chief constituent of its glycerides is the saturated fatty acid palmitic (Reeves et al., 1979). Palm oil fruit comes on large bunches called Fresh Fruit Bunches (FFB) (Fig.2.3) wavering in weight from 10 to 40 kgs.

The single fruit, (Fig.2.4) extending from 6 to 20 gm, and are made up of an outer skin (the exocarp), a pulp (mesocarp) containing the palm oil in a fibrous matrix; a central nut consisting of a shell (endocarp); and the kernel, which encloses an oil, fairly dissimilar to palm oil, similar to coconut oil (Poku, 2002).

Figure 2.3: Fresh Fruit Bunches (FFB) (Poku, 2002).

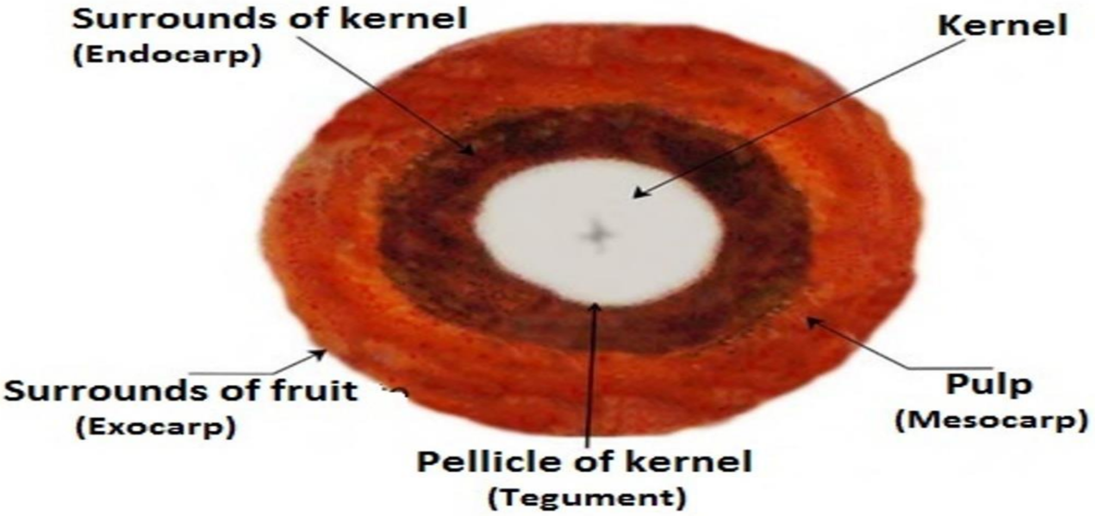

Figure 2.4: Anatomy/cross section of an individual mature licuri palm fruit (Poku, 2002).

The Central and West Africa wild oil palm coppices entails primarily of a copious-shelled diversity with a thin mesocarp, called Dura. Upbringing work, predominantly crosses between Dura and a shell-less variety (Pisifera), have directed to the growth of an amalgam with a plentiful heavier mesocarp and a thinner shell, named Tenera. All refinement and planting programs at the present time use this last type, the fruits of which have a much advanced content of palm oil than the natural Dura (Poku, 2002). However, most of the palm oil is expended as food is cooking oil, to a certain extent oxidized rather than in the fresh state, and this oxidation is in charge for the health risk related with utilizing palm oil (Edem, 2002). Typically, individuals have spent 17 pounds (7.7 kg) of palm oil per person in 2015 around the world (Raghu, 2017).

The extremely high potential productivity has motivated far-reaching growth of oil palm industries in numerous tropical countries. Compared to any other crop, the oil palm produces the maximum revenue of oil per unit area, and manufactures two diverse oils - palm oil and palm kernel oil – that are both important in world trade. Under supreme climatologic circumstances and good management, contemporary high-yielding variations industrialized by background programs, can produce surplus of 20 tonnes of bunches/ha/yr, with palm oil in bunch content of 25%. This corresponds to a yield of 5 tonnes oil/ha/yr (eliminating the palm kernel oil), that exceeds any other source of eatable oil (Poku, 2002).

Table 2.1: Ideal composition of palm fruit bunch

Bunch weight	23-27 kg
Fruit/bunch	60-65 %
Oil/bunch	21-23 %
Kernel/bunch	5-7 %
Mesocarp/bunch	44-46 %
Mesocarp/fruit	71-76 %
Kernel/fruit	21-22
Shell/fruit	10-11

Nonetheless, since climatic environments are habitually less than superlative, high revenues are infrequently accomplished in practice. In Central and West Africa, rain water is inconsistent, hereafter, the tree suffer water-related stresses (Poku, 2002).

2.2.1 Palm oil facts, (Figure 2.5):

- Combined together, palm oil and palm kernel oil exemplify **38**% of the universal vegetable oil manufacture.
- 62 million tons of palm oil are manufactured per annum.
- 40 kilogrammes of palm oil are produced by a single palm tree once a year.
- On average, 3.8 tons of oil are produced in one hectare of oil palm trees yearly.
- Oil palm accounts for **7**% of all the cultivated land for vegetable oils globally, but has the highest output, producing 38% of all oils and fats.

- 85% of the palm oil used globally are supplied by Indonesia and Malaysia together.
- Around 4.5 million people earn a living from palm oil in Indonesia and Malaysia jointly.
- The use of palm oil in human nutrition dates is back to **10,000** years.

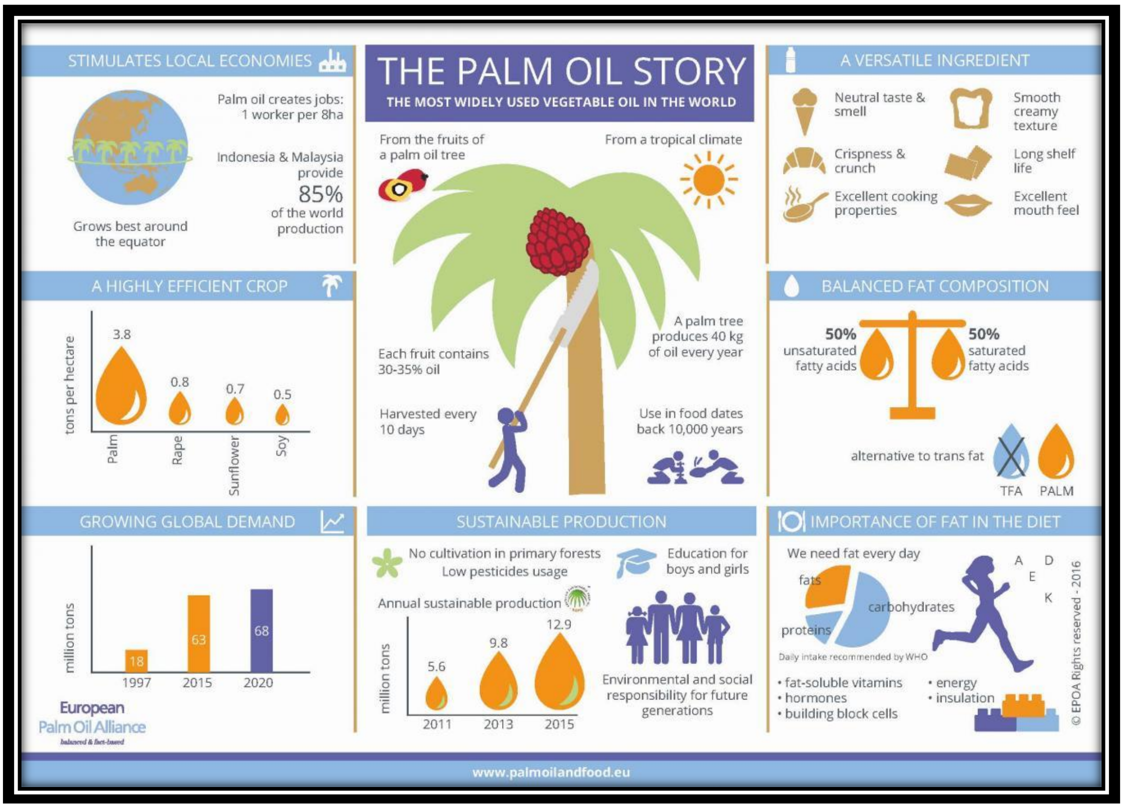

Figure 2.5: The palm story. Source: www.palmoilandfood.eu.

2.3 Biomass and Bioenergy of Palm Oil

Biomass is an organic matter that can be converted into energy." Shared instances of biomass consist of food crops, crop residues, crops for energy, wood waste and by products, and animal manure. Recently, the perception of biomass developed to contain such miscellaneous sources as algae, production wreckage, public solid waste, backyard waste, and food waste.

Others say that biomass is a renewable resource that is extensively accessible, with minimal cost, and that may yield less greenhouse gas than fossil fuels beneath definite locations. Some oppose that biomass has seen inadequate use as an energy source since it is not willingly obtainable as a year-round material, is frequently situated at isolated sites, could be costly to convey, shortages long-dated act data, requires expensive technology to change into energy, and may not encounter quality terms to dependably fuel electric generators (Bracmort, 2015)

Mainly, palm oil is used to generate methyl ester and hydrideoxygenated biodiesel (Rojas, 2007) . Palm oil methyl ester is formed across a procedure named transesterification[1], while palm oil biodiesel is frequently merged with further fuels to produce palm oil biodiesel blends. Palm oil biodiesel fulfills the European EN 14214[2] standard for biodiesels. Direct hydrogenolysis of the fat into alkanes and propane has produced Hydrodeoxygenated biodiesel. Nevertheless, the use of palm oil-based biodiesel is growing as a result of dense production growth in tropical countries like Indonesia, Malaysia. Palm oil is an encouraging raw materials for biodiesel production because of its little price and high output per unit of planted land (Rojas, 2007).

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[1] Transesterification: a general term "used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety" (Schuchardt et al., 1998).

[2] "The European standard for biodiesel is EN 14214, which is translated into the respective national standards for each country that forms the CEN (European Committee for Standardization) area e.g., for the United Kingdom, BS EN 14214 and for Germany DIN EN 14214. It may be used outside the CEN area as well. The main difference that exists between EN 14214 standards of different countries is the national annex detailing climate related requirements of biodiesel in different CEN member countries (Aatola et al., 2008)."

The domain's principal palm oil biodiesel plant is the Finnish-operated in Singapore, largest palm oil biodiesel plant in the world which opened in 2011 and produces hydride oxygenated NEXBTL[1] biodiesel (Yasmine, 2011).

The biological waste stock which is created when handling oil palm, comprising oil palm fruit and bunches oil palm shells, can also be used to produce energy. The leftover substance can be transformed into balls that can be used as a biofuel (Choong, 2012). Moreover, palm oil that has been used to cook foods can be changed into methyl esters for biodiesel. Chemically, the utilized cooking oil is preserved to generate a biodiesel identical to petroleum diesel (Kheang et al., 2006).

2.4 Epoxy Resins

2.4.1 Synthesis:

Epoxy resins are composites encompassing more than one epoxide group/molecule on average, or equivalent of oxirane/mole of compound. Oxirane, which is also known as epoxy, is highly responsive attributable to the polar union construction and can give a large diversity of chemical reactions. Profitable epoxy resins comprise cycloaliphatic, aliphatic, or aromatic supports. However, they are set from either epichlorohydrin or by

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[1] Neste Renewable Diesel (formerly NEXBTL) is "a renewable diesel fuel production process commercialized by the Finnish oil and refining company Neste. Whether as an admixture or in its pure form, Neste Renewable Diesel is able to supplement or partially replace diesel fuel without problems. Unblended Neste Renewable Diesel meets the requirements set by the European pre-standard CEN TS 15940. Fuel blends meet the European diesel fuel standard EN 590" (Aatola et al., 2008).

direct epoxidation of olefins with peracids, while the most imperative intermediary for epoxy resins is the diglycidyl ether of bisphenol A (DGEBA). (Riew and Gillham, 1984; Pham Marks, 2002).

2.4.2 Curing Agents:

Management of epoxy resins with curing agents or hardeners gives three-dimensional infusible and insoluble networks. They can be preserved with an inclusive variety of remedial agents. The option of curing agents relies on the mandatory physical and chemical characteristics, processing methods and therapeutic situations. Epoxy resins can be treated with either catalytic or core active curing agents. Catalytic curing agents behave as motivators for epoxy ring-opening homopolymerization or as supplemental curing agents or accelerators for other curing agents like anhydrides or amines. Epoxy resins can be catalytically cured by Lewis acids such as boron trifluoride monoethylamine or Lewis bases[1] such as tertiary amines,. Photoinitiated cationic curing of epoxy resins got a great consideration for the application of coatings from solvent-free or high solid systems. The epoxide ring can retort with chemicals with diverse assemblies, particularly those that motivated hydrogen atoms for instance amines, carboxylic acids, and alcohols.

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[1] Lewis bases and acids: A Lewis acid is "a chemical species that contains an empty orbital which is capable of accepting an electron pair from a Lewis base to form a Lewis adduct. A Lewis base, then, is any species that has a filled orbital containing an electron pair which is not involved in bonding but may form a dative bond with a Lewis acid to form a Lewis adduct".

2.5 Base Resins

The "epoxy resin" expression portrays an extensive group of thermosetting polymers in which the principal cross-linking takes place throughout the reaction of an epoxide group. Since the molecule is defined as an epoxide, the molecular base where it is devoted may differ extensively, setting numerous epoxy resins modules (Lee and Neville, 1967).

The cluster of epoxy which is correspondingly termed the glycidyl set has through its special presence specified the name epoxy. It is also a molecule with additional epoxy cluster that can be hardened into a serviceable plastic. Epoxy resins are a domestic of synthetic resins, as well as products which fluctuate from viscid solutions to high melting point solids. The resin molecule includes as responsive site one or more oxirane or epoxide groups, frequently in a formula of the glycidyl group, moreover, they regularly comprise hydroxyl groups (Lee and Neville, 1967).

There is an oxygen atom on the outer of the string of carbon. Epi denotes "on the outside of", while the other portion of the term originates from oxygen. There are two spellings, explicitly epoxi and epoxy. The first comes from the ozygen's simple basic chemicals that are readily available. The simplest epoxy model is a three-member ring structure recognized by the idiom 'alpha-epoxy' or '1,2-epoxy', while the typical chemical construction is exposed in the figure below, and recognized distinctive of any more complex epoxy molecule (Tesoro, 1988).

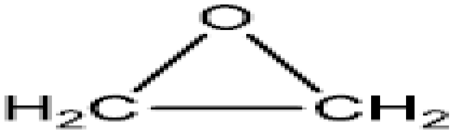

Figure 2.6: Simple chemical structure of epoxy group.

The furthermost commercially significant resin is the glycidyl ether of bisphenol-A created by the concentration of epichlorohydrin (ECH) and diphenylpropane (DPP), similarly identified as bisphenol-A (BPA). Epoxy resins with diverse features are furthermore formed commercially by countering Epichlorohydrin (ECH) with other materials (Tesoro, 1988).

The resins ought to be cross-linked by means of a curing agent or a hardener. The option of curing agent is of dominant significance in scheming an epoxy resin for a relevance. The chief combative groups in the resin – the epoxide or hydroxyl groups – are able to interact with many clusters so as numerous forms of chemical matters can be operated as curing agents. They embrace acid anhydrides, aliphatic and aromatic amines and polyaminoamides. Several curing agents will cross-link the resin at surrounding temperature whilst others necessitate the application of heat. Nevertheless, the undemanding combination of resin and curing agent not often supplies a material encompassing all the wanted properties for a precise submission. Therefore, further ingredients are supplemented in subediting the scheme (Lee and Neville, 1967).

It is very imperative to understand rudimentary production techniques to appreciate the obtainable resins and how they differ from each other base molecules form epoxy resins from comprising an unsaturated carbon-carbon bond. Two processes can be used to convert this double bond into an oxirane ring:

1. Dehydrohalogenation[1] of a halohydrin intermediate,

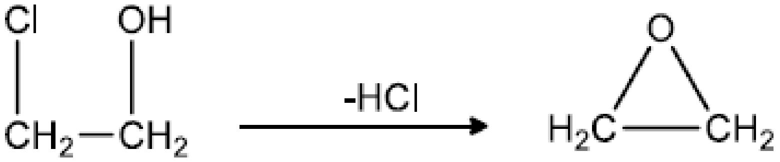

Figure 2.7: Dehydrohalogenation process to convert double bond into an oxirane ring.

2. Direct peracid epoxidation[2].

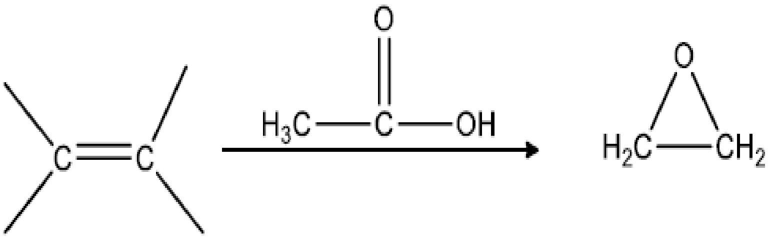

Figure 2.8: Direct peracid epoxidation process to convert this double bond into an oxirane ring

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[1] **Dehydrohalogenation**: "Traditionally, alkyl halides are substrates for this dehydrohalogenations. The alkyl halide must be able to form an alkene, thus methyl and benzy halides are not suitable substrates. Aryl halides are also unsuitable. Upon treatment with strong base, chlorobenzene dehydrohalogenates to give phenol via a benzyne intermediate" (March, 1985)

[2] **Epoxidation:** "the conversion of an olefin (an unsaturated alkene hydrocarbon) to a cyclic ether through reaction with hydrogen peroxide, a peracid, or oxygen, is an important chemical technique."

The halohydrin itinerary is more reciprocated and is used to yield an extensive assortment of materials despite that both processes are used to produce marketable epoxy resins. The most vital raw material used in epoxy resin production is epichlorohydrin, which is used as a precursor for virtually every commercially available epoxy resin with the exception of the cycloaliphatic resins (Maureen et al., 2006).

Epoxy resins are unevenly sectioned into three modules: aliphatic, cycloaliphatic and aromatic. The diglycidyl ether of bisphenol A (DGEBA) structure, which is made from the concentration reaction of bisphenol A (BPA) and epichlorohydrin (EPCH), is the most collective, commercially existing epoxy resin. In a multi-step process, propylene produce EPCH. Glycerol can also be used to produce EPCH and has been recently commercialized (Santacesaria et al., 2012).

2.6 Uses of Epoxy Resin

After curing, the resins are considered, in high chemical and standing bond to several pillars, pretty electrical traits and capability to be managed under a range of conditions. (Negoita et al., 2016).

The epoxy resins are used at metallic roofs, at anti-corrosive treatment, at manufacturing the electric insulating materials, at manufacturing the dyes, the electronic components, but also the decorative floors. The applications go to areas absolutely indescribable, from manufacturing the components for ships, planes and cars or vehicles of high tonnage, up to plastic pieces which replace the metal or wood pieces. But, the epoxy resins have entered also in other domains in which one might hardly believe they are used: in art (painting, sculpture, reconditioning the artifacts) or in medicine (artificial organs, stomatology). Still the indispensable mobile phones contain epoxy resins which cover the essential components of the device. The enormous accomplishment of the discovery of the 20th century which burst out on the market in the 1960s was due to improving the methods for attaining the epoxy resins, but also to the publicity made to the new products by the civil media, which gave it extraordinary consideration, as more and more fields of activity were circumscribed to this subject (Negoita et al., 2016).

Epoxy resins are customarily employed as adhesives, coverings, encapsulate, molding substances, potting complexes, and wrappers. Other most remarkable applications are the aerospace and entertaining businesses where resins and fibers are joined to fabricate multifaceted merged configurations. However, epoxy technologies could fulfill a range of nonmetallic amalgamated enterprises in marketable and martial aerospace solicitations, as well as floor covering panels, piping, stabilizers, and even the fuselage (the main body of an aircraft). Correspondingly, is now being used to produce lightweight bicycle structures, snowboards, racing cars, as well as harmonic devices (Maureen et al., 2006).

Numerous substantial developments in the past years are controlled by plastics and polymers. Nearly 95% of those supplies are attained from petroleum and nowadays the use of non-renewable properties in the manufacture of plastics calculates for around 7% of international oil. A few years ago, the worry with petroleum diminution in addition to the conservational effect of such materials has managed to a concern in different, environmentally-friendly ingredients. Likewise, bio-based polymers have confirmed to be progressively more common substitutes in the last years (Lochab et al., 2012).

In a brief and scientifically vulgarized formulation, epoxy resins symbolize a group of unbending polymers, with high mechanical properties, with resistance to temperature and rust (Negoita et al., 2016).

2.7 Economic Aspects on the Epoxy Resin

Since its first epoxy resins products that were synthesized early 1891 (Lee and Neville, 1967a), the commercial epoxy resins work of Pierre Castan in Switzerland and Sylvan Greenlee in the United States was promoted in the 1940s, though alike resins had been endorsed in the 1930s. Commercially, epoxy resins were first proposed in 1946 that are now used in a widespread range of industries. The reaction products of bisphenol A and epichlorohydrin were epoxy resins early sold, while this is still the chief path for the manufacturing of most resins currently marketed (Ellis, 1993).

From the economic point of view, the composite industry represents both a challenge and a continuously growing market due imperatives of the environmental protection. In latest years, (55%) of epoxy resins used were in organizational uses such as coats and complexes, tooling, decoration, building, bonding and adhesives, while the rest (45%) of entirety epoxy resins sold were used in protective coatings. Furthermore, being such a familiar material in all industries, revealing its importance on the economy of the countries, economically, worldwide request on epoxy resin was projected at unevenly US$21.5 billion in 2016. Encouraging growing is predictable because of robust signs of economic environment, predominantly in the US markets. In recent years, raw material prices have been risen, and expected to escalate in the subsequent years. Predictably, market value will reach US$27.5 billion by 2020 and upsurge to US$37.3 billion by 2025, succeeding the yearly increase rate of 6.3% in the pending years. Sturdiest request is projected from epoxy combination market and epoxy adhesive market. Requests for long-term availability, price drops, disquiets for environmental concerns, and reasonable advantages are the roots for the expansion of new bio-based materials. Moreover, (VO) has drawn growing consideration to be one of most encouraging opportunities due to its prepared handiness, comparatively low price, and low eco-toxicity (Acmite Market Intelligence, 2017).

In the universal epoxy resin market, the following major applications were taken into account: paints and coverings, glues, compounds, electrical and electronics, wind turbine and others. The foremost application in terms of use of epoxy resins is paints and coatings. A number of factors is determining the market, for instance growing demand from the paints and coatings industry, and rising demand from the electrical and electronics sector. Yet, the market confronts definite shortcomings, for example high cost of the raw materials, and environmental worries. The aforesaid factors may operate as a barricade to the market progression. The universal epoxy resin market, on the basis of raw materials, can be largely segmented into DGBEA (Bisphenol A & ECH), DGBEF (Bisphenol F & ECH), Novolac (Formaldehyde & Phenols), Aliphatic (Aliphatic Alcohols), Glycidylamine (Aromatic Amines & ECH), and others. Geographically, market has been sectioned into Asia-Pacific, North America, Europe, South America, and Middle-East and Africa. Asia-Pacific grips the major portion in the market. Presently, China takes over the international market in terms of volume, and accounts for about 45% of the global share as of 2014, while in North America, growing mandate for epoxy resins-based composites from the aerospace industry is projected to lead the market (Mordor Intelligence, 2017).

2.8 Health Problems of Epoxy Resins

There is an emergent work on the effects of epoxy resins, curing agents, hardeners, and the blends of these resins with other chemical compounds adequate to merit an examination of the conceivable reasons of the complications which have resulted from the manufacture and use of these materials. Extreme hazards may be avoided by good engineering installations and "no touch" technique, but these are not always relevant to use, and also depend significantly on the magnitudes of raw materials used. While considerable experimental work is being executed with amended systems and new materials, trivial is known of the systemic effects of the newer chemicals used in these processes. There are limited reports of introductory work on the toxicity of the chemicals. In addition, the position is convoluted by international patent problems which have stimulated some manufacturers of the primary materials to be cagey about giving this information (Bourne et al., 1959).

It is the hardener constituent and not to the epoxy resin that causes the primary risk associated with epoxy use. Specifically, amine hardeners are usually disfiguring, nevertheless, may correspondingly ranked as toxic or carcinogenic. Fragrant amines pose a specific health hazard, nonetheless their use is currently circumscribed to definite industrial submissions, and not dangerous aliphatic or cycloaliphatic amines are generally engaged. Solid epoxy resins are normally more secure than liquid ones, and many are categorized harmless materials. Liquid epoxy resins in their uncured shape are typically categorized as irritant to the eyes and skin, besides toxic to aquatic organisms (water creatures). A specific hazard related with epoxy resins is sensitization which is more noticeable in epoxy resins encompassing low molecular weight epoxy diluents (TWI, 2003).

2.8.1 Dermatitis:

Skin inflammation or (acute contact dermatitis) is the furthermost public reaction caused by epoxy resin and hardener. Distress can be severe, but generally vanishes once ceasing contact with the irritant. When overexposed to epoxy resin or hardener, less than 10% of epoxy users' act in response, nevertheless, recurrent skin contact with resins as well as hardeners could furthermore instigate chronic contact dermatitis, which is commonly minor but long-lasting. Nonetheless, if unprocessed for long times, it may develop to eczema, that is a form of dermatitis that can embrace swelling, pimples and itching. Moderately treated epoxy sanding powder, if settled on the skin, can also guide to approach dermatitis (Jolanki et al., 2000).

2.8.2 Allergic Dermatitis (Sensitization):

Fewer than 2% of epoxy operators are expected to acquire allergic dermatitis which is a more serious problem. When the body overreacts to an allergen, it causes allergic dermatitis (sensitization); the state of being allergic to a substance. The immune system and the grade and incidence of introduction to epoxy affects the chance of becoming sensitized. The body is vulnerable when exceptionally overexposed to epoxy or if ingrained sensitized or allergic to a constituent of epoxy. Likewise, extra liable if has fine skin, or when previously showing to other sensitizing materials, or if has high fever, or are under tension. One may develop sensitization to epoxy after just one or several exposures. It may need 10 days of exposure, a month, or even years, but, it is best to sidestep exposures since it is unknown how much one can tolerate before becoming allergic. Moreover, experiencing epoxy resins can tempt an allergic reaction. Sensitization commonly arises because of recurrent exposure such as the poor disinfection or absence of defensive tools) across long durations. Allergic reaction occasionally takes place post quite a few days from the exposure.

It is repeatedly detectible in figuration of dermatitis, mainly forearms and hands (Wheaf, 2000).

Respiratory problems or irritated skin (more common) may be resulted in as allergic reactions to epoxy can. Frequently, it may embrace puffiness, irritating and red eyes. Yet, irritation can be trivial or severe, acute or chronic only with poison bindweed. If done repeatedly or for extended periods, inhaling concentrated epoxy vapors can infuriate the respiratory tract, while exposing delicate skin parts, like the eyelids, to vastly concentrated epoxy vapors may breed itching and swelling. Nonetheless, there is no definite remedy for epoxy sensitization, but indications can occasionally be cured with medicine. On the other hand, when sensitized, further feedbacks become probably upon future exposures, even to reduced quantities of epoxy while it is possible to prevent recurrences (Kanerva et al., 1991).

2.8.3 Severe Irritation and Chemical Burns[1]:

Solidification or hardener burns are infrequent. Epoxy hardeners are moderately corrosive, while variegated epoxy is improbable to cause burns. Duration of time for a hardener to instigate a chemical burn relies on the part of interaction and hardener condensation. They can harshly irritate the skin and cause moderate chemical burns when left in contact with skin. Progressively, chemical burns evolve and initially affect irritation and

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[1] Chemical burn: A caustic burn (chemical burn) is an acute, severe irritant reaction by which the cells have been damaged to a point where there is no return to viability; in other words, a necrosis develops (Cartotto et al., 1996).

trivial pain. The burn may stain and to some extent wound the skin. The hardener is diluted and not as much corrosive when resin and hardener are mingled (Three Bond Technical News, 1992).

2.8.4 Respiratory Irritation

Epoxy vapors at room temperature are questionable to be extremely concentrated. Nevertheless, if sensitized to epoxy, exposure to low concentrations of epoxy vapors can generate an allergic reaction, while at deeper temperatures and in stuffy spaces, the epoxy vapor levels escalate. Extremely breathing intense epoxy vapor may infuriate the respiratory system and trigger sensitization. While the epoxy chemicals keep on volatile till they have alleviated, and the reactive material may affect intense respiratory irritation or respiratory allergies (Solano et al., 2016).

2.9 Epoxidation

2.9.1 Epoxidation of Vegetable Oils:

Epoxidation is a "way of employing vegetable oils and its byproducts, consists to some extent oxidizing the fat acids presenting an atom of oxygen where it is present an unsaturation in the chain of the molecule" (Saurabh et al., 2011).

Epoxidation is one of the most imperative dual bond totaling reactions. Frequently, it is achieved *in situ* by means of the performic acid method, which is previously industrially achieved in a huge gauge (Figure 2.7) (Baumann et al., 1988).

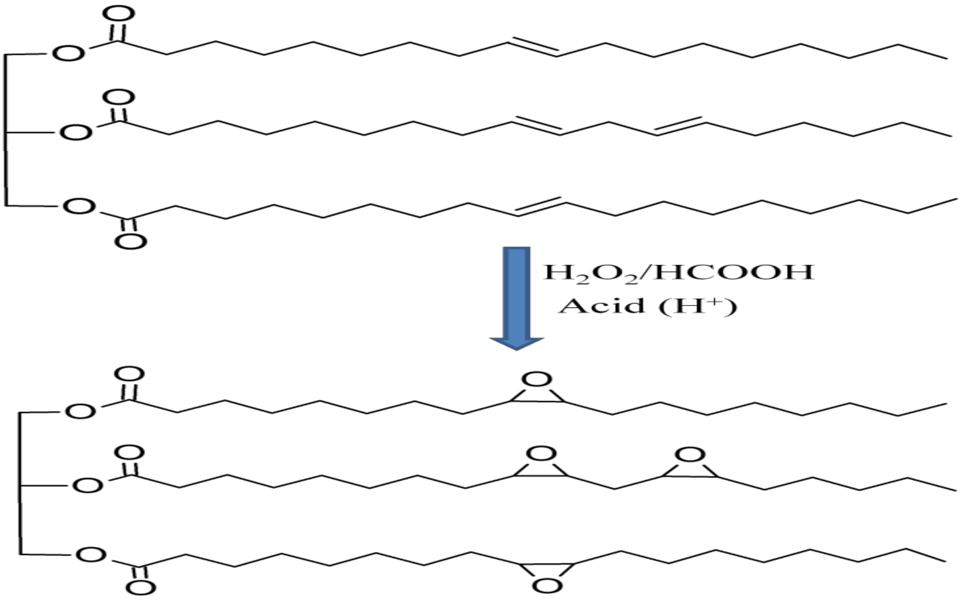

Figure.2.9: Epoxidation reaction of vegetable oils using the performic acid method

Naturally, vegetable oils have definite amounts of unsaturation alongside the string. Thus, it is likely to bypass from unsaturated oil to epoxidated oil. Industrially, the epoxidation of vegetable oils is a recognized reaction, with unproved submissions since 1946 (Terry and Wheeler, 1949).

Epoxidated oils are engaged as intercession for different products for instance alcohols, carbonyl or olefinic compounds and polyols for essential polymers containing polyurethanes and polyesters (Aguilera et al., 2016)

There are numerous techniques to attain epoxidated oils. Chavan et al. and Dinda et al. suggest a categorization which involves four central methods:

1. Epoxidation with peroxycarboxilic acids. The utmost technologically technique. It is non-toxic and the derivative is merely water.
2. Epoxidation with organic and inorganic peroxides, comprising alkaline and nitrile hydrogen peroxide epoxidation.
3. Epoxidation with halohydrines, using hypohalous acids (HOX) and their salts.

4. Epoxidation with molecular oxygen utilizing silver as catalyst. Yet, this is the easiest and low-priced method, nonetheless, just a low vintage could be acquired.

Since 1946, the creation of epoxidated vegetable oils in industry has been accomplished with patented application (Sepulveda et al., 2006).

Multiphase epoxidation: electrochemical technique using oil, gaseous O_2, formic and hydrochloric acid (Biermann et al., 2000). The enormous benefits of this technique are the well-managed and in situ production of H_2O_2 and the lowered reaction time.

Epoxides, (oxiranes), are recurrent atmospheres with a responsive tri-membered loop. Epoxides are significant intermediates in the production of several chemical composites through the ring opening reaction, which can be originated by each nucleophiles or electrophiles, or catalyzed by either acids or bases. There is an extensive assortment of epoxide conversions, for example hydrogenation, rearrangement to the ketone (Kyunghoon, 2012).

As a result of the high reaction of the oxirane ring, epoxides likewise can proceed as a raw material for synthesis of diversity of chemicals for instance alcohols (polyols), glycols, olefinic compounds, lubricants, plasticizer and stabilizer for polymers (Dinda et al., 2007). (VO) symbolizes the low-cost and supreme plentiful organic feedstock existing in huge amounts and its use as starting material offers frequent advantages such as low toxicity and inherent biodegradability (Biermann et al., 2000). Consequently, the commercial significance of the (VO) may be improved by converting the (VO) into epoxidized vegetable oil (EVO). However, the double bonds in (VO) are used as reactive sites in the coatings and they can be employed by epoxidation. Hence, the high molecular weight yields can be attained by expanding the cross linking (Petrovic et al., 2002; Mungroo et al., 2008; Goud et al., 2006).

As a consequence of opening up an extensive scope of reactions that can be executed beneath trivial circumstances, epoxidation of the double bond is considered an interesting reaction. The molded epoxide is a medium that can be transformed to a range of results, by adding nucleophiles to form lubricants as a consequence of high reactivity of the oxirane ring. Depending upon the kind of nucleophiles added, the physical and chemical properties could be altered. The epoxidation of plant oils has been executed equivalently by way of percarboxylic acid, like peracetic acid and performic acid, acquired by oxidation with hydrogen peroxide, using mineral acid, like sulfuric acid, as catalyst (Rios et al., 2011).

2.9.2 Process of Epoxidation:

Lately, the employment of epoxidized vegetable oil (EVO) has become more public. Epoxidized oil encompasses epoxide groups or oxirane rings. The term epoxide is expressed as cyclic ethers which made up of three rudiments in the epoxide ring. The common route for the synthesis of the epoxide groups is recognized as an epoxidation reaction in which an alkene is reacted with an organic peroxy acid. Well-known methods of epoxidation are as follows:

- Epoxidation via Conventional Method

- Epoxidation via acid ion exchange resin (AIER)
- Epoxidation via enzymes
- Epoxidation via metal catalyst
- Other Systems

2.10 Literature Review

Sahoo et al., 2015, carried out a study about sisal fiber strengthened biocomposites that are industrialized consuming in cooperation basic petrol-based epoxy and bioresin modified epoxy as base background. However, two bioresins, epoxidized soybean oil and epoxy methyl soyate (EMS) are utilized to adapt the epoxy matrix for operative hardening and afterwards two coatings of sisal fiber mat are combined to mend the mechanical and thermo-mechanical properties. Important power and modulus of the EMS adjusted epoxy composites reveals good interfacial bonding of matrix with the fibers. Fracture toughness parameters KIC and GIC are indomitable and found to be considerably improved. Uneven effect power is observed to be higher for unmodified epoxy composite, while protraction at break is found to be much higher for adjusted epoxy mixture. Dynamic mechanical analysis displays an enhancement in the packing modulus for bioresin hardened composites on the toughness conveyed by fibers. Damage modulus is higher for epoxy methyl soyate (EMS) modified epoxy composite as a result of strong fiber–matrix interfacial closeness. Damage refraction curves display a robust impact of bioresin on inhibiting performance of epoxy composite. Strong fiber–matrix crossing point is found in adjusted epoxy compound by inspecting electron microscopic analysis.

Hong and Wool, 2005, conducted a study about novel bio-based composite substance, fit for electronic along with automotive and aeronautical applications that was prepared from soybean oils and keratin feather fibers (KFs). This ecologically sociable, cheap composite may be a supernumerary for petroleum-based composite materials. Yet, (KFs) are a deep, light, and tough material and are attuned with several soybean resins, like acrylated epoxidized soybean oil (AESO). The new KFS lightweight composites have a density $\rho \approx 1$ g/cm^3, when the KF volume fraction is 30%. The resonating keratin fibers were not packed by resin infusion and the composite engaged a substantial volume of air in the deep structure of the fibers. The amalgamation of (KFs) in the soy oil polymer improved the mechanical structures like storage modulus, fracture durability and bowing characteristics. Significant enhancements in the KFS multifactorial features are possible by optimizing the resin structure and fiber assortment.

Senoz et al., 2013, proposed a friendly environment, green compound scheme that was verified by generating entirely bio-renewable and reasonable material. Somewhat pyrolyzed chicken feather fibers (PCFF) were combined in acrylated epoxidized soybean oil (AESO) and methacrylated lauric acid (MLAU)-based thermosetting resin to offer strengthening in low density and rubbery polymer applications. While the mechanical properties of the polymer composite, such as storage modulus, tensile modulus, tensile strength, and fracture energy were directly proportional to the fiber content, thermally stabilized PCFF have the possibility for application in composite construction, where classic manufacturing temperatures, specifically in thermoplastic defamation, surpass the unprocessed biobased fiber degradation temperature (215°C).

Gammon 2011, surveyed a study about a first-hand procedure changes waste chicken feathers into biodegradable plastic. Chicken feathers are commonly composed of keratin, the protein which controls the strength of wool, hair, fingernails and ungues. Previous hard work to form plastic from feathers resulted in crops that didn’t hold up mechanically or weren't totally water-proof. To create the innovative plastic, investigators started with chicken and turkey feathers scrubbed and crushed into a delicate powder. Then, they appended chemicals to make the keratin molecules link all together to form elongated restraints by polymerization. However, the plastic they synthesized was tougher than comparable materials made from starch or soy proteins, and it withstood water. Furthermore, rise in temperature treatment of the feathers at the onset of the process would boom any probable contagion, like from bird flu. The new material is a thermoplastic. Heating it to an unassertive (for industrial manufacturing) 170 degrees’ Celsius permits the plastic to be formed into some preferred outline, and it can be liquefied and remolded many times. Contrasting most thermoplastics, which are petroleum-based, chicken-feather plastic uses no fossil fuels. The feather-based plastic could be used for all kinds of products, from plastic cups and plates to furniture. Over and above to benefit from feathers that would else finish in garbage dumps, it is extremely decomposable. The efficacy of biopolymer, such as the feather plastic, relies on the price and adaptability of the end product.

Wang 2014, issued a study on epoxidized vegetable oil (EVO) which is extensively employed as a plasticizer and as a synthetic intermediate for polyol or unsaturated polyester. Nevertheless, the effectiveness of EVO as monomer for high concert epoxy thermoset polymer is partial by its reflection and by the consequential physical merits. VO-based epoxy monomers, i.e., glycidyl esters of epoxidized fatty acids resulting from soybean oil (EGS) or linseed oil (EGL), have been synthesized and were compared against commercial available diglycidyl ether of bisphenol A (DGEBA) and also epoxidized soybean oil (ESO) controls. EGS and EGL controlled higher oxirane content, more reactivity and lower viscosity than ESO or epoxidized linseed oil (ELO), provided better compatibility with DGEBA as a responsive diluent, and produced thermally and mechanically stronger polymers than polymers obtained using ESO. Glass transition temperatures (Tg) of the VO-based epoxy thermoset polymers were mostly a function of monomer oxirane content with some extra structural impacts of epoxy reactivity, and manifestation of an incomplete string. Organo-modified montmorillonite clay (OMMT) and long glass fiber reinforced composites (FRC) were proficiently created using anhydride cured EGS as matrices. The OMMT nanocomposites displayed higher mechanical and thermal strength than the immaculate polymers, but were also built on the scattering techniques and the mud deliberation. Unexpectedly, the neat EGS-anhydride matrix FRC indicated equivalent properties, such as curvature and power strengths and marginally lower glass transition temperature °C (*T*g), versus DGEBA based equivalents. These high performance monomers, polymers, and composites have prospective to substitute petroleum-based epoxy as value-added products from VOs compared to EVOs.

Additionally, Islam et al., 2015, conducted a study concerning palm oil as non-drying oil owing to its low iodine value. An endeavor was carried out to rise the unsaturation in the fatty acid chains of palm oil for the formulation of alkyds. To rise the unsaturation in the palm oil, sulphuric acid (SA) and para-toluene sulphonic acid (PTSA) were used preceding to alcoholysis for the desiccation activity. Moreover, the iodine number of the oil trials was checked for the unsaturation measurement by Wijs method. Alkyd resin was prepared using the dehydrated palm oil by succeeding alcoholysis and esterification reaction. To mend the film properties, 0.5wt.%[1] multi-wall carbon nano tubes (MWCNTs) were used to create polymeric film. The traits of the resins were categorized by various physico-chemical properties such as compactness, viscosity, iodine value and saponification value. The structural interpretation was established by Fourier transform of infrared spectroscopy and proton nuclear magnetic resonance; surfaces of the films were inspected by field-emission scanning electron microscope. Moreover, pencil hardness and chemical resistivity was also assessed by means of ordinary approaches. The outcome of augmentation of the unsaturation in the fatty acid chain found noteworthy

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wt%: "Multiplying mass fraction by 100 gives the mass percentage. It is sometimes called weight percent (wt%) or weight-weight percentage".

and stimulating. The resin formulated with dehydrated palm oil displayed amended properties concerning hardness and chemical resistivity analysis. Furthermore, the amalgamation of MWCNTs improved the thermal stability and hardness of the films.

Furthermore, a study conducted by Ratna and Banthia, 2012, about epoxidized soybean oil (ESO) that has been prepared to harden epoxy resin treated with surroundings temperature hardener, Tris-2,4,6-(*N*,*N*-dimethyl amino methyl) phenol. The ESO was prepolymerized with the amine hardener to achieve the liquid epoxidized soybean rubber (ESR). The ESR adjusted epoxy networks were appraised for their thermal, influence and bond properties. The epoxy/ESR compositions were thoroughly mixed to examine the influence of modifier concentration on the adhesion and effect power. The finest properties were found at a concentration of 20 wt% ESR. The DSC and DMTA analyses designated phase separation between the epoxy-rich phase and ESO-rich phase.

Sarwono et al., 2012, conducted a study about epoxy resin equipped by the reaction of a diglycidyl ether of bisphenol A (DGEBA) and *m*-xylylenediamine (*m*-XDA) was adjusted with 10% wt of epoxidized palm oil (EPO). The EPO was first pre-polymerized with *m*-XDA at several temperatures and reaction periods. The following outcome was then blended with the epoxy resin at 40 °C and permitted to react at 120 °C for extra 3 hours. The entirely reacted DGEBA/*m*-XDA/EPO mixture was categorized by using scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermal gravimetric analysis, tensile test, hardness indentation and dynamic mechanical analysis. The SEM study displays that dissimilar forms of morphology, extending from phase separated to admixture blends were acquired. A combination blend was found when the *m*-XDA and EPO were reacted for more than 2 hours. The outcomes from DSC analysis reveal that the integration of EPO at 10% wt in the epoxy blend degraded the glass transition temperature (T_g). The lowered T_g and mechanical properties of the adjusted epoxy resins are caused by a reduction in crosslinking density and plasticizer effect.

Chapter Three

Experimental

3.1 Materials and Methods

All equations were taken from the study of Shagal et al., 2013.

1. Epoxy resin prepared for the epoxidation reaction include PO, glacial acetic acid (99-100 wt%), aqueous hydrogen peroxide (30 wt%), sulphuric acid (98wt %). However, chemicals used for the determination characteristics of PO include ethanol, phenolphalein indicator, 0.1N KOH, iodine, glacial acetic acid, bromine water, chloroform, potassium, iodide, sodium thiosulfate and starch.
2. Materials used for the characterization of gas chromatography include methanolic NaOH, 14% BF_3 in methanol, n-heptane.
3. Materials used for the determination of mechanical properties of epoxidized palm oil (EPO) include epoxy resin (diglycidyl) ether of (bisphenol A), diethylenetriamine (DETA) and chicken feathers.

Apparatuses:

1. FTIR spectrum was used to check for the presence of the double bond group in PO and epoxy group in EPO**.**
2. Gas Chromatography Mass Spectrometry (GC-MS) was used to determine type of fatty acid present in PO, and the percentage for each category.
3. Compression machine was used to determine toughness of epoxy.

4. Instron was used to determine tensile strength of epoxy.

3.2 Determination of Acid Value (AV) in Palm Oil

2 g of PO to 30 ml ethanol. The mixture was heated until bubbles appeared. Two to three (2-3) drops of phenolphalein indicators were added and titrated with 0.1N KOH until the pink color appeared (Deshpande, 2013). The Acid value was calculated by using the following equation.

$$\text{A.V} = \frac{M.N.56.1}{W} \tag{3.1}$$

Where, M: is volume of KOH,

N is the normality of KOH (mole/L), 56.1g is atomic weight of KOH,

W is the mass of PO used (g).

3.3 Iodine Value (I.V.)

Iodine value is defined as indicators for unsaturated bond components of oils and fat**.**

3.3.1 Preparation of Hanus Solution:

Hanus solution was prepared to determinate I.V. To prepare Hanus solution, we dissolved 1.32 g of iodine in 100 ml glacial acetic acid. The solution was heated to dissolve iodine in acid. After cooling the solution, we added 0.3ml bromine water to increase the halogen content.

3.3.2 Determination of Iodine Value (I.V.) to PO:

A 0.25 g of PO; was weighed into a 250 conical flask. Ten (10) ml of chloroform were added to PO, and 30 ml of Hanus solution were added, and then closed the conical flask by Para film. The solution was left at room temperature for 30 minutes with shaking uninterruptedly, then 10 ml of 15% potassium iodide solution were added with incessant shaking, and added 100 ml of distilled water (DW). A titration was made then to the iodine solution with 0.1 N sodium thiosulfate solution until the yellow color appeared, then added 2-3 drops of starch solution. The blue color was formed with constant shaking with titration until the blue color disappeared. The volume of $Na_2S_2O_3$ represented (S) at the end (Thomas, 2002).

The same above procedure was done, but without PO. The volume of $Na_2S_2O_3$ at represented (B) the end.

The Iodine value is calculated by using the following equation.

$$\text{I.V} = \frac{(B-S).N.12.69}{W} \tag{3.2}$$

Where,

B is volume of $Na_2S_2O_3$ required to titrate the iodine solution without PO,

S is volume of $Na_2S_2O_3$ required to titrate the iodine solution with PO,

N is the normality of $Na_2S_2O_3$ (mole/L), 126.9g is atomic weight of iodine,

Moreover, W is the mass of PO used (g).

3.3.3 Determination of Fatty Acid in PO

Fatty acid composition of PO was determined by gas chromatography mass spectrometry (GC-MS) using methylation of PO for the determination of the volume required to epoxidation reaction.

methylation of PO was carried out as follows, a 0.1 g PO was weighed and put in a 250ml round bottom flask, then, to it was we added 10ml methanolic NaOH solution by dissolving 2 g NaOH in methanol. Moreover, we attached a condenser to the flask, heated and refluxed for a 10 min duration. A (10ml) 0f 14% BF_3 Borontrifluoride (BF_3) in methanol was added from top of condenser to the flask of PO. In addition, the mixture was refluxed for another 5 min, then added 10 ml n-heptane, through top of condenser and refluxed for 1min. Eventually, analysis was carried on (GCMS).

3.4 Epoxidation

3.4.1 Total amount of fatty acids in PO

The most widely used process of epoxidation, using a hydrogen peroxide catalyzed by liquid inorganic acids such as H_2SO_4 and used carboxylic acid as oxygen carrier (Saurabh et al., 2011)

Total mole of fatty acid in 100g PO calculated by using the following equation:

$$n \text{ fatty acid} = \frac{percentage\ of\ fatty\ acid\ in\ P.O \times weight\ of\ P.O}{Molecular\ weight\ of\ P.O}$$

n Linoleic acid = $\frac{0.228\times100}{280.45}$= 0.08129

n Margaric acid =$\frac{0.00359\times100}{270.45}$ = 0.001327

n Oleic acid = $\frac{0.233\times100}{282.46}$= 0.08248

n Stearic acid = $\frac{0.0138\times100}{284.48}$ = 0.00485

n Palmitic acid = $\frac{0.49\times100}{256.42}$ = 0.191

n Eicosanoic acid = $\frac{0.014\times100}{312.538}$ = 0.00447

Total mole of PO = 0.08129 + 0.001327 + 0.08248 + 0.00485 + 0.191+0.00447 = 0.36541 mole.

3.4.2 Determination of Volume of Acetic Acid Required to Epoxidation in 100 g PO

Mole ratio of glacial acetic acid to PO = 0.5:1, acetic acid (99.5 wt%), molecular weight= 60.05, density =1.05 g/ml.

Mole of acetic acid =0.5× 0.3654 = 0.1827 mol

Mass of acetic acid = 0.1827 ×60.05 = 10.97 g

Mass of glacial acetic acid $\frac{100}{99.5}$ × 10.97 = 11.02 g

Volume of glacial acetic acid = $\frac{11.02}{1.05}$ = 10.49 ml

3.4.3 Determination of Volume of Hydrogen Peroxide Required to Epoxidation in 100 g PO

Mole of hydrogen peroxide to PO = 1.5:1

Hydrogen peroxide (30 wt%), molecular weight = 34.01, density = 1.10 g/ml.

Mole of hydrogen peroxide = 1.5× 0.3654 = 0.548 mol

Mass of hydrogen peroxide = 0.548× 34.01 = 18.637 g

Mass of hydrogen peroxide solution = $\frac{100}{30} \times 18.637 = 62.123$ g

Volume of hydrogen peroxide = $\frac{62.123}{1.10} = 56.47$ ml

3.4.4 Determination of Volume of Catalyst

Mass of sulfuric acid in mixture is 3% of total mass of hydrogen peroxide and acetic acid.

H_2SO_4 (98wt.%), molecular weight = 98.08. density = 1.84 g/ml.

Mass of H_2SO_4 = $(\frac{3}{100})$ × (volume of Hydrogen peroxide + volume of acetic acid)= $(\frac{3}{100}) \times (56.47 + 10.49) = 0.2$ ml

3.5 Epoxidation Reaction

Initially, 10.49 ml acetic acid and 0.2ml of H_2SO_4 was added to 100g PO in a 250 ml three neck round bottom flask equipped with a thermometer reflux condenser and magnetic stirrer. The three neck round bottom flask was fixed by a metal clamp in a water bath at different temperatures. In the 1st day, 6 samples were taken at 30°C, in the 2nd day, 6 samples were also taken but at 40°C, in the 3rd and 4th days also 12 samples evenly were taken at 50 and 60°C evenly and respectively. A volume of 56.47 ml of hydrogen peroxide (H_2O_2) was slowly added drop wisely within 1 hour through a needle. An hour later, after completing adding of H_2O_2,a sample of the oil was taken out and thoroughly washed with sodium bicarbonate (5 wt%), and washed with distilled water (DW), and then washed with sodium chloride (5 wt%) to separate the organic layer by separator funnel from the mixture. This process was repeated after 2, 3, 4, 5, and 6 hours and at each temperature, used different times and temperatures to optimize the epoxidation of palm oil using the time-temperature-transformations (TTT) (Figures 3.1, 3.2 and 3.3).

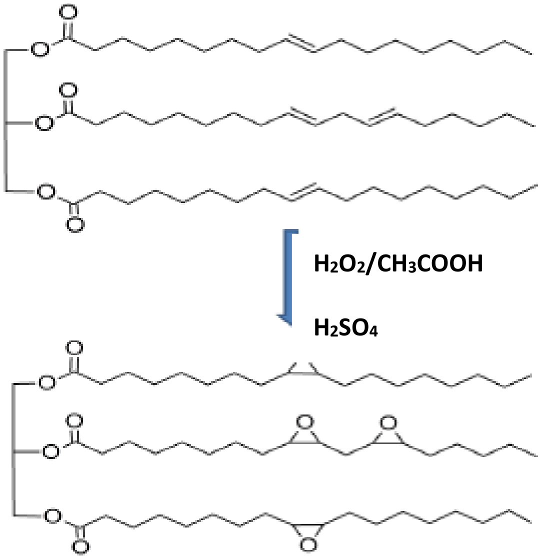


Figure 3.1: Epoxidation reaction of palm oil .

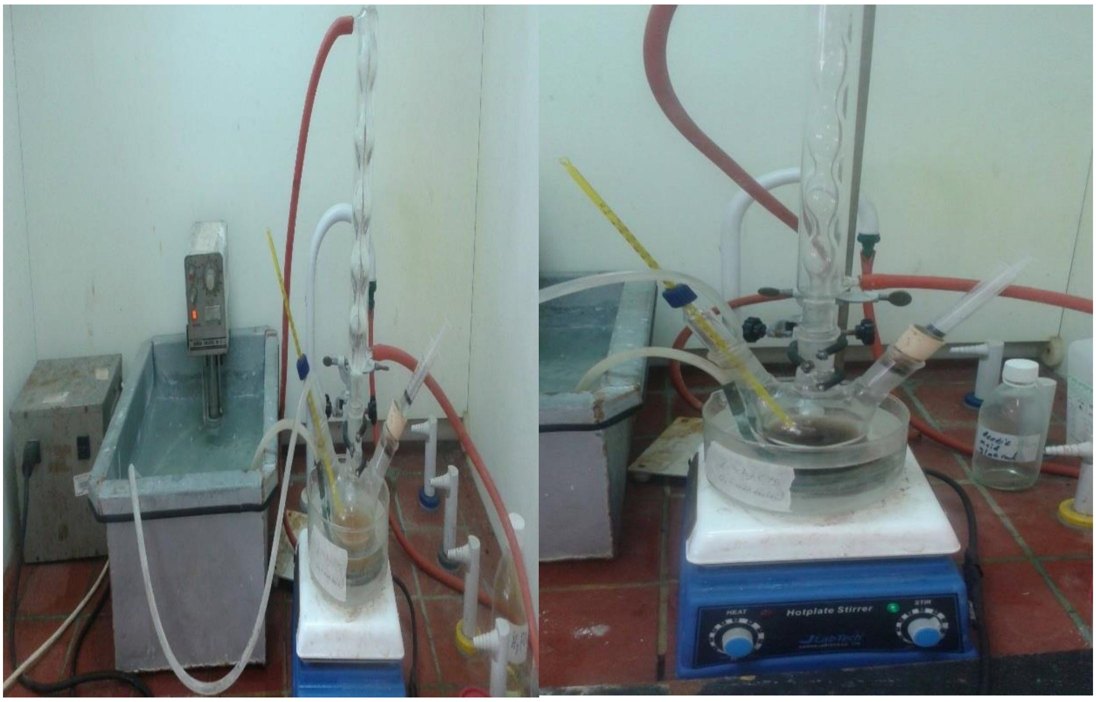


Figure 3.2: Epoxidation reaction of palm oil carried out *in-situ*.

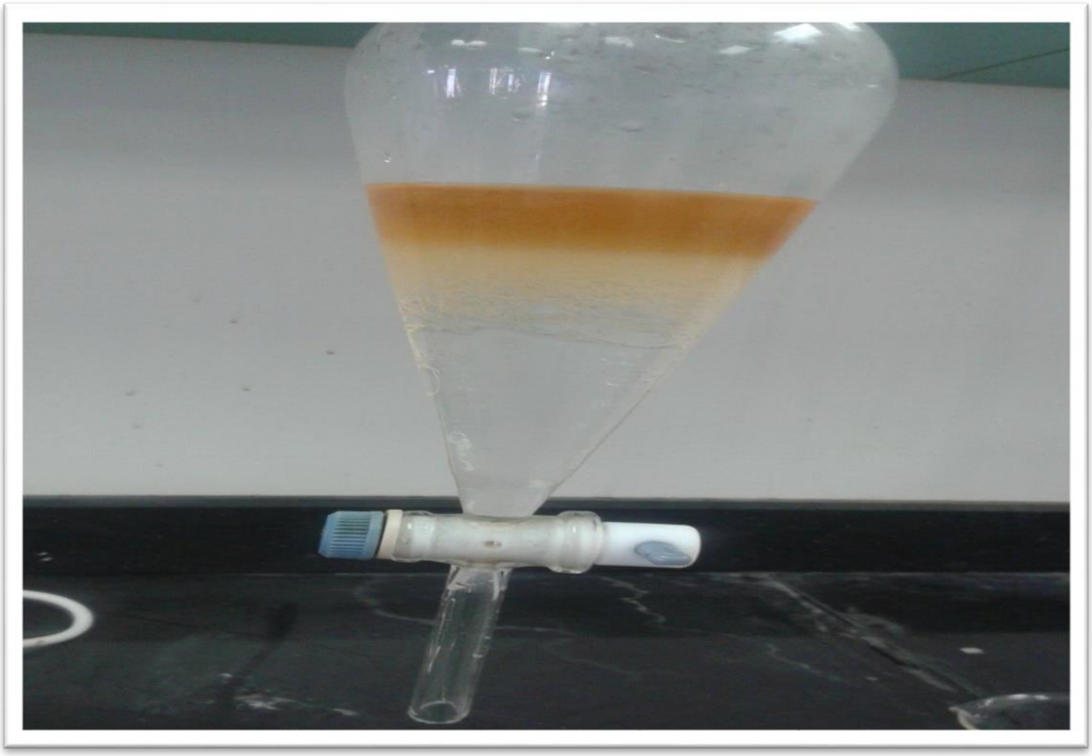


Figure 3.3: The oil was thoroughly washed with sodium bicarbonate, distilled water, and then washed with sodium chloride separated by separatory funnel.

3.6 FTIR Spectrum

Two samples were taken; the first was from PO, while the other was from epoxidized palm oil (EPO) in a Fourier transform infrared (FT-IR) spectrum, for the determination of the double bond group in PO and epoxy group in epoxidized palm oil (EPO).

3.7 The Conversion of PO into Epoxidized PO

The conversion of double bond group in the palm oil to epoxy group in epoxidized palm oil (EPO) is calculated on basis of determined value of iodine for the oil before epoxidation and value of iodine after epoxidation (Shagal et al., 2013).

To determine iodine value before epoxidation,

$$\left(\text{I.V} = \frac{(B-S).N.12.69}{W} \qquad (3.2)\right),$$

and to determine iodine value after epoxidation, did the same procedure, but used the EPO instead of PO.

The equation of double bond conversion to epoxy formation using the following equation before and after:

$$C_{IN} = \frac{\text{IVbe} - \text{IV ae}}{\text{IVbe}} \times 100\%$$

Where:

C_{IV}: conversion of PO to epoxidized PO

IV_{be}: iodine value before epoxidation

IV_{ae}: iodine value after epoxidation

3.8 The Oxirane (Epoxy Group) Content Values

The oxirane content values means the weight percent of oxirane oxygen in a molecule (He et al., 2014).

To determine the oxirane content values, approximately 0.2g of epoxied palm oil (EPO) were weighed, and put it in a 250ml conical flask. We added 25ml of 0.2 N HCl to EPO, then added 2-3 drops of phenolphthalein indicator, and then titrated with 0.1NaOH solution until the pink color appears. The volume of NaOH at end point represented (S), and did the same above procedure but without EPO, which is the volume of NaOH represented (B) at end.

The percentage of oxirane content was calculated using the equation:

$$\text{The oxirane content} = \frac{(B-S).M.1.6}{W}$$

Where:

B is volume of NaOH required to titrate with 0.2 N HCl solution without EPO,

S: is volume of NaOH required to titrate with 0.2 N HCl solution with EPO,

N: is the normality of NaOH 0.1(mole/L),

W: is the mass of EPO used (g).

3.8.1 Mechanical Properties of Epoxidized Palm Oil (EPO)/Epoxy Resin (ER)

To determine the weight of hardener diethylenetriamine (DETA) which is added to Epoxy Resin (diglycidyl ether of bisphenol A), we use the following equation: (Meng et al., 2010)

Equivalent weight of amine = $\frac{\text{Molecular weight of amine}}{\text{Number of active hydrogen atoms of amine}}$

Equivalent weight of epoxy resin = $\frac{\text{Molecular weight of epoxy resin}}{\text{Number of epoxy groups}}$

Weight of hardener = $\frac{\text{Equivalent weight of amine}}{\text{Equivalent weight of epoxy resin}} \times$ Weight of ER

Where:

molecular weight of diethylenetriamine (DETA) is around 103 g/mol,

Number of active hydrogen atoms of DETA is 5,

Molecular weight of the epoxy resin (diglycidyl ether of bisphenol A) is about 340 g/mol,

and number of epoxy groups of the epoxy resin is 2.

Equivalent weight of amine = $\frac{103}{5}$ = 20.6

Equivalent weight of epoxy resin = $\frac{340}{2}$ =170

Weight of hardener=$\frac{20.6}{170} \times$ Weight of ER

3.8.2 Determination of Toughness of Epoxy Resin

First, to determine the toughness of epoxy resin, we mixed 50g of epoxy resin (diglycidyl ether of bisphenol A) with 6g of hardener diethylenetriamine (DETA), and then we poured them into a cylindrical container 4.55cm diameter and 2.38 cm height. After 24 hours, we examined the toughness by compression machine (Figures 3.4).

Figure 3.4: An epoxy sample in a cylinder after 24 hours compression strength by compression machine.

3.8.3 Determination of Toughness by Blending Epoxidized Palm Oil/Epoxy Resin

We prepared three samples of EPO/ER in three beakers. In the 1st one, we put 45 g ER and 5 g EPO and 6 g hardener (DETA). In the 2nd beaker, we put 40g ER, 10 g EPO, and 6g DETA. In the 3rd beaker, we put 35 g ER, 15 g EPO, and 6 g DETA. All samples were mixed well. Each sample was poured into a cylindrical container. The diameters of all cylindrical containers were 4.49cm. After 24 hours, we examined the toughness by compression machine (Figure 3.5).

Figure 3.5: An epoxy with EPO sample after 24 hours' compression strength by compression machine.

3.8.4 Determination of Toughness by Blending Chicken Feathers/Epoxy Resin

We prepared three samples of chicken feathers /ER in three beakers. In the 1st one, we put 45 g ER and 5 g chicken feathers and 6 g hardener (DETA). In the 2nd beaker, we put 40 g ER, 10g Chicken feathers, and 6 g DETA. In the 3rd beaker, we put 35 g ER, 15 g Chicken feathers, and 6 g DETA. All samples were mixed well. Each sample was poured into a cylindrical container. The diameters of all cylindrical containers were 4.49 cm. After

24 hours, we examined the toughness by compression machine (Figure 3.6).

Figure 3.6: An epoxy with chicken feathers sample after 24 hours compression strength by compression machine.

3.8.5 Determination of Toughness by Blending Chicken Feathers/ EPO/Epoxy Resin

We prepared three samples of chicken feathers/EPO/ER in three beakers. In the 1st one, we put 45 g ER and 2.5 g chicken feathers, and 2.5 g EPO, and 6 g hardener (DETA). In the 2nd beaker, we put 40g ER, 5g chicken feathers, and 5 g EPO, and 6g DETA. In the 3rd beaker, we put 35 g ER, 7.5 g chicken feathers, and 7.5 g EPO, and 6 g DETA. All samples were mixed well. Each sample was poured into a cylindrical container. The diameters of all cylindrical containers were 4.49 cm. After 24 hours, we examined the toughness by compression machine (Figure 3.7).

Figure 3.7: An epoxy with EPO/chicken feathers sample after 24 hours compression strength by compression machine.

3.9 Determination of Tensile Strength of Epoxy Resin

First, to determine the tensile of epoxy resin, we mixed 60 g of epoxy resin (diglycidyl ether of bisphenol A) with 7.2 g of hardener diethylenetriamine (DETA), and then we poured into a 31 mm width and 5 mm thickness rectangular container. After 24 hours, we examined the tensile by tensile machine (Figures 3.8, 3.9).

Figure 3.8: An epoxy sample before testing tensile strength by tensile machine.

Figure 3.9: An epoxy sample after 24 hours tensile strength by tensile machine.

3.9.1 Determination of Tensile Strength by Blending Epoxidized Palm Oil/Epoxy Resin

We prepared three samples of EPO/ER in three beakers. In the1st one, we put 54 g ER and 6g EPO and 7.2 g hardener (DETA). In the 2nd beaker, we put 48g ER, 12g EPO, and 7.2 g DETA. In the 3rd beaker, we put 42 g ER, 18 g EPO, and 7.2 g DETA. All samples were mixed well. Each sample was poured into a rectangular container. The width of all rectangular containers were 31 mm, and 5 mm thickness. After 24 hours, we examined the tensile by tensile machine (Figure 3.10).

Figure 3.10: An epoxy blended with EPO sample after 24 hours tensile strength by tensile machine.

3.9.2 Determination of Tensile Strength by Blending Chicken Feathers/Epoxy Resin

We prepared three samples of chicken feathers/ER in three beakers. In the1st beaker, we put 54 g ER and 6g chicken feathers and 7.2 g hardener (DETA). In the 2nd beaker, we put 48g ER, 12g chicken feathers, and 7.2 g DETA. In the 3rd beaker, we put 42g ER, 18g chicken feathers, and 7.2 g DETA. All samples were mixed well. Each sample was poured into a rectangular container. The width of all rectangular containers were 31mm, and 5mm thickness. After 24 hours, we examined the tensile by tensile machine (Figure 3.11).

Figure 3.11: An epoxy blended with chicken feathers sample after 24 hours tensile strength by tensile machine.

3.9.3 Determination of Tensile Strength by Blending Chicken Feathers/EPO/Epoxy Resin

We prepared three samples of chicken feathers/ER in three beakers. In the 1st one, we put 54 g ER and 3 g chicken feathers, and 3g EPO, and 7.2g hardener (DETA). In the 2nd beaker, we put 48 g ER, 6 g chicken feathers, and 6 g EPO and 7.2 g DETA. In the 3rd beaker, we put 42 g ER, 9 g chicken feathers, and 9 EPO, and 7.2 g DETA. All samples were mixed well. Each sample was poured into a rectangular container. The width of all rectangular containers were 31mm, and 5mm thickness. After 24 hours, we examined the tensile by tensile machine (Figure 3.12).

Figure 3.12: An epoxy/EPO with chicken feathers sample after 24 hours tensile strength by tensile machine.

Chapter Four

Results and Discussion

4.1 Determination Acid Value (AV):

The acid value (AV) is a common parameter in the specification of oil.

It is defined as the weight of Potassium Hydroxide (KOH) in mg needed to neutralize the organic acids present in 1g of fat and it is a measure of the free fatty acids (FFA) present in the fat or oil (Patterson, 2015).

An increment in the amount of FFA in a sample of oil or fat indicates hydrolysis of triglycerides.

The Acid value was then calculated by using the following equation.

$$A.V=\frac{M.N.56.1}{W}=\frac{1.8\times 0.1\times 56.1}{2}=5.103$$

Where,

M is volume of KOH= 1.8 ml,

N is the normality of KOH=0.1 mole/L,

56.1g is atomic weight of KOH,

W is the mass of PO =2 g.

4.2 Determination Iodine value (IV):

The Acid value was then calculated by using the following equation.

$$I.V=\frac{(B-S).N.126.9}{W}=\frac{(42.3-32.7)\times 0.1\times 126.9}{0.25}=48.768$$

Where,

B is volume of $Na_2S_2O_3$required to titrate the iodine solution without PO = 42.3ml,

S is volume of $Na_2S_2O_3$ required to titrate the iodine solution with PO = 32.7 ml,

N is the normality of $Na_2S_2O_3$ = 0.1mole/L,

126.9 g is the atomic weight of iodine,

W is the mass of PO = 0.25 g.

4.3 Fatty Acid Composition of Palm Oil

Gas Chromatography Mass Spectrometry (GC-MS) determined the fatty acid composition of PO. The main components of the PO from GC-MS are palmitic, oleic, and linoleic acids. The fatty acids percentages are shown in Table 4.1 below.

The most abundant fatty acid in PO was palmitic acid; where 16 is the carbon atom, and zero (0) is the saturated acid, (16:0),approximately 49% , then comes next is oleic acid (18:1) approximately 23.3%, then linoleic acid (18:2) approximately 22.8%, eicosanoic acid (20:0), stearic acid (18:0), margaric acid(17:0), was 1.4%,1.38%, 0.359% , respectively.

These percentages were used for the calculation of chemicals required for epoxidation reaction.

Table 4.1: Fatty acid composition of palm oil measured on GCMS

Fatty Acids	Composition (wt %)	Molecular Weight
Palmitic acid	49	256.42
Oleic acid	23.3	282.46
Linoleic acid	22.8	280.45
Eicosanoic acid	1.4	312.538
Stearic acid	1.38	284.48
Margaric acid	0.359	270.45

4.4 Fourier Transform Infrared (FTIR) Spectroscopy Analysis

The FTIR spectra of PO is show in figure 4.1.

Oxirane ring (epoxy group) can be detected at bands between1070-1020 cm^{-1}, =CH group can be detected at wave number 3000-3050 cm^{-1}, and HC=CH group can be detected at wave number 1620-1680 cm^{-1}.

Based on Figure 4.1, FTIR spectrum of PO showed bonding peak of HC=CH at wave number 1647.49 cm^{-1} (Orange arrow), and stretching vibration peak of =CH 3008.97 cm^{1}; this was attributed to the hydroxyl O–H stretching, indicating that the epoxy group might be opened. (Blue arrow).

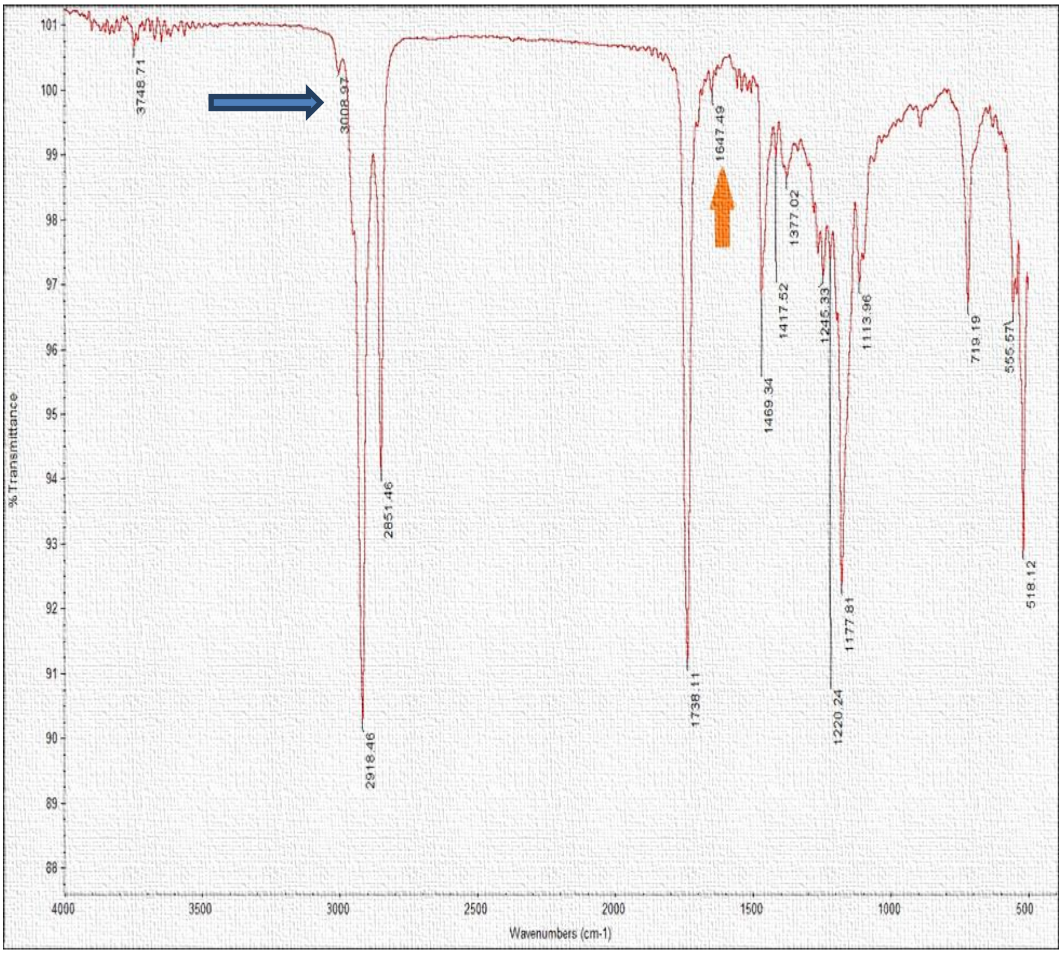


Figure 4.1: FTIR spectra of PO.

While, in Figure 4.2, for the FTIR spectrum of EPO, the unsaturation bonding peak HC=CH and stretching vibration peak of =CH for PO have been disappeared. However, the oxirane ring peak was detected at wave number 1104.76 cm^{-1}. (Red arrow).

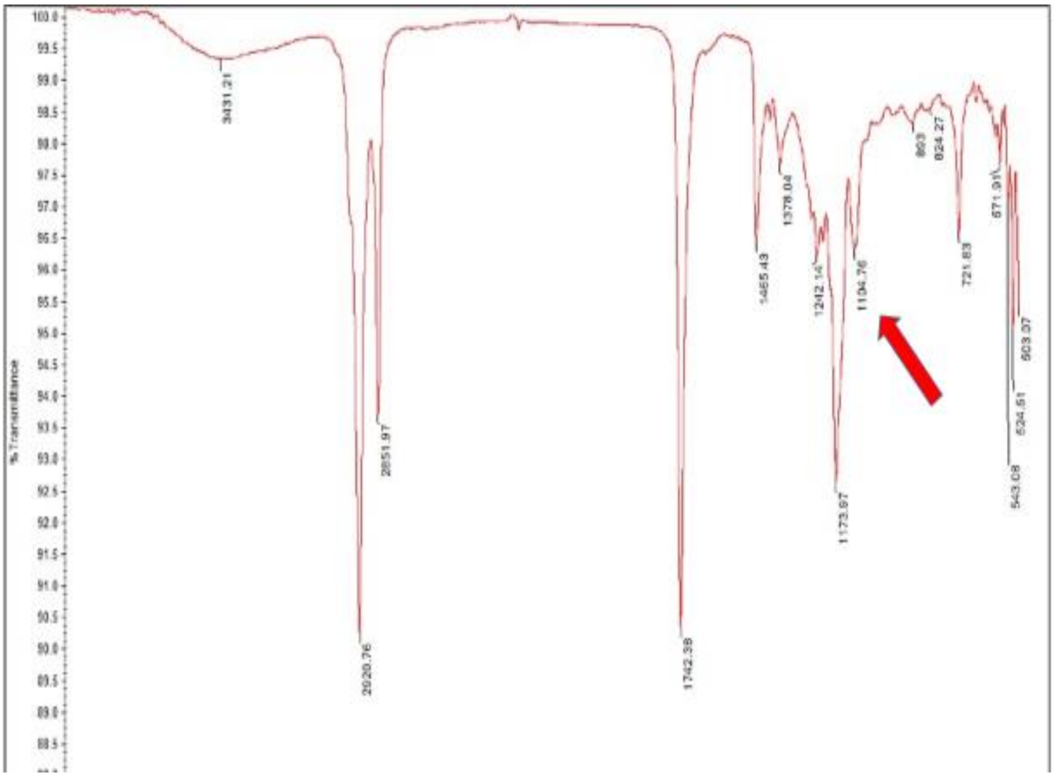


Figure4.2: FTIR spectra of EPO. Samples.

4.5 Effect of Time and Temperature on Epoxidation Reaction

4.5.1 Effect of Time and Temperature on Conversion

In order to obtain high conversion value, there are some factors to consider such as reaction temperature and reaction time.

Carbon double bonds of unsaturated fatty acids were epoxidized via acid catalysis producing epoxy functional groups.

There are parameter factors that affect epoxidation reaction time and temperature are the most important factors.

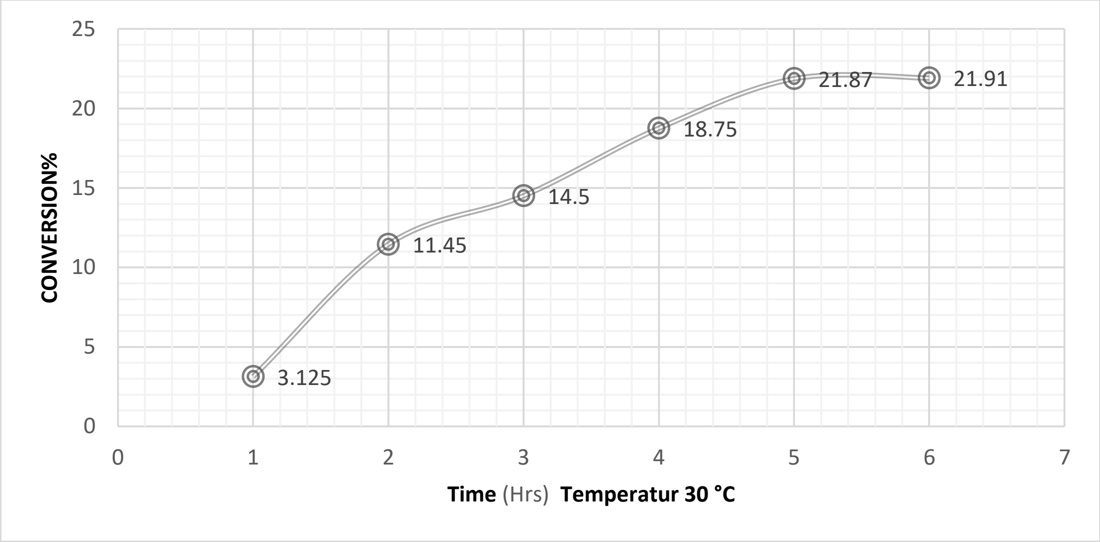


Figure 4.3: Effect of time at temperature 30°C on conversion %.

Figure 4.3 shows the effect of time on epoxidation reaction when the temperature is 30°C.

During the increase of time, while the epoxidation reaction at 30°C, from 1-5 hours, the percentage of conversion has increased noticeably, but from 5-6 hours the increment was very little.

The maximum relative conversion obtained at temperature 30°C after 6 hours from the beginning of the reaction was (21.91%).

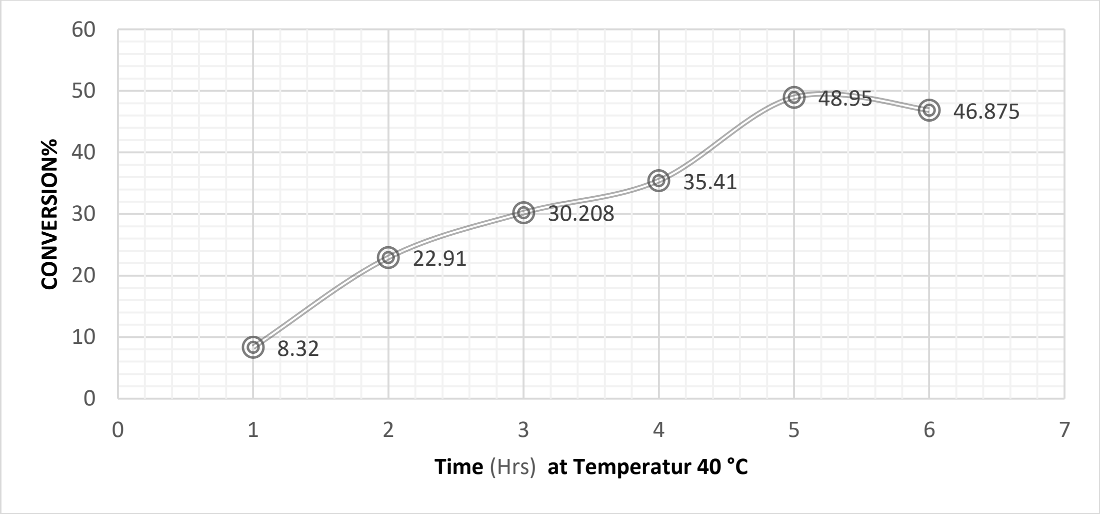


Figure 4.4: Effect of time at temperature 40°C on conversion %

Figure 4.4 reveals the effect of time on epoxidation reaction when the temperature is 40°C.

During the increase of time, while the epoxidation reaction at 40°C, from 1-5 hours, the percentage of conversion has increased obviously, but from 5-6 hours the conversion has was decreased about 2%.

The maximum relative conversion obtained at temperature 40°C after 5 hours from the beginning of the reaction was (48.95%).

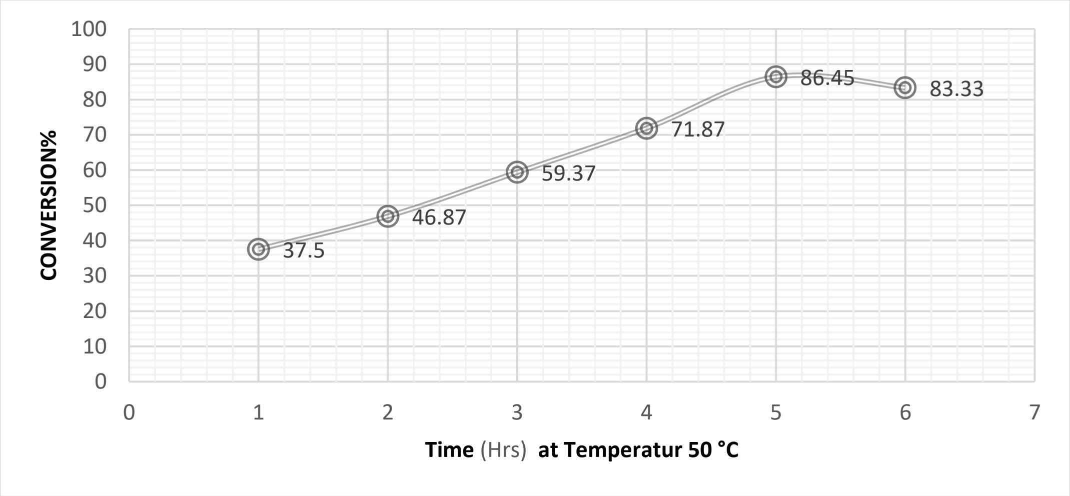


Figure 4.5: Effect of time at temperature 50°C on conversion %

Figure 4.5 displays the effect of time on epoxidation reaction when the temperature is 50°C.

During the increase of time, while the epoxidation reaction at 50°C, from 1-5 hours, the percentage of conversion has increased obviously, but from 5-6 hours the conversion has was decreased about 3%.

The maximum relative conversion obtained at temperature 50°C after 5 hours from the beginning of the reaction was (86.45%).

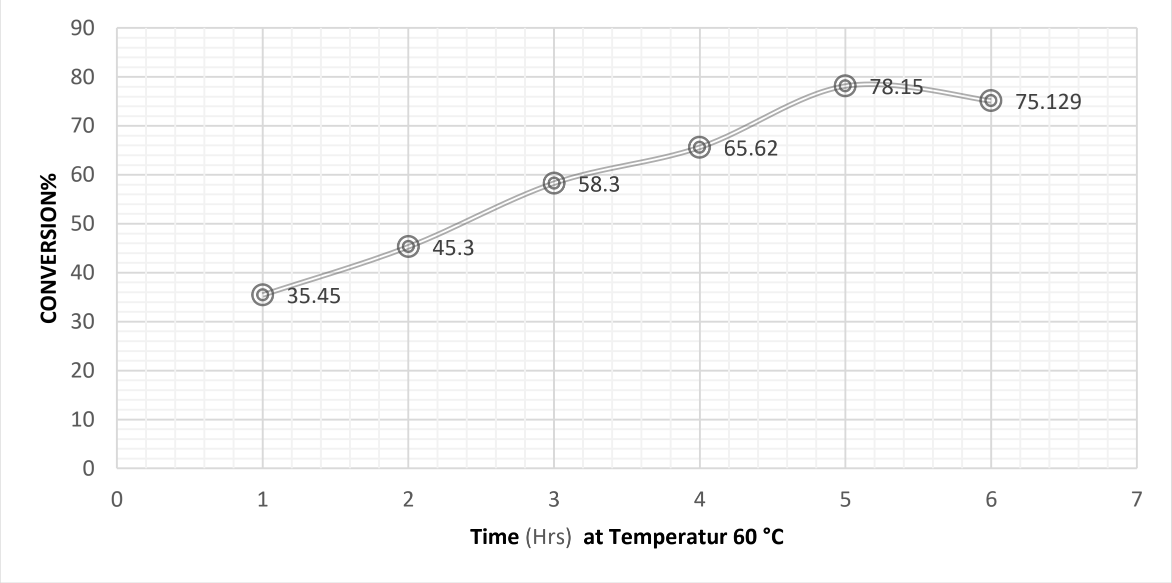


Figure 4.6: Effect of time at temperature 60°C on conversion %

Figure 4.6 shows the effect of time on epoxidation reaction when the temperature is 60°C.

During the increase of time, while the epoxidation reaction at 60 °C, from 1-5 hours, the percentage of conversion has increased obviously, but from 5-6 hours the conversion has was decreased about 3%.

The maximum relative conversion obtained at temperature 60°C after 5 hours from the beginning of the reaction was (78.15%).

Grossly, it was noticed that the topmost relative conversion obtained at temperature 50°C after 5 hours from the beginning of the reaction was (86.45%).

4.5.2 Effect of Time and Temperature on the Oxirane Oxygen %

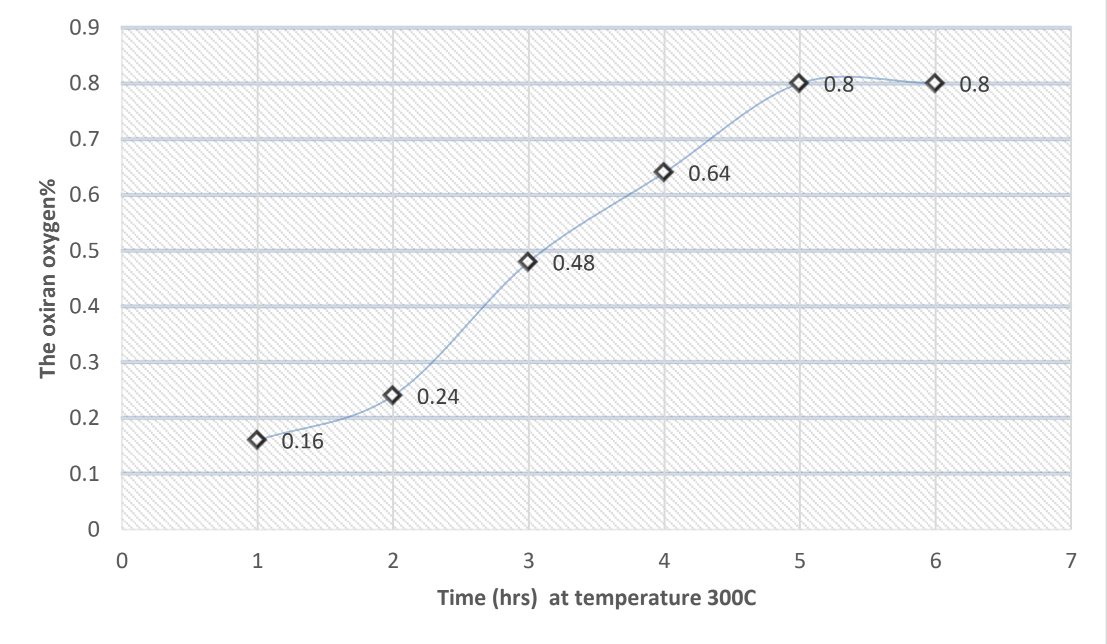


Figure 4.7: Effect of time at temperature 30°C on the oxirane oxygen **%**

In the increment of time, during the epoxidation reaction at 30°C from 1-5 hours, to obtain the epoxy group (the oxirane oxygen %), the percentage has increased, but not exceeding 0.8%, while from 5-6 hours has not changed.

The maximum oxirane oxygen percentage obtained at temperature 30°C at 5 and 6 hours from the beginning of the reaction was (0.8%).**(Figure 4.7**).

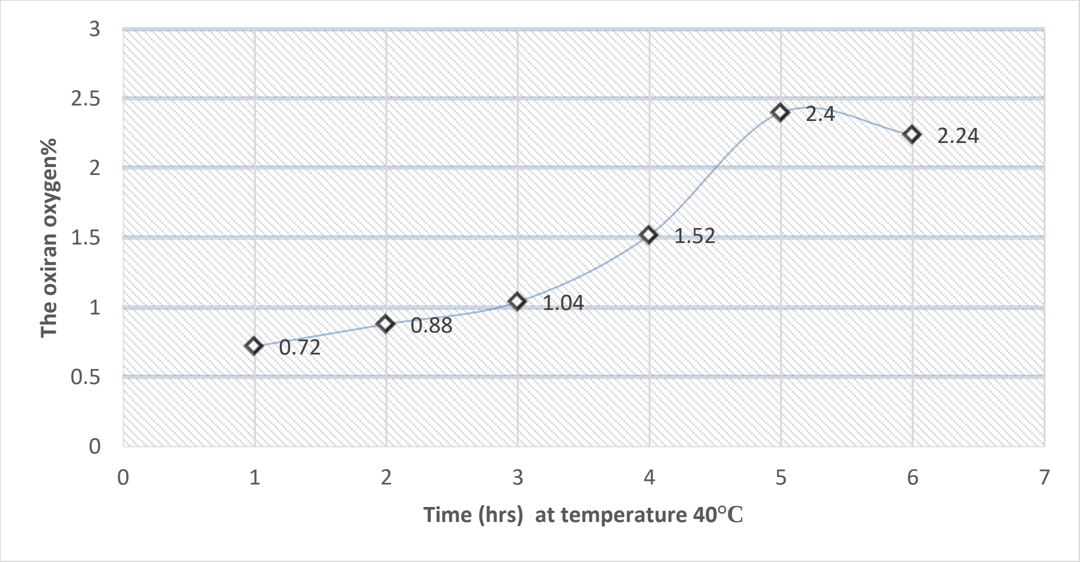


Figure 4.8: Effect of time at temperature 40°C on the oxirane oxygen **%**

In the increment of time, during the epoxidation reaction at 40°C from 1-5 hours, to obtain the epoxy group (the oxirane oxygen %) the percentage has increased, but with a percent, which did not exceed 2.4%, while from 5-6 hours has decreased. **(Figure 4.8**).

The maximum oxirane oxygen percentage obtained at temperature 40°C at 5 hours from the beginning of the reaction was (2.4%).

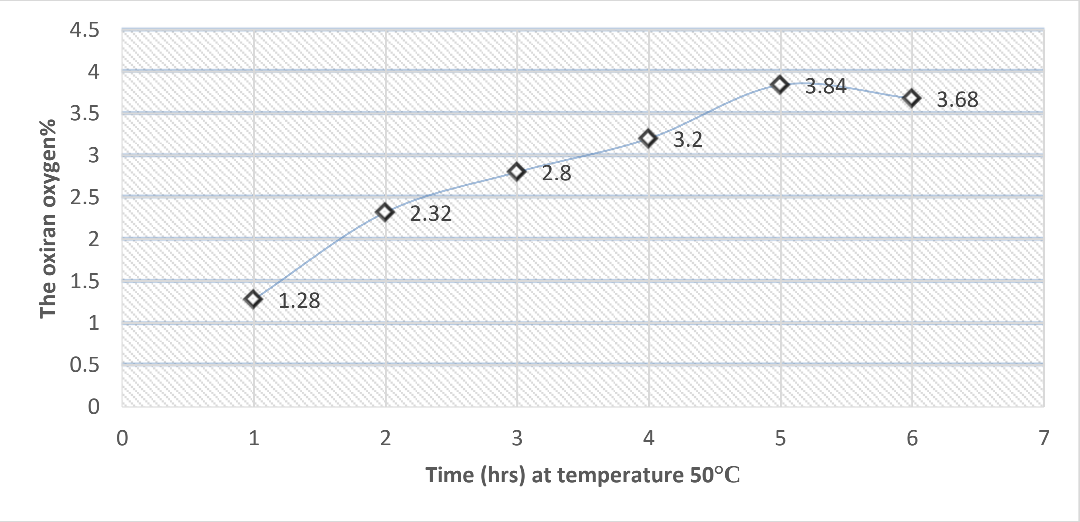


Figure 4.9: Effect of time at temperature 50°C on the oxirane oxygen %

In the increment of time, during the epoxidation reaction at 50°C from 1-5 hours, to obtain the epoxy group (the oxirane oxygen %) the percentage has increased, while from 5-6 hours has decreased.

The maximum oxirane oxygen percentage obtained at temperature 50°C at 5 hours from the beginning of the reaction was (3.84%).(**Figure 4.9**).

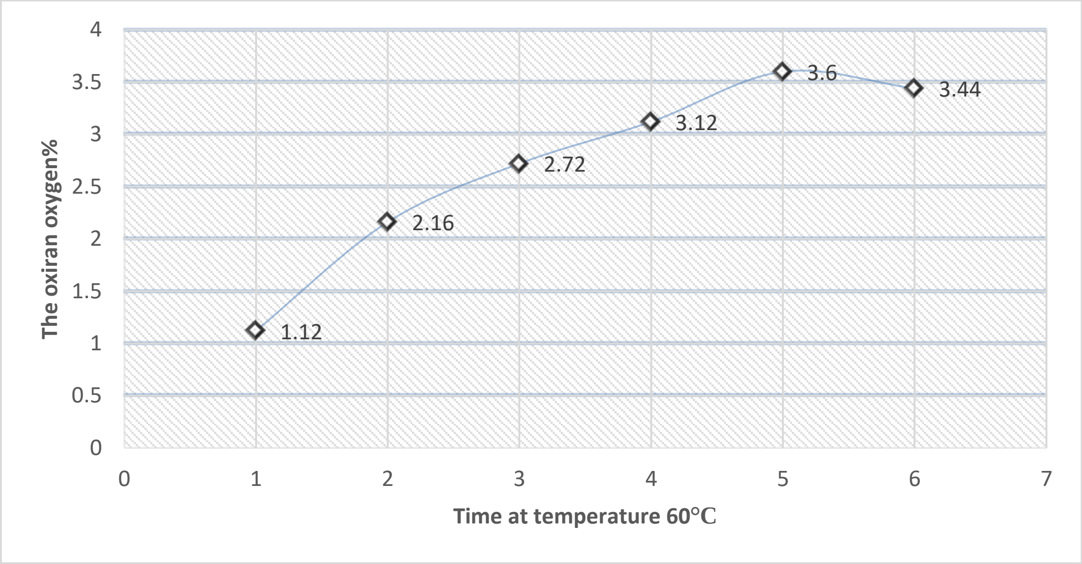


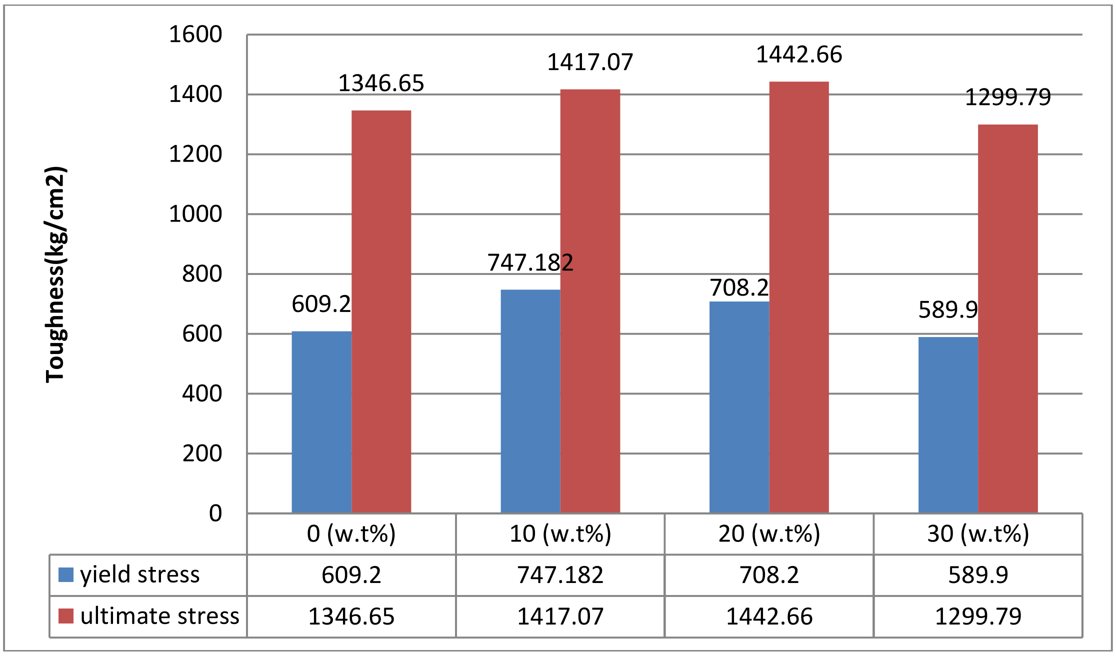
Figure 4.10: Effect of time at temperature 60°C on the oxirane oxygen %

In the increment of time, during the epoxidation reaction at 60°C from 1-5 hours, to obtain the epoxy group (the oxirane oxygen %), the percentage has increased, while from 5-6 hours has decreased.

The maximum oxirane oxygen percentage obtained at temperature 60°C at 5 hours from the beginning of the reaction was (3.6%).(**Figure 4.10**).

Grossly, it was noticed that the topmost relative oxirane oxygen percentage obtained at temperature 60°C after 5 hours from the beginning of the reaction was (3.6%).

4.5.3 Effect of Addition of EPO on the Toughness of Epoxy



	0 (w.t%)	10 (w.t%)	20 (w.t%)	30 (w.t%)
🟦 yield stress	609.2	747.182	708.2	589.9
🟥 ultimate stress	1346.65	1417.07	1442.66	1299.79

Figure 4.11: Effect of adding EPO to ER on toughness

Yield strength or yield stress[1] is the maximum stress up to which a body undergoes elastic deformation (I.e., the body comes back to its original conformation after the withdrawal of the stress

As shown in Fig. 4.11, that the toughness (yield stress), epoxy has increased by 137.98kg/cm^2 when adding 10% EPO of the weight of epoxy. Moreover, the ultimate stress[2] has increased by 70.42 kg/cm^2 when adding the same weight of EPO.

Furthermore, the toughness (yield stress), epoxy has increased by 99kg/cm^2 when adding 20% EPO of the epoxy weight.

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[1] **Yield stress:** The stress level at which a metal or other material ceases to behave elastically. The stress divided by the strain is no longer constant. The point at which this occurs is known as the yield point (Christensen, 2013).

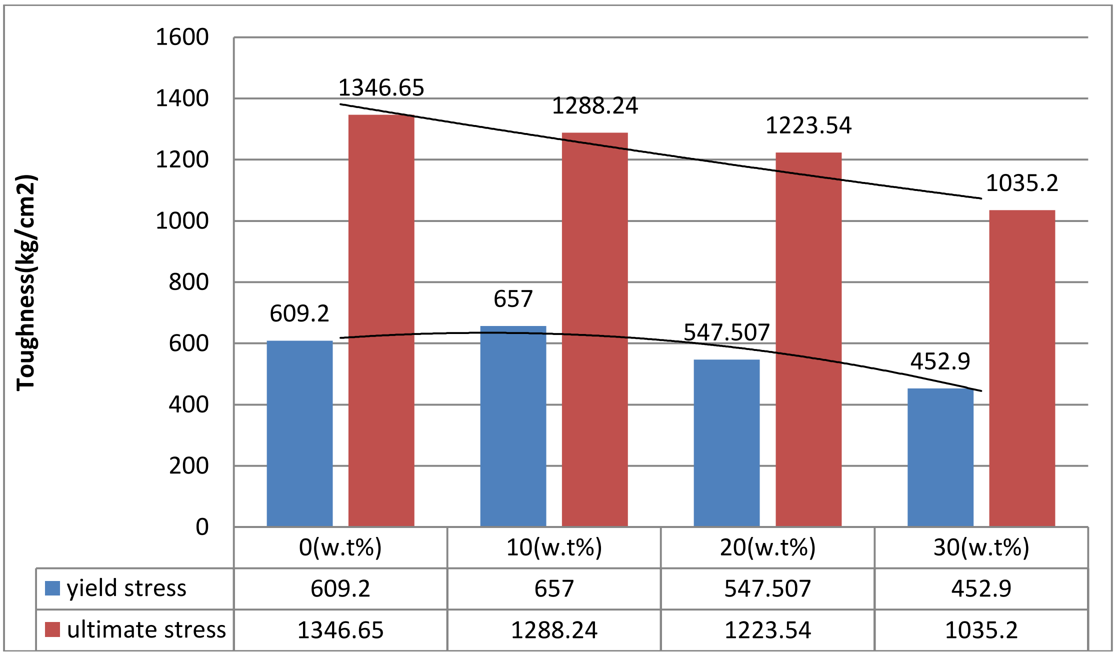
[2] **Ultimate tensile strength**: is measured by the maximum stress that a material can withstand while being stretched or compression before breaking. In the study of strength of materials, tensile strength, compressive strength, and shear strength can be analyzed independently.

In addition, the ultimate stress has increased by 96.01kg/cm^2 when adding the same weight of EPO.

Also, the toughness (yield stress), epoxy has decreased by 19.3kg/cm^2 when adding 30% EPO of the epoxy weight.

Moreover, the ultimate stress has decreased by 46.86kg/cm^2 when adding the same weight of EPO.

4.5.4 Effect of Addition of Chicken Feathers on the Toughness of Epoxy



	0(w.t%)	10(w.t%)	20(w.t%)	30(w.t%)
🟦 yield stress	609.2	657	547.507	452.9
🟥 ultimate stress	1346.65	1288.24	1223.54	1035.2

Figure 4.12: Effect adding chicken feathers to ER on toughness

It is clear in Fig. 4.12 that the toughness (yield stress), epoxy has increased by 47.8kg/cm^2 when adding 10% chicken feathers of the weight of epoxy.

Besides, the ultimate stress has decreased by 58.41kg/cm^2 when adding the same weight of chicken feathers.

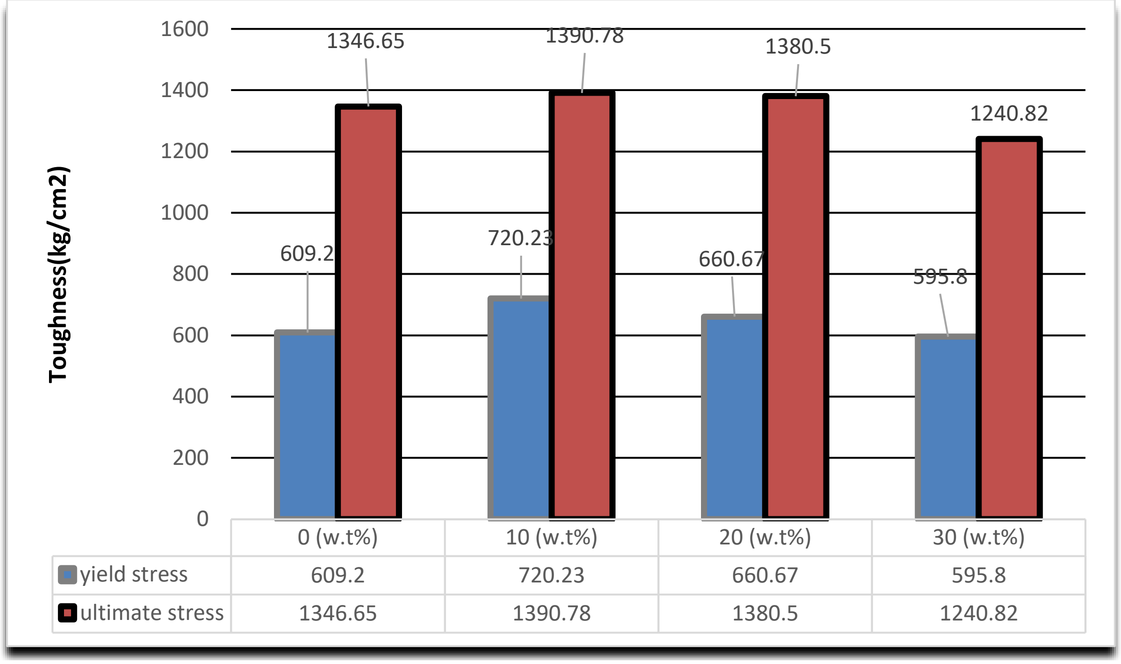
Additionally, the toughness (yield stress), epoxy has decreased by 61.70kg/cm^2 when adding 20% chicken feathers of the weight of epoxy.

Moreover, the ultimate stress has decreased by 123.11kg/cm^2 when adding the same weight of chicken feathers.

Likewise, the toughness (yield stress), epoxy has decreased by 156.3kg/cm^2 when adding 30% chicken feathers of the weight of epoxy.

Furthermore, the ultimate stress has decreased by 311.45kg/cm^2 when adding the same weight of chicken feathers.

4.5.5 Effect of Addition of EPO/Chicken Feathers on the Toughness of Epoxy



	0 (w.t%)	10 (w.t%)	20 (w.t%)	30 (w.t%)
yield stress	609.2	720.23	660.67	595.8
ultimate stress	1346.65	1390.78	1380.5	1240.82

Figure 4.13: Effect adding EPO and chicken feathers to ER on toughness

It is clear in Fig. 4.13 that the toughness (yield stress), epoxy has increased by 111.03kg/cm^2 when adding 5% EPO and 5% chicken feathers of the weight of epoxy.

Besides, the ultimate stress has increased by 44.13 kg/cm^2 when adding the same weight of EPO/chicken feathers.

Additionally, the toughness (yield stress), epoxy has increased by 51.47 kg/cm^2 when adding 10% EPO and 10% chicken feathers of the weight of epoxy.

Besides, the ultimate stress has increased by 33.85 kg/cm^2 when adding the same weight of chicken feathers.

Likewise, the toughness (yield stress), epoxy has decreased by 13.4 kg/cm^2 when adding 15% EPO and 15% chicken feathers of the weight of epoxy.

Moreover, the ultimate stress has decreased by 105.83 kg/cm^2 when adding the same weight of chicken feathers.

4.5.6 Effect of Addition of EPO on the Tensile Of Epoxy

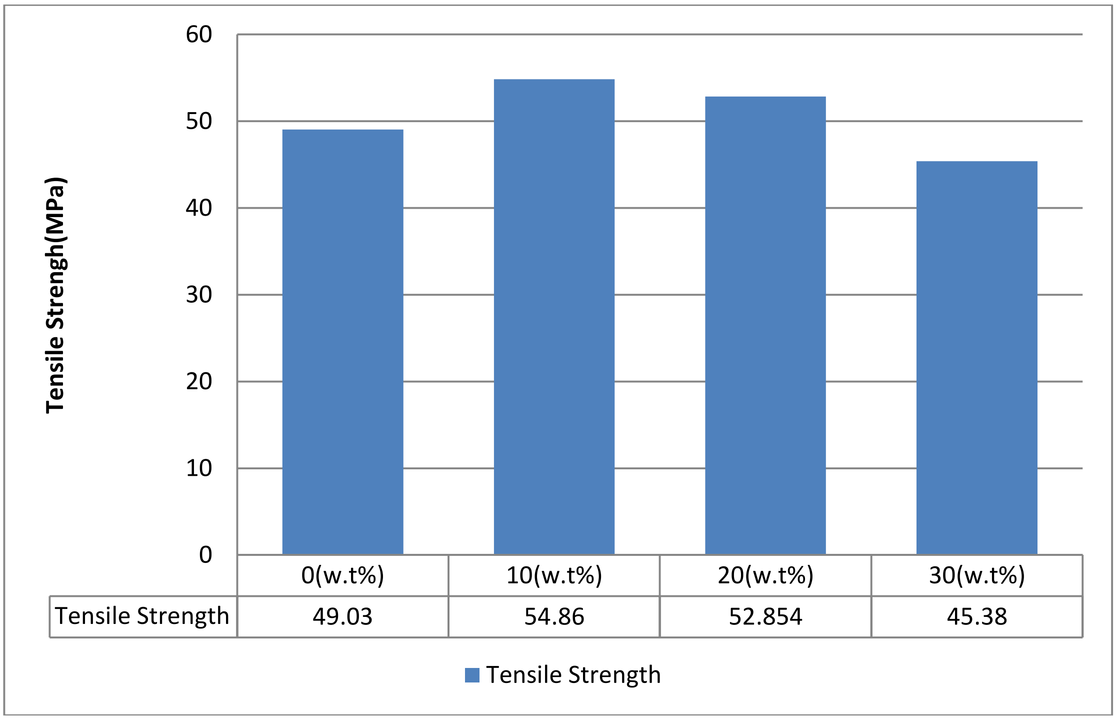


Figure 4.14: Effect of adding EPO to ER on tensile strength

The effect of EPO content on the tensile strength of the epoxy resin is shown in Figure 4.14.

It is observed that the tensile strength increased from 49.03 MPa to 54.86 MPa when we added 10% EPO, and increased from 49.03 MPa to 52.854 MPa when we added 20% EPO, but when added 30% EPO, tensile strength decreased from 49.03 MPa to 45.38 MPa.

In another word, increasing the amount of EPO from 10 to 30 w.t% caused decreasing the values of tensile strength by amount of 3.65 MPa. This is consistent with the study results of Alsagayar et al., 2014,who indicated that by adding the EPO (10, 20 and 30 wt%), the tensile strength was reduced as compared to composite without EPO, signifying that increasing the amount of EPO from 10 to 30 w.t% caused decreasing the values of tensile by amount of 13.85%.

Moreover, a similar result was achieved in a work of epoxidized soya bean oil/epoxy resin blends by Zhu et al., 2004 when the result designated that tensile properties decreased when the amount of epoxidized soya oil ESO was increased.

4.5.7 Effect of Addition of Chicken Feathers on the Tensile of Epoxy

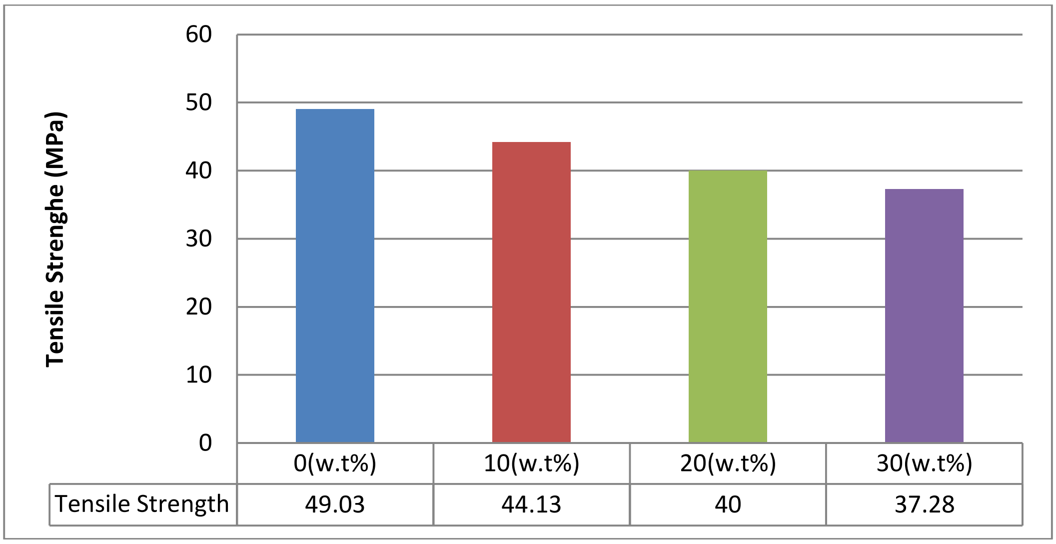


Figure 4.15: Effect of adding chicken feathers to ER on tensile strength

The effect of EPO content on the tensile strength of the epoxy resin is shown in Figure 4.15

It is observed that the tensile strength decreased from 49.03 MPa to 44.13 MPa when we added 10% chicken feathers, and decreased from 49.03 MPa to 40 MPa when we added 20% chicken feathers, and when added 30% chicken feathers, tensile strength decreased from 49.03 MPa to 37.28 MPa.

4.5.8 Effect of Addition of EPO and Chicken Feathers on the Tensile of Epoxy

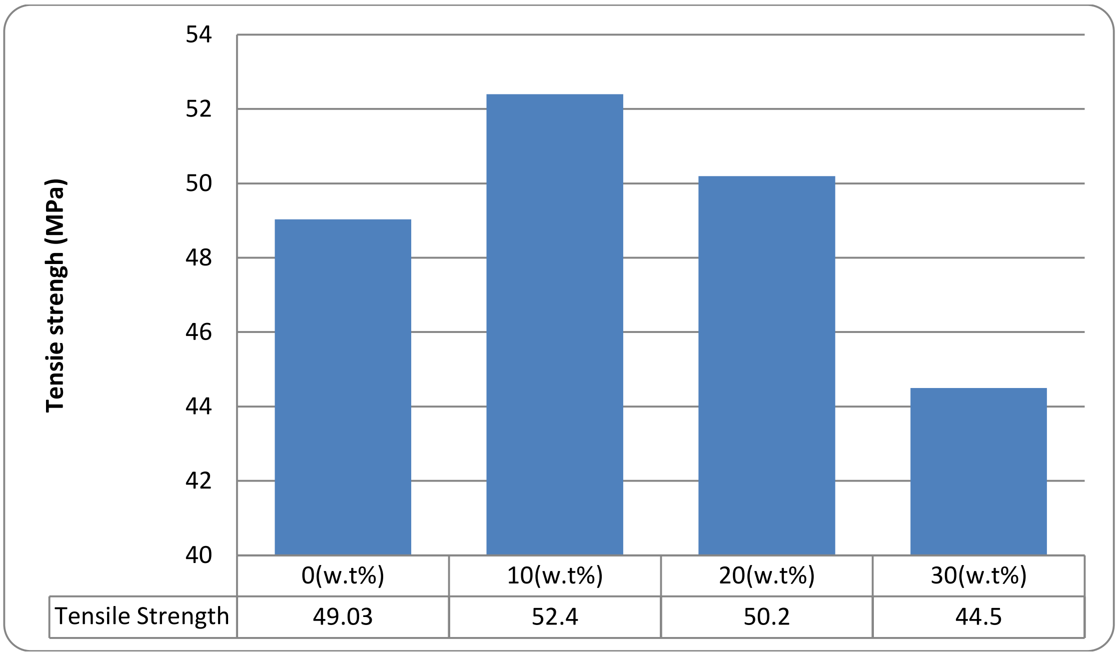


Figure 4.16: Effect of adding EPO/chicken feathers to ER on tensile strength

Figure 4.16 summarises the test results of adding EPO/chicken feathers to ER on tensile strength. It was observed that the tensile strength increased from 49.03 MPa to 52.4 MPa when we added 5% EPO and 5% chicken feathers, and increased from 49.03 MPa to 50.2MPa when we added 10% EPO and 10% chicken feathers, however, when added 15% EPO and 15% chicken feathers, tensile strength decreased from 49.03 MPa to 44.5 MPa.

4.6 Conclusions

In this work, we showed that epoxy resin could enhance the properties of epoxy prepared with a combination of EPO and chicken feathers. Tests have shown that the addition of EPO enhances the tensile and toughness properties of the base epoxy resin system. Therefore, epoxidized EPO additives hold great potential for environmentally friendly and lower cost raw materials for the fabrication of epoxy composites for structural applications.

Advance materials from chicken feathers and palm oil are a prodigious feedstock for the synthesis of advanced materials due to the substantial amounts of feathers that are wasted in agriculture. One aspect of this research is clearance of the environment from huge amounts of chicken feathers, utilization of a renewable resource for the use of inexpensive, high-performance fibers which may then be used in reinforcement of composites, as well as the enhancement of the mechanical properties of the base epoxy resin. This process will eliminate the feather disposal problem, minimize the health problem and generate an economically valuable new bio-based product. Yet, alone, the chicken feathers did not give positive results, then, when blend with epoxy, chicken feathers lessened the tensile and toughness of the epoxy. Nevertheless, the addition of EPO enhanced the tensile and toughness properties of the epoxy resin.

The most important conclusions are shown as follow:

1. FTIR seems to be a valuable device for both qualitative analysis and quantification of epoxy.
2. It has been shown how to disentangle relevant information from spectra to identify typical components of resins and hardeners.
3. Following time, variations of specific bands allow extracting relevant kinetic parameters to get more insight about the specific reaction mechanism of curing process.

4. The highest percentage of fatty acid in PO for Palmitic acid was 49%.
5. Optimum percent of conversion double bond by epoxidation reaction was 86.45% at temperature 50°C at 5 hours from the beginning of the reaction.
6. The maximum oxirane oxygen percentage obtained at temperature 50°C at 5 hours from the beginning of the reaction was (3.48%).
7. The toughness of epoxy increased when adding 10% and 20% EPO of the weight of epoxy, but decreased when adding 30% EPO of weight of epoxy.
8. The toughness of epoxy increased when adding 10% chicken feathers of the weight of epoxy, but decreased when adding 20% and chicken feathers 30% EPO of weight of epoxy.
9. The toughness of epoxy increased when adding 10% and 20% EPO blend with chicken feathers of the weight of epoxy, but decreased when adding 30% EPO blend with chicken feathers of weight of epoxy.
10. The tensile strength of the epoxy increased when adding 10% and 20% EPO of the weight of epoxy, but decreased when adding 30% EPO of weight of epoxy.
11. The tensile strength of the epoxy increased when adding 10% and 20% EPO blend with chicken feathers of the weight of epoxy, but decreased when adding 30% EPO blend chicken feathers of weight of epoxy.

4.7 Suggestions for Future Work

Although this research studies many properties of P.O, factors affecting on epoxidation reaction and mechanical properties of epoxy resin, there are many areas need further investigation. These include:

1. Use another oil such as soybean oil, linseed, or a mixture of epoxidized palm oil and epoxidized soybean oil (EPSO).
2. Use other methods for epoxidation reaction such as metal catalyst epoxidation, catalytic acidic ion exchange resin epoxidation, or chemoenzymatic epoxidation.
3. Study thermal properties of epoxy resin such as thermal gravimetric analysis (TGA), Differential scanning calorimetry (DSC).
4. Replace chicken feathers with other biomaterials such as sheep wool.

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كلية الدراسات العليا

إنتاج مواد حيوية من منتجات متجددة: ريش الدواجن وزيت النخيل

إعداد

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قُدمت هذه الأطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في العلوم البيئية، كلية الدراسات العليا، جامعة النجاح الوطنية، نابلس، فلسطين.

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الملخص

تمثل زيوت النباتات أو زيوت الخضراوات مصدراً متجددًا يمكن استخدامها كمواد أولية موثوقة للوصول إلى منتجات جديدة مع مجموعة واسعة من التنويعات الهيكلية والوظيفية. في السنوات الأخيرة، تعتبر الزيوت النباتية الإيبوكسيدي (EVO) مواد صديقة للبيئة أكثر من المواد الأخرى مثل الوقود الأحفوري والمواد منخفضة التكلفة.المواد المطورة من زيت النخيل وريش الدجاج هي مواد خام بارزة لتخليق مواد مطورة نظراً للكميات الهائلة للريش التي تُهدر وتؤثر على البيئة.

هدفت هذه الدراسة إلى توصيف الخصائص الوظيفية الأساسية والمركبات الحيوية لزيت النخيل، وكذلك عمل إيبوكسيد (Epoxidation) زيت النخيل من أجل تحسين خصائص الايبوكسي، وتحسين خصائص زيت النخيل المرتبط إيبوكسياً(EPO) ثم استكشاف التطبيقات الممكنة لتحسين خصائص راتينجات الايبوكسي من خلال إضافة إيبوكسيد زيت نخيل جديد وريش دجاج، وأيضا تخليص البيئة من ريش الدجاج.

سُخرت في هذا العمل مجموعة من الطرائق وتقانات القياس المعيارية التي تلبي الغرض من هذا العمل، وتمثلت هذه التقانات في جهاز مطيافية الأشعة تحت الحمراء (FTIR)، وجهاز الإستشراب الغازي-مطياف الكتلة (GC-MS)، وكذلك جهازا الشد والضغط لدراسة تغيرات القساوة وخواص الشد. ومن أجل توصيف الخواص الكيميائية، عُرضتْ عينات متعددة منه لعدد من المؤثرات الكيميائية خلال مدد زمنية مختلفةبحيث تم تنفيذ تفاعل إبوكسيديشن لزيت النخيل لمدة أربعة (4) أيام مع ست (6) عينات لكل يوم، ومع درجات حرارة متنوعة (30 درجة مئوية، 40 درجة مئوية، 50 درجة مئوية و60 درجة مئوية).

أجريت تجارب لاستكشاف تأثير إضافة ريش الدجاج/زيت النخيل المرتبط إيبوكسياً(EPO) على صلابة وشد الإيبوكسي (10 wt%, 20 wt% and 30 wt%) بشكل فردي/ مجتمع.

أظهرت النتائج أن جهاز مطيافية الأشعة تحت الحمراء (FTIR) لذروة ترابط زيت النخيل تضمن عصابة الإمتصاص عند العدد الموجي 1647.49 cm^{-1} العائدة إلى حلقة الإيبوكسي HC=CH، وذروة التردد الإهتزازي الممتدة =CH 3008.97 cm^{1}، بينما لزيت النخيل المرتبط إيبوكسياً (EPO) كانت ذروة الترابط غير المشبع (cis) HC=CH، وذروة التردد الإهتزازي الممتدة =CH كانت قد اختفت تماماً. غير أنه تم تحديد مجموعة الإيبوكسي عن ذروة حلقة الأوكسيران(oxirane) على عدد موجي 1104.76 cm^{-1}. استُخدم زيت النخيل المرتبط إيبوكسياً (EPO) حتى تتصلب راتنجات الإيبوكسي المُعالجة بمقسي ذي درجة حرارة محيطة. النسبة المثلى من رابطة التحويل المزدوج بتفاعل الإبوكسدة كانت 86.45% عند درجة حرارة 50°C في 5 ساعات من بداية التفاعل، وقد زادت قساوة الإيبوكسي عند إضافة 10% و 20% من زيت النخيل المرتبط إيبوكسياً (EPO) من وزن الإيبوكسي، بينما تناقصت عند إضافة 30% من وزن الإيبوكسي. كما أن قوة الشد قد زادت من الإيبوكسي عند إضافة 10% و 20% من زيت النخيل المرتبط إيبوكسياً (EPO) من وزن الإيبوكسي المخلوط مع ريش الدجاج من وزن الإيبوكسي، لكنه انخفض عند إضافة 30% من وزن الإيبوكسي المخلوط مع ريش الدجاج. لم يكن ريش الدجاج ليعطي نتائج إيجابية بشكل منفرد، ولكن، عند مزجه مع الإيبوكسي، قلل ريش الدجاج من قوة الشد والضغط للإيبوكسي. ومع ذلك، فإن إضافة زيت النخيل المرتبط إيبوكسياً (EPO) قد عزز خصائص الشد والضغط لراتينج الإيبوكسي.