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SYNTHESIS OF POLYESTER FROM EPOXIDIZED VEGETABLE OIL AND PHTHALIC ANHYDRIDE

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งานวิจัยนี้มุ่งศึกษาการสังเคราะห์พอลิเอสเทอร์จากน้ำมันพืช อิพ็อกซิไดซ์ที่อุณหภูมิต่างๆ (110-240 องศาเซลเซียส)น้ำมันถั่วเหลือง น้ำมันปาล์ม น้ำมันทานตะวัน อิพ็อกซิไดซ์สังเคราะห์ขึ้นโดยปฏิกิริยาอิพ็อกซิเดชันกับกรดเปอร์แอซิติก ร้อยละอิพ็อกซิเดชันของน้ำมันถั่วเหลือง น้ำมันปาล์ม และน้ำมันทานตะวันที่อิพ็อกซิไดซ์ คือ ร้อยละ 86 ร้อยละ 78 และร้อยละ 87 ตามลำดับ พอลิเอสเทอร์จากน้ำมันถั่วเหลือง น้ำมันปาล์มและน้ำมันทานตะวันอิพ็อกซิไดซ์ กลีเซอรอลและแทลิกแอนไฮไดรด์ที่อัตราส่วน 1.1:1:1.5 สามารถสังเคราะห์ในภาวะที่ไม่มีตัวเร่งปฏิกิริยา พบว่าพอลิเอสเทอร์ถูกสังเคราะห์ได้ที่อุณหภูมิสูงกว่า 110 องศาเซลเซียส มวลโมเลกุลของพอลิเอสเทอร์ที่สังเคราะห์ได้อยู่ในช่วง 1.19×10^5-10.5×10^5 ได้ศึกษาความแข็งแรงของวัสดุภายใต้แรงดึง ความยืดหยุ่นภายใต้แรงดึง โมดูลัสความยืดหยุ่นภายใต้แรงดึงและความต้านทานต่อการผิดรูปของพอลิเอสเทอร์ด้วยเช่นกัน

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PIYATIDA RUKSAYOT: SYNTHESIS POLYESTER FROM EPOXIDIZED VEGETABLE OIL AND PHTHALIC ANHYDRIDE. THESIS ADVISOR: ASSOC. PROF. SURACHAI PORNPAKAKUL, Ph.D., 94 pp.

This research aimed to synthesize polyester from epoxidized vegetable oils at various temperatures (110-240°C). Epoxidized Soybean oil, palm oil and sunflower oil were synthesized via epoxidation reaction with peracetic acid. The percent epoxidation of epoxidized soybean oil, palm oil and sunflower oil were 86%, 78% and 87%, respectively. The polyesters from epoxidized soybean, palm and sunflower oils, glycerol and phthalic anhydride at ratio 1.1:1:1.5 could be synthesized in the absence of catalyst. It was found that the polyesters were synthesized at above 110°C. The molecular weight of synthesized polyesters were in the range of 1.19×10^5-10.5×10^5. The tensile strength, elongation, Young's modulus and hardness of polyesters were also investigated.

Field of Study : Petrochemistry and Polymer Science Student's Signature
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LIST OF ABBREVIATIONS

ASTM	American Standard Test Method
$^{\circ}C$	Degree Celsius
cSt	Centistroke
FT-IR	Fourier Transform Infrared Spectroscopy
g	gram
GC	Gas-liquid chromatography
hr	hour
NMR	Nuclear Magnetic Resonance Spectroscopy
kg/mm^2	Kilogram per milimetre
ml	Milliter
mm	Millimeter
ppm	part per million
%wt	percent weight
δ_H	Chemical shift of ^1H NMR
δ_C	Chemical shift of ^{13}C NMR

CHAPTER I

INTRODUCTION

Polyester is generally achieved by polycondensation reaction of polybasic and polyhydric alcohol to form a series of ester linkages. There are many categories of polyesters depending on the types of acids and alcohols selected. One of the most favourable type of polyesters is alkyd resin which refer to oil-modified polyester used for surface coating (paints, enamels, lacquers and varnishes) in which the resins function as binders, forming a tough, continuous film due to their unique properties such as film hardness, durability gloss, gloss retention and resistance to abrasion, etc. Alkyd resins can be synthesized by alcoholysis process of polyhydric alcohol, dibasic acid and monobasic acid which normally are glycerol, phthalic anhydride and fatty acid of oil, respectively. The natural oils such as soybean oil, sunflower oil and palm oil containing large amounts of triglycerides can be used as monobasic acid to obtain biopolymer in the sense that they are generated from renewable natural sources and they are also biodegradable as well as non-toxic. In addition, natural oils can be modified before using as monobasic acid by epoxidation reaction. The double bonds of alkenes in natural oils are formed into three-membered cyclic ether (oxirane). Epoxidized oils are used as plasticizers, crosslinking agents, stabilizers, pre-polymers and intermediates for polyol production used in polyurethane, polyester and plastic resins after the oxirane ring is opened by hydroxylation or alcoholysis.

Generally, natural oils without modifying are used as a raw material for synthesizing polyesters at the relative high temperature (240^{o}C). In this research, epoxidized oils were used instead of natural oils to enhance the efficiency of obtained polyesters. The temperature reaction of polyesters at low temperature and the properties of synthesized polyesters were also studied.

Objectives of the research:

1. To synthesized polyester from epoxidized oil and phthalic anhydride
2. To study physical and mechanical properties of polyester from epoxidized oil.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Vegetable oil chemistry

Chemically the oils/fats consist of triglyceride molecules of three long chain fatty acids that are ester bonded to a single glycerol molecule. These fatty acids differ by the length of carbon chains, the number, orientation and position of double bonds in these chains and the structure notation as shown in Figure 2.1.

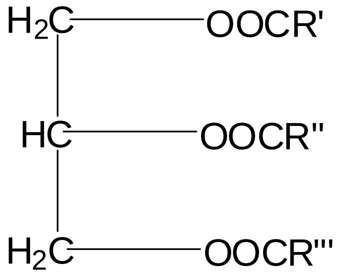


Figure 2.1 Structure of a triglyceride.

where R’, R’’, R’’’ represent hydrocarbon chain of fatty acids. Fatty acids vary in carbon chain length and in the number of unsaturated bonds (double bonds). The structures of common fatty acids are given in Table 2.1, and fatty acid compositions of some vegetable oils are given in Table 2.2.

Vegetable oils have about 10% less heating value than diesel due to the oxygen content in the molecule. In addition, the viscosity of mineral diesel is several times lower than that of vegetable oil due to high molecular weight and complex chemical structure in vegetable oil. Physical and thermal properties of some of the vegetable oils are listed in Table 2.3.

Table 2.1 Chemical structure of common fatty acids [1]

Fatty acid	Systermatic name	Structure	Formular
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$
Linoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$
Oleic	*cis*-9-Octadecenoic	18:1	$C_{18}H_{34}O_2$
Linoleic	*cis*-9,*cis*-12-Octadecadienoic	18:2	$C_{18}H_{32}O_2$
Linolenic	*cis*-9,*cis*-12,*cis*-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Erucic	*cis*-13-Docosenoic	22:1	$C_{22}H_{42}O_2$

Table 2.2 Chemical composition of vegetable oils [1]

Vegetable oil	Fatty acid composition (%wt)									
	C14:0	C16:0	C18:0	C20:0	C22:0	C24:0	C18:1	C22:1	C18:2	C18:3
Corn	0	12	2	*Tr*	0	0	25	0	60	*Tr*
Cottonseed	0	28	1	0	0	0	13	0	58	0
Crambe	0	2	1	2	1	1	19	59	9	7
Linseed	0	5	2	0	0	0	20	0	18	55
Peanut	0	11	2	1	2	1	48	0	32	1
Rapeseed	0	3	1	0	0	0	64	0	22	8
Safflower	0	9	2	0	0	0	12	0	78	0
Sesame	0	13	4	0	0	0	53	0	30	0
Soya bean	0	12	3	0	0	0	23	0	55	6
Rice-bran	0.4-0.6	11.7-16.5	1.7-2.5	0.4-0.6	—	0.4-0.9	39.2-43.7	—	26.4-35.1	—
Mahua	—	16-28.2	20-25.1	0.0-3.3	—	—	41.0-51.0	—	8.9-13.7	—
Neem	0.2-0.26	13.6-16.2	14.4-24.1	0.8-3.4	—	—	49.1-61.9	—	2.3-15.8	—
Karanja	—	3.7-7.9	2.4-8.9	—	—	1.1-3.5	44.5-71.3	—	10.8-18.3	—

Tr:Trace

Table 2.3 Physical and thermal properties of vegetable oils [1]

Vegetable oil	Kinematic viscosity	Cetane number	Heating value (MJ/kg)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (Kg/l)	Carbon residue (wt%)	Ash (wt%)
Corn	34.9	37.6	39.5	−1.1	−40.0	277	0.9095	0.24	0.01
Cotton seed	33.5	41.8	39.5	1.7	−15.0	234	0.9148	0.24	0.01
Cramble	53.6	44.6	40.5	10.0	−12.2	274	0.9044	0.23	0.05
Linseed	22.2	34.6	39.3	1.7	−15.0	241	0.9236	0.22	<0.01
Peanut	39.6	41.8	49.8	12.8	−6.7	271	0.9026	0.24	0.005
Rapeseed	37.0	37.6	39.7	−3.9	−31.7	246	0.9115	0.30	0.054
Safflower	31.3	41.3	39.5	18.3	−6.7	260	0.9114	0.25	0.006
Sesame	35.5	40.2	39.3	−3.9	−9.4	260	0.9133	0.25	<0.01
Soyabean	32.6	37.9	39.6	−3.9	−12.2	254	0.9138	0.27	<0.01
Sunflower	33.9	37.1	39.6	7.2	−15.0	274	0.9161	0.23	<0.01
Palm	39.6	42.0	—	31.0	—	267	0.9180	—	—
Tallow	—	—	40.0	—	—	201	—	6.21	—

The high viscosity of vegetable oil, 35–60 cSt compared to 4 cSt for diesel at 40°C, leads to problem in pumping and spray characteristics (atomization and penetration etc.). The inefficient mixing of oil with air contributes to incomplete combustion. High flash point attributes to its lower volatility characteristics. This results in high carbon deposit formation, injector coking, piston ring sticking and lubrication oil dilution and oil degradation. The combination of high viscosity and low volatility of vegetable oils cause poor cold starting, misfire and ignition delay.

2.1.1 Oil types

Three kinds of oil are classified by drying property as follow: [2]

1) Drying oils: They are fastest dried oil due to oxidation reaction that changing liquid to dry film, which are insoluble in oil-solvent, and are durable to chemicals and moisture penetration. This oil is mostly composing of fatty acid, which have double bond more than three, for example, linseed oil and tung oil etc.

Alkyd resin produced from these oils type would have a water resistance property, the latter changes are always occurred as alkyd resin film have losses their gloss and broken faster than the other producing from lower unsaturation.

2) Semi-drying oils: It is able to absorb lesser oxygen from the air, resulting film is more slowly dried than from drying oil. Fatty acids in this kind of oil have two double bonds and usually have been used as the ingredient in non-yellowing alkyd. These oils type are tall oil, soybean oil, dehydrated castor oil, sunflower oil and wordfiber oil etc. Usually, this oil has iodine value of 120-160 g of I_2/100g., that can give a moderate polymerization.

3) Non-drying oils: this oil cannot be dried by themselves, composing of subjective amount of saturated fatty acid. It can be used as plasticizer for binder in lacquer. For examples, castor oil and palm oil etc. They are usually has iodine value of < 120 g of I_2/100g., causing low polymerization reaction.

2.1.2 Fatty acid

The properties of oil are depending on fatty acid in oil, which affect to dry property of oil [3]. Fatty acid comprise of carboxyl group connected to hydrocarbon chain of 9 to 22 carbon atoms, while carbon atoms are mostly presented. They are classified in to two groups as follows:

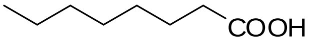
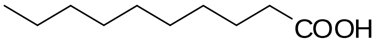
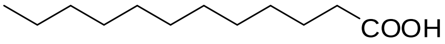
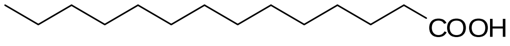
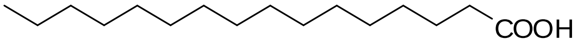
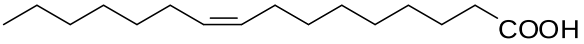
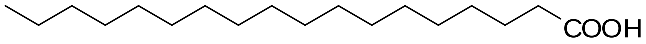
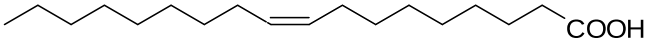
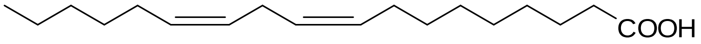
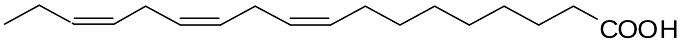
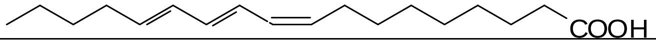
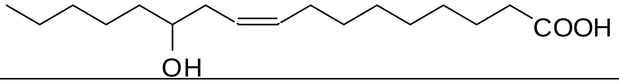
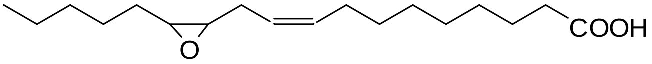
1. Saturated fatty acids:

It is fatty acid with no double bond in molecular structure. Each carbon on molecular chain is attached to at least two atoms of hydrogen. By these reasons, oils with only saturated fatty acids such as stearic acid and palmitic acid etc have non-properties.

2. Unsaturated fatty acids:

It is fatty acid with double bond in carbon chain. However, different position of double bond will also give rise to different kind of fatty acid. Double bond in fatty acid are most affecting to drying property f oil, due to drying reaction of oil is the reaction of oxygen and double bond in oil. In addition, positioning of double bond in the structure are also affecting to the drying property, conjugated double bond structure can give rise to more rapidly dry than isolated double bond. For instance, unsaturated fatty acid are oleic acid and linoleic acid etc.

Table 2.4 Formulas and structures of the most important fatty acids. [3]

Fatty Acid	**Formula**	**Structure**
Caprylic	$C_8H_{16}O_2$	
Capric	$C_{10}H_{20}O_2$	
Lauric	$C_{12}H_{24}O_2$	
Myristic	$C_{14}H_{28}O_2$	
Palmitic	$C_{16}H_{32}O_2$	
Palmitoleic	$C_{16}H_{30}O_2$	
Stearic	$C_{18}H_{36}O_2$	
Oleic	$C_{18}H_{34}O_2$	
Linoleic	$C_{18}H_{32}O_2$	
Linolenic	$C_{18}H_{30}O_2$	
a-Eleostearic	$C_{18}H_{30}O_2$	
Ricinoleic	$C_{18}H_{34}O_2$	
Vernolic	$C_{18}H_{32}O_2$	

2.2 Soybean oil [4]

Soybean oil, obtained from the seed of the legume ***Soja max***, is the hight volume vegetable oil produced in the world. The crude of oil is obtained by processing or solvent extraction methods. The main use of the oil after refining, bleaching and deodorization, and partial hydrogenation are in the manufacture of margarine and shortenings. Soybean oil is also used exclusively in the manufacture of drying oil products.

Crude soybean oil of good quality has a light amber color, which upon alkali refining, is reduced to the light yellow color of most vegetable seed oils. Fatty acid composition of soybean oil usually contains 5-9% of linolenic acid and generally

43-56% of linoleic acid. The following figure shows the chemical structure of linolenic acid.

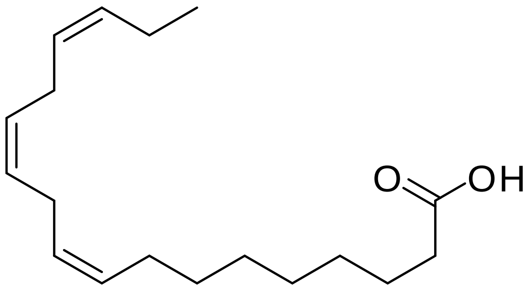


Figure 2.2 structure of linolenic acid.

Soybean oil is a biodegradable vegetable oil dominating today's food oil market. About 80% of the soybean oil produced each year is used for human food. Another 6% is used for animal feed, while the remainder (14%) finds nonfood uses (soap, fatty acids, lubricants, coatings, etc.) [4]. The polyunsaturation of soybean oil and low saturation soybean oil (LoSatSoy), with still higher polyunsaturated fatty acid content, makes it possible to polymerize or copolymerize these natural oils into useful new materials.

Figure 2.3 Seed of the legume ***Soja max***.

Table 2.5 Physical properties of Soybean oil and Their Representative value. [4]

Property	Unit	Value
Specific gravity at 25° C	g/mm^3	0.9175
Refractive index, n^{25}_D	/	1.4728
Specific refraction, r^{30}_D	/	0.3054
Viscosity at 25° C	Centipoise	50.09
Solidification point	° C	-10 to -16
Specific heat at 19.7 ° C	Cal/g	0.458
Heat of combustion	Cal/g	9478
Smoke point	° C	234
Flash point	° C	328
Fire point	° C	363

2.3 Palm oil [5]

The oil palm is a monocotyledon belonging to the genus *Elaeis.* It is a perennial tree crop and the highest oil producing plant. The crop is unique in that it produces two types of oil. The fleshy mesocarp produces palm oil, which is used mainly for its edible properties and the kernel produces palm kernel oil, which has wide application in the oleochemical industry. The genus *Elaeis* comprises two species, namely *E. guineensis*, *E. oleifera.* Currently, most of the world's production of palm oil comes from South-East Asia, in particular Malaysia and Indonesia.

Like all oils, TGs are the major constituents of palm oil. Over 95% of palm oil consists of mixtures of TGs. During oil extraction from the mesocarp, the hydrophobic TGs attract other fat- or oil-soluble cellular components. These are the minor components of palm oil such as phosphatides, sterols, pigments, tocopherols, tocotrienols and trace metals. Other components in palm oil are the metabolites in the biosynthesis of TGs and products from lipolytic activity. These include the monoglycerols (MGs), diglycerols (DGs) and free fatty acids (FFAs). The oil palm fruit is a drupe, which forms in a tight bunch. The pericarp comprises three layers:

the exocarp (skin); mesocarp (outer pulp containing palm oil); and endocarp (a hard shell enclosing the kernel (the endosperm) which contains oil and carbohydrate reserves for the embryo). Composition of palm oil fruit is shown in Figure 2.4.

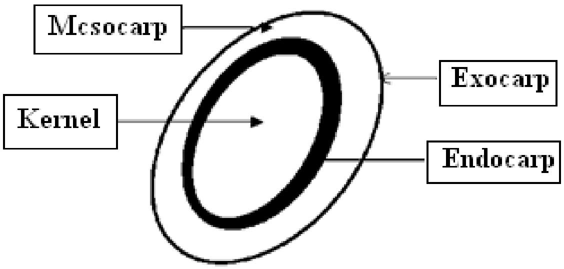


Figure 2.4 Composition of palm oil fruit.

Table 2.6 Fatty acid composition of palm oil. [5]

Fatty acid	**Formular**	**Palm oil (PO)**
Saturated fatty acid (%)		**42.62**
C 12:0 Lauric acid	$C_{12}H_{24}O_2$	0.32
C 14:0 Myristic acid	$C_{14}H_{28}O_2$	0.95
C 16:0 Palmitic acid	$C_{16}H_{32}O_2$	37.47
C 18:0 Stearic acid	$C_{18}H_{36}O_2$	3.88
Unsaturated fatty acid (%)		**57.39**
C 18:1 Oleic acid	$C_{18}H_{34}O_2$	45.92
C 18:2 Linoleic acid	$C_{18}H_{32}O_2$	11.12
C 20:0	$C_{20}H_{40}O_2$	0.35

2.4 Sunflower oil [4]

Sunflower oil is the non-volatile oil expressed from sunflower (*Helianthus annuus*) seeds. Sunflower oil is commonly used in food as a frying oil, and in cosmetic formulations as an emollient. There are several types of sunflower oils produced, such as high linoleic, high oleic and mid oleic. Mid linoleic sunflower oil typically has at least 69% linoleic acid. High oleic sunflower oil has at least 82% oleic acid. Variation in unsaturated fatty acids profile is strongly influenced by both genetics and climate. In the last decade, high stearic sunflower lines have been developed in Spain to avoid the use of partially, hydrogenated vegetable oil in the food industry. Sunflower oil also contains lecithin, tocopherols, carotenoids and waxes. Sunflower oil's properties are typical of a vegetable triglyceride oil. Sunflower oil is produced from oil type sunflower seeds.

Table 2.7 Fatty acid composition of sunflower oil. [4]

Fatty acid	Formular	Sunflower oil (SFO)
Saturated fatty acid (%)		**12.00**
C 16:0 Palmitic acid	$C_{16}H_{32}O_2$	7.00
C 18:0 Stearic acid	$C_{18}H_{36}O_2$	5.00
Unsaturated fatty acid (%)		**88.00**
C 18:1 Oleic acid	$C_{18}H_{34}O_2$	19.00
C 18:2 Linoleic acid	$C_{18}H_{32}O_2$	68.00
C 18:3 Linolenic acid	$C_{18}H_{30}O_2$	1.00

2.5 Polyester resin [6]

By chemical definition a polyester is formed by the reaction of polybasic and polyhydric alcohol to form a series (poly=many) of ester linkages. The particular types of acids and alcohols selected and other modification of the polyester structure determine into which of the following categories the resulting polyester will fall:

1. Unsaturated polyester resin: linear polyester resins based on dibasic acids and dihydric alcohols capable of crosslinking with vinyl monomer to from thermoset copolymers.

2. Alkyds: generally used to refer to oil-modified polyesters used for coatings (some crosslinking polyester systems are referred to as alkyd molding compounds).

3. Plasticizer: certain completely saturated polyesters used to plasticize other plastic compositions are referred to as polymeric plasticizer.

4. Fiber and film: high molecular weight highly oriented polyesters based on rather specific acids and alcohols are used to from fiber and film.

5. Polyester foams: polyester with a high concentration of hydroxyl groups, which are cross-linked with isocyanates to from foam, coatings, elastomers etc.

2.5.1 Saturated polyester [6]

The saturated polyester prepared principally from acids and alcohols by condensation Polymerization have been highly developed on a commercial basis in the form of fiber and films. In the fiber and woven form these polyesters are among the most amazing of the miracle fabrics. As films, they are displacing other plastic film and pioneering in new application because of their strength, toughness and electrical properties. The repeat unit of saturated linear polyester as shown in Figure 2.5.

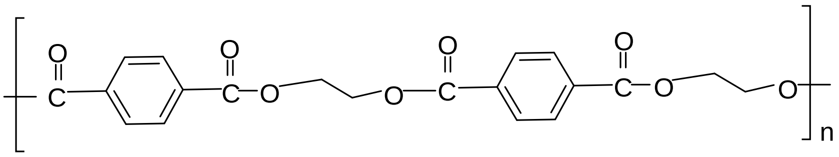


Figure 2.5 Segment of the saturated linear polyester.

The saturated linear polyester cannot be cross-linking monomer. Other saturated polyester of different composition is reacted with diisocyanate compounds through terminal hydroxyl groups to produce foams, costing, adhesivers and rubbers.

2.5.2 Unsaturated polyester [6]

Unsaturated polyester resins are polymers formed by condensation polymerization of dibasic acids and dihydric alcohols, with ester bonds linking the repeating units. The resins are able to form crosslinking to thermoset copolymer because each repeat unit contains an active carbon-carbon double bond that can react with vinyl monomer usually styrene by the addition polymerization mechanism. Reaction of carbon–carbon double bonds by addition polymerization requires that a free radical be formed and attack the double bond to initiate the reaction sequence.

Usually heat-activated or time-activated peroxide or some other free radical source is added to the resin as an initiator at a concentration of 1-2% to initiate the crosslinking reaction. The resin is normally cured at room temperature followed by a post cure at higher temperature to complete the reaction. A repeat unit of unsaturated polyester resin containing a carbon-carbon double bond as shown in Figure 2.6.

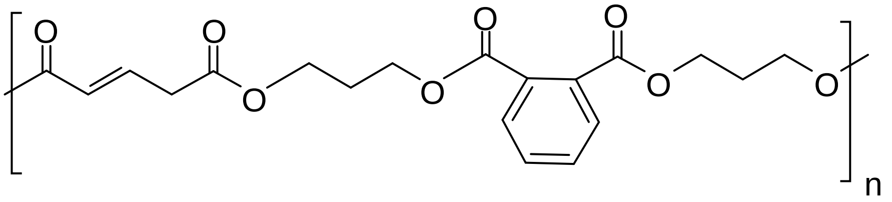


Figure 2.6 Segment of an unsaturated polyester resin chain [6].

2.6 Polymerization theory [7]

When a difunctional acid or anhydride (AA) and a difunction alcohol (BB) are heart together, a stepwise reaction occurs that builds up liner chain molecular.

Composition containing short chains (3 to about 20 monomer units per chain) are called ―oilgomers”. Those containing long chains are ―polymers”. Under ideal condition polymer chains containing thousands of monomer units can be made. Conditions necessary for formation of very high molecular mass chains include the following:

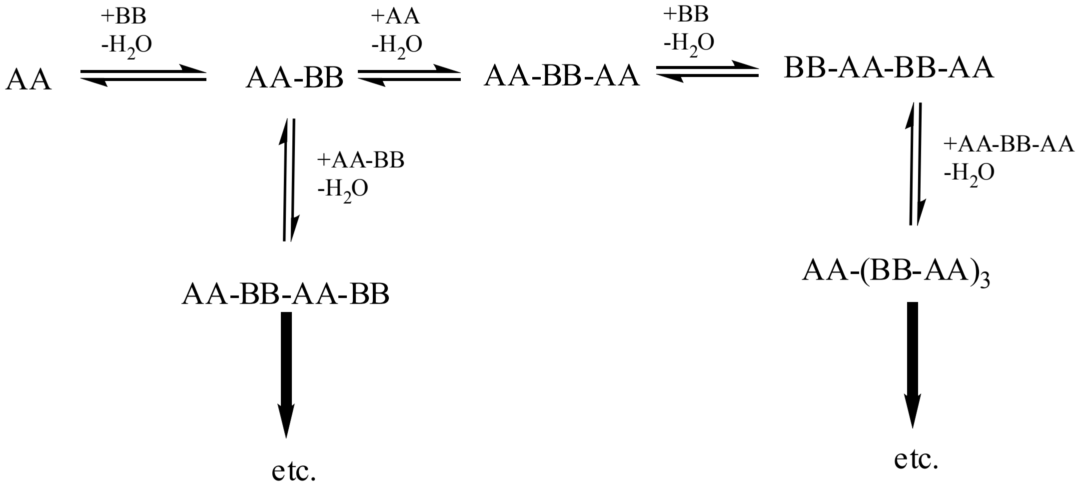


Figure 2.7 Polymerization reaction of anhydride and alcohol.

- The mixture must be heated long to complete the reaction.
- Equimolar quantities of AA and BB must be present.
- No alternative reactions may be possible.
- AA and BB must contain no monofunctional reactive impurities.

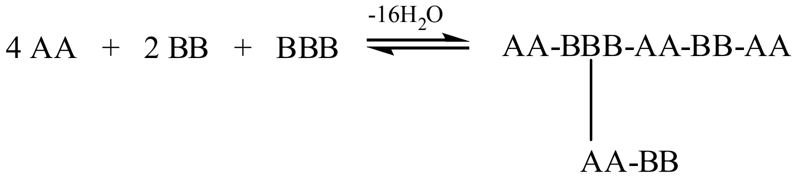
The average molecular mass can be deliberately held at lower levels by altering any of the above ideal condition, for example:

$$9\,\mathrm{AA} + 8\,\mathrm{BB} \xrightleftharpoons{-16\mathrm{H_2O}} \mathrm{AA\text{-}(BB\text{-}AA)_8} \tag{2.1}$$

$$9\,\mathrm{AA} + 10\,\mathrm{BB} + 2\mathrm{A} \xrightleftharpoons{-20\mathrm{H_2O}} \mathrm{A\text{-}(BB\text{-}AA)_9\text{-}BB\text{-}A} \tag{2.2}$$

A represent a monofunctional acid. Of course the actual products of such reaction are mixtures of various chain lengths.

If a trifunctional monomer, BBB is added, chain branching occurs:



$$4\,AA + 2\,BB + BBB \overset{-16H_2O}{\rightleftharpoons} \underset{\substack{|\\ AA\text{-}BB}}{AA\text{-}BBB\text{-}AA\text{-}BB\text{-}AA} \qquad (2.3)$$

If substantial amounts of BBB present, continued polymerization leads to formation of a three-dimensional network, or gel.

One of the goals in alkyd resin synthesis is to prepare structures that are branched but are not quite gelled. A fairly close approach to gelation is needed to form a polymer which readily forms cross-linked networks after application as a coating. However, gelation in the reactor causes a total loss of materials and a difficult clean-up job.

Many researches have been directed toward understanding polymerization and developing general principles to help the alkyd formulator achieve the desired degree of polymerization and to optimize properties. Early theories of polymerization were developed by Carothers and by Kienle and co-workers. Carothers hypothesized a uniform, stepwise polymerization process. In model, gelation occurs as the polymer molecular mass approaches infinity. The condition for gelation would be:

$$P_g = \frac{2}{F_{Av}} \qquad (2.4)$$

When

P_g is the extent of reaction at the gel point.

F_{Av} is the average functionality of the monomer mixture.

According to this equation pure difunctional monomers can never be gel but a mixture of glycerol and phthalic anhydride ($F_{Av} = 2.5$) would gel at $P_g = 0.8$; That is, it would gel when 80% of the functional groups have reacted.

In practice, gelation usually occurs at lower P_g than predicted by this theory. To explain this fact Flory and co-workers proposed probabilistic theory: gelation occurs when a relatively small proportion of the monomer molecules first become bonded into a three-dimensional network. Flory's theory is satisfactory for predicting polymerization of the chemically straightforward monomers used to make polyesters. However, alkyd formulators must deal with monomers that are far from straightforward. Complications include [7]:

- Variable starting materials
- Competing side reactions
- Reaction reversibility
- Differential reactivity of the functional groups
- Differential solubility effects
- Nonuniform process conditions

Gradual progress has been made toward a general and reliable theory of alkyd formation by several authors. A completely precise theory is unlikely, mainly because alkyd polymerizations probably are not homogeneous during the late stages of reaction. Most alkyd contain small, soft get particles as well as soluble material and these gel particles are in some cases essential to the attainment of optimum properties. Despite this difficulty, certain alkyd polymerizations can accurately modeled with the aid of computers and advanced statistical techniques. Such theoretical methods offer considerable help and insight to the alkyd formulator. They can reduce reliance future.

2.7 Alkyd resin

Alkyd came from **al** (**al**cohol) and cid (phthalic acid). It combines **alcid.** Then it pronounce to be similar to the word that acid It has changed to alkyd. The some people producer calls that **glyptal** [**gly**cerol + **p**(h) t(h) **al**ic [6].

Alkyd resins are literally, polyester that are made by condensation polymerization of polyhydric alcohol, dibasic acid and monobasic acid. The largest use of alkyd resins is for surface coating (paints, enamels, lacguers and varnishes) in which the resins function as binders, forming a tough, continuous film that adheres to the object coat. Alkyd resins are the most versatile of coating binders and they are used extensively in all major categories of coating such as architectural, industrial and special pupose. It is estimated that about one third of all organic coating applied worldwide use alkyd resins as a primary binder and perhaps another one fourth of all coating contain smaller amounts of alkyd resins. Alkyd resins are also important ink binders. Other uses include caulks, adhesives and plasticizers [6].

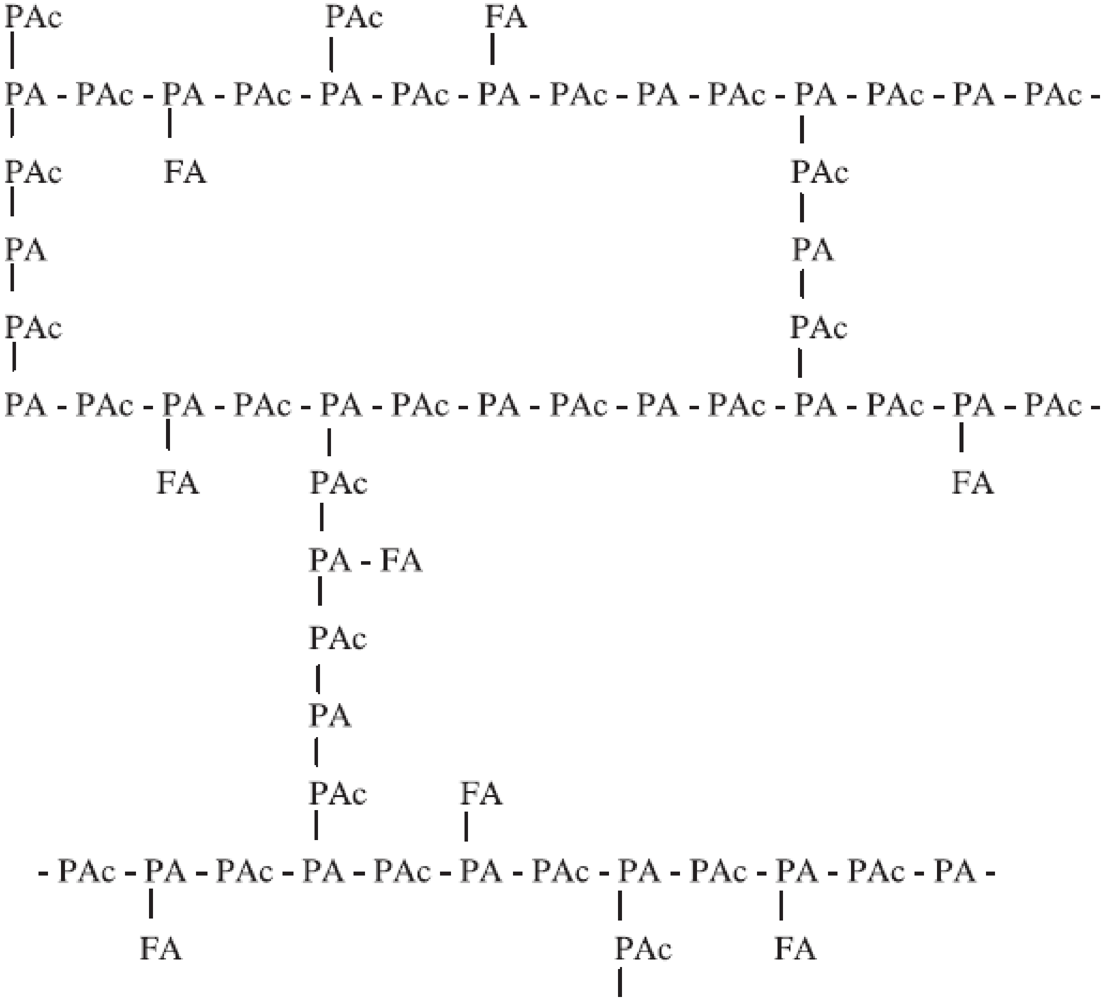


Figure 2.8 Structure of alkyd resin.
(PA: polyalcohol, PAc: poly acid, FA: fatty acid).

2.7.1 Classification of alkyd resin

2.7.1.1 Classified by type of oil

Alkyd resins classified by type of oil are as follows: [6]

1. Drying alkyds:

Drying alkyd are alkyd resins containing enough unsaturated Fatty acids to make curing by oxygen possible.

2. Nondrying alkyds:

Nondrying alkyds are alkyd resins containing lower levels of unsaturated fatty acids and are not polymerized appreciably with oxgen.

2.7.1.2 Classified by oil content

Alkyd resins classified by oil content are as followes:[6]

- Short-oil alkyds: As alkyds contain oil below 40%
  Classified to two types as:
    - Drying oil is components.
    - Nondrying oil is the components.
- Medium oil alkyd resin: As alkyds contain oil between 60% and 40%
- Long oil alkyd resin: As Alkds contain oil above 60%
  Classified to two types as:
    - It have a non-volatile matter 70 %w/w.
    - It have a non-volatile matter 75 %w/w.

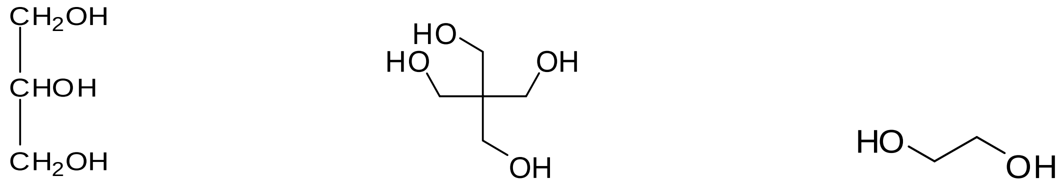
2.7.2 Raw materials

The main raw material used in alkyd resins production are given as follows.[8]

2.7.2.1 Polyhydric alcohol

1. Glycerol is the traditional alcohol used in alkyd resin production. It is a trihydric alcohol containing two primary and one secondary hydroxyl group, as shown in Figure 28.

2. Pentaerythritol is the main polyhydric alcohol used in long oil alkyd today. It posses four primary hydroxyl group, as shown in Figure 28, which confer the potential for building more complex molecules than with trihydric alcohols, hence its alkyd derivatives are characterized by higher viscosity, faster dry and superior water resistance. In practical terms, this allows the development of long oil alkyds with freer brushing properties for the same drying times. However, the high reactivity of pentaerythriol limits its use in short oil alkyds, where it can cause gelation unless its functionality is lowered by the use of dihydric alcohols and/or monobasic acid such as rosin or benzoic acid. Blends of pentaerythritol and ethylene glycol lead to lower cost alkyds than those made on glycerol and produce short oil alkyds of excellent durability.



Glycerol Pentaerythritol Ethylene Glycol

Figure 2.9 Structure of polyhydric alcohol.

2.7.2.2 Dibasic acid [9]

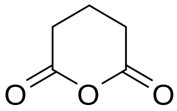
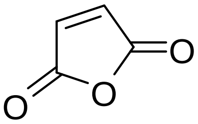
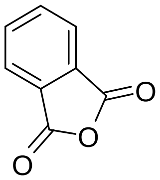
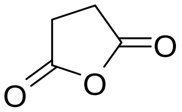
1. Phthalic anhydride has traditionally been the leading dibasic acid used for alkyd production

2. Isophthalic acid produces alkyd resins of higher viscosity and slightly faster drying, but the batch conditions for cooking vary from the phthalic anhydride cook, because isophthalic acid is not soluble in oil at low temperatures, and batch temperarure must be high enough to eliminate –isophthalic haze”.

3. Maleic anhydride undergoes a Diels-Alder reaction across the unsaturation of the oil produce alkyd of high viscosity and fast dry. However, its functionality is high and early gelation may occur if maleic anhydride is used alone. It is often employed in very small amounts as a viscosity controller.

In case of dibasic acid, phthalic anhydric is the most favorite use because its low cost, stable at synthetic varnish’s temperature and good resistance to ultraviolet ray [10,21]. Then, phthalic anhydride are always use for preparing to alkyd resin in most of research works [11, 14-17, 20-21, 27]. However, using maleic anhydride as disbasic acids is appeared in some work [16]. Form history of phthalic anhydride usage it was rather the same as glycerol because both substances were used as material for alkyd resin at the same time [22].

Table 2.8 The chemical structures, molecular weights and acid values of anhydrides.

Anhydride	Code	Acid Value	Formula
Glutaric anhydride	GA	983.4	
Maleic anhydride	MA	1144.2	
Phthalic anhydride	PA	757.5	
Succinic anhydride	SA	1121.1	

2.7.2.3 Monobasic acid

While the preparation of alkyd resin involves hydroxyl and carboxylic acid groups, the cross-linking reaction may depend on excess of these functionality groups. Thus, monobasic acid from fatty acid of oil in nature are used for decrease reactivity of polyhydric alcohol.

The natural oil used as monobasic acid are soybean [17], sunflower seed oil [9,13], peanut seed oil [6], rice bran oil [11], rubber seed oil [11], linseed [6], Nahar seed oil [9] and castor oil [15, 22-23] etc.

2.7.2.4 Solvents

Types of solvents used for alkyd resin dilition are also classified using oil content as follow: [9, 2]

1. Short-oil alkyds: suitable solvent for aromatic such as xylene and toluene.

2. Medium-oil alkyds: suitable for aliphatic solvent or a mixture solvent of aliphathatic and aromatic solvent such as a mixture solvent of white spirit and toluene.

3. Long-oil alkyds: have a suitable solvent as aliphatic solvent such as white spirit.

2.8 Alkyd resin processin

Various production processes of alkyd resin have reported, but only 2 processes are practically well know [8, 27] as follows:

2.8.1 Fatty acid process [27]

Free fatty acid from hydrolysis of oil is mixed by glycerol and phthalic anhydride. They have been heat at 240 ± 5°C and flushed with nitrogen gas for eliminate oxygen gas. Alkyd resin were prepared to have a light color.

2.8.2 Alcoholysis process [8]

Glycerol and oil were heated at T1 = 240 ± 5°C, which is temperature of monoglyceride process and flushed with nitrogen gas, and has the alkaline as catalyst. Products were prepared as diglyceride and monoglyceride. Next, it was cooled to T2 = 230 ± 5°C, which is alkyd resin process, and added phthalic anhydride, as the reaction show in figure 2.9[8].

However, the alcoholysis process is more favorite than fatty acid process, because oil can be used as monbasic acid without fatty acid separation from oil.

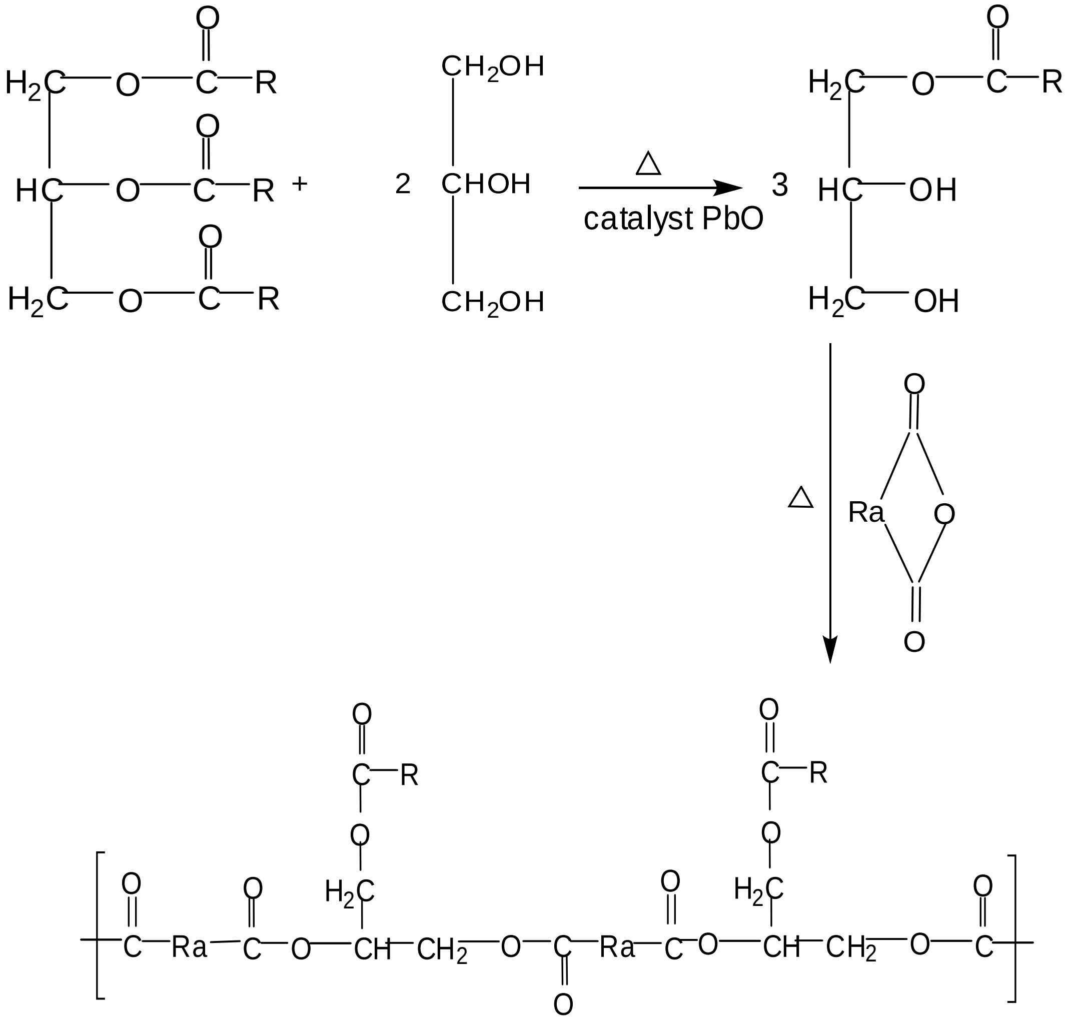


Figure 2.10 Polymerization reaction of alkyd resin from alcoholysis process [8].

2.9 Modified alkyd resin

The advantages and disadvantages of modification alkyd resins with modifiers are shown in Table 2.7 [9]

Table 2.7 Modified alkyd resins.

Modifier	Advantages	Disadvantages
rosin or rosin ester	- fast dry - better brushing - greater harness - better mar resistance - better adhesion	- more yellowing - decrease exterior - durability when - use in excess
phenolic	- greater hardness - better water resistance - better alkali resistance - better solvent resistance	- more yellowing - poorer stability - drier problems
styrene, vinyl toluene methyl methacrylate	- faster dry improved color and gloss	- poorer solvent resistance
acrylonitrile	- improved color and gloss retention - improved chemical resistance	
silicones	- improved heat resistance - greater hardness - more resistance to thermal shock	- higher cost - higher curing temperature
Hydroabietyl Alcohol (Abitol,trademark Hercules powder Co.)	- better brushing - reduce alkyd - functionality and acts as gelation inhibitor solubility (in aliphatic solvent) - better gloss - better flow - greater hardness	- slightly more yellowing - slightly decrease - durability - used in exess
p-tert-butylbenzoic acid, benzoic acid	- reduces alkyd functionality and acts as a gelation inhibitor - greater hardness - higher viscosity - faster dry - improved color and gloss - improved chemical resistance	- poorer solubility - poorer flexibility
epoxides	- improved adhesion - better alkali resistance - better detergent resistance - better solvent resistance	- poorer color - retention - rapid chalking
isocyanates	- better water resistance - faster dry - better abrasion resistance	- Greating yellowing - toxicity problem (in manufacture)

2.10 Applications of alkyd resins

Alkyd resins are polyester-based materials that are normally modified with oil or fatty acids. These products may be further modified with a variety of other chemical materials. Various polybasic acid, polyhydric alcohol, oils, fatty, acid and modifying agents may be combined to produce alkyd with specially desighed properties. The precise combination of the ingredients used, together with the careful control of the reaction, influences the final properties of the alkyd produced. For this reason, many alkyds are available o the coating formulator. In considering the applicatons of alkyd resins, it is convenient to take them in order of decreasing oil length [9].

2.9.1 Long oil alkyds: (>60%oil)

Long oil length is usually prepard from drying and semi-drying oils, with pentaerythritol being the preferred polyhydric alcohol. The most common oils used are linseed and the semi-drying oils, soya, safflower, sunflower and tall oil.

All the resins in this range are soluble in low order aliphatic solvents, permitting excellent brushing properties with good maintenance as brushing enamels, undercoats and primers and also marine paints. Their slowness to dry and lack of response to force drying has prevented their use in industrial finishes.

2.9.2 Medium oil alkyd : (40-60%)

Products in this range are probably the most versatile of all the alkyd. In general, all-round durability is better than among their longer or short relations. They still maintain solution in low boiling aliphatic solvents, enabling brushing paints to be prepared but they can also be produced in faster evaporating solvents for industrial spray applications.

The most commonly used unmodified medium oil length alkyd are based on linseed oil. Color retention is not a problem since they are generally used in exterior situations. Alkyds of this type are extensively used in anti-corrosive primers and in general maintenance painting applications. Fish oil based medium oil length alkyds are also employed in such paints.

2.9.3 Short oil alkyds : (<40%oil)

Unmodified short drying oil alkyds are typically made of linseed, soya or dehydrated caster oils. The linseed-based alkyds are used in automotive refinishing enamels and in general purpose industrial air drying enamels. They also perform well in force dry and low bake situations. Soya and dehydrated castor oils can be used in air drying system but they tend to be too slow-drying for most applications. They perform well in force drying and baking system, either with metal driers or when modified with amino resins. In these cases, they have good baking properties with excellent film characteristies; their color retention is only fair and they are not used in light colored paints that are liable to be overbaked. Low-rosin-containing tall oil alkyds have good color retention on baking with amino resins and are used as basis for most industrial baking enamels where high durability is not required.

2.11 Epoxidation theory [10]

Epoxidation means the oxidation of alkenes which we usually mean the reactions of alkenes that form carbon-oxygen bonds. These reaction are particularly important because many of the common functional groups contain oxygen, and alkene oxidations are some of the best methods for introducing oxygen into organic molecules. We consider methods for epoxidation, hydroxylation, and oxidative cleavage of the double bonds of alkenes.

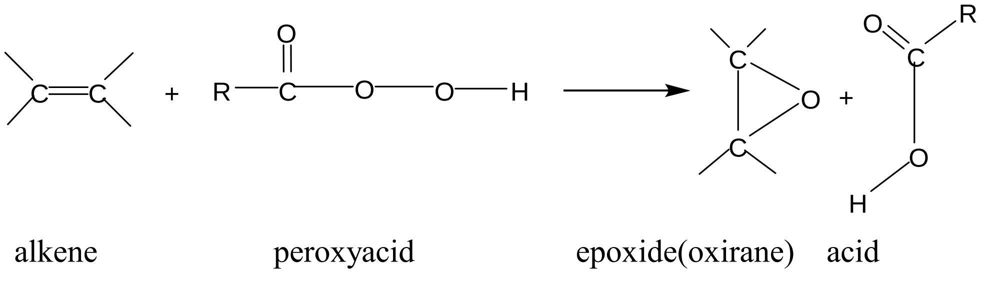
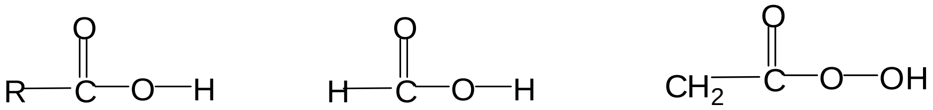


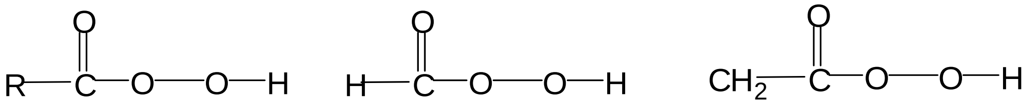
Figure 2.11 Segment of the epoxidation of alkenes.

An epoxide is a three-membered cyclic ether, sometimes called an oxirane. Epoxides are valuable synthetic intermediates, used to convert to an epoxide by a peroxyacid, a carboxylic acid that has an extra oxygen atom in a –O-O- (peroxy) linkage. The epoxidation of an alkene is clearly an oxidation since an oxygen atom is added. Some common peroxyacids (sometimes called peracids) and their corresponding carboxylic acid are shown below.



$R-\overset{O}{\overset{\|}{C}}-O-H \qquad H-\overset{O}{\overset{\|}{C}}-O-H \qquad CH_2-\overset{O}{\overset{\|}{C}}-O-OH$

Carboxylic acid formic acid acetic acid



$R-\overset{O}{\overset{\|}{C}}-O-O-H \qquad H-\overset{O}{\overset{\|}{C}}-O-O-H \qquad CH_2-\overset{O}{\overset{\|}{C}}-O-O-H$

Peroxyacid peroxyformic acid peroxyacetic acid

Benzoic acid peroxybenzoic acid

Figure 2.12 Structure of some common peroxyacids.

A peroxyacid epoxidizes an alkene by a concented eletrophilic reaction where seven bonds are broken and several bonds are formed at the same time. Starting with the alkene and the peroxyacid, a one-step reaction gives the epoxide and the acid directly. Synthesis and reactions of epoxides are unlike those of other ether. How we review the epoxidantion techniques already covered, and see how the Williamson ether synthesis is applied to the synthesis of epoxides.

Peroxyacids are used to convert alkenes to epoxides. Since the peroxyacid is strongly acidic, the epoxide opens to a glycol. Therefore, a weak peroxyacid is used to make an epoxide. The epoxidation takes place in a one-step, concerted reaction that maintains the stereochemistry of any substituents on the double bond.

2.12 Literature reviews

In 1995, Aigbodion A. et al. [11] The kinetics of the polyesterification of glycerol, phthalic anhydride and rubber seed oil leading to the formation of alkyd resins were studied at temperatures between 230 and 250°C. Six samples of the resin having oil contents of 20% (I), 30% (II), 35% (III), 40% (IV), 50% (V) and 60% (VI) were prepared. The extent of reaction (PA) and average degree of polymerization (Dp) were calculated from end group analysis of aliquots of the reaction mixture withdrawn at various intervals of time. The average degree of polymerization calculated in the region of deviation from second order kinetics suggests the occurrence of chain branching at relatively short intervals along the polymer chain. The second order rate constants were found to be of the order of 10^{-5} g (mg KOH)$^{-1}$ min^{-1}.

In 2001, Derouet D. et al. [12] Studied addition of alcohols into 4,5-epoxy-4-methyloctane using cerium ammonium nitrate as catalyst with the aim to generalize the procedure to the alcoholysis of epoxidized polyisoprene. The formation of each identified product could be explained by S_N2 mechanism. The results showed that decreasing in β-alkoxy alcohol yield was always compensated by an increasing of the yield in two side products, epoxide rearrangement products and β-nitrato alcohol, which results from a direct reaction between the epoxide and the catalyst. However, the rearrangement of epoxide was still highly predominant compared to β-nitrato alcohol formation.

In 2002, Antolin G. et al. [13] Studied the optimization of biodiesel production of sunflower oil transesterification. The results showed that 96% of methyl ester was achieved at 70°C using 0.28% w/w of potassium hydroxide as a catalyst with an excess amount of methanol. According to European standard, the sunflower methyl ester could be used as diesel fuels.

In 2004, Aydin S. et al. [9] Studied the effect of anhydride type and amount on viscosity and film properties of alkyd resin from sunflower oil which was prepared by modified method compared with classical method. The results showed that modified method gave low viscosity resins and resins with the same or better film properties than resins from classical method. In addition, high solid content alkyd resin could be prepared with the modified method because of their low viscosity and good film properties.

In 2005, Weerawatsophon U. [14] Prepared of oil-modified alkyd resin from waste cooking oil using alcoholysis process compared with alkyd resin from palm olein oil was studied. Waste cooking oil, glycerol, phthalic anhydride and mixture of NaOH, H_2O and glycerol were used as monobasic acid, polyhydric alcohol, dibasic acid and catalyst, respectively. The results showed that waste cooking oil could be used as raw material for alkyd resin production. The optimum condition, 35% w/w oil with the reaction time of 160 min, gave acid value, viscosity and non-volatile matter of 13.28 mg.KOH/g., 17.60 stoke and 59.05% w/w, respectively. For environmental consideration, although alkyd resin from waste cooking oil used more reaction time than alkyd resin from palm olein oil but it is reasonable that using waste cooking oil as monobasic acid is better alternative for oil-modified alkyd resin production.

In 2008, Nway N.H. et al. [15] The Oil-modified alkyd resin was prepared from crude castor oil. The experiment started with investigating the optimum conditions for neutralization of crude castor oil and bleaching of neutralized oil. These results showed that the refined oil was qualified to prepare dehydrated castor oil. Dehydration of refined oil was carried out at 210-220°C under 600-640 mmHg with the help of 1%(wt%) $NaHSO_4$ catalyst. The dehydrated castor oils were analyzed for iodine value, viscosity and its set to touch time and drying time were also investigated. Dehydrated castor oil has iodine value of 140, kinemetic viscosity of 1.6 St, set to touch time of 4 hr and drying time of 5 days. And then, oil modified alkyd resin (acid value 6.6) was prepared from dehydrated castor oil by alcoholysis method in excess of glycerol and phthalic anhydride in the presence of 0.3% (wt%) NaOH catalyst. The physico-chemical properties and high chemical resistance of alkyd resin film showed that they were promising in formulating of paint.

CHAPTER III

MATERIALS AND METHODS

3.1 Materials

3.1.1 Chemicals

1. Anhydrous sodium sulfate: analytical grade; Carlo Erba
2. Chloroform-d: NMR spectroscopy grade; Merck
3. Commercial palm oil; Morakot
4. Dimethyl sulfoxide
5. 99.5% Glycerol: analytical grade; Carlo Erba
6. Glacial acetic acid: analytical grade; Merck
7. Hexane: analytical grade; Lab-Scan
8. 37% Hydrochloric acid: analytical grade; Merck
9. Methanol: analytical grade; Merck
10. 95-97% Sulfuric acid analytical grade; Merck
11. Phthalic anhydride: analytical grade; Sigma-aldrich

3.2 Instrument

3.2.1 Fourier transform Infrared Spectrometer (FT_IR)

The FT-IR spectra were recorded on a Perkin Elmer, Nicolet Impact 410 Fourier Transform Infrared Spectrophotometer. Soild samples were formally examined by incorporating the sample with potassium bromide (KBr) to form a pellet. Liquid sample was coated on the KBr disk.

3.2.2 Nuclear Magnetic Resonance Resonance Spectroscopy (NMR)

The ^1H NMR spectra and ^{13}C NMR spectra were recorded on a Varian, model Mercury+400 nuclear magnetic resonance spectrometer operating at 400 MHz. Chemical shifts (δ) are reported in part per million (ppm) relative to tetramethylsilane (TMS) or using the residual protonated solvent singnal δ_H 5.1-5.4, 2.5-2.7, 2.7-3.1, 74.6 and 173 ppm as a reference.

3.3 Experiments

3.3.1 Properties of vegetable oils.

The properties of soybean oil (SBO), palm oil (PO) and sunflower oil (SFO) including iodine value and saponification value were determined according to ASTM D5555, ASTM D5558 and ASTM D5554 standards, respectively.

3.3.2 Preparation of epoxidized soybean oil (SBO), palm oil (PO) and sunflower oil (SFO). [25]

Epoxidation of Soybean oil was carried out in a 250-ml two-necked round-bottom flask with a stopper and stirrer. Soybean oil (SBO) (65 g, 0.075 mol) was placed in the round-bottom flask. Peracetic acid prepared *in-situ* by reacting with 99.5% glacial acetic acid (16 g, 0.27 mol) with 35% H_2O_2 (46.24 g, 0.68 mol) in the presence of small quantities of concentrated sulphuric acid for about 3 hr was added slowly to the SBO in the round-bottom flask. The reaction mixture was stirred with a mechanical stirrer and heated to maintain the reaction temperature at 80°C.

At the end the mixture was quenched by cooling with ice bath to stop the epoxidation reaction. The mixture was separated by separation funnel. The oil layer was washed with saturated sodium carbonate solution until the pH was neutral. Then the oil layer was washed with saturated sodium chloride solution and distilled water. The oil phase was dried over anhydrous sodium sulfate and then filtered.

To obtain EP_PO and EP_SFO, the procedure was carried out as above mentioned by using palm oil (PO) and sunflower oil (SFO) instead of SBO.

3.3.3 Preparation of polyester

To a three-necked round-bottomed flask equipped with condenser and nitrogen gas inlet epoxidized soybean oil (EP_SBO) (20 g, 0.024 mol) and glycerol (2 g, 0.022 mol) were added and the reactor was flushed with nitrogen gas throughout the reaction. The mixture was heated at various temperture; 110°C, 130°C, 150°C, 170°C and 240°C for 1 hour and phthalic anhydride (5 g, 0.034 mol) was then added. The reaction mixture was stirred with a magnetic stirrer and heated to maintain the reaction temperature for 2 hour. The product was allowed to cool to room temperature and charaterized by using FT-IR spectroscopy.

The same procedure as above was pereformed with sulfuric acid (0.05g, 0.00051 mol) and glacial acetic acid (2 g, 0.0083 mol) as a catalyst.

3.4 Viscosity average molecular weight (M_v)

Intrinsic viscosity $[\eta]$ of the polymer solutions was measured by using an Ubbelohde viscometer at 30°C in DMSO to calculate for viscosity average molecular weight (M_v) following by equations. The solutions were filtered through a disposable membrane filter (0.2 μm) prior to the measurement**.**

$$[\eta] = KM_V{}^{a}$$

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_{re})}}{C}$$

where, η_{re} is relative viscosity or viscosity ratio (efflux time ratio between the solution (t) in a determined concentration, and the solvent (t_0), i.e. $\eta_{re} = t / t_0$); η_{sp} is specific viscosity ($\eta_{sp} = \eta_{re} - 1$); C (g/mL) is polymer solution concentration; $[\eta]$ is intrinsic viscosity; K and a are related to the "stiffness" of the chain depending on the type of polymer, solvent, and temperature [28].

3.5 Measurement of mechanical properties.

3.5.1 Tensile strength

The tensile strength of the polyester was determined according to ASTM D638 using the dumbbell-shaped specimens as shown in Figure 5.1. ASTM D638 : Standard test method for tensile properties. The test specimen dimension was presented in Figure 5.1.

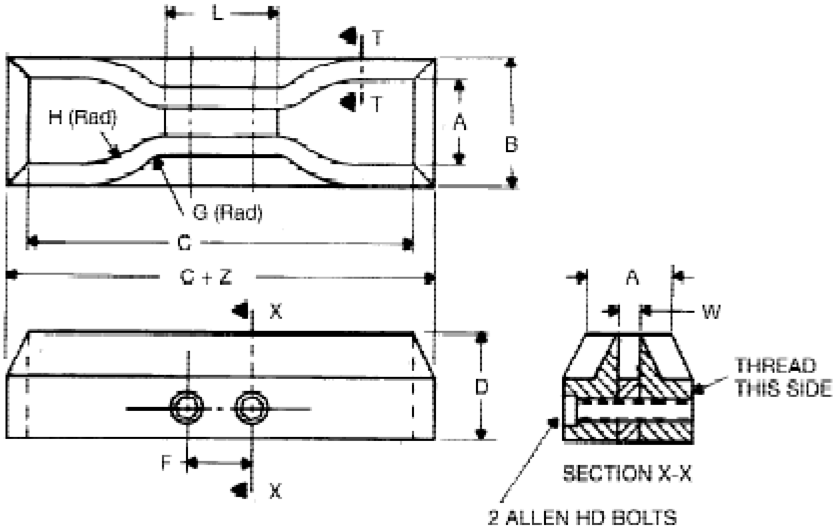


Figure 3.1 Specimen for tensile testing.

Where A = width of narrow section 25 mm.
L = length of narrow section 33 mm.
B = width of over-all 40 mm.
C+Z = length of over-all 155 mm.
G = gauge length 25 mm.
R = radius 14 mm.

Procedure

A specimen was gripped at the ends and pulled by the machine until fracture took place. The ultimate tensile strength was calculated from the applied load at a breaking point and the cross-sectional area of the specimen. Therefore, the tensile strength can be represented in terms of the following equation.

$$\text{Tensile Strength} = L/A$$

Where L = load at break, kgf
A = area, square mm^2

3.5.2 Hardness

Hardness by pencil test of the polyester was determined according to ASTM D3363-05: Standard test method for film hardness by pencil test.

Procedure

A coated panel is placed on a firm horizontal surface. The pencil is held firmly against the film at a 45^o angle (point away from the operator) and pushed away from the operator in a 6.5 mm ($^1/_4$ in.) stroke. The process is started with the hardest pencil and continued down the scale of hardness to either of two end points: one, the pencil that will not cut into or gouge the film (pencil hardness), or two, the pencil that will not scratch the film (scratch hardness). The pencil test for film hardness was measured by using mechanized scratch test apparatus as shown in figure 3.2.

Figure 3.2 Mechanized scratch test apparatus.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Determination of vegetable oils properties

The properties of soybean oil (SBO), palm oil (PO) and sunflower oil (SFO) including iodine value saponification number and fatty acid composition were determined by ASTM D5554, ASTM D5558 and gas chromatographic analysis, respectively. The results are shown in Table 4.1, it could be seen that SFO had the highest iodine value referred to the highest amount of double bond in the structure when compared to SBO and PO. The saponification number of PO was highest due to the shortest chain length of hydrocarbon in the structure. Considering the fatty acid compositions of oils, PO contained the highest amount of saturated fatty acids, whereas, SFO contained the highest amount of unsaturated fatty acids which related to the highest iodine value in the oil.

In this research, polyesters were prepared by condensation polymerization from the epoxidized soybean oil (EP_SBO), palm oil (EP_PO) and sunflower oil (EP_SFO) as vegetable oils. Glycerol and phthalic anhydride had been used as polyhydric alcohol and dibasic acid, respectively.

Table 4.1 Properties of Vegetable Oils.

Properties	**Soybean oil (SBO)**	**Palm oil (PO)**	**Sunflower oil (SFO)**
Iodine value (mg.I_2/100 g.)	**120.58**	**61.33**	**130.50**
Saponification number (mg KOH/g)	**188.23**	**202.74**	**191.00**
Saturated fatty acid (%)	**20.22**	**42.97**	**12.00**
C 12:0 Lauric acid	-	0.32	-
C 14:0 Myristic acid	-	0.95	-
C 16:0 Palmitic acid	10.93	37.47	7.00
C 18:0 Stearic acid	8.28	3.88	5.00
C 20:0	0.34	0.35	-
C 22:0	0.4	-	-
C 23:0	0.12	-	-
C 24:0	0.15	-	-
Unsaturated fatty acid (%)	**79.78**	**57.04**	**88.00**
C 18:1 Oleic acid	19.9	45.92	19.00
C 18:2 Linoleic acid	52.7	11.12	68.00
C 18:3 Linolenic acid	5.87	-	1.00
C 20:1	0.33	-	-
Unknown	0.98	-	-
Average molecular weight* (g/mol)	867.02	853.76	876.00

** Calculation method Average molecular weight (see appendix B)*

4.2 Preparation of epoxidized soybean oil (EP_SBO), epoxidized palm oil (EP_PO) and epoxidized sunflower oil (EP_SFO).

Vegetable oils (SBO, PO and SFO) were epoxidized by peracetic acid, obtaining from the reaction of glacial acetic acid with hydrogen peroxide in a presence of small amount of conc. sulfuric acid as a catalyst. The vegetable oils and epoxidized vegetable oils were characterized by using ^{1}H-NMR and FT-IR spectroscopy. The results of ^{1}H-NMR were shown in Figure 4.1 - 4.3 and the results of FT-IR Spectroscopy were shown in Figure 4.4 - 4.6.

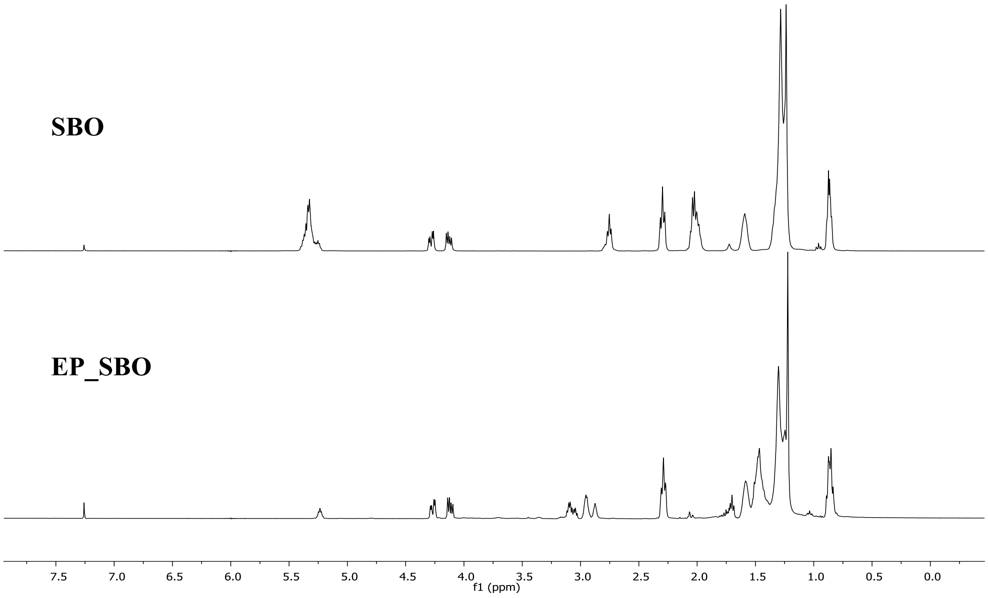


Figure 4.1 ^{1}H-NMR spectra of SBO and EP_SBO (in $CDCl_3$).

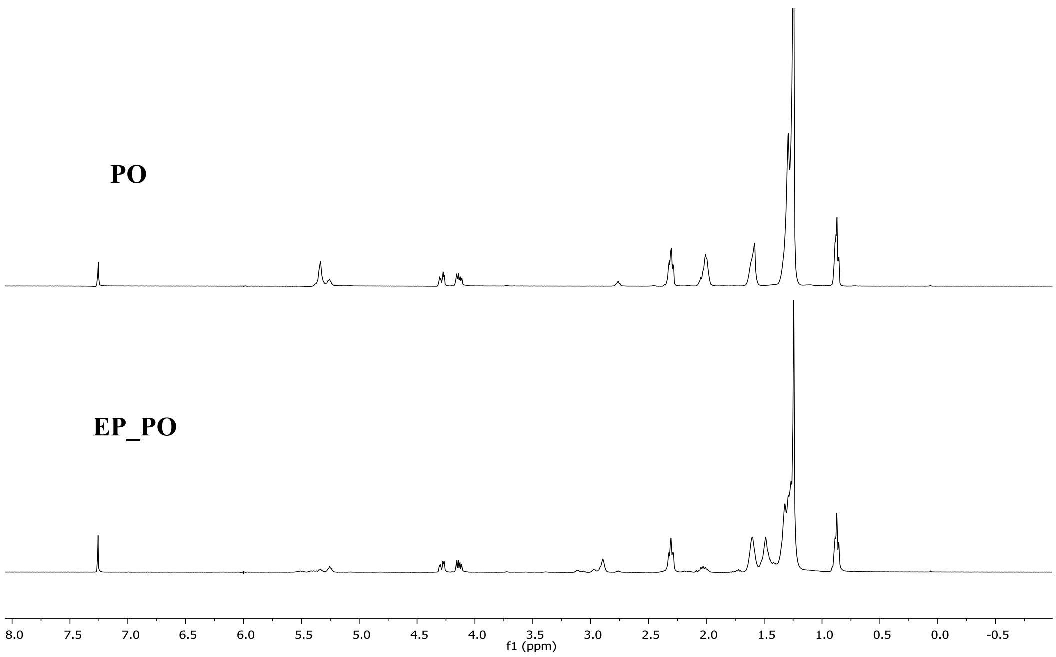


Figure 4.2 ^{1}H-NMR spectra of PO and EP_PO (in $CDCl_3$).

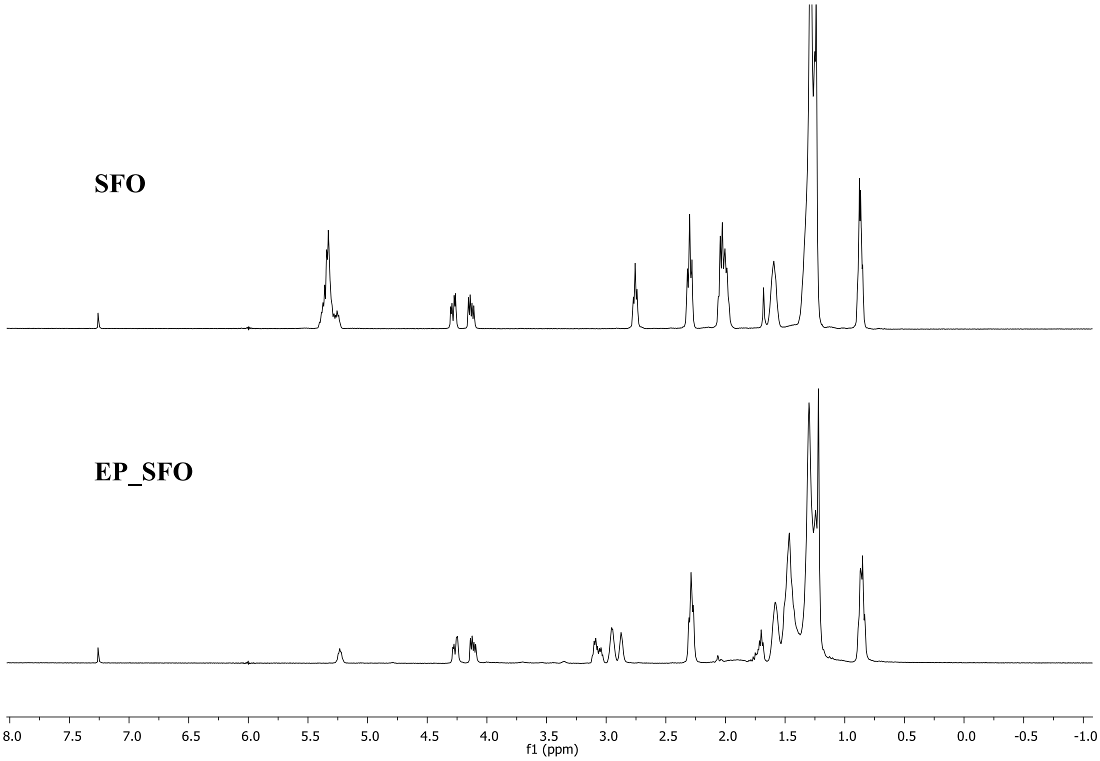


Figure 4.3 ^{1}H-NMR spectra of SFO and EP_SFO (in $CDCl_3$).

^{1}H-NMR spectra of the epoxidized oil in Figure 4.1-4.3 showed that signals of olefinic protons (<u>H</u>C=C<u>H</u>) at δ_H 5.1-5.4 ppm was decreased and the signal of allylic protons at δ_H 2.5-2.7 ppm was disappeared while signals of protons of oxirane moiety at δ_H 2.7-3.1 ppm were displayed and glyceride protons at δ_H 4.1-4.3 ppm still remained. Thus, it could be confirmed that the epoxidation was occurred at the double bond site. The percent conversion of EP_SBO, EP_PO and EP_SFO calculated using integral values of protons of oxirane moiety and of olefinic protons (see appendix B) were 86%, 78% and 87%, respectively.

As can be seen in Table 4.2, average molecular weight of vegetable oils (SBO, PO and SFO) were increased after the epoxidation reactions were carried out. The average molecular weight of epoxidized oils (EP_SBO, EP_PO and EP_SFO) had the same trend as percent conversion of epoxidized oils which were 1853, 1621.10 and 2357.56 g/mol, respectively.

Table4.2 Average molecular weight vegetable oils and epoxidized oils.

Vegetable oils	Average molecular weight (g/mol)	Epoxidized oils	Average molecular weight (g/mol)
SBO	867.02	EP_SBO	880.78
PO	853.76	EP_PO	866.24
SFO	876.00	EP_SFO	889.92

From Figure 4.4-4.6, IR spectra of epoxidized vegetable oils (EP_SBO, EP_PO and EP_SFO) were almost identical, indicating the same functional groups and crucial IR absorptions were summarized in Table 4.3. The IR absorption of functional groups of polyester comprised of carbonyl absorption of esters (1745-1746 cm^{-1}) and C-O stretching absorption of ester (1237-1241 cm^{-1} and 1160-1164 cm^{-1}). The C-H stretching absorption of aliphatics were shown at 2853-2926 cm^{-1}. In addition, the absence of C-H vinyl aborption (3005-3008 cm^{-1}) indicated that vegetable oils could be mostly converted to epoxidized oils.

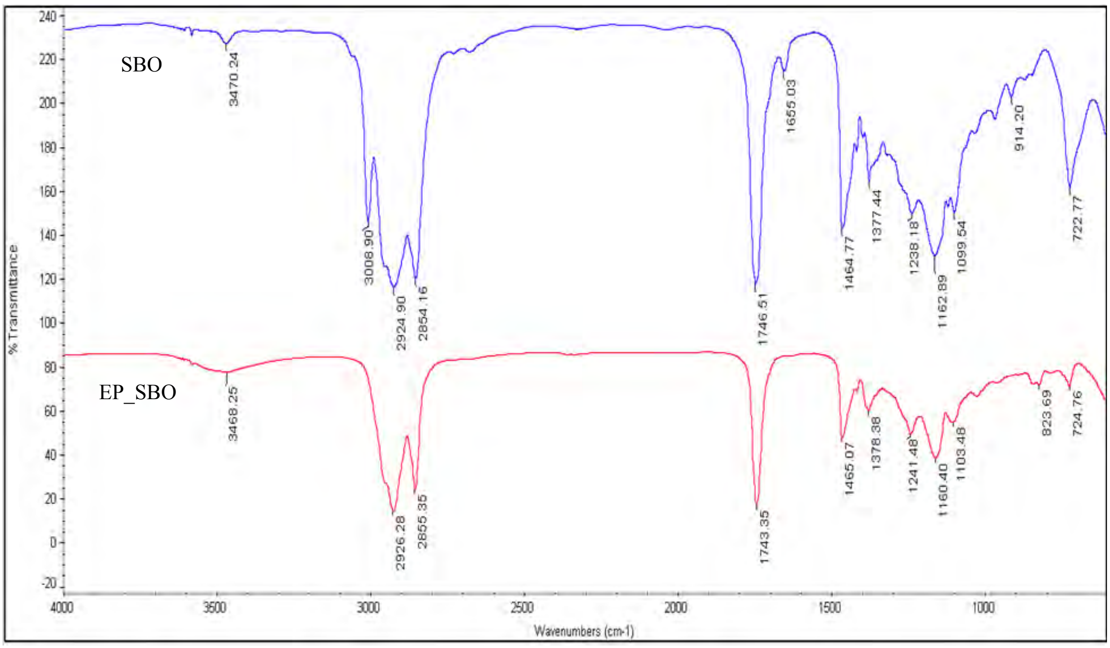


Figure 4.4 IR spectra of SBO and EP_SBO.

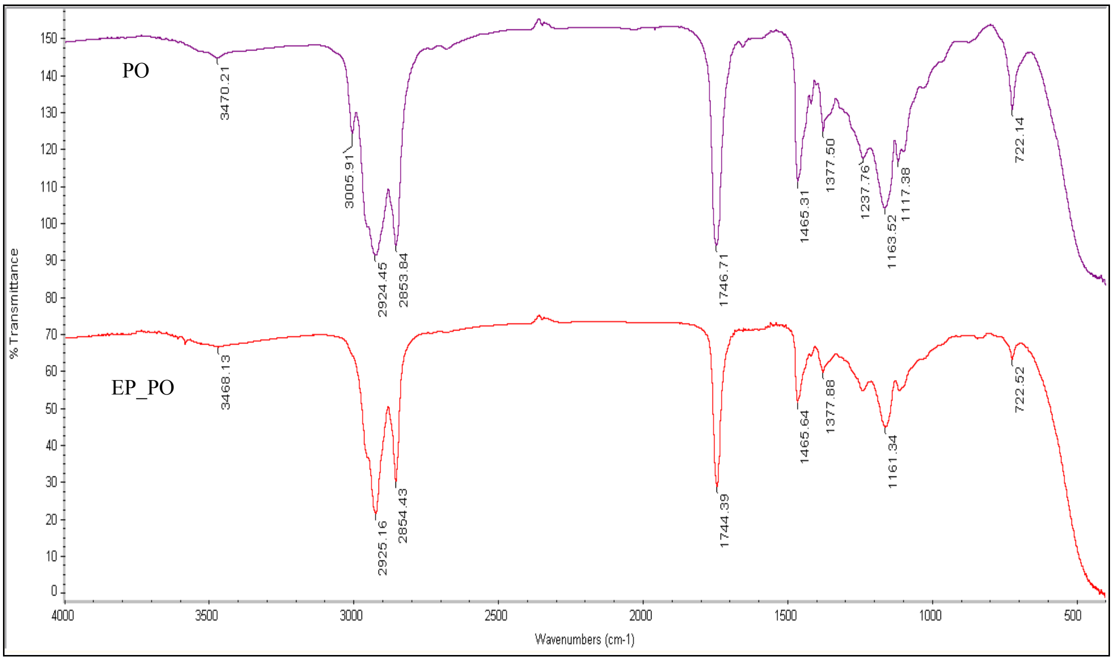


Figure 4.5 IR spectra of PO and EP_PO.

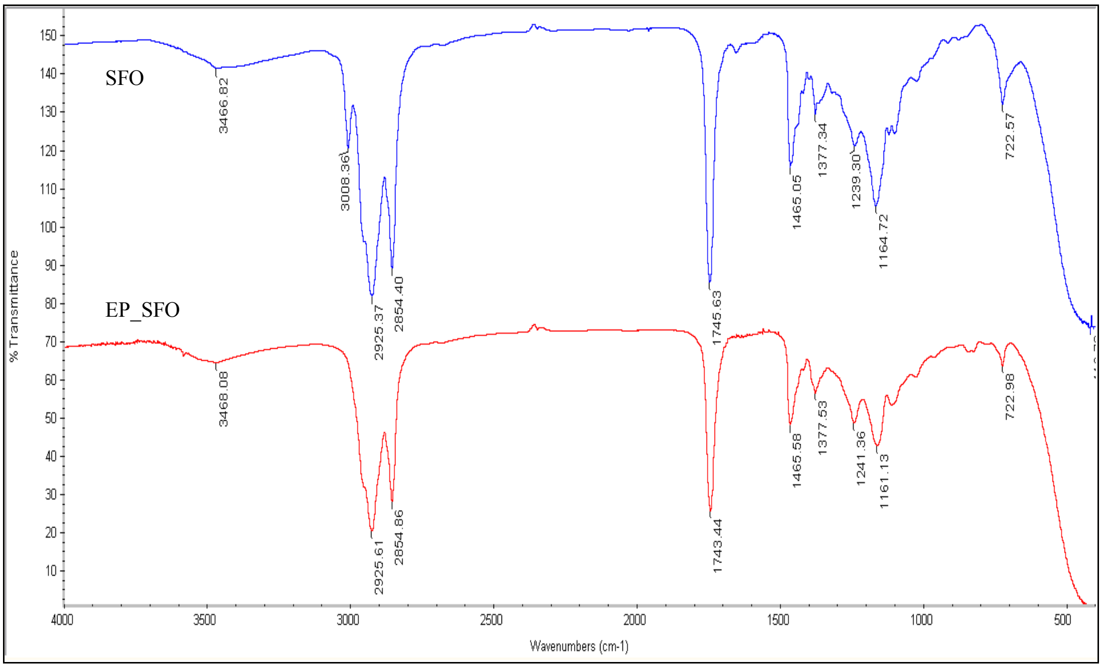


Figure 4.6 IR spectra of SFO and EP_SFO.

Table 4.3 Crucial IR absorption bands assignment of oils and epoxidized oils.

Absorption band (cm^{-1})						Functionality
SBO	EP_SBO	PO	EP_PO	SFO	EP_SFO	
1163 and 1230	1160 and 1241	1163 and 1237	1161 and 1237	1164 and 1239	1161 and 1241	C-O stretching peaks of ester
1746	1743	1746	1744	1745	1743	C=O carbonyl of ester
2854 and 2924	2855 and 2926	2853 and 2924	2854 and 2925	2854 and 2925	2854 and 2925	C-H stretching of aliphatic
3008	-	3005	-	3008	-	C-H vinyl
-	904	-	838	-	847	C-O stretching of oxirane moiety

4.3 Preparation of polyester

4.3.1. Optimization condition of condensation polymerization of polyester

To determine the ester produced in epoxidized oils before synthesizing polyesters, the ratio of carbonyl ester and aliphatic C-H stretching absorptions could be calculated by using the absorption area of carbonyl group of ester at 1723-1732 cm^{-1} compared to C-H stretching absorption at 2850-2923 cm^{-1}. The ratio of ester of EP_SBO, EP_PO and EP_SFO were shown in Table 4.4.

Table 4.4 Ratios of carbonyl ester and aliphatic C-H stretching absorptions of epoxidized oils before synthesizing polyesters.

Oils (mol)	Glacial acetic (mol)	35% H_2O_2 (mol)	Vegetable oils	Ratios of carbonyl ester absorption and aliphatic C-H stretching absorption
0.075	0.27	0.68	EP_SBO	0.32
0.076	0.27	0.68	EP_PO	0.29
0.074	0.27	0.68	EP_SFO	0.31

4.3.1.1 Effect of flowing Ar (gas)

From Figure 4.7, IR spectra of polyester from soybean oil (PS_SBO) at 110°C under conditions with and without Ar (gas) were identical and the absorption of carbonyl group of ester and C-O stretching of ester were at 1732 cm^{-1} and 1266 cm^{-1}, respectively. The C-H stretching of aliphatics were shown at 2854-2924 cm^{-1}. It could be concluded that Ar (gas) had no effect on synthesizing polyester.

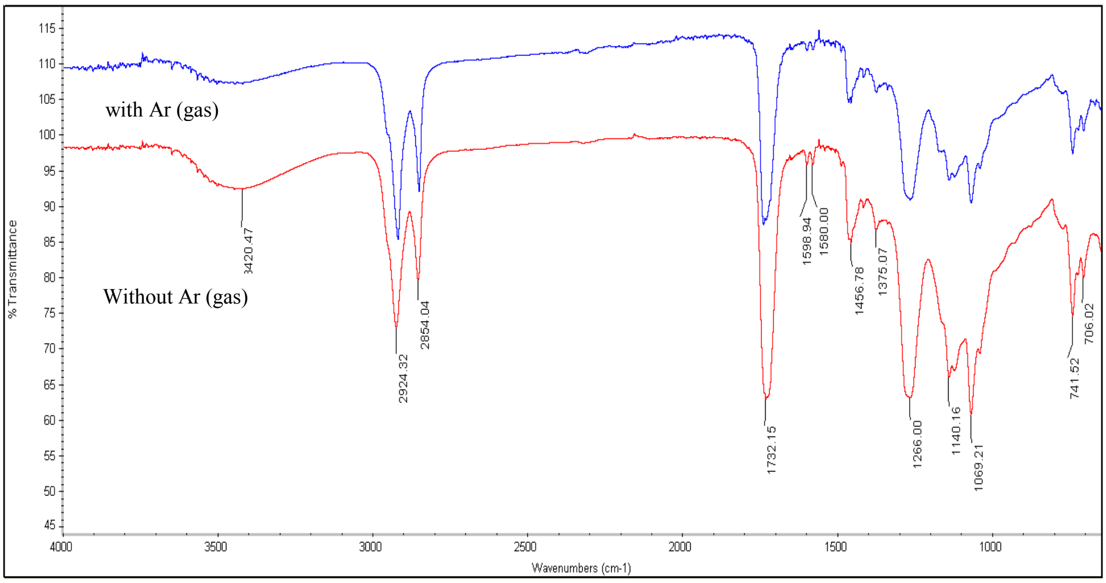


Figure 4.7 IR spectra of PS_SBO under the condition with and without Ar (gas) at 110°C for 3 hr.

4.3.1.2 Effect of the amount of glycerol on condensation into polyester

The effect of the amount of glycerol on condensation into polyester were investigated and condition for these investigation were shown in Table 4.5 and Table 4.6.

Table 4.5 Synthesized conditions of PS_SBO from EP_SBO using 0.0022 mol of glycerol.

Epoxidized Soybean Oils (Ep.SBO) (mol)	Glycerol (mol)	phthalic anhydride (mol)	Temp. (°C)	Time (hr.)
0.011	0.0022	0.034	240	3
0.011	0.0022	0.034	170	3
0.011	0.0022	0.034	150	3

From Figure 4.8, IR spectra of the PS_SBO at various temperatures were approximately similar. Since absorption of oxirane ring at 898-904 cm^{-1} and the absorption of C=O stretching of phthalic anhydride at 1724-1852 cm^{-1} were presented when using 0.0022 mol of glycerol, it was indicated that amount of glycerol was not enough for the reaction. In addition, higher temperature of the reaction resulted in increasing condensation into ester. In comparison of IR spectra in Figure 4.9, when using 0.022 mol of glycerol, the absorption of oxirane and phthalic anhydride were disappeared.

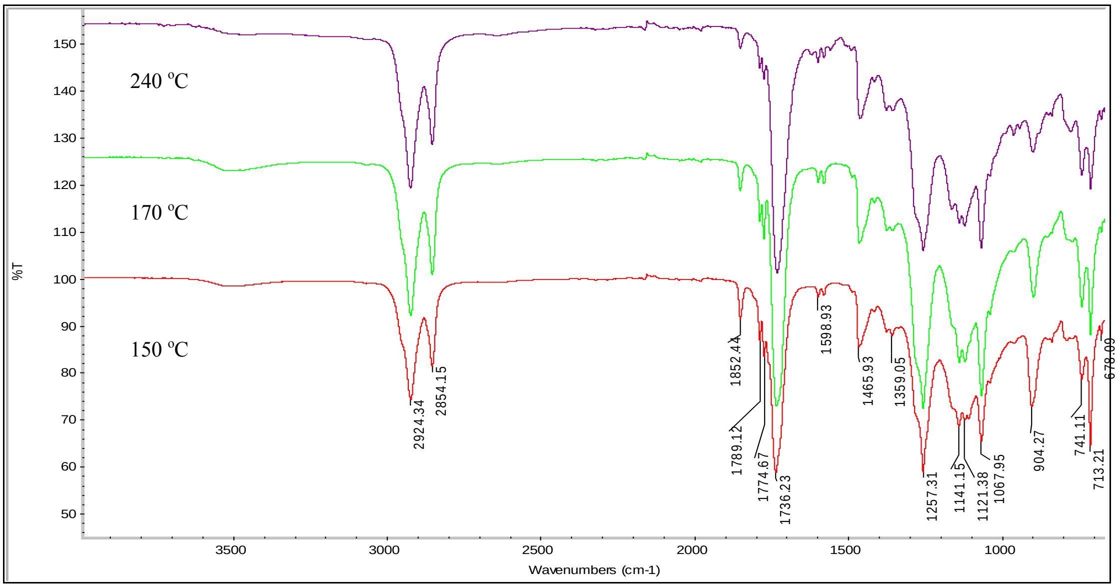


Figure 4.8 IR spectra of PS_SBO from condensation of phthalic anhydride, 0.0022 mol of glycerol for 3 hr.

Table 4.6 Synthesized conditions of PS_SBO from EP_SBO using 0.022 mol of glycerol.

Epoxidized Soybean Oils (Ep.SBO) (mol)	Glycerol (mol)	phthalic anhydride (mol)	Temp. (°C)	Time (hr.)
0.011	0.022	0.034	240	3
0.011	0.022	0.034	170	3
0.011	0.022	0.034	150	3

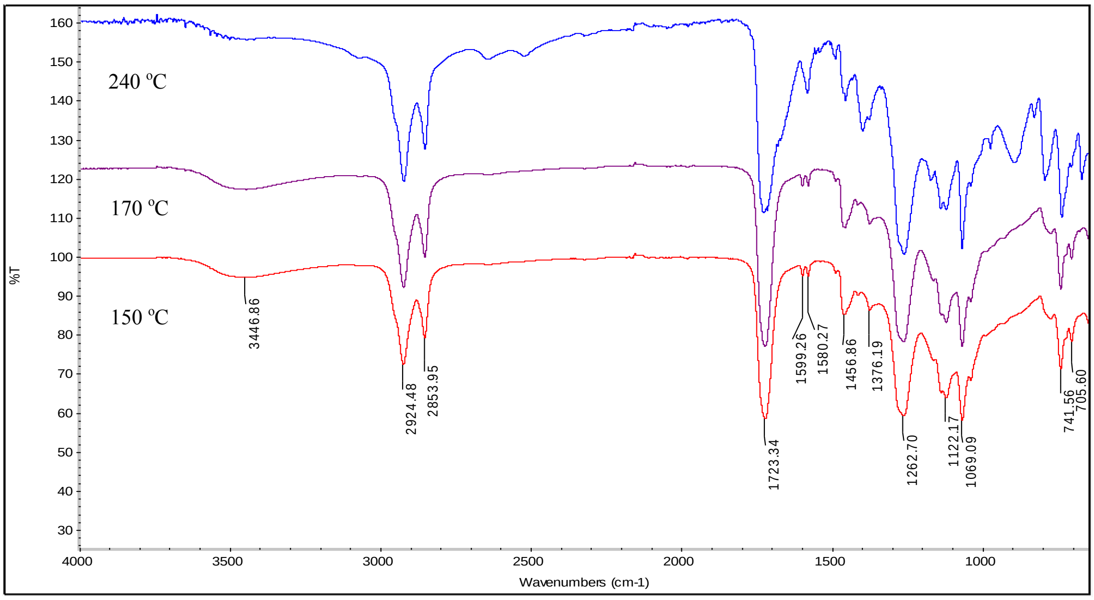


Figure 4.9 IR spectra of PS_SBO from condensation of phthalic anhydride, 0.022 mol of glycerol for 3 hr.

4.3.1.3 Effect of reaction time

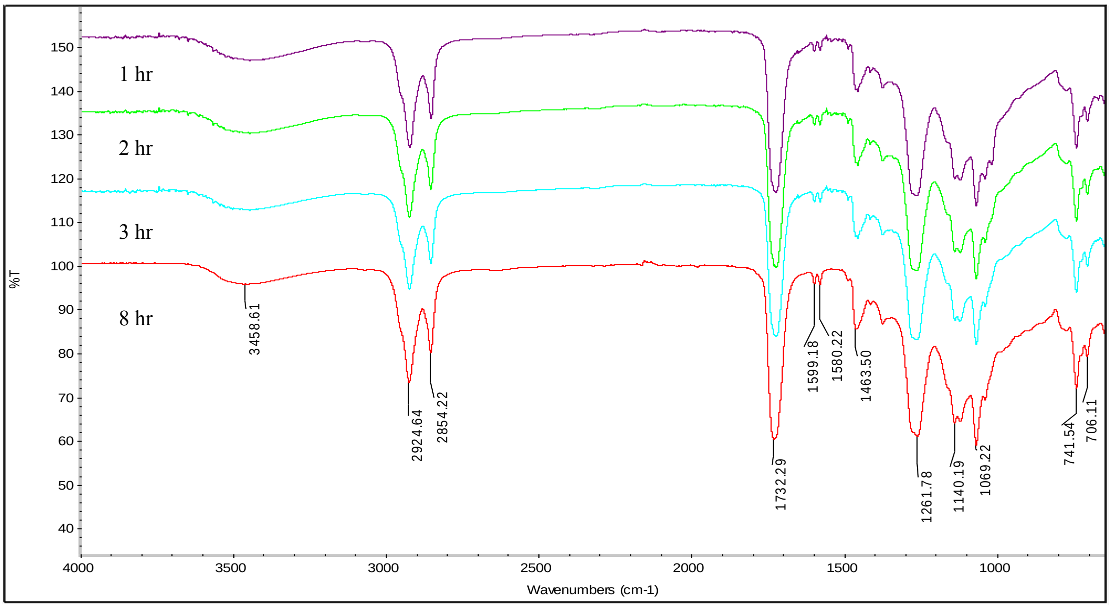


Figure 4.10 IR spectra of PS_SBO at various reaction times; 1 hr, 2 hr, 3 hr and 8 hr.

Polyesters were synthesized by using 0.022 mol of glycerol at various reaction times: 1hr, 2 hr, 3 hr and 8 hr. IR spectra (Figure 4.10) showed absorptions corresponding to esters similar to the section 4.3.1.1 (page 47).

Table 4.7 Ratios of carbonyl ester and aliphatic C-H stretching absorptions of PS_SBO at various reaction times.

Epoxidized Soybean Oils (Ep.SBO) (mol)	Glycerol (mol)	phthalic anhydride (mol)	Temp. (^{o}C)	Time (hr)	Ratios of carbonyl ester and aliphatic C-H stretching absorptions
0.011	0.022	0.034	110	1	1.03
0.011	0.022	0.034	110	2	1.04
0.011	0.022	0.034	110	3	1.05
0.011	0.022	0.034	110	8	1.05

From Table 4.7, the result showed that when using longer reaction time, the higher ratio of carbonyl ester and aliphatic C-H stretching absorptions was obtained. The intensity of carbonyl ester absorption was increased and the oxirane ring absorption was disappeared when the longer time was used due to the increasing of condensation polymerization. In addition, polyesters were darker at the higher temperature. At the reaction time of 3 hr, the ratio of carbonyl ester and aliphatic C-H stretching absorptions was the same as the reaction time of 8 hr. Due to the saving production time, the reaction time at 3 hr was chosen to perform in further studies.

4.3.1.4 Effect of the amount of phthalic anhydride

Polyesters were synthesized by using higher quanitity of glycerol at 110°C for 3 hr. The amounts of phthalic anhydride (PA) were varied from 0.020, 0.027 and 0.034 mol. The ratios of carbonyl ester and aliphatic C-H stretching absorptions were shown in Table 4.8.

Table 4.8 Ratios of carbonyl ester and aliphatic C-H stretching absorptions of PS_SBO at various amount of phthalic anhydride (PA).

Epoxidized Soybean Oils (Ep.SBO) (mol)	Glycerol (mol)	phthalic anhydride (mol)	Temp. (^{o}C)	Time (hr)	Ratios of carbonyl ester and aliphatic C-H stretching absorptions
0.011	0.022	0.020	110	3	1.05
0.011	0.022	0.027	110	3	1.10
0.011	0.022	0.034	110	3	1.20

From Table 4.8, it could be seen that the ratios of carbonyl ester and aliphatic C-H stretching absorptions were obtained when using higher amount of PA. The highest ratio was obtained when using 0.034 mol of PA. In addition, if the amount of PA was higher than 0.034 mol, the reaction could not be carried out because PA could not dissolve in the mixture.

4.3.1.5 Effect of catalyst

To determine the effect of catalysts on the condensation polymerization of polyester, the reaction could be performed by using 0.022 mol of glycerol and 0.034 mol of phthalic anhydride for 3 hr without flowing Ar (gas). The IR spectra of PS_SBO at various temperatures under 3 conditions such as using sulfuric acid (H_2SO_4) and glacial acetic acid (CH_3COOH) as a catalyst and without any catalyst were shown in Figure 4.11-4.13

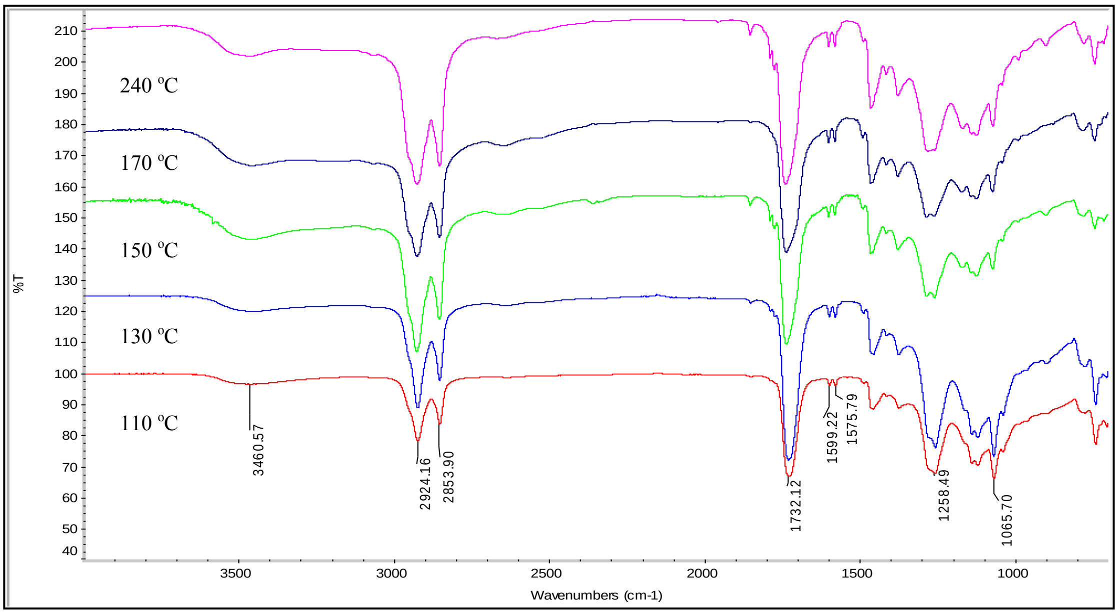


Figure 4.11 IR spectra of PS_SBO at various temperature using H_2SO_4 as a catalyst for 3 hr.

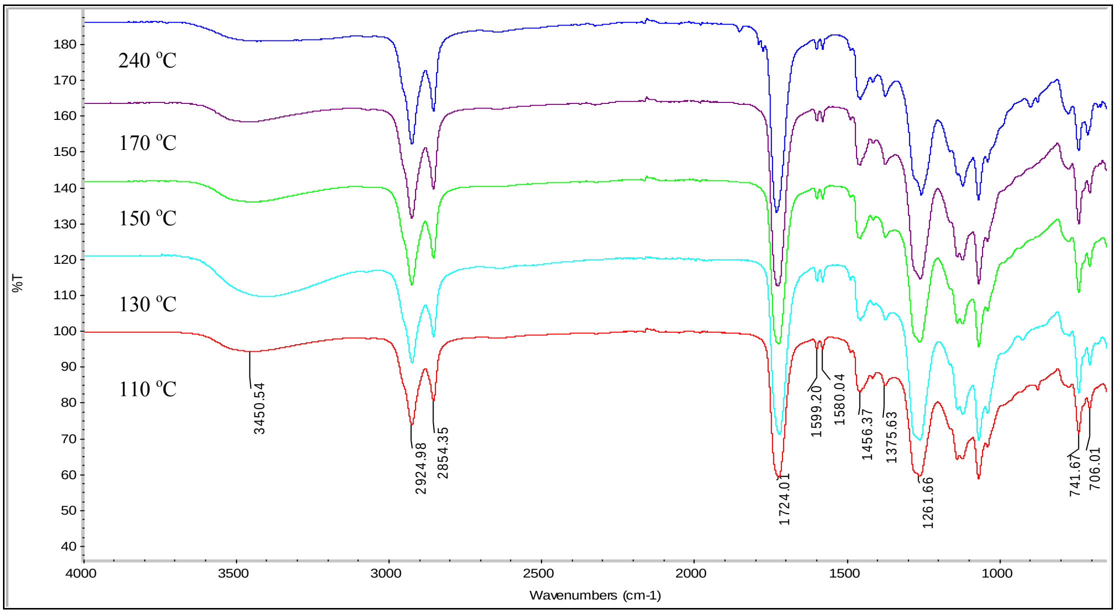


Figure 4.12 IR spectra of PS_SBO at various temperature using CH_3COOH as a catalyst for 3 hr.

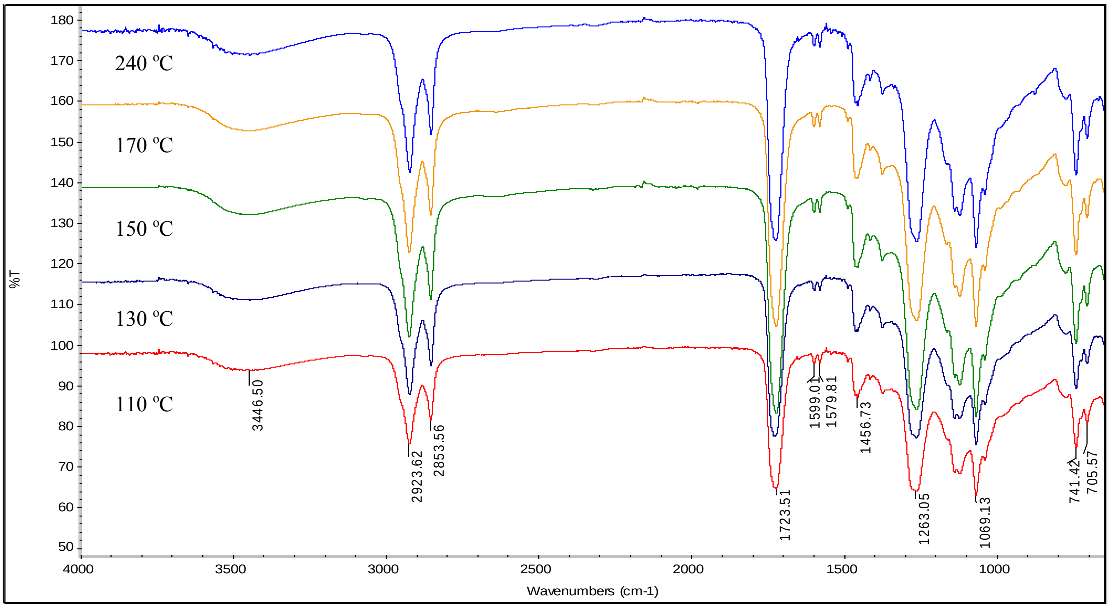


Figure 4.13 IR spectra of PS_SBO at various temperature without catalyst for 3 hr.

From Figure 4.11-4.13, IR spectra of PS_SBO under the conditions using sulfuric acid, glacial acetic acid and without using catalyst gave the same identical absorptions indicating the corresponding esters.

Table 4.9 Ratios of carbonyl ester and aliphatic C-H stretching absorptions of PS_SBO under various conditions of catalyst.

Epoxidized Soybean Oils (Ep_SBO) (mol)	Glycerol (mol)	phthalic anhydride (mol)	Temp. (°C)	Time (hr)	Ratios of carbonyl ester and aliphatic C-H stretching absorptions		
					Using H_2SO_4	Using CH_3COOH	Without catalyst
0.011	0.022	0.034	240	3	1.18	1.23	1.49
0.011	0.022	0.034	170	3	1.07	1.11	1.27
0.011	0.022	0.034	150	3	1.05	1.08	1.10
0.011	0.022	0.034	130	3	1.03	1.08	1.10
0.011	0.022	0.034	110	3	1.03	1.07	1.06

From Table 4.9, the ratios of carbonyl ester and aliphatic C-H stretching absorptions of PS_SBO at any temperatures were increased when compared to EP_SBO in Table 4.3 because carbonyl group absorption of esters at 1723-1724 cm^{-1} were increased due to the open ring of epoxide. In addition, the absorptions of C-O stretching absorption of ester at 1216-1263 cm^{-1} were also increased and the absorption of oxirane ring at 898-904 $cm\text{-}^{1}$ was disappeared at the same time. However, it could be seen that when using H_2SO_4 as a catalyst at 240°C, the absorption of C=O stretching absorption of phathalic at 1724-1852 cm^{-1} and the absorption oxirane ring at 904 $cm\text{-}^{1}$ were found because the epoxide ring was not mostly convert to ester.

As can be seen in Table 4.9, the ratios of carbonyl ester and aliphatic C-H stretching absorptions were lowest when using H_2SO_4 as a catalyst. When using CH_3COOH as a catalyst, the ratios were slightly different from the ratios of the absence of catalyst. In comparison of ratios of carbonyl ester and aliphatic C-H stretching absorptions, the highest ratio was obtained when catalyst did not use. Therefore, the optimum condition for synthesizing polyester should be performed without using catalyst for saving the production cost.

Considering the ratios of carbonyl ester and aliphatic C-H stretching absorptions of PS_SBO, the ratios were higher when using higher temperature. In the absence of catalyst, the ratio at 240°C was slightly higher than 110°C which were 1.49 and 1.06, respectively. It could be concluded that polyester could be synthesized at low temperature.

To determine the polyester from epoxidized palm oil (EP_PO, 0.012 mol) and sunflower oil (EP_SFO, 0.0085 mol), the reaction could be performed by using 0.022 mol of glycerol and 0.034 mol of phthalic anhydride for 3 hr without flowing Ar (gas) in the absence of catalyst.

4.3.2 Polyester from epoxidized palm oil

The polyesters from epoxidized palm oil on condensation polymerization were carried out by conditions as shown in Table 4.10.

Table 4.10 Synthesized conditions of PS_PO from EP_PO using 0.012 mol of glycerol.

Epoxidized Palm Oils (Ep_PO) (mol)	Glycerol (mol)	phthalic anhydride (mol)	Temp. (°C)	Time (hr)
0.012	0.022	0.034	240	3
0.012	0.022	0.034	170	3
0.012	0.022	0.034	150	3
0.012	0.022	0.034	130	3
0.012	0.022	0.034	110	3

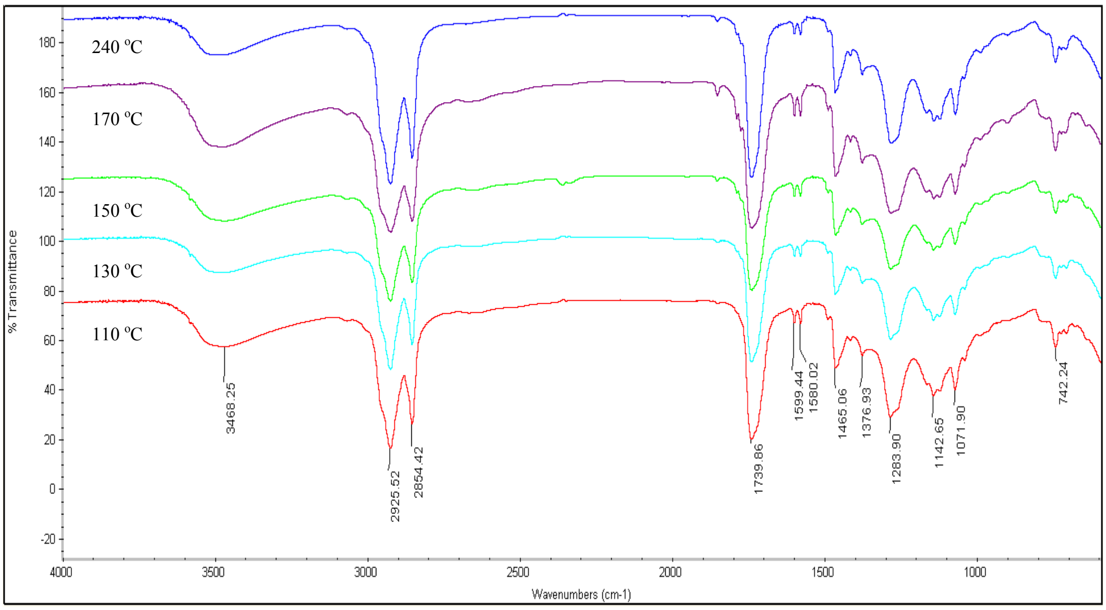


Figure 4.14 IR spectra of PS_PO at various temperatures under the optimum condition.

From Figure 4.14, the IR spectra of PS_PO at various temperatures under the optimum conditions obtained from the section 4.3.1 were identical comparing to the IR spectra of PS_SBO, indicating the same functional groups of polyester. The absorption of carbonyl group of ester was at 1739 cm^{-1} and C-O stretching absorptions of ester were at 1282-1283 cm^{-1}. The C-H stretching of aliphatic was shown at 2854-2925 cm^{-1}.

4.3.3 Polyester from epoxidized sunflower oil

The polyesters from epoxidized sunflower oil on condensation polymerization were carried out by conditions as shown in Table 4.11.

Table 4.11 Synthesized conditions of PS_SFO from EP_SFO using 0.0085 mol of glycerol.

Epoxidized sunflower Oils (Ep_SFO) (mol)	Glycerol (mol)	phthalic anhydride (mol)	Temp. (^{o}C)	Time (hr)
0.0085	0.022	0.034	240	3
0.0085	0.022	0.034	170	3
0.0085	0.022	0.034	150	3
0.0085	0.022	0.034	130	3
0.0085	0.022	0.034	110	3

The PS_SFO were synthesized at various temperatures under the optimum conditions. The functional groups of esters were characterized by using FT-IR Spectroscopy. The results were shown in Figure 4.15.

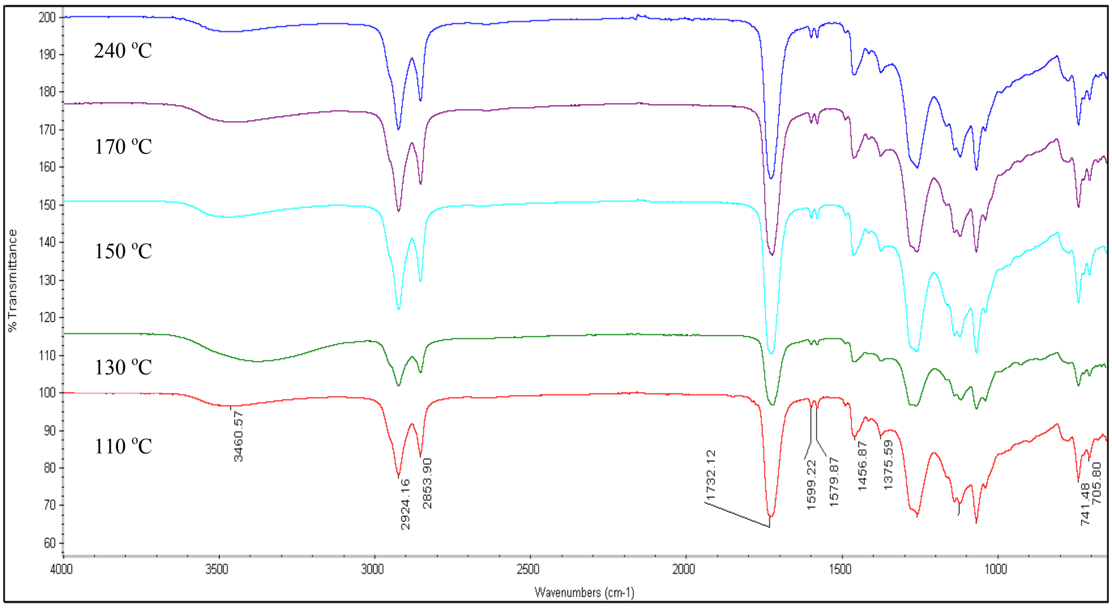


Figure 4.15 IR spectra of PS_SFO at various temperatures under the optimum condition.

The IR spectra of PS_SFO in Figure 4.15 were identical comparing to the IR spectra of PS_SBO and PS_PO, indicating the same functional groups of polyester. The absorption of carbonyl group of ester was at 1723-1727 cm^{-1} and C-O stretching absorptions of ester were at 1258-1262 cm^{-1}. The C-H stretching of aliphatic was shown at 2853-2924 cm^{-1}.

Table 4.12 Ratios of carbonyl ester and aliphatic C-H stretching absorptions of PS_SBO, PS_PO and PS_SFO under the optimum conditions.

Temperature (°C)	Ratios of carbonyl ester and aliphatic C-H stretching absorptions		
	PS_SBO	PS_PO	PS_SFO
240	1.49	0.65	1.04
170	1.27	0.62	1.02
150	1.10	0.60	1.01
130	1.10	0.59	1.02
110	1.06	0.53	1.00

From Table 4.7, the ratios of ester of PS_SBO, PS_PO and PS_SFO were the same trends by increasing the ratios of carbonyl ester and aliphatic C-H stretching absorptions, when the temperature was increased. In comparison of all synthesized polyesters, the carbonyl ester absorptions : C-H stretching absorptions ratios of PS_SBO and PS_SFO polyester were similar due to the composition of unsaturated fatty acids in the oils affecting the high percentage of epoxy (oxirane ring) which were 86% and 87%, respectively. Conversely, palm oil consisted of the large amount of saturated fatty acids affected the lower ratio of ester. Furthermore, the ratios of all synthesized polyesters at low reaction temperature were slightly different from high temperature which was the conventional reaction temperature. It could be concluded that polyesters from epoxidized oils could be synthesized at low temperature.

4.3.4 Structural analysis of polyesters

To investigate bonding in polyester molecules transesterification reaction of polyester with BF_3/MeOH was performed and the transesterified product were characterized by ^{13}C-NMR spectroscopy. The tranesterification products of the ester from condensation of SBO (0.011 mol), glycerol (0.022 mol) and phthalic anhydride (0.034 mol) at 240 ^{o}C and 110 ^{o}C were characterized by ^{13}C-NMR spectroscopy.

The results (Figure 4.16 and 4.17) showed the carbonyl carbon signals of ester at δ_H 173 ppm ester bond between polyester molecules at δ_H 57-88 ppm. The signal of phthalic moiety were displayed at δ_H 128-133 ppm. In addition a presence of carbon signals at δ_H 80 and 75 ppm, in Figure 4.16 and 4.17, indicated a crosslinking between fatty and chain via oxirane ring opening (see Figuare 4.18).

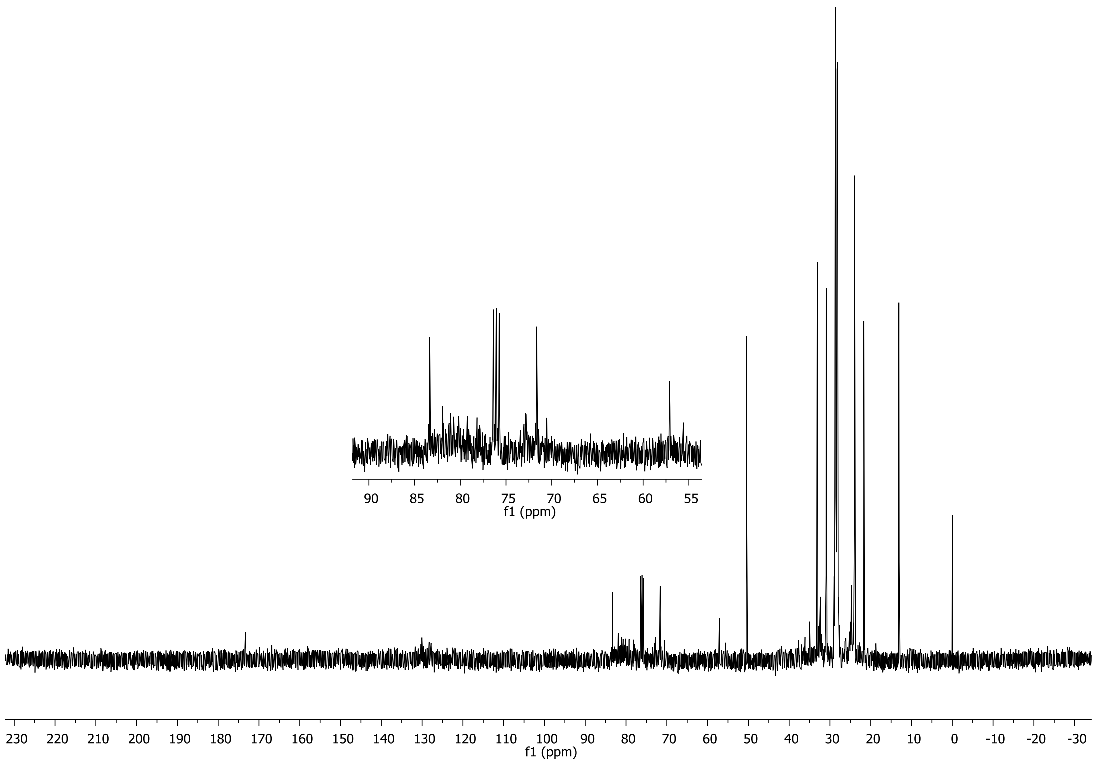


Figure 4.16 ^{13}C-NMR spectra of PS_SBO obtained from condensation polymerization at 110°C transesterified.

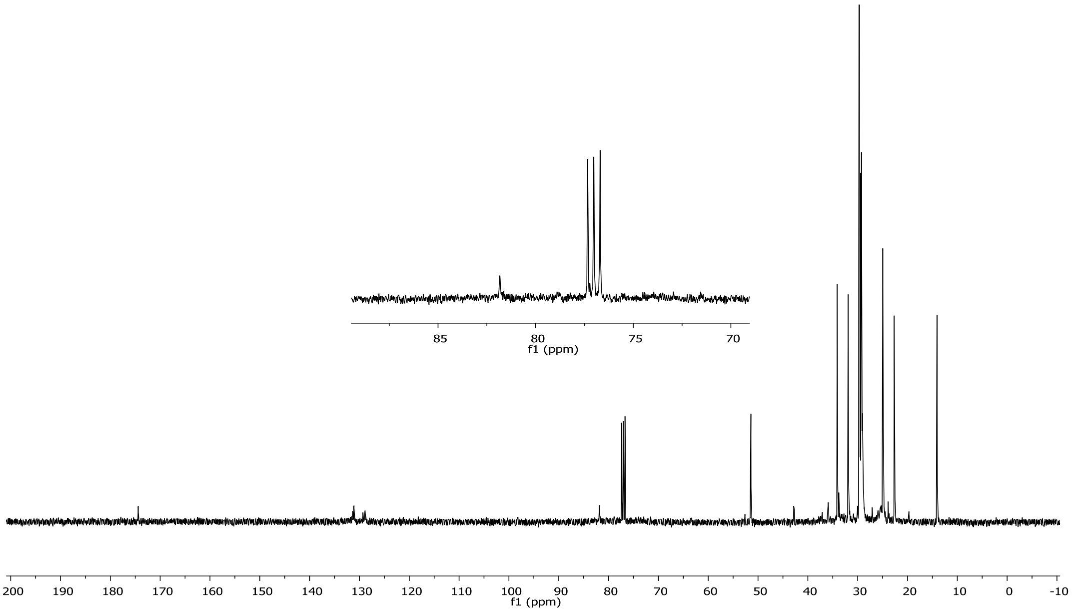


Figure 4.17 ^{13}C-NMR spectra of PS_SBO obtained from condensation polymerization at 240°C transesterified.

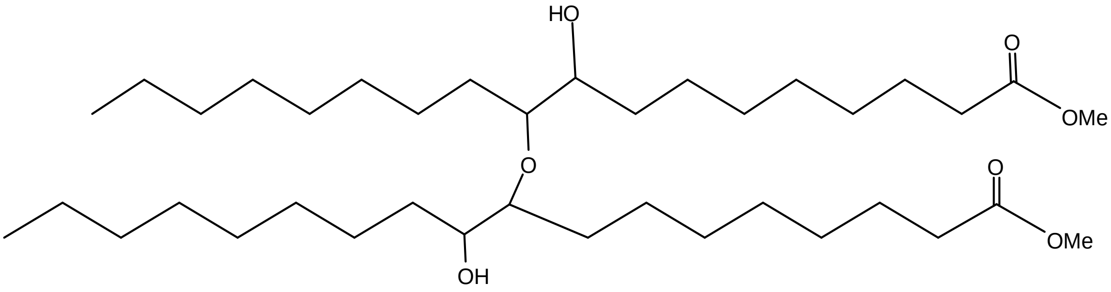


Figure 4.18 Fatty acid methyl ester of PS_SBO.

4.3.5 Average Molecular weight of synthesized polyesters, [η]

Average Molecular weight of the polyester was determined using literature method [28] and average Molecular weight were shown in Table 4.8

Table 4.13 Viscosity of PS_SBO, PS_PO and PS_SFO under the optimum conditions at various condensation temperatures.

Temperature (^{o}C)	**[η] (Cst)**			**M$_V$ (x10^5)**		
	PS_SBO	**PS_PO**	**PS_SFO**	**PS_SBO**	**PS_PO**	**PS_SFO**
240	165.07	134.44	153.21	10.5	8.53	9.77
170	136.42	121.33	128.56	8.66	7.66	8.14
150	95.74	81.65	81.65	5.99	5.07	5.07
130	57.73	40.82	54.01	3.53	2.46	3.30
110	44.09	33.33	20.41	2.67	1.99	1.19

At condensation temperature 240^{o}C, the highest average molecular weight of polyester (Table 4.13) was obtained the increasing this temperature of condensation resulted in increasing should be concluded that degree of polymerization.

4.4 Measurement of mechanical properties.

The measurement of mechanical properties such as tensile strength, Young's modulus, elongation and hardness were determined according to the ASTM D 638 and ASTM D3363-05. Only PS_SBO and PS_SFO could be measured in this section while PS_PO derived from palm oil could not be casted.

4.41 Tensile strength

The tensile strength of the PS_SBO and PS_SFO were performed at 240°C, 150 °C and 110 °C. The results were shown in Table 4.14.

Table 4.14 Tensile strength of PS_SBO and PS_SFO obtained at condensation temperatures under the optimum condition.

Type of oils	**Epoxidized Oils (mol)**	**Glycerol (mol)**	**Phthalic anhydride (mol)**	**Temp. (°C)**	**Time (hr)**	**% Elongation**	**Tensile Strength at breaking point (kgf/mm^2)**
EP_SBO							
	0.011	0.022	0.034	240	3	42.25	0.0514
	0.011	0.022	0.034	150	3	50.15	0.0422
	0.011	0.022	0.034	110	3	85.39	0.0354
EP_SFO							
	0.0085	0.022	0.034	240	3	42.25	0.0219
	0.0085	0.022	0.034	150	3	72.60	0.0160
	0.0085	0.022	0.034	110	3	93.92	0.0130

From Table 4.13 and 4.14, the results showed that average molecular weight and tensile strength at breaking point were increased, when condensation temperature are increased. These indicated the increasing degree of condensation polymerization and crosslinking of polyester. The synthesized polyester could be classified as a thermosetting polymer since it did not melt when heated and could not be molded when first set. In comparison of PS_SFO and PS_SBO, PS_SBO had a greater tensile strength at breaking point. This should be caused by different fatty acid composition. The maximum tensile strength at breaking point was obtained when synthesizing PS_SBO at 240°C.

4.4.2 Elongation

The percent elongation at break of the PS_SBO and PS_SFO obtained at condensation temperture 110°C, 150 °C and 240 °C. The result was shown in Table 4.14, it could be described that the percent elongation at break was decreased, when condensation temperature was increased. These indicated that the increasing of condensation polymerization of polyester resulting in the strength of synthesized polyester. In comparison of PS_SBO and PS_SFO, PS_SFO had a greater elongation at break because the average molecular weight affecting the increasing of crosslinking between the ester molecules. The maximum elongation at break was obtained when synthesizing PS_SFO at 110°C.

4.4.3 Young's modulus

Table 4.15 The Young's modulus of PS_SBO and PS_SFO obtained at condensation temperatures under the optimum condition.

Type of oils	**Temp. (^{o}C)**	**Epoxidized Oils (mol)**	**Glycerol (mol)**	**phthalic anhydride (mol)**	**Time (hr)**
EP_SBO	240	0.011	0.022	0.034	3
	150	0.011	0.022	0.034	3
	110	0.011	0.022	0.034	3
EP_SFO	240	0.0085	0.022	0.034	3
	150	0.0085	0.022	0.034	3
	110	0.0085	0.022	0.034	3

Young's modulus of PS_SBO and PS_SFO

	Temp. (^{o}C)	**5 kgf/mm^2**	**10 kgf/mm^2**	**25 kgf/mm^2**	**50 kgf/mm^2**	**75 kgf/mm^2**
EP_ SBO	240	0.0059	0.0085	0.0137	0.0277	0.075
	150	0.0043	0.0118	0.0303	0.0373	0.038
	110	0.0124	0.0201	0.0300	0.0350	0.036
EP_ SFO	240	0.0038	0.0067	0.0346	0.0365	0.046
	150	0.0061	0.0075	0.0130	0.0211	0.023
	110	0.0033	0.0062	0.0121	0.0215	0.020

From Table 4.15, the Young's modulus of PS_SBO and PS_SFO were increased when the temperature were increased. In comparison of PS_SFO and PS_SBO, PS_SBO had a greater Young's modulus. The maximum Young's modulus was obtained when synthesizing PS_SBO at 240^{o}C.

4.4.4 Hardness

Table 4.16 Hardness of PS_SBO and PS_SFO obtained at condensation temperatures under the optimum condition.

Temperature (^{o}C)	Hardness	
	PS_SBO	PS_SFO
240	5H	5H
170	4H	4H
150	3H	3H
130	3H	3H
110	3H	3H

From Table 4.16, the hardness of PS_SBO and PS_SFO were determined by pencil test for film hardness using mechanized scratch test from the following scale of 6B-6H. The hardness of PS_SBO and PS_SFO were decreased when the temperature were decreased.

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

This research aimed to synthesize polyester from epoxidized vegetable oils at various temperatures. Soybean oil, palm oil and sunflower oil were synthesized via epoxidation reaction which will convert the double bond in the oils to the oxirane ring. The percent conversion of epoxidized soybean oil (EP_SBO), palm oil (EP_PO) and sunflower oil (EP_SFO) were 86%, 78% and 87%, respectively. The average molecular weight of vegetable oils (SBO, PO and SFO) were increased after the epoxidation reactions were carried out which were 1853, 1621.10 and 2357.56 g/mol,respectively.

The polyesters from epoxidized soybean, palm and sunflower oils, glycerol and phthalic anhydride at ratio 1.1:1:1.5 could be synthesized in the absence of catalyst for 3 hr. To determine the ester produced in polyesters, the ratio of carbonyl ester and aliphatic C-H stretching absorptions calculating from the peak area of carbonyl group of ester at 1723-1732 cm^{-1} compared to C-H stretching at 2850-2923 cm^{-1}. The ester bonds between polyester molecules were found by using transesterification reaction. It could be seen that when the temperature was increasing, the ratio of carbonyl ester and aliphatic C-H stretching absorptions, the viscosity, the molecular weight and the mechanical properties of polyesters were increased. The ratios of PS_SBO and PS_SFO were similar due to the composition of unsaturated fatty acids in the oils affecting the high percentage of epoxy. Conversely, palm oil consisted of the large amount of saturated fatty acids affected the lower ratio. The viscosity of polyesters related to the molecular weight which were in the range of 1.19×10^{-5}-10.5×10^{-5}. Increasing of degree of polymerization and the higher condensation temperature resulted in the higher molecular weight of polyester. Furthermore, the synthesized polyester could be classified as a thermosetting polymer since it did not melt when heated and could not be molded when first set. It could be concluded that polyesters from epoxidized oils could be synthesized at low temperature.

5.2 Suggestion

Study various properties of polyester with adding different types of additives and study synthesized polyester in industrial field.

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APPENDICES

APPENDIX A

A1 FT-IR SPECTROSCOPY

A2 ^{1}H-NMR AND ^{13}C-NMR SPECTRA OF POLYESTER AND EPOXIDIZED OILS

A1 FT-IR Spectroscopic data

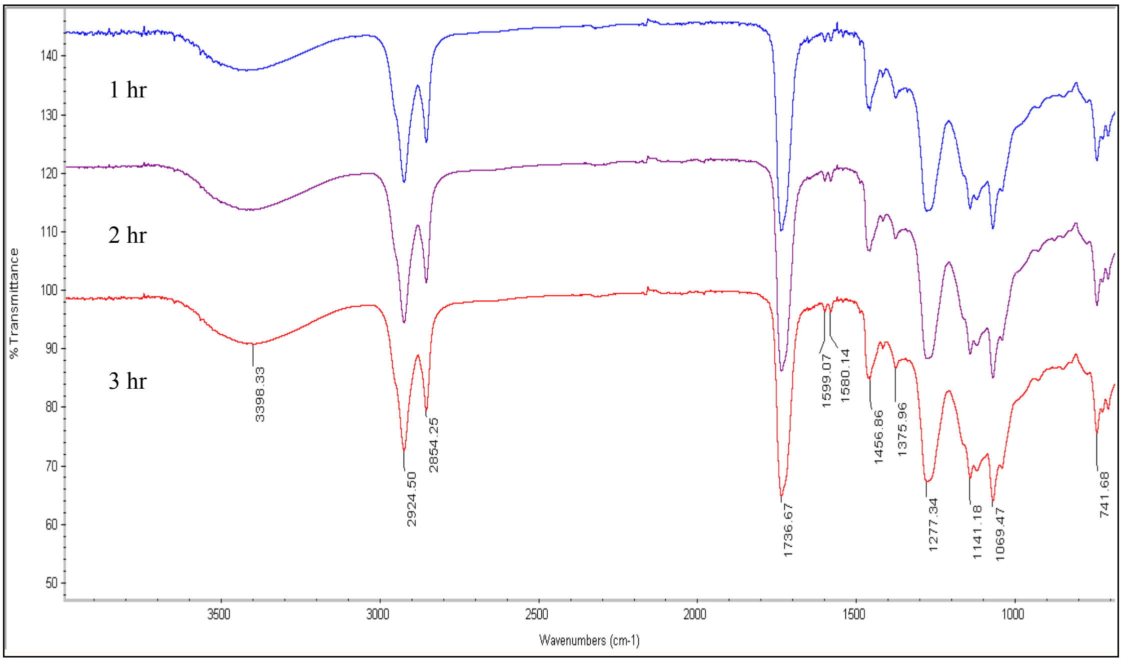


Figure A1.1 IR spectra of PS_SBO at various time using PA 0.020 mol at 110°C.

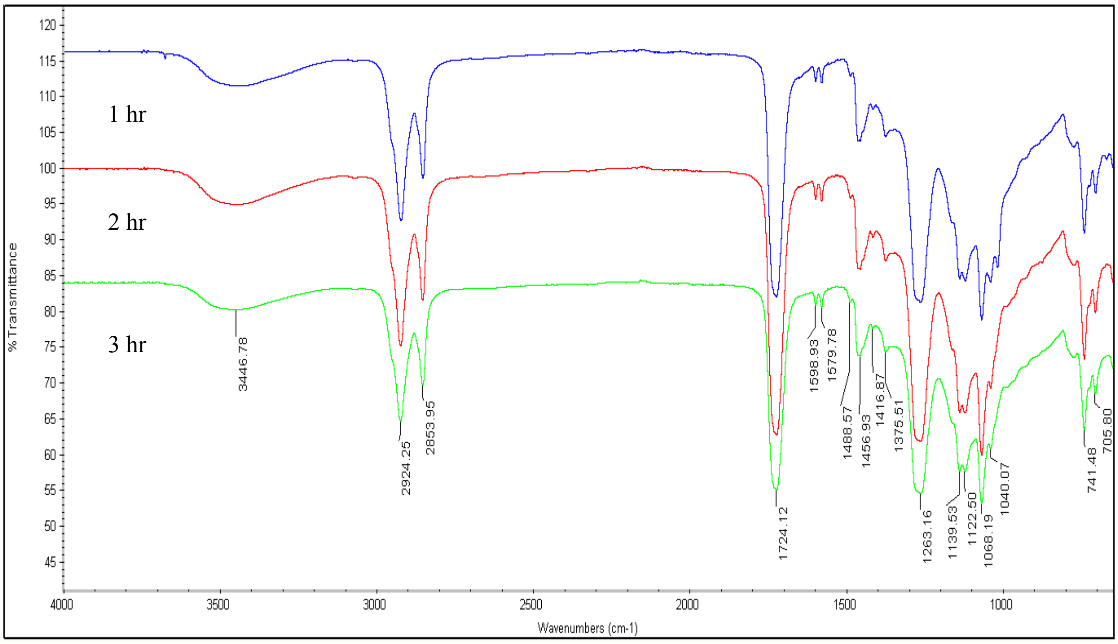


Figure A1.2 IR spectra of PS_SBO at various time using PA 0.034 mol at 110°C.

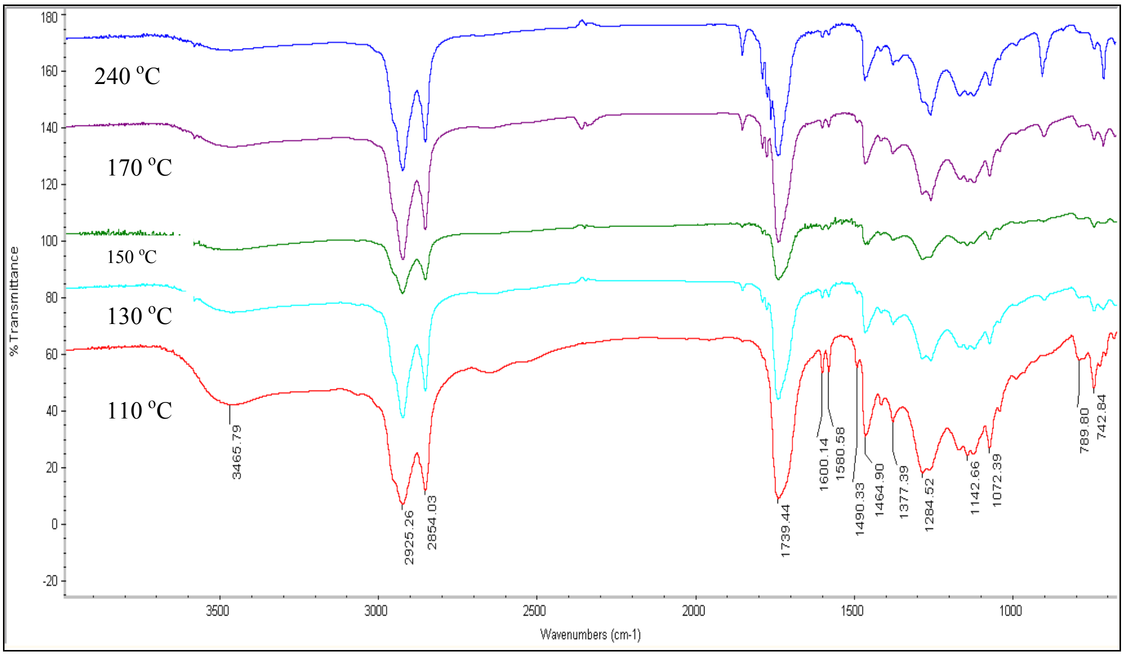


Figure A1.3 IR spectra of PS_PO using H_2SO_4 as a catalyst.

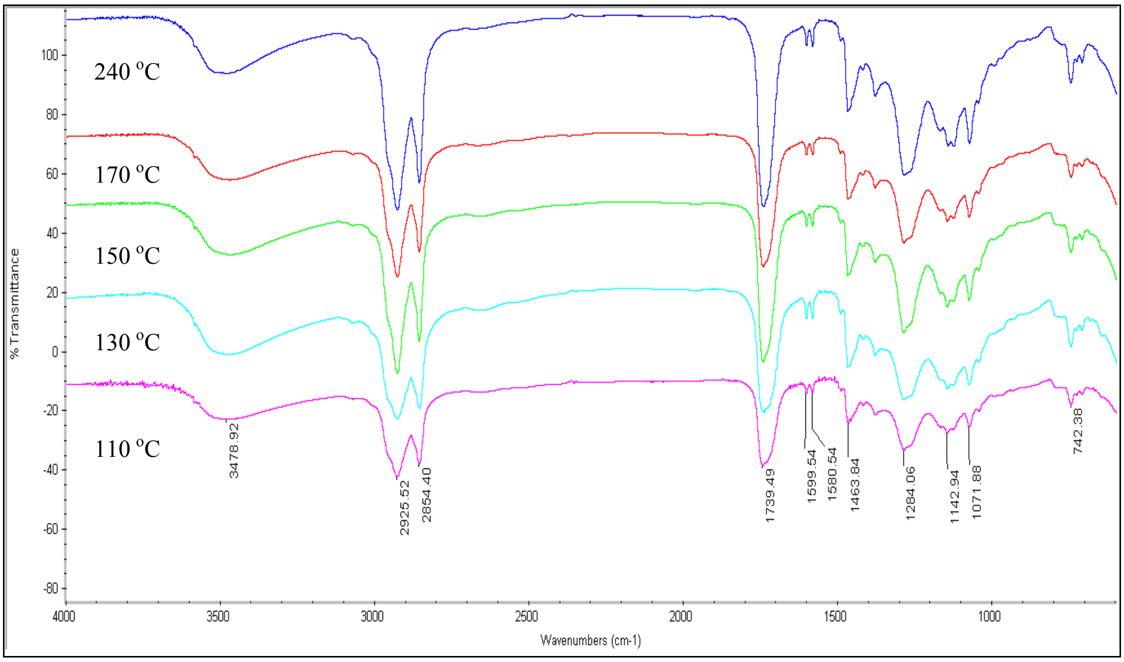


Figure A1.4 IR spectra of PS_PO using CH_3COOH as a catalyst.

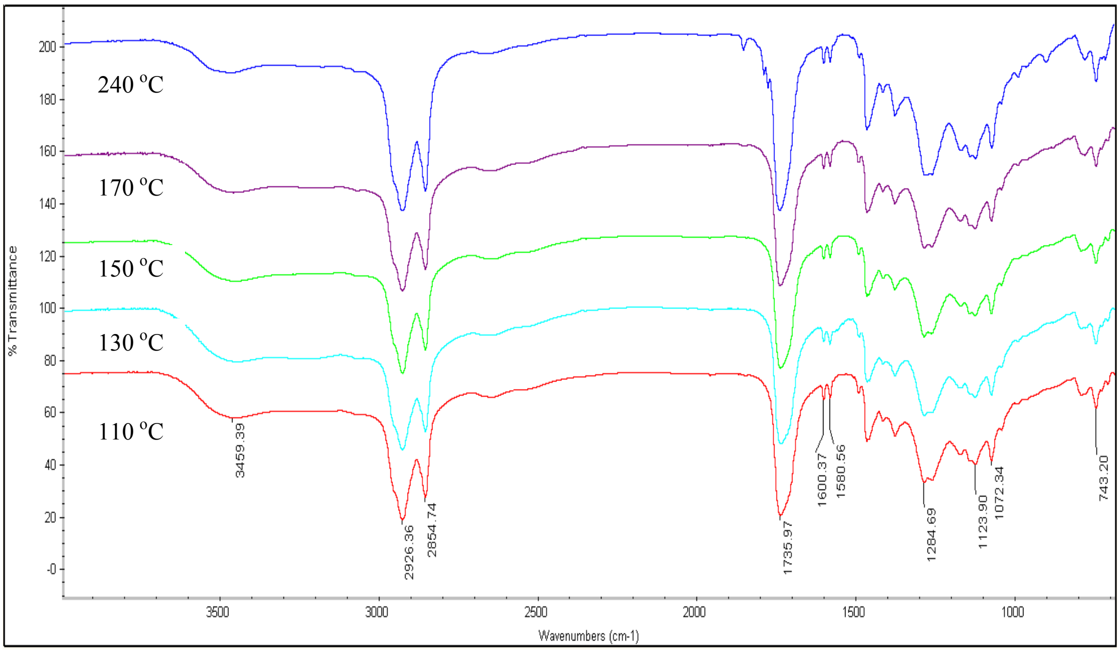


Figure A1.5 IR spectra of PS_SFO using H_2SO_4 as a catalyst.

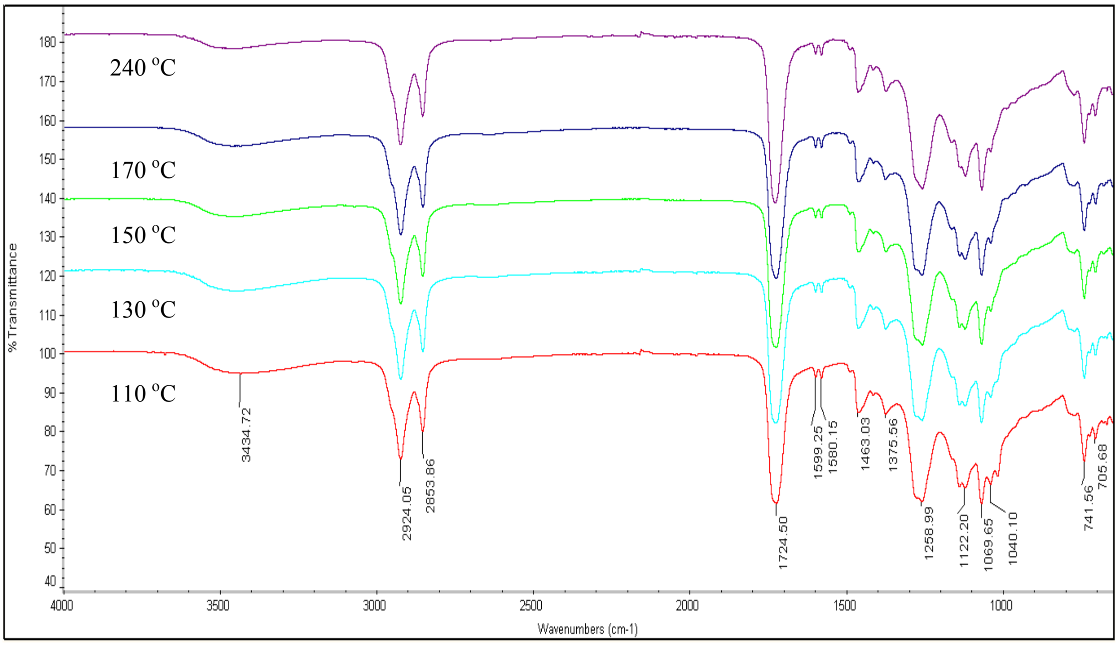


Figure A1.6 IR spectra of PS_SFO using CH_3COOH as a catalyst.

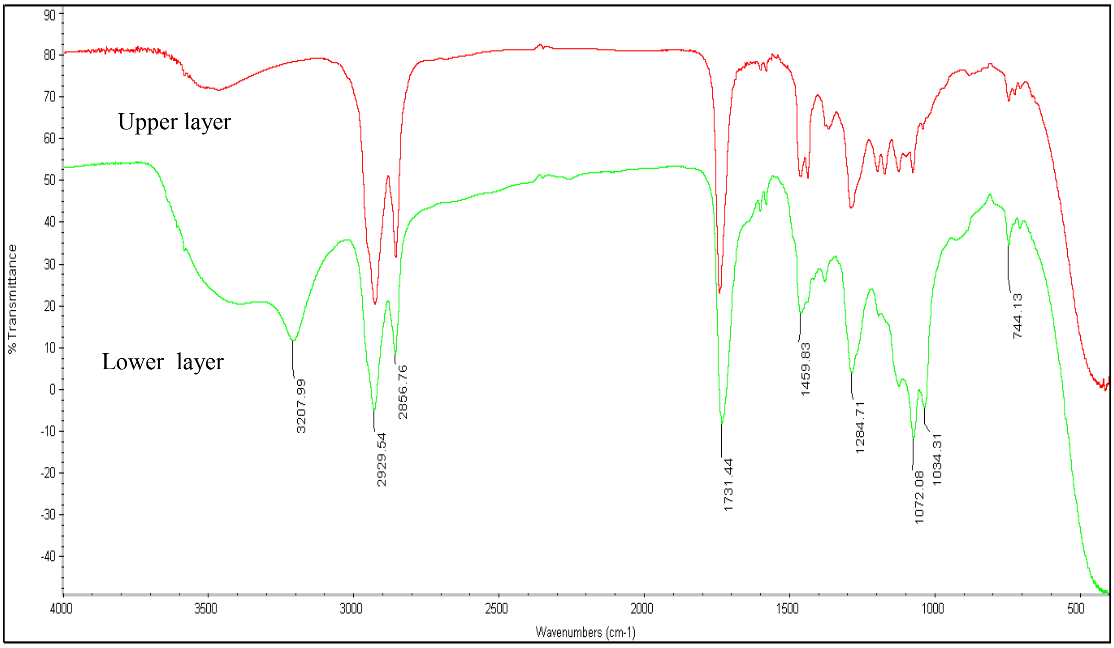


Figure A1.7 IR spectra of tranesterification of PS_SBO with BF_3 at 120°C

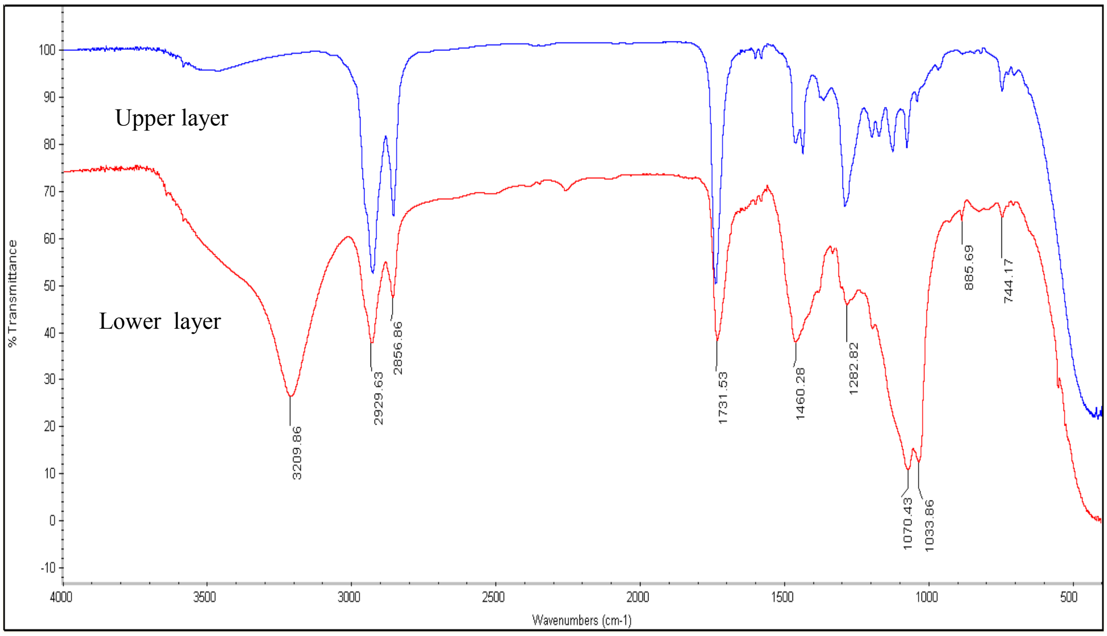


Figure A1.8 IR spectra of tranesterification of PS_SBO with BF_3 at 240°C

A2 NMR Spectroscopic data

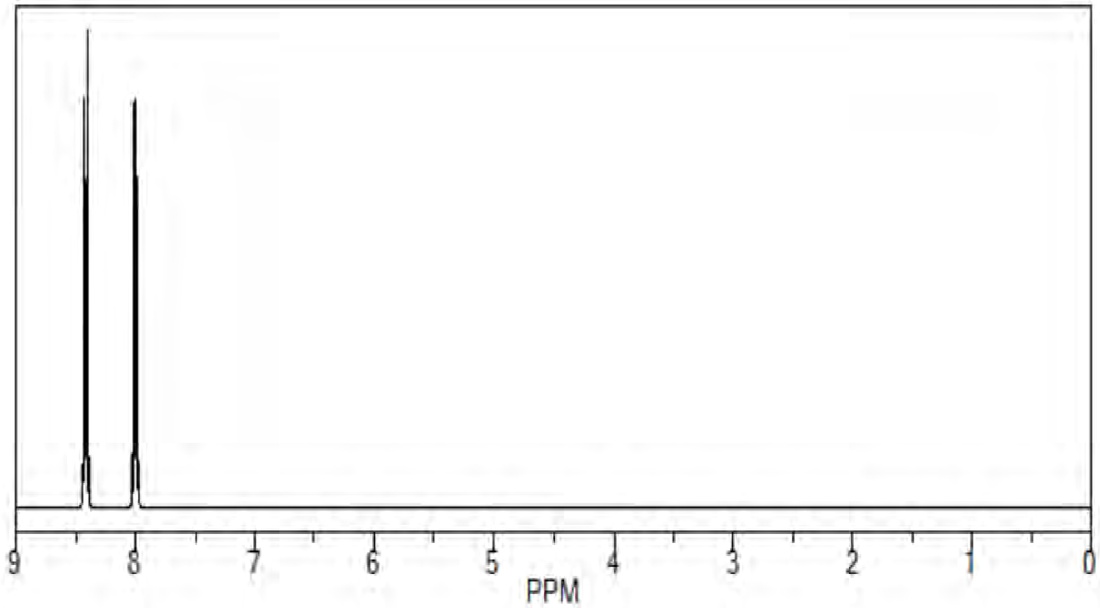


Figure A2.1 ^{1}H-NMR spectra of phathalic anhydride (PA).

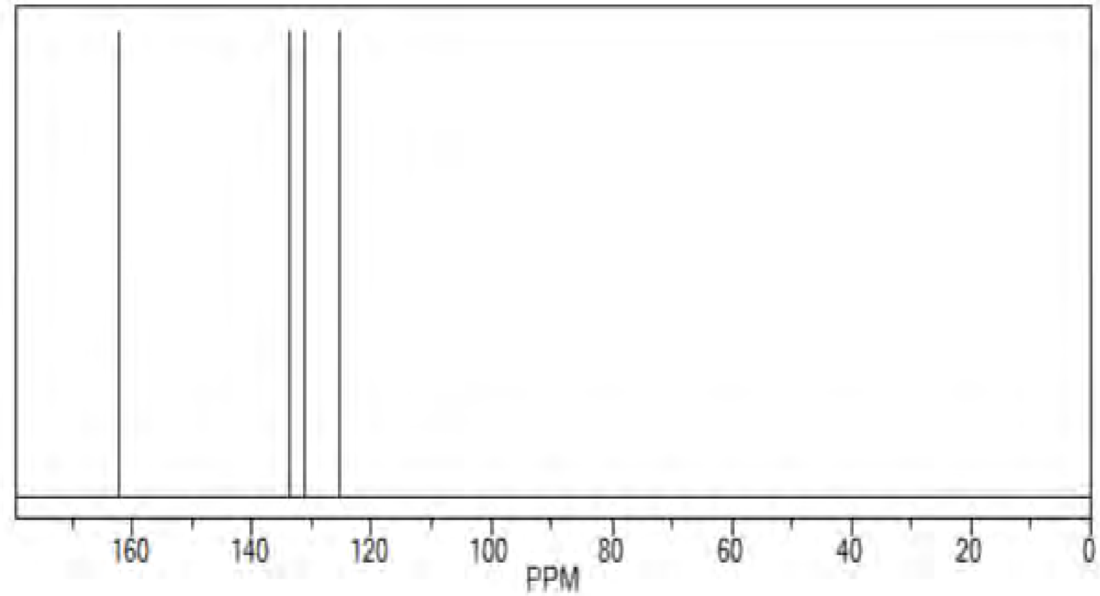


Figure A2.2 ^{13}C-NMR spectra of phathalic anhydride (PA).

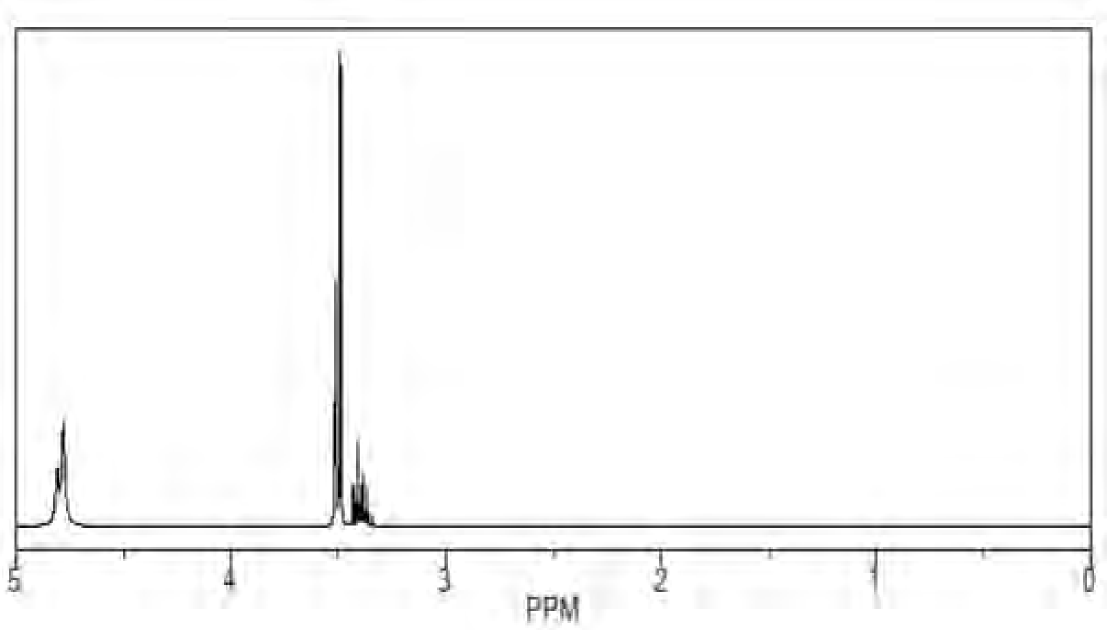


Figure A2.3 ^{1}H-NMR spectra of glycerol.

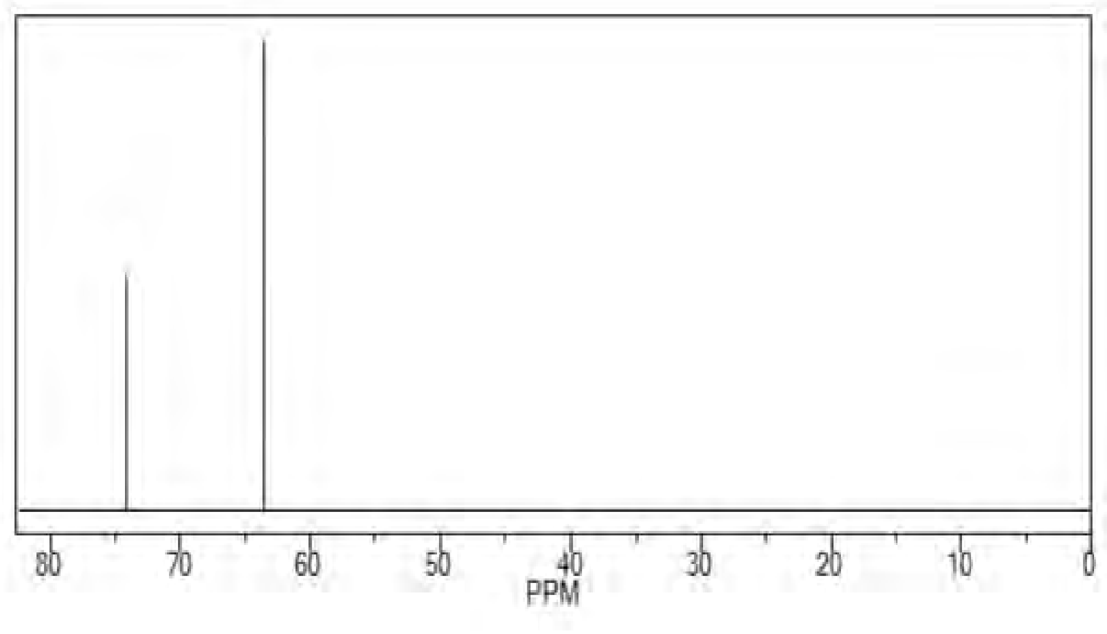


Figure A2.4 ^{13}C-NMR spectra of glycerol.

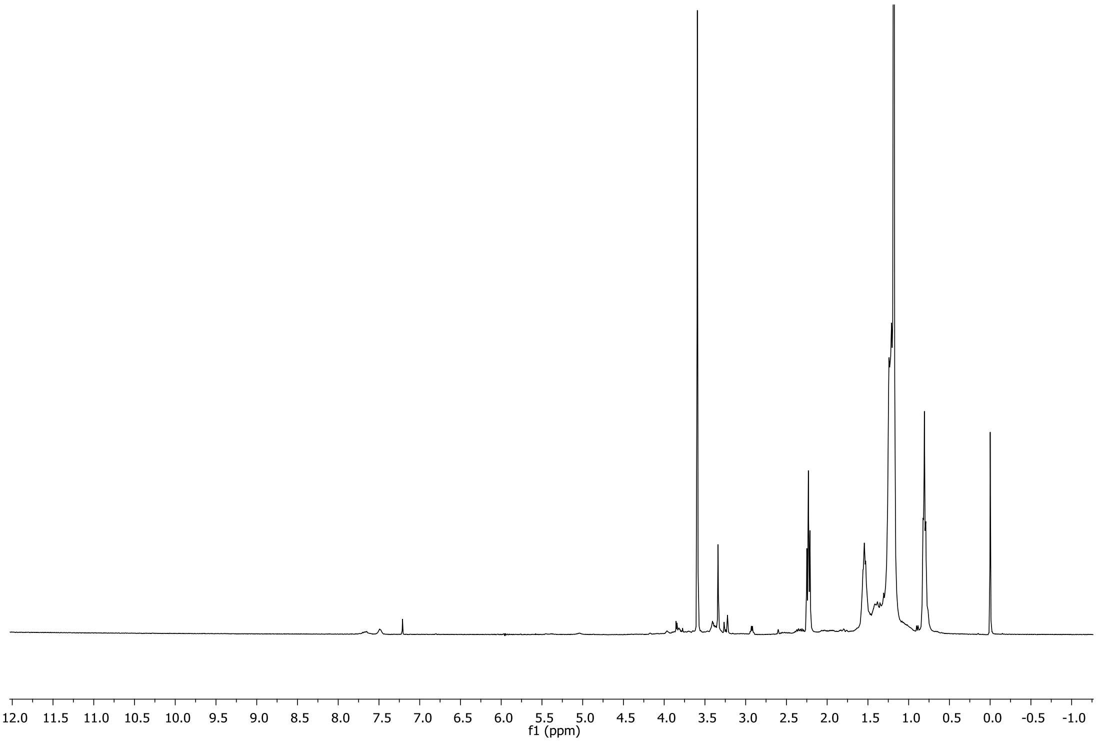


Figure A2.5 ^{1}H-NMR spectra of PS_SBO obtained from condensation polymerization at 110°C transesterified.

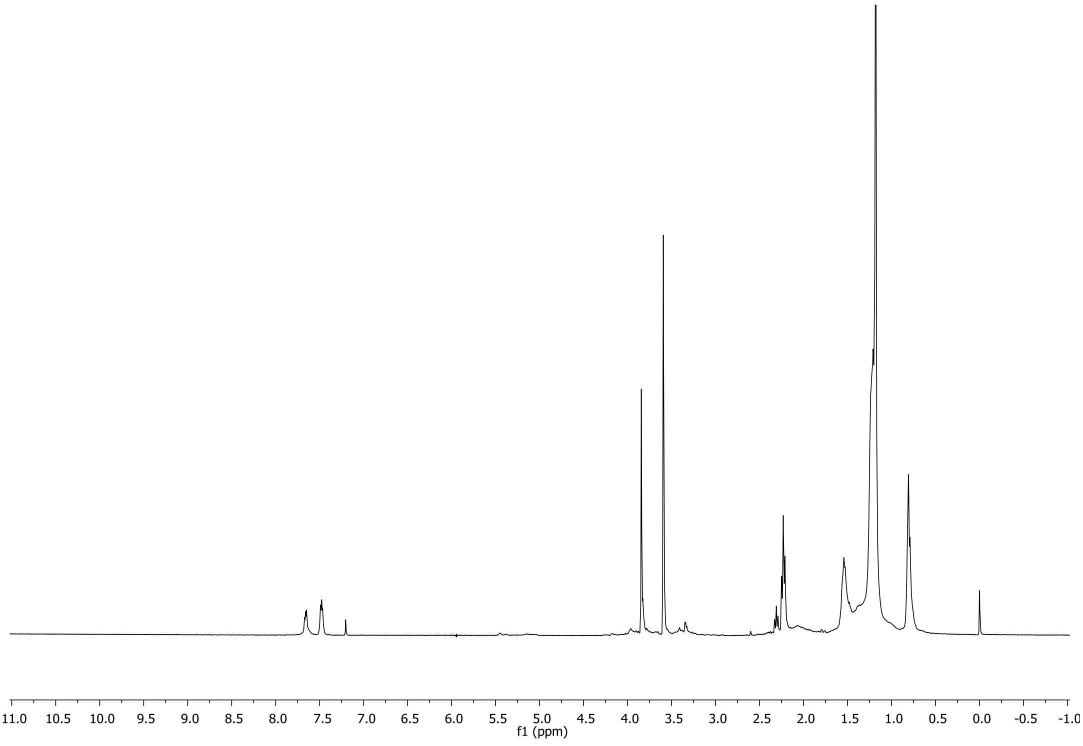


Figure A2.6 ^{1}H-NMR spectra of PS_SBO obtained from condensation polymerization at 240°C transesterified.

APPENDIX B

CALCULATIONS

B1 CALCULATION OF %EPOXIDATION OF VEGETABLE OILS

B2 AVERAGE MOLECULAR WEIGHT VEGETABLE OILS AND EPOXIDIZED OILS

B3 MECANICAL PROPERTIES

B1. Calculation of %Epoxidation of vegetable oils

B1.1 Calculation of %Epoxidation of soybean oil (SBO) and epoxidized soybean oil (EP_SBO).

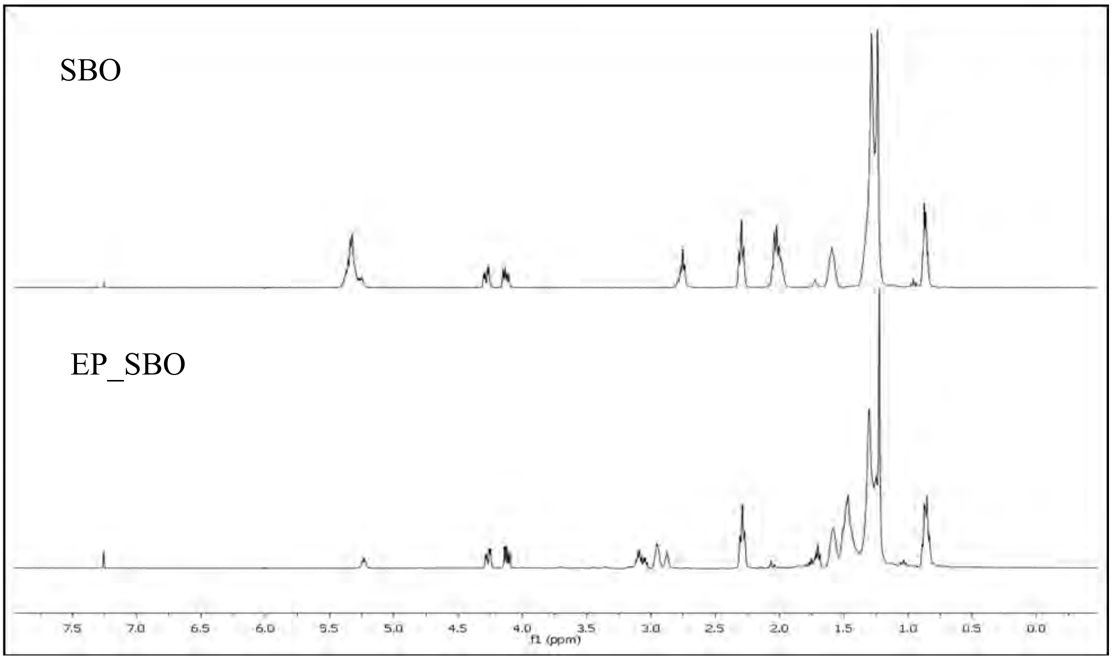
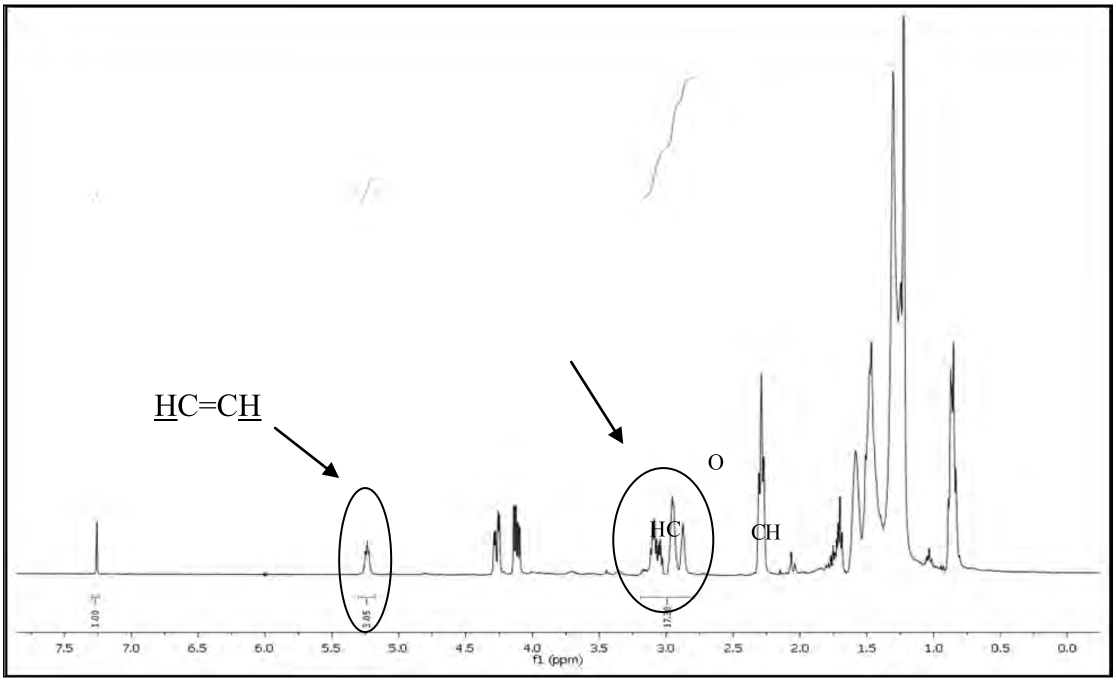


Figure B1.1 ^{1}H NMR spectrum of soybean oil and epoxidized soybean oil.

$$\%\text{Epoxidation} = \frac{\text{integration of oxirane moiety per one mole equivalent}}{(\text{integration of olefinic protons} + \text{integration of oxirane moiety})}$$



% Epoxidation = $(17.30)/(17.30+3.05)\times 100 = 86.00\%$

B1.2 Calculation of %Epoxidation of palm oil (PO) and epoxidized palm oil (EP_PO).

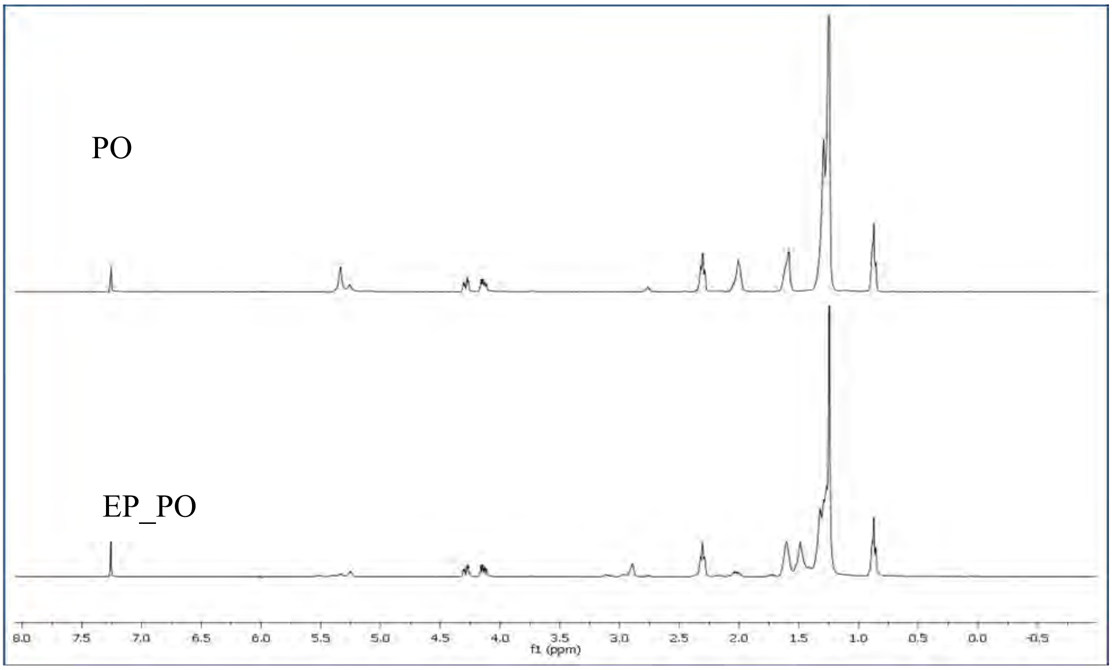
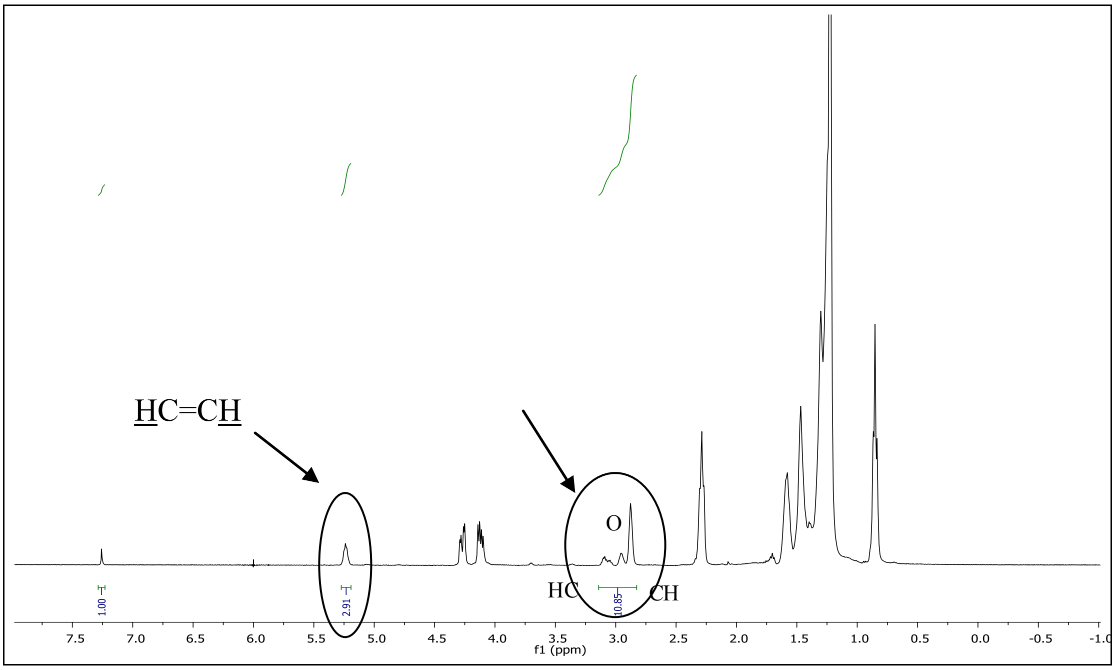


Figure B1.2 ^{1}H NMR spectrum of palm oil and epoxidized palm oil.

$$\%\text{Epoxidation} = \frac{\text{integration of oxirane moiety per one mole equivalent}}{(\text{integration of olefinic protons} + \text{integration of oxirane moiety})}$$



% Epoxidation = (10.85)/(10.85+2.91) × 100 = 78.00%

B1.3 Calculation of %Epoxidation of sunflower oil (SFO) and epoxidized sunflower oil (EP_SFO).

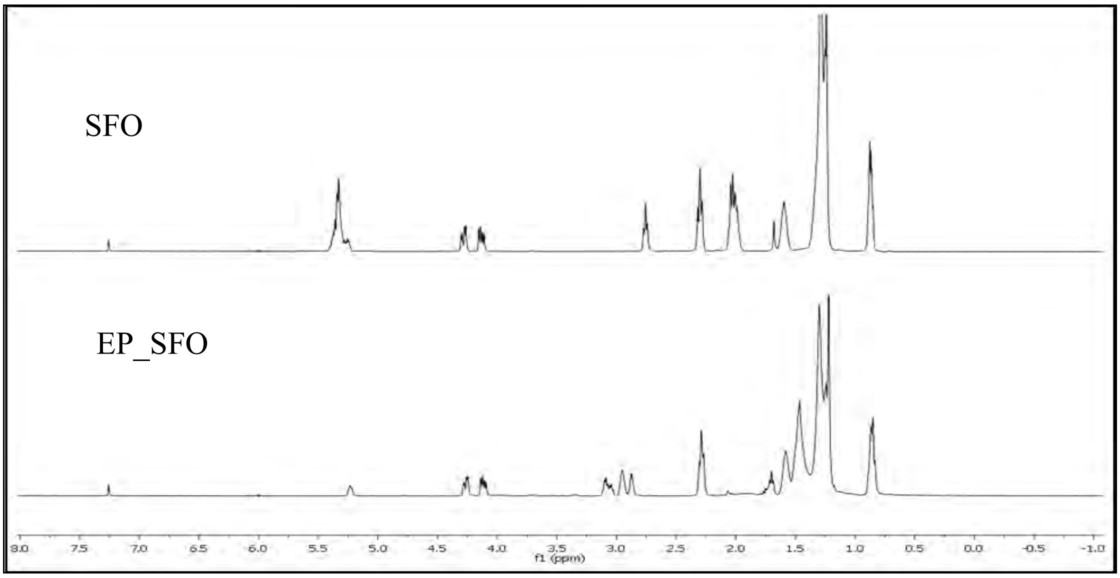
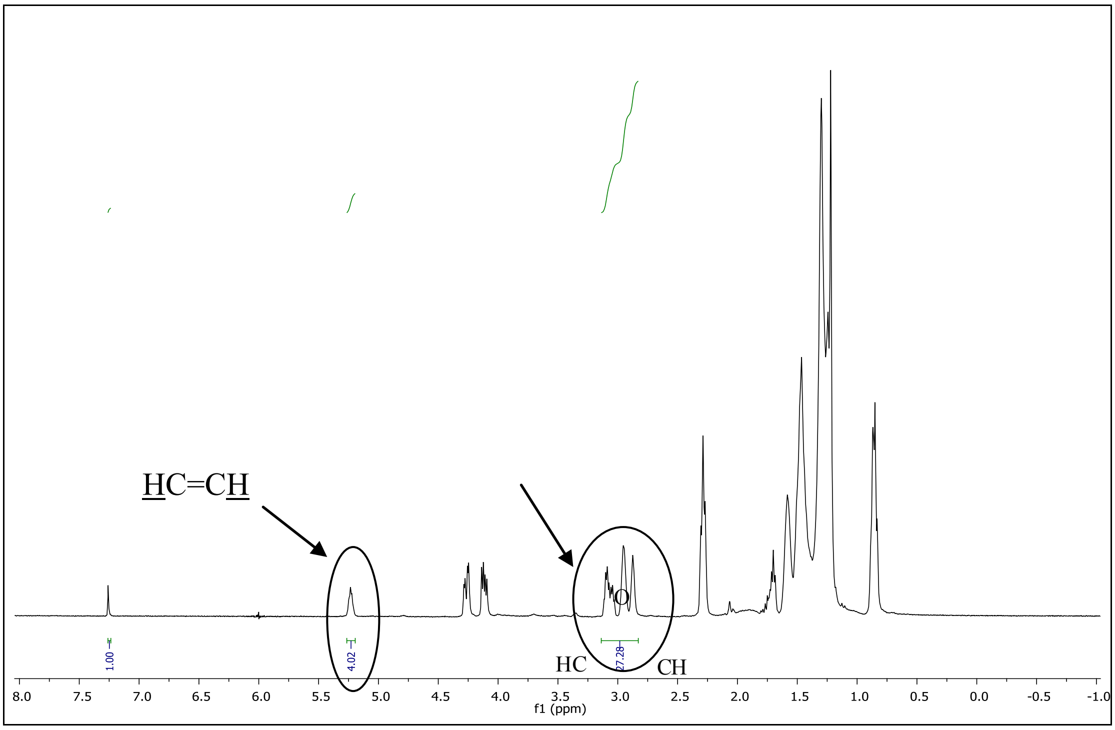


Figure B1.3 ^{1}H NMR spectrum of sunflower oil and epoxidized sunflower oil.

$$\%\text{Epoxidation} = \frac{\text{integration of oxirane moiety per one mole equivalent}}{(\text{ integration of olefinic protons} + \text{integration of oxirane moiety})}$$



$\%\ \text{Epoxidation} = (27.28)/(27.28+4.02)\times 100 = 87.00\%$

B2. Average molecular weight vegetable oils and epoxidized oils.

Table B2.1 Properties of Vegetable Oils

Properties	**Soybean oil (SBO)**	**Palm oil (PO)**	**Sunflower oil (SFO)**
Iodine value (mg.I_2/100 g.)	**120.58**	**61.33**	**130.50**
Saponification number (mg KOH/g)	**188.23**	**202.74**	**191.00**
Saturated fatty acid (%)	**20.22**	**42.97**	**12.00**
C 12:0 Lauric acid	-	0.32	-
C 14:0 Myristic acid	-	0.95	-
C 16:0 Palmitic acid	10.93	37.47	7.00
C 18:0 Stearic acid	8.28	3.88	5.00
C 20:0	0.34	0.35	-
C 22:0	0.4	-	-
C 23:0	0.12	-	-
C 24:0	0.15	-	-
Unsaturated fatty acid (%)	**79.78**	**57.04**	**88.00**
C 18:1 Oleic acid	19.9	45.92	19.00
C 18:2 Linoleic acid	52.7	11.12	68.00
C 18:3 Linolenic acid	5.87	-	1.00
C 20:1	0.33	-	-
Unknown	0.98	-	-
Average molecular weight* (g/mol)	867.02	853.76	876.00

B2.1 Soybean oil (SBO)

$$M_{av} = \text{MW of } C_3H_5O_3 + (\text{Average Molecular weight of fatty acids} - 17) \text{x} 3$$

$$M_{av} \text{ of SBO} = 89 + [(256.42\text{x}0.1093) + (284.4846\times0.0828) + (282.46\text{x}0.199)\ldots] - 17]\text{x}3$$

$$M_{av} \text{ of SBO} = 867.02 \text{ g/mol}$$

Converted to epoxidized SBO (EP_SBO) (The percent conversion of epoxidation = 86%)

$$M_{av} \text{ of EP\_SBO} = \left(\frac{\text{integration of oxirane moiety}}{\text{integration of olefinic protons}}\right) \text{x \% Epoxidation x MW of oxygen x3} \left(\frac{\text{Integration value of the methylene protons}}{\text{integration of olefinic protons}}\right)$$

So, M_{av} of EP_SBO = $867.02 + [(17.30/3.05)\text{x}(86/100)\text{x}16\text{x}3(12.85/3.05)]$

$$M_{av} \text{ of EP\_SBO} = 1853 \text{ g/mol}$$

B2.2 Palm oil (PO)

$$M_{av} = \text{MW of } C_3H_5O_3 + (\text{Average Molecular weight of fatty acids} - 17) \text{x} 3$$

$$M_{av} \text{ of PO} = 89 + [(200.32\text{x}0.0032) + (288.37\times0.0095) + (256.42\text{x}0.03747)\ldots] - 17]\text{x}3$$

$$M_{av} \text{ of PO} = 853.76 \text{ g/mol}$$

Converted to epoxidized PO (EP_PO) (The percent conversion of epoxidation = 78%)

So, M_{av} of PO = 853.76 + [(10.85/2.91)x(78/100)x16x3(16/2.91)]

M_{av} of PO = 1621.07 g/mol

B2.3 Sunflower oil (SFO)

M_{av} = MW of $C_3H_5O_3$ + (Average Molecular weight of fatty acids -17)x3

M_{av} of SFO = 89+ [(256.42x0.07) + (284.48×0.05) +(282.46.42x0.19)…]-17]x3

M_{av} of SFO = 876.00 g/mol

Converted to epoxidized SFO (EP_SFO) (The percent conversion of epoxidation = 87%)

So, M_{av} of SFO = 876 + [(27.28/4.02)x(87/100)x16x3(21.80/4.02)]

M_{av} of SFO = 2357.56 g/mol

B3. Mecanical Properties

Table B3.1 Results for product code: PS_SBO 110°C.
Individual Specimens:

Unit	Thickness (mm)	Width (mm)	Elongation (%)	Tensile strength (kgf/mm^2)
1-1	3.20	12.43	85.69	0.0315
1-2	3.21	12.44	84.90	0.0412
1-3	3.22	12.43	85.72	0.0317
1-4	3.22	12.44	84.95	0.0413
1-5	3.21	12.43	85.69	0.0315
Mean	3.21	12.43	85.39	0.0354

Table B3.2 Results for product code: PS_SBO 150°C.
Individual Specimens:

Unit	Thickness (mm)	Width (mm)	Elongation (%)	Tensile strength (kgf/mm^2)
1-1	3.22	12.40	50.35	0.0439
1-2	3.20	12.41	50.27	0.0442
1-3	3.21	12.42	49.87	0.0395
1-4	3.22	12.42	49.98	0.0398
1-5	3.23	12.41	50.30	0.0438
mean	3.22	12.41	50.15	0.0422

Table B3.3 Results for product code: PS_SBO 240°C.

Individual Specimens:

Unit	Thickness (mm)	Width (mm)	Elongation (%)	Tensile strength (kgf/mm^2)
1-1	3.23	12.45	42.43	0.0523
1-2	3.22	12.44	42.38	0.0525
1-3	3.23	12.45	41.97	0.0497
1-4	3.21	12.43	42.50	0.0499
1-5	3.22	12.45	41.98	0.0526
mean	3.22	12.44	42.25	0.0514

Table B3.4 Results for product code: PS_SFO 110°C.

Individual Specimens:

Unit	Thickness (mm)	Width (mm)	Elongation (%)	Tensile strength (kgf/mm^2)
1-1	3.23	12.45	93.42	0.012
1-2	3.22	12.44	94.39	0.014
1-3	3.23	12.45	93.98	0.013
1-4	3.21	12.43	94.53	0.012
1-5	3.22	12.45	93.28	0.014
Mean	3.22	12.44	93.92	0.013

Table B3.5 Results for product code: PS_SFO 150°C.

Individual Specimens:

Unit	Thickness (mm)	Width (mm)	Elongation (%)	Tensile strength (kgf/mm^2)
1-1	3.22	12.40	71.15	0.0156
1-2	3.20	12.41	72.23	0.0164
1-3	3.21	12.42	73.46	0.0167
1-4	3.22	12.42	73.28	0.0157
1-5	3.23	12.41	72.89	0.0155
Mean	3.22	12.41	72.60	0.0160

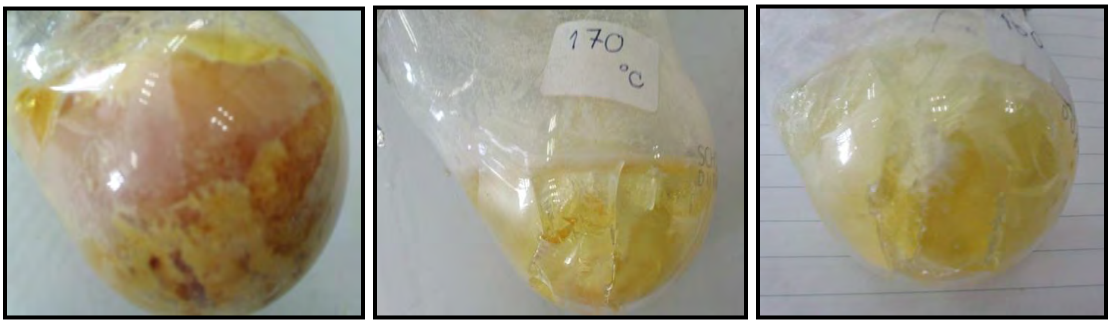
Table B3.6 Results for product code: PS_SFO 240°C.

Individual Specimens:

Unit	Thickness (mm)	Width (mm)	Elongation (%)	Tensile strength (kgf/mm^2)
1-1	3.20	12.43	49.80	0.0215
1-2	3.21	12.44	50.65	0.0219
1-3	3.22	12.43	49.54	0.0225
1-4	3.22	12.44	50.56	0.0214
1-5	3.21	12.43	50.64	0.0220
mean	3.21	12.43	42.25	0.0219

APPENDIX C

PICTURES OF POLYESTER FROM EPOXIDIZED VEGETABLE OILS



240°C 170°C 150°C

Figure C1 PS_SBO obtained from condensation of phthalic anhydride, 0.0022 mol of glycerol for 3 hr.

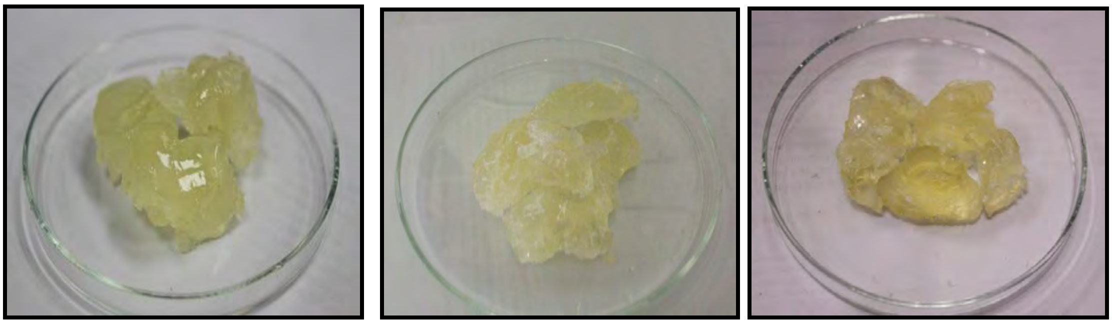
240°C 170°C 150°C

Figure C2 PS_SBO obtained from condensation of phthalic anhydride, 0.022 mol of glycerol for 3 hr.

110°C/1 hr 110°C/2 hr

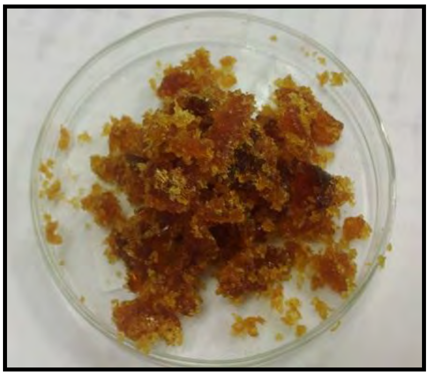
110°C/3 hr 110°C/8 hr

Figure C3 PS_SBO obtained at various reaction times; 1 hr, 2 hr, 3 hr and 8 hr at 110^{o}C.



PA 0.020 PA 0.027 PA 0.034

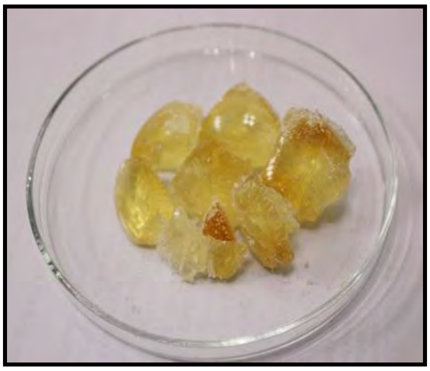
Figure C4 PS_SBO obtained at various of amount of phthalic anhydride at 110^{o}C.



240°C

170°C

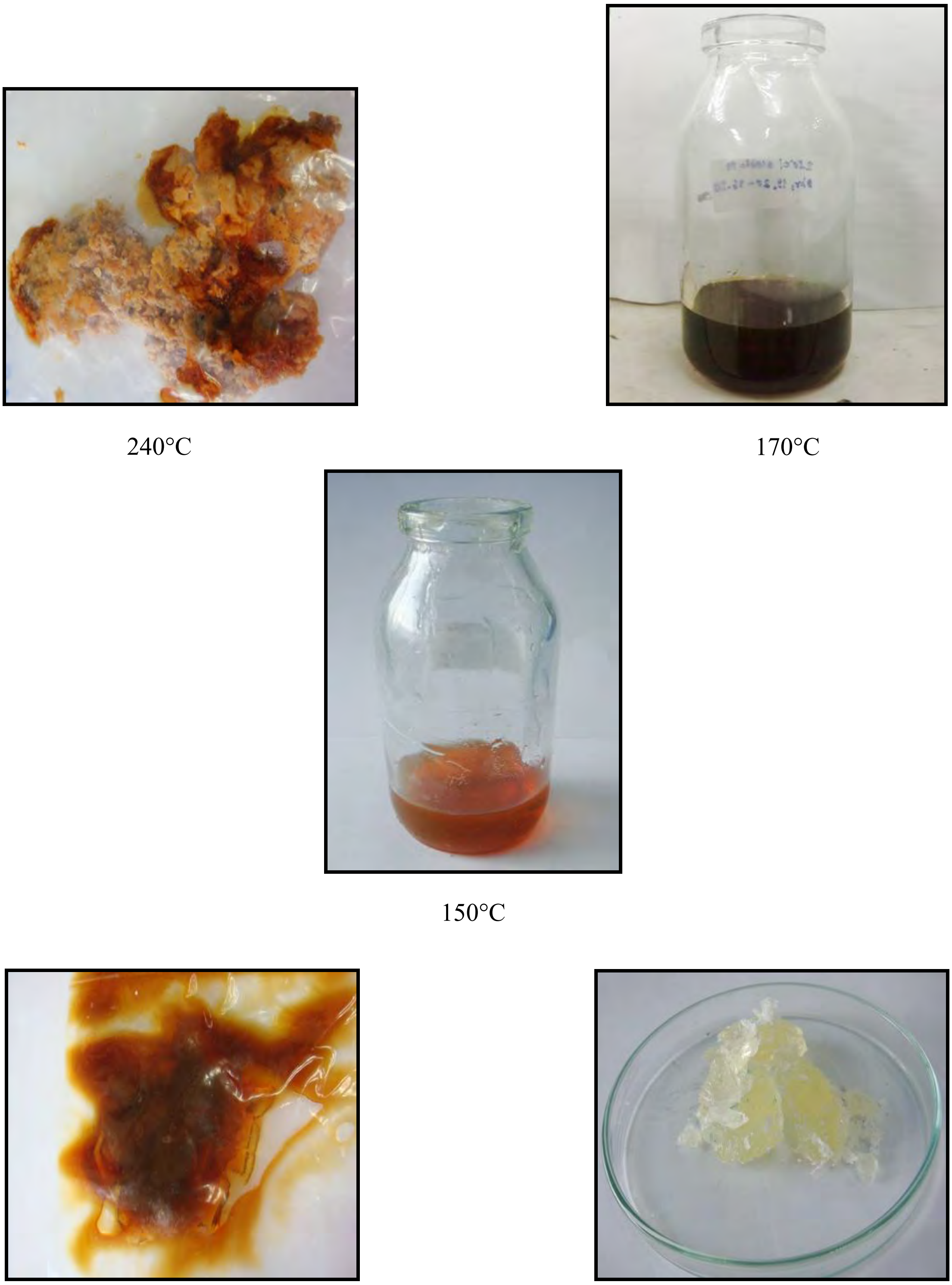
150°C



130°C

110°C

Figure C5 PS_SBO obtained at various condensation temperature without catalyst for 3 hr.



240°C

170°C

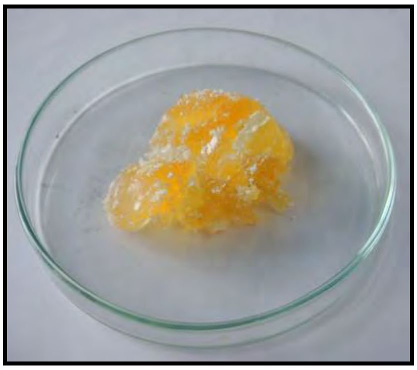
150°C

130°C

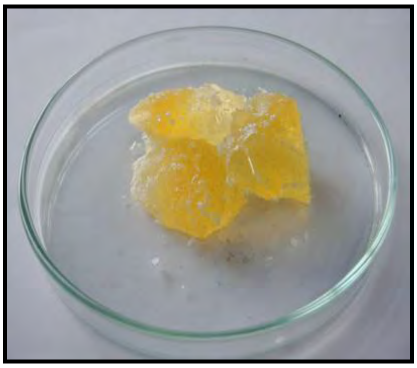
110°C

Figure C6 PS_SBO obtained at various condensation temperature using H_2SO_4 as a catalyst for 3 hr.

240°C

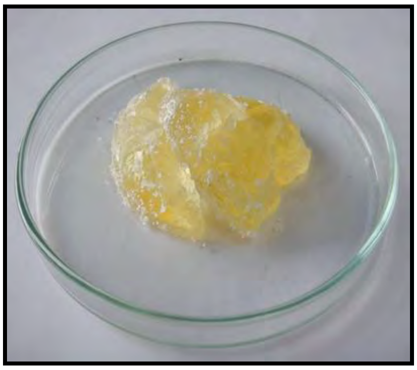


170°C



150°C

130°C



110°C

Figure C7 PS_SBO obtained at various condensation temperature using CH_3COOH as a catalyst for 3 hr.

240°C

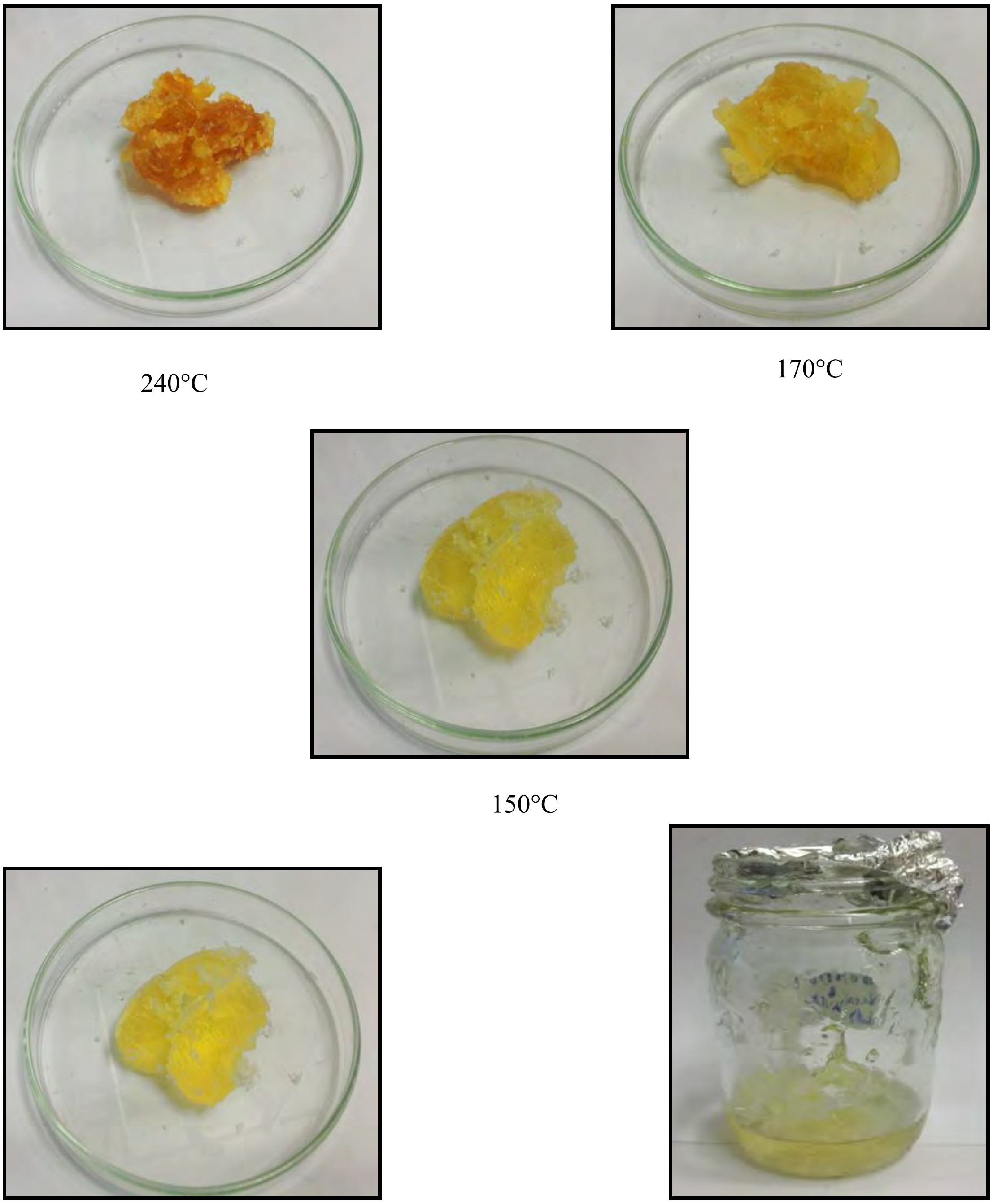
170°C

150°C

130°C

110°C

Figure C8 PS_PO obtained at various condensation temperature without catalyst for 3 hr.



240°C

170°C

150°C

130°C

110°C

Figure C9 PS_SFO obtained at various condensation at various temperature without catalyst for 3 hr.

VITA

Miss Piyathida Ruksayot was born on March 5, 1985 in Bangkok, Thailand. She graduated with Bachelor Degree of Industrial chemistry, from Department of Industrial chemistry, Faculty of Applied Science, King Mongkut's Institute of Technology North Bangkok in 2007. She was admitted to the Master degree of Science in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 2007 and completed the program in 2010.

Conference

5-7 January 2011 "SYNTHESIS OF POLYESTER FROM EPOXIDIZED VEGETABLE OIL AND PHTHALIC ANHYDRIDE"

Pure and Applied Chemistry International Conference 2011
Miracle Grand Hotel Bangkok, Thailand.