UNIVERSITI TEKNOLOGI MARA

PREPARATION AND CHARACTERIZATION OF ACRYLATED EPOXIDIZED SOYBEAN OIL IN THE MAKING OF VEGETABLE OIL BASED - FILM

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Final year project report submitted in partial fulfillment of the requirement for the degree of **Degree of Bachelor of Sciences (Hons.) Polymer Technology**

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CONFIRMATION BY PANEL OF EXAMINERS

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ABSTRACT

PREPARATION AND CHARACTERIZATION OF ACRYLATED EPOXIDIZED SOYBEAN OIL IN THE MAKING OF VEGETABLE OIL-BASED FILM

The demand of bio-based coating has been greatly increased in order to solve the environmental issues. Petroleum-based coating is expensive, hard to recycle and all the sources come from non-renewable fossil fuel. Therefore, solution needed to overcome the problem. This study was carried to synthesize ESO to produce AESO film coating. The acrylation of epoxidized soybean oil (AESO) was successfully synthesized by introducing acrylic acid, which is an unsaturated monomer into oxirane groups of the epoxidized oil (ESO). Then, AESO has been reacted with trimethylolpropane triacrylate as monomer and 3-(Triethoxysilyl)-propylamine as the curing agent to produce AESO film with varying formulation of TMPTA: amine were 70:30, 50:50 and 30:70 respectively. The oxirane oxygen content, viscosity, FTIR and acid value were obtained to know the amount of unsaturation in the synthesized product. Based on the successfulness of esterification process, FTIR result showed the hydroxyl group that exists in the AESO structure at peak 3618 cm^{-1}. In addition, the hydroxyl group presence in the AESO film for sample ratio with 30:70 at peak 3459.6 cm^{-1}. The viscosity of AESO was found within desirable range and higher compared to ESO which were 835.96 cP and 329.62 cP. Moreover, the result revealed that AESO has lower VOC than AESO film which was 4%. In the pencil hardness result, AESO film with ratio 30monomer:70curing agent had high scratching resistance with pencil grade 2H and indicates that the film had better properties than the others. In overall, AESO is suitable to replace petroleum-based film and used as vegetable oil-based film.

ABSTRAK

PENYEDIAAN DAN PENCIRIAN KEEPOSIDAAN AKRILIK MINYAK KACANG SOYA DALAM PEMBUATAN FILEM BERASASKAN MINYAK SAYURAN.

Permintaan salutan berasaskan bio telah banyak meningkat untuk menyelesaikan isu-isu alam sekitar. Salutan berasaskan minyak mahal, sukar dikitar semula dan semua sumber berasal dari bahan api fosil yang tidak boleh diperbaharui. Oleh itu, penyelesaian di perlukan untuk mengatasi masalah tersebut. Kajian ini menjalankan sintesis ESO untuk menghasilkan salutan filem AESO. Penyerapan minyak kacang soya epoxidized (AESO) berjaya disintesis dengan memperkenalkan asid akrilik, yang merupakan monomer tak tepu ke dalam kumpulan oxirane dari minyak epoxidized (ESO). Kemudian, AESO telah bertindak balas dengan trimethylolpropane triacrylate sebagai monomer dan 3 (Triethoxysilyl) -propilamina sebagai agen pengawetan untuk menghasilkan filem AESO dengan pelbagai rumusan TMPTA: amina adalah 70:30, 50:50 dan 30:70 masing-masing. Kandungan oksir oksida, kelikatan, FTIR dan nilai asid diperolehi untuk mengetahui jumlah unsaturation dalam produk yang disintesis. Berdasarkan kejayaan proses pengesteran, hasil FTIR menunjukkan kumpulan hidroksil yang terdapat dalam struktur AESO pada puncak 3618 cm-1. Di samping itu, kehadiran kumpulan hidroksil dalam filem AESO untuk nisbah sampel dengan 30:70 pada puncak 3459.6 cm-1. Kelikatan AESO didapati dalam julat yang wajar dan lebih tinggi berbanding dengan ESO iaitu 835.96 cP dan 329.62 cP. Selain itu, hasilnya menunjukkan AESO mempunyai VOC yang lebih rendah daripada filem AESO yang 4%. Dalam hasil kekerasan pensil, filem AESO dengan nisbah 30monomer: 70curing agen mempunyai rintangan menggaru tinggi dengan gred 2H pensil dan menunjukkan bahawa filem itu mempunyai sifat yang lebih baik daripada yang lain. Secara keseluruhan, AESO sesuai untuk menggantikan filem berasaskan petroleum dan digunakan sebagai filem berasaskan minyak sayuran.

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All praises to Allah, I’m finally successfully complete my final project. During completing this project, I have gained extra knowledge on making film coating with epoxidized vegetable oil. I would like to thank for those were involved in finishing this project. First and foremost, I have to thank my supervisor, Pn. Sharifah Nafisah bt Syed Ismail. Without her assistance and dedicated involvement in every step throughout the process, this paper would have never been accomplished. Not forget to lab assistances, Pn. Hadayu, Pn. Nurul, Pn. Ziana and other lab assistances for helping me in conducting the synthesis process and testing of sample and the guidance in handling laboratory work. I would also like to show gratitude to my friends especially whose are in same supervisor with me. Last but not least, an honorable mention goes to my parents and family members for their support and encouragement in morale and financial during completing my final year project. This dissertation stands as a testament to all unconditional love and encouragement.

TABLE OF CONTENTS

CHAPTER ONE: INTRODUCTION

CHAPTER TWO: LITERATURE REVIEW

CHAPTER THREE: METHODOLOGY

CHAPTER FOUR: RESULT AND DISCUSSION

CHAPTER FIVE: CONCLUSION AND RECOMMENDATION

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AEPO	Acrylated Epoxidized Palm Oil
AESO	Acrylated Epoxidized Soybean Oil
DOE	Degree of Epoxidation
EPC	Epichlorohydrin
EPO	Epoxidized Palm Oil
ESO	Epoxidized Soybean Oil
FTIR	Fourier Transform Infra-Red
HBr	Hydrobromic Acid
KHP	Potassium Hydrogen Phthalate
KOH	Potassium Hydroxide
MAESO	Maleinized Acrylated Epoxidized Soybean Oil
OOC	Oxirane Oxygen Content
PVA	Polyvinyl Alcohol
PVC	Polyvinyl Chloride
SOPERMA	Soybean Oil Penaerythritol Maleates
TMPTMA	Trimethylolpropane trimethacrylate
UV	Ultra Violet
VO	Vegetable Oil
VOC	Volatile Organic Compound

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Vegetable oils (VO) is the only one single, biggest, effortlessly accessible, low cost, non-toxic and biodegradable family that produce materials are able of competing with fossil fuel determined petro-based products. In recent years, using vegetable oils as renewable resources become a growing trend especially in chemical productions. The growing interest is to produce biopolymers. Recently, more environmental friendly manufacturing procedures have been introduced for polyurethane production using bio-renewable sources.

One of the current priorities in polymer chemistry is to explore bio-based polymers from renewable resources. For packaging applications, several bio-based polymers such as proteins and polysaccharides have been researched as raw materials but they are poor water resistance because of their hydrophilic natures (Sung, 2014). Vegetable oils are most suitable as ideal raw materials to prepare economical polymers because they are abundant, readily available, and reasonable price.

In addition, vegetable oils are expected to be an ideal chemical feedstock due to the numerous applications and environmental friendly. Besides that, their availability in worldwide and versatile chemistry are including in interesting properties of vegetable oils. Vegetable oils have many excellent properties that can be used in the production of valuable polymeric materials (Habib and Bajpai, 2011) as shown in Figure 1.1 below. Moreover, the long fatty acid chains of vegetable oils impart desirable flexibility and toughness to some brittle resin systems such as epoxy, urethane and polyester resins. Polymeric materials film shows good abrasion resistance and physical strength on their process but vegetable oils showed excellent to optimize the properties of polymeric materials.

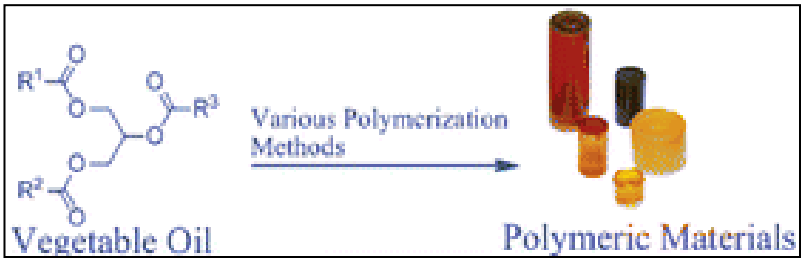


Figure 1.1 Reaction of vegetable oil in making polymeric materials

However, the epoxy groups are accessible for assist chemical modification reactions. The presence of acrylate functions in polymer is the most part made for the purpose of polymerizing or copolymerizing of double bonds driving to network or grafted copolymers. Besides that, the development of the soy-based resins is still challenging for the polymer and composite industries for structural applications. Eventough the materials are not costly but it still hard to handle due to the synthesize process which take long time to carry out. To produce the bio-based coating will be affected in cycle time.

Soybean oil is the most important resources and available across the world. Soybean is regenerated through photosynthesis by means of a chemical process with organic peroxide in which carbon from double bonds of unsaturated fatty acids has been epoxidized to produce epoxy functional group. Soy protein-based adhesives become major benefit as the soybean is low cost raw material. Many new techniques have been developing in many years for the conversion of soybean oil to epoxidized soybean oil. Soybean oil becomes epoxidized soybean oil after the epoxidation process. In epoxidation reaction, antioxidants that are commonly applied in this reaction include homogenous and heterogeneous catalytic systems using hydrogen peroxide (Chen, *et al*., 2018).

Epoxidized soybean oils containing different numbers of epoxide groups/molecule were synthesized. Epoxidized soybean oil (ESO) has used as plasticizer, stabilizer, lubricant and polyol (Alam, *et al*., 2014; Pantone, *et al*, 2017). Currently, ESO mostly produced at industrial scale by the per acid process (Chen, *et al*., 2018) in organic oxidation corresponding carboxylic acid in the presence of mineral acids. ESO has shown promising effects when it used as reactive modifier because of the presence of unsaturated epoxy compounds that available for further chemical modifications. Examples of chemical modification include the introduction of acrylic acid into epoxidized soybean oil by acrylation process to produce acrylated epoxidized soybean oil (AESO).

To prepare AESO, the fatty acid was in corporation between trifunctional acrylate monomer and trimethylolpropane trimethacrylate (TMPTMA) along with the photoinitiator benzophenone and activator and cured with UV (Xiaoyan, *et al., 2019*, Habib & Bajpai, 2011). The process carried out in oil bath to control the temperature. AESO is used widely in the fields of UV-curing coatings, biodegradable foam and composite materials. AESO cured film also has also slow assimilation rates, strong adhesion, low hardness, and good thermal stability (Chu, *et al.*, 2014).

UV curing is widely used in technology to ensure the uniformity of curing for coated panels. Other than that, it also to develop the appearance and low emission of organic volatile compounds (Seung, *et al*., 2012). The majority of UV-curing produced highly crosslinked polymers through photoinitiated radical polymerization. Usually, this type of curing were used in coating and some company used in paint ink. UV-curing widely used in automotive coating in order to improve the profit and reduce time consuming. For thermal coating, biomedical devices widely used protein repellent coatings to minimize the unspecific adhesion that tend to failure of the device. High technology modification techniques for surface can be used in this application to give antifouling properties to objects.

In this work, ESO was reacted with acrylic acid that acts as ring-opening reagent in order to produce AESO and thin film. It has low viscosity, low skin irritation and excellent pigment wetting characteristics (Chu, *et al*., 2014). A development on AESO has been done to reduce the moisture sensitivity and enhance gas permeability of starch-based film (Xiaoyan, *et al*., 2019). The AESO resin was cured by using thermal technique to produce thin film bio-based coating. It also can be used in the plastic production.

1.2 Problem Statement

Production of epoxy resin based vegetable oil friendly is rather environment friendly and become as promising raw materials for manufacturing of bio-based film because of its biodegradability, recyclability, good processability and high transparency.

In spite of its numerous advantages, there are several drawbacks that epoxy resin based vegetable oil faces. One of the problems with epoxy resin is the low production of polymer crosslinking and tends to produce low thermal and mechanical properties, which make the usage of ESO loss attractive.

To eliminate this problem, acrylated epoxidized soybean oil has been identified to produce thin bio-film from the reaction of ESO with acrylic acid via acrylation process. AESO has the ability to be crosslink with active functional group to produce AESO thin film that is less expensive and have good mechanical strength.

Moreover, highly demanded on biodegradable film nowadays has creates many researches to look into potential resources to be used to eliminate or reduce the dependent on petroleum based product. Epoxy resins from petroleum oil are produced by the reaction of bisphenol-A and epichlorohydrin (EPC) that harm to human and environment. The chemical also acts as endocrine disruptor which can disrupt the physiological function which can have a negative biological effect in humans.

The petrol-based polymers are not biodegradable. Therefore, it has become major problem for coating production. In addition, sources from under sea also will decrease from year by year. By using bio-based materials, reduction of global warming issues can be help by replacing petroleum based products with almost have same functions.

1.3 Significance of Study

AESO produced from natural resources which is processed soybean oil and making thin film from soybean oil. Soybean oil is less toxic and good lubricity eventough contain high degree of unsaturation chain. They are relatively low in reactivity. However, to make useful functional polymers by modified the unsaturated sites of fatty acids in various ways including chemically modified. One of the methods is by converting the internal double bond into epoxy functionality. This oxirane ring can be used further in numerous coatings innovations such as epoxy-amine and epoxy-anhydride crosslinking and acrylated for utilize in UV-cured systems.

Besides that, soybean oil has been used widely to produce coating, inks and lubricants (Lopez, *et al.*, 2013). AESO is one of the important subordinate of soybean oil and a very attractive monomer deliver very low critical fractions under copolymerization. AESO give preferential distribution (Lopez, *et al.*, 2013) due to the 3D-crosslinking direction which is bonded to polar functional groups.

Thus, the current researches intend to utilize AESO as a replacement of conventional raw material of epoxy resin to produce AESO. AESO is solventless and will reduce volatile hazardous gasses. In addition, amine and anhydride used in the conventional epoxy resins may be eliminated. The process and cost of new green epoxy and the intensity the environment can be minimize by reducing the chemical waste. The research are expected to produce coating resin from acrylated epoxidized soybean oil (AESO) with amine functionalized which is low in cost of production and can benefit the environment through this technique.

1.4 Objectives of Study

The objectives of this study are:

1. To synthesize an acrylated epoxidized soybean oil from the reaction of acrylic acid and epoxidized soybean oil by the acrylation process.
2. To characterize Acrylated Epoxidized Soybean Oil by using oxirane oxygen content test, viscosity test, acid value test and Fourier Transform Infra-Red (FTIR) Spectroscopy test.
3. To characterize the acrylated epoxidized soybean oil film coating by using volatile organic compound (VOC) test, pencil hardness and FTIR.

CHAPTER 2

LITERATURE REVIEW

2.1 Soybean Oil

Soybean oil is categorized in vegetable oil because it has natural fatty acid. Hydrogen are fully filled the saturated fatty acid chains. It has carbon-carbon double bonds either one or more on their chains (Guner *et al.*, 2006). The fatty acid contain double bonds, epoxies, and other functional group which are functionalities in the backbone that able to undergo several suitable chemical reactions like hydrogenation, transesterification, auto-oxidation, epoxidation, hydroxylation, acrylation, isocyanation and others (Alam, *et al.*, 2014). Fatty acid presented in the soybean oil showed in Figure 2.1. This vegetable oil tends to dry or form films by their own virgin form.

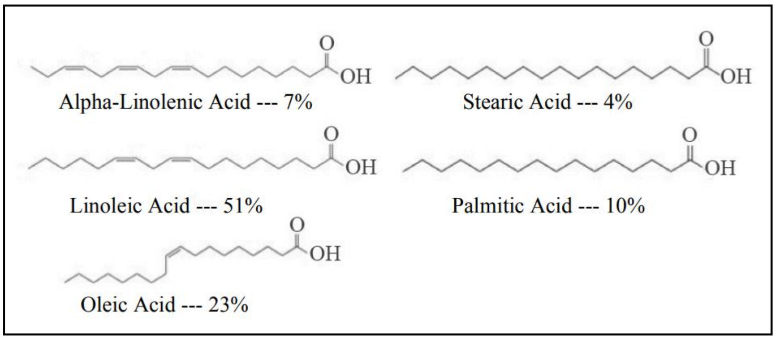


Figure 2.1 Major fatty acids in soybean oil

According to Habib and Bajpai (2011), soybean oil is categorized as triglyceride oil which is one of the most important sources for biopolymers that can be found in sunflower, castor oil, linseed oil, palm and soybean. The most common modification reaction carried out is epoxidation reaction. In order to have more reactive functional groups that can be used in the free radical polymerization, double bond in the soybean oil must be converted (Saithai *et al*., 2013). Figure 2.2 shows the structure of soybean oil.

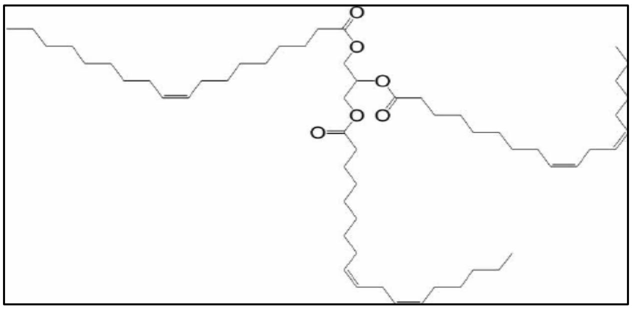


Figure 2.2 Structure of soybean oil.

Soybean oil known as bio-based oil because it comes from the natural sources. This vegetable oil can replace petrol based oil which is unfriendly to environment. Soybean oil were produced about 80% of each year is used for human food. Another 6% is exploiting for animal feed, while the remainder (14%) has nonfood uses (Lopez, *et al*., 2013). Soybean oil is prepared with saturated and unsaturated fatty acid which 80-85% from unsaturated fatty acids (Mihail and Petrovic, 2011). Other than that, they estimated that in a mole of soybean oil has average molecular weight by 874 g/mol and 4.6 carbon carbon double bonds.

In the surface coating, vegetable oil (VO) used semi-drying or drying. It depends on their unsaturated portion such as an arrangement of double bonds which is cis or trans (Alam *et al*., 2014). A study by Chu, *et al*. said, “American Soybean Association annual set aside ten millions dollar to fund the comprehensive utilization of soybean oil”. When using conventional oxidative drying oil, the process was very time-consuming but with UV curing less than fraction of seconds, the drying can be done. (Habib and Bajpai, 2011). Water resistance in coating increases due to the hydrophobic nature of soy. The cross linkable double bonds and contribute to the hardness of film imparting durability and impact resistance.

To introduce hydroxyl group, different methods from Zhang, (2015) were used into composition oil in order to prepare polyols for polyurethane production. The methods are including epoxidation or ring opening, ozonolysis, hydroformulation/reduction with syngas and transesterification (amidation). As the primary component in coatings and paints, vegetable oil or soybean oil was used (Alam *et al*., 2014) to produce those applications (Sung, 2014) state that without the functional group such as epoxy and hydroxyl group, the carbon double bond cannot directly used to convert polymer even though unsaturated fatty acids have olefins as active sites.

2.2 Epoxidized Soybean Oil

Epoxidized soybean oil is well-known as renewable resources which applicable to polymer products include coatings and adhesives. It has been produced from 30 years ago and still available in various trade names. The epoxidized soybean oil (ESO) was widely used as plasticizer instead of phthalates in plastic industry. Flexibility, stability and processability in plastic products can be increase by using ESO as plasticizer. Besides, Guner (2006), Liu (2005) and Petrovic (2008) claimed that by using epoxidized soybean oil can improved the stability of commercial polymer such as polyvinyl chloride (PVC) and polyvinyl alcohol (PVA).

Epoxidized soybean oil have functional epoxy group where it able to react with suitable curing agents to form elastomeric network by apply in UV curable coating system (Habib and Bajpai, 2011). Epoxy groups been polymerized by ring opening reaction to form ESO and can be hydrogels by hydrolyzed where it could be find in medical application. The structure of epoxidized soybean oil is shows in Figure 2.3. Soybean oil is the first preferred oil in the synthesis compared to the other vegetable oils due to its number of carbon double bonds approximately 4.6 per triglyceride (Acik, *et al*., 2018). From modified ESO, rigid and glassy thermoset materials were derived. ESO was synthesized by chemical and chemo-enzymatic epoxidation methods.

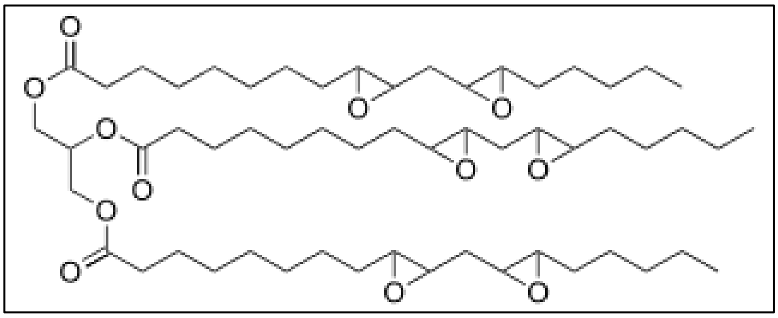


Figure 2.3 Epoxidized soybean oil structure.

Allylic double bond added to oxirane rings of ESO by using reaction of oxirane ring-opening then copolymerized by using free radical polymerization and esterification the allylated ESO with maleic anhydride to form thermosets. Increase in maleic anhydride content, the modulus, glass transition temperature (Tg) increase up to 123°C and tensile strength up to 29 MPa respectively. Meanwhile, the elongation drop down to the lowest was 7% (Sung, 2014).

Peroxyacids are produced *in situ* in the reaction vessel for safety reasons by adding acid catalyzed oxidation of the corresponding organic acid with hydrogen peroxide (Habib and Bajpai, 2011). Their mechanical properties make some of the polymers suitable for advanced composite applications (Zhang, *et al.*, 2015). The degree of epoxidation after synthesis process was calculated from below equation in order to get stable epoxidized soybean oil.

$$\text{DOE} = \frac{number\ of\ epoxide\ group}{number\ of\ starting\ double\ bonds} \text{ x } 100$$

An experiment was carried out to determine oxirane oxygen content (OOC) by synthesis the soybean oil to get epoxidized soybean oil using ASTM D1652-11. High OOC value indicates high degree of epoxidized number in the modified oil. OOC test result obtained from titration method where the low value is not necessary but it is possible for degradation of epoxide groups’ eventough the value is low (Meadow, *et al.*, 2017).

2.3 Acrylic Acid

Acrylic acid acts as the ring-opening reagent to be esterified with epoxidized soybean oil. Acrylic monomer and oligomers are the free radical photopolymerization components as main raw materials in UV-curing coating industries. Besides, acrylic acid was used in oil treatment chemicals, manufacture of plastics as a tackifier and as flocculants. Acrylic acid able to produce hydroxyacrylates where it is employed as a comonomer with acrylamide in anionic polyacrylamide for use in industrial coating formulations.

It is miscible in water, alcohol, benzene and acetone. It polymerized in presence of oxygen. Acrylic acid is sensitive towards sunlight and heat. The boiling point is 141°C and melts within 14°C. In addition, it able to drying faster because of it evaporates behavior. Figure 2.4 illustrated the structure of acrylic acid.

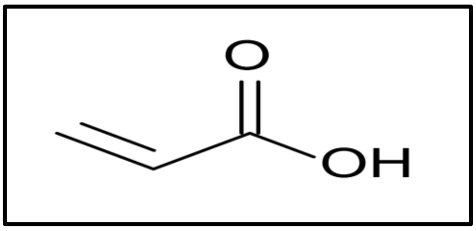


Figure 2.4 Structure of acrylic acid.

From the structure above, vinyl group is attach to carbonyl group. The double bond and functional carboxylic acid group play a crucial role by giving acrylic acid behavior similar with carboxylic acid. The acrylic acid market has high demand over the years. It is used in industries as a chemical preparation of polymers, plastics, coating and food packaging. Because of it is easily evaporate and corrosive behavior, they must be stored in the tanks made from steel, glass or iron and keep in closed condition.

2.4 Acrylated Epoxidized Soybean Oil Film

Acrylated epoxidized soybean oil (AESO) was prepared by reacting epoxidized soybean oil and acrylic acid. Figure 2.5 illustrates the chemical reaction of epoxidized soybean oil and acrylic acid with addition of photoinitiator such as trimethylamine or hydroquinone under temperature of 80°C (Habib and Bajpai, 2011). Acid value must be calculated in order to get extent of reaction**.** Acrylated epoxidized soybean oil can be achieved by the synthesis reaction of acrylic acid as ring opener and epoxidized triglyceride which react as additional polymerization.

AESO coating were created to diminish moisture effect and permeability of starch-based materials. Coating that applied on the substrate act as protective layer. Other than that, it can help enhance the wettability (Zhuang, 2011), wear resistance and other properties of the substrate surface. Reduce in volatile organic compound (VOC), sustainability and consumer demand are key drivers encourage interesting developments in soy technology.

FTIR result shows that the moisture sensitivity was decreased since the crosslinked AESO enforce as hydrophobic layer (Xiaoyan, *et al.*, 2019). Therefore, it is proven that very thin layer of AESO might accomplish good water resistance. It is one of the largest bio-based industrial and one of the interesting techniques in preparing bio-based oil polymers (Saithai, *et al.*, 2013). AESO is produced by the epoxidation of ESO followed by substitution of epoxide groups into acrylate group. The mechanical properties of AESO show higher than ESO which has been established from the experiment. It has high weather resistance rather than ESO.

AESO cured film need huge amount of reactive diluents because it has low rate assimilation, strong adhesion, low hardness and good thermal stability (Chu, *et al.*, 2014). However, for past few years, nanosized fillers incorporate on preparing AESO composite in order to improve the thermal and mechanical properties (Dong, *et al.*, 2018).

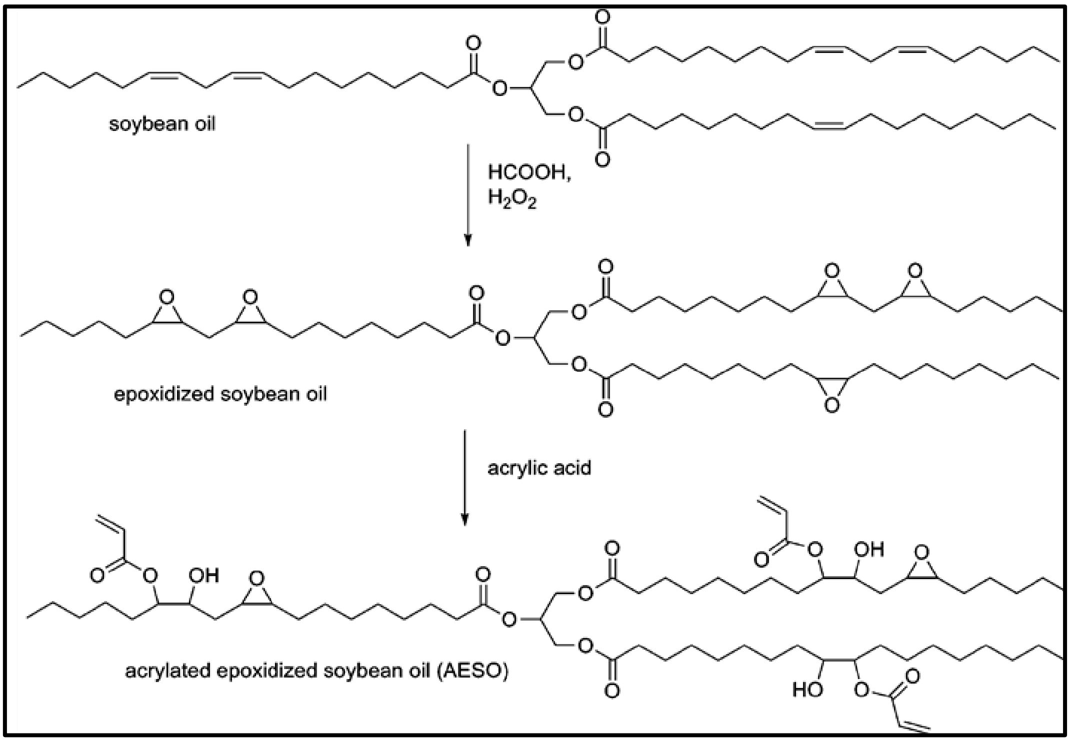


Figure 2.5 Full reaction of acrylated epoxidized soybean oil (AESO).

Lu (2004) reported a study in the preparation of soybean oil based polymer to make the functionalized soybean oil such as AESO, maleinized acrylated epoxidized soybean oil (MAESO), and soybean oil pentaerythritol maleates (SOPERMA) were respectively combined with styrene to become polymer matrix, and clay nanocomposites. The monomers showed better miscibility with nanoclay compared with unmodified soybean oil because high solubility parameter and polarity caused by the chemical modification of soybean oil. The bending modulus and storage modulus were increased by nanoclay additions, but thermal decomposition temperatures of the composites were not significantly improved. The important parameter is degree of esterification that may affect the coating property (Habib and Bajpai, 2011), and the reaction was performed until the acid value reached below 6 mgKOH/gm. The higher concentration of reactive sites gives change in the acid value occurs with the reaction time because the acid and epoxide groups are more likely to associate.

2.5 Fourier Transform Infra-Red Spectra

The FTIR spectroscopy of AESO shows that the hydroxyl group is successfully converted to the acrylated functionality through condensation esterification. This is indicated by the presence of hydroxyl functionality of resin at absorption band of 3508 cm^{-1}, associated with hydrogen bond of –OH and a strong absorption band for the carbonyl group, C═O of the acrylated compound at 1723 cm^{-1} (Kasetaite, *et al*, 2018). Figure 2.6 shows the result of FTIR for acrylated epoxidized soybean oil (AESO).

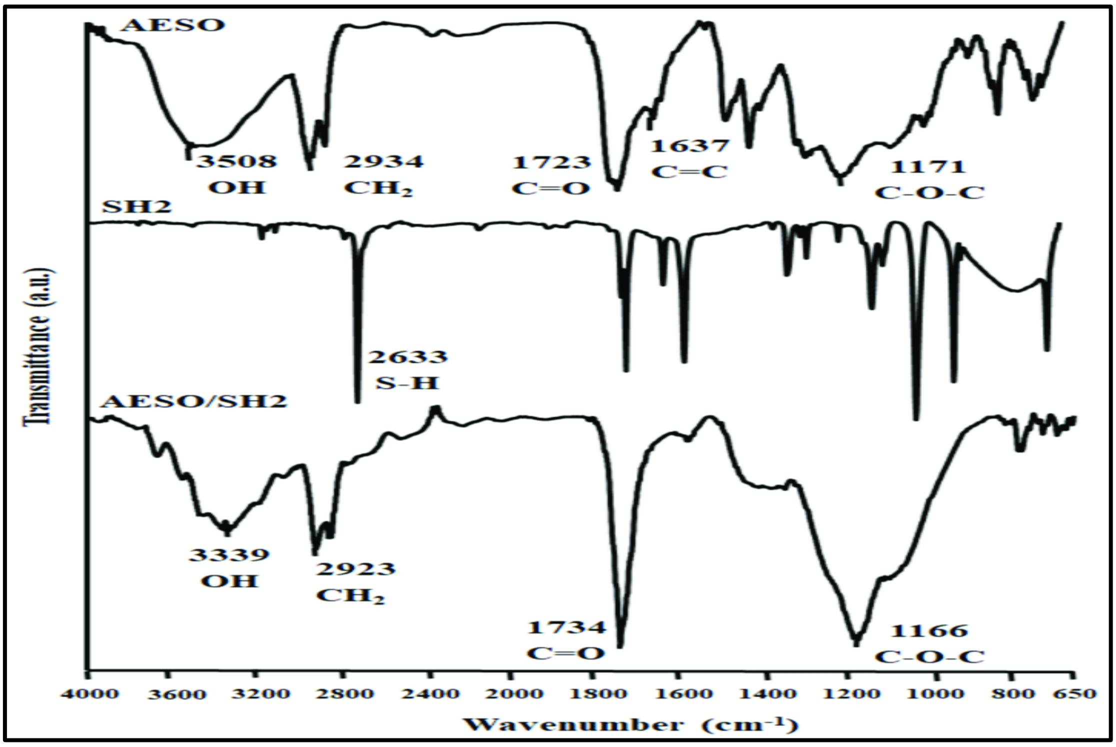


Figure 2.6 FTIR result for acrylated epoxidized soybean oil (AESO).

Some of the researches produce thin films based on different types of epoxidized vegetable oils with acrylic acid and the result for FTIR on palm oil (Salih, *et al*, 2015) shown as in Figure 2.7 as followed. One of the studies on different vegetable oil was epoxidized palm oil (EPO). The stretching vibration for C-O-C groups clearly showed in FTIR spectra of EPO at wavenumber 1240 cm^{-1}, the wavenumber around 850-830 cm-1 indicates other characteristic band of the epoxy rings. In the saturated fatty acid backbone showed methylene moieties (CH_2) appear at 2853 cm^{-1} stretching band, terminal methyl groups (CH_3) of the triglyceride chains showed a strong band of C-H stretching at 2924 cm^{-1}, and in-plane deformation band of C-H at 1378 cm^{-1}. Clearly, the comparison between the FTIR spectra of EPO and AEPO uncovers that there are unused IR assimilation bands in the spectrum of AEPO, such as the absorption band at 810 cm^{-1}, which is credited to the out-of-plane deformation of the C=C of the vinyl moieties of the acrylate groups, other than that, the band at 1636 cm^{-1}.

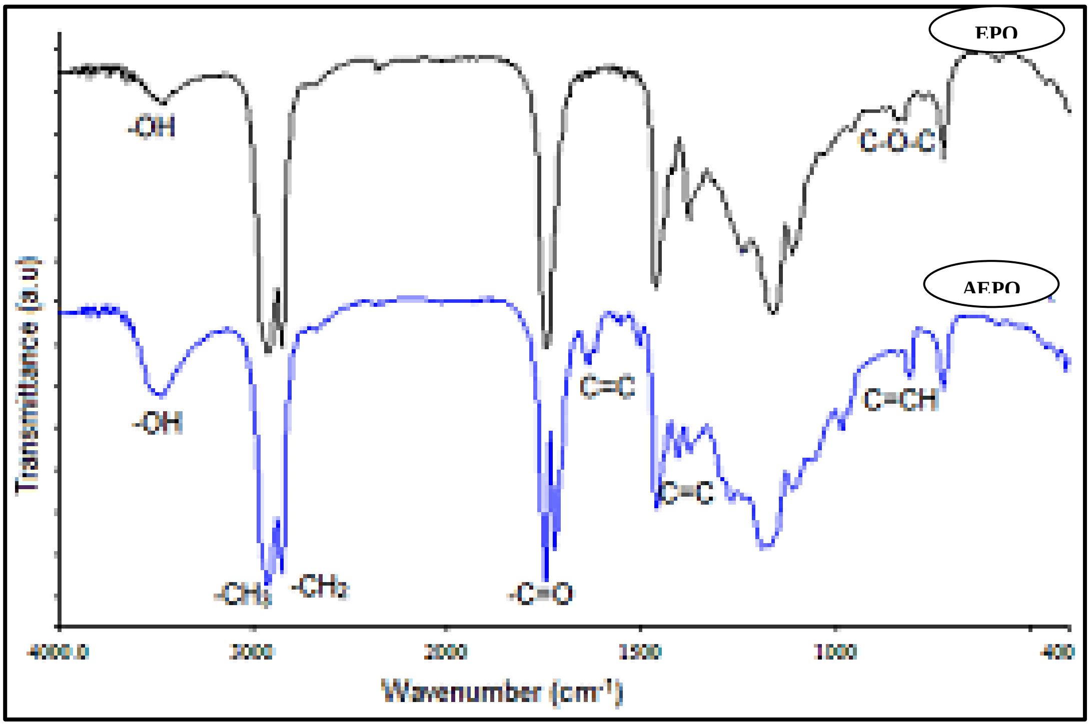


Figure 2.7 FTIR result on epoxidized palm oil (EPO) and acrylated epoxidized palm oil (AEPO).

CHAPTER 3

METHODOLOGY

3.1 List of Materials

a) Epoxidized soybean oil, $C_{57}H_{98}O_{12}$ was purchased from Parchem (ESBO, New York).

b) Acrylic acid, $C_3H_4O_2$ with molecular weight 71.08 g/mol was purchased from E. Merck

c) Triethyl amine, $C_6H_{15}N$ was purchased from E. Merck.

d) Hydrobromic Acid, HBr with molecular weight 80.91 g/mol was purchased from Sigma Aldrich.

e) Diethyl ether was obtained from S.D.Fine Chemicals.

f) Hydroquinone, $C_6H_6O_2$ with molecular weight 138.16 g/mol was purchased from Sigma Aldrich.

g) Toluene, $C_6H_5CH_3$ with molecular weight 92.14 g/mol was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

h) Potassium Hydrogen Phthalate, KHP with molecular weight 204.22 g/mol was purchased from Sigma Aldrich.

i) Acetic Acid glacial, CH_3COOH with molecular weight 60.052 g/mol was purchased from Sigma Aldrich.

j) 3-(Triethoxysilyl)-propylamine, $C_9H_{23}O_3Si$ with molecular weight 221.37 g/mol was purchased from Sigma Aldrich.

k) Trimethylolpropane triacrylate, $C_{15}H_{20}O_6$ with molecular weight 296.319 g/mol was purchased from Sigma Aldrich.

l) Sodium Chloride, $NaCl_2$ was purchased from E. Merck.

3.2 List of Apparatus/Instruments

a) Magnetic stirrer
b) Thermometer
c) Reactor vessel
d) Volumetric flask
e) Oven
f) Liebig condenser
g) Burette
h) Brookfield viscometer
i) Fourier Transform Infra-Red Spectroscopy (FTIR)
j) Heating mantel
k) Glass slide
l) Petri dish
m) Rotary evaporator
n) Retort stand
o) Mechanical stirrer

3.3 Experiment Methods

3.3.1 Preparation of Acrylated Epoxidized Soybean Oil (AESO)

Acrylated Epoxidized Soybean Oil (AESO) was synthesized by mixing 150g of epoxidized soybean oil with 118g acrylic acid in the presence of triethylamine as catalyst and 2g of hydroquinone act as an inhibitor. Then process was placed in an oil bath at temperature 80°C for 5 hours in the reaction vessel equipped with Liebig condenser and using mechanical stirrer at 400 rpm. The inhibitor was added into the flask and the glacial acetic acid was put by drop wise using dropper. The acid value was checked every 1 hour until the value reached to 5 mgKOH/g or less. Oxirane Oxygen Content (OOC) value test was conducted at the beginning of the reaction until the acrylation process was completed. The oil turns to deep yellow or caramel color and transfer into separating funnel. Then, distilled water was added to separate them followed by addition of diethyl ether and sodium chloride. The excesses water and diethyl ether were removed through water base extraction by using rotary evaporator to purify it.

3.3.2 Preparation of AESO Film Coating

The cured thin film was prepared by the addition of AESO with 3-(Triethoxysilyi)-propylamine and trimethylolpropane triacrylate. Prior to sample curing, glass slide were used as substrate. The solution was stirred at room temperature until homogenous. Prepared resin was dropped onto glass slide until all surface of the substrate was covered with the resin. The solution was cured in an oven at 150°C for 24 hours to produce cured thin film. Then, AESO film was undergone several tests such as volatile organic compound test, pencil hardness test and gel content test. The formulation for each resin sample was showed in Table 3.1 while the set up of apparatus for AESO was shown in Figure 3.1.

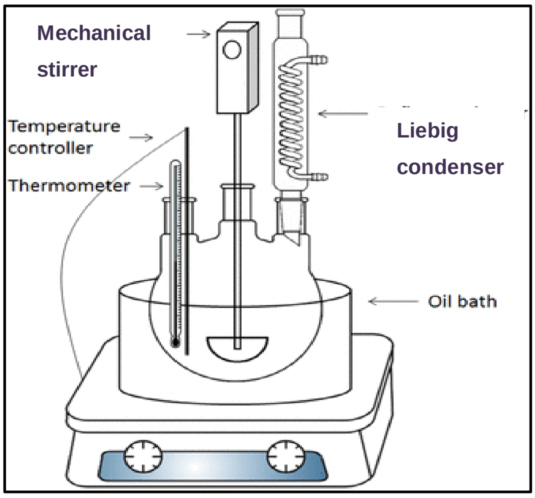


Figure 3.1 Illustration on synthesis process for Acrylated Epoxidized Soybean Oil (AESO)

Table 3.1 Formulation of mixture in sample 1, sample 2 and sample 3

Sample	Ratio mixture of Trimethylolpropane triacrylate to 3-(Triethoxysilyl)-propylamine
1	30:70
2	50:50
3	70:30

3.4 Characterization of Acrylated Epoxidized Soybean Oil

3.4.1 Oxirane Oxygen Content (OOC) Test

The oxirane oxygen content (OOC) test was used for the characterization of acrylated soybean oil. It is used to define the number of oxirane groups produced in place double bonds. Potassium Hydrogen Phthalate (KHP) and acetic acid were calculated according to ASTM D1652-11 using titration process. OOC test involves the determination the standardization of 0.1N Hydrobromic acid, HBr before the test was conducted. Indicator was dropped to get the color changes from violet to green petronas. The perchloric acid reagent will be calculated using an Equation (1) as below, where N is Normality.

$$N = \frac{\text{W of KHP,g}}{0.2042 \text{ x amount of HBr used,mL}} \qquad \text{Eq. (1)}$$

Where, W is the mass of potassium acid phthalate while HBr is Hydrobromic Acid. The percentage relative conversion to oxirane can be calculated by using Equation (2). The AESO weight have been used was 0.3-0.5g respectively.

$$\% \text{ OOC} = \frac{\text{W of HBr x N x 1.6}}{\text{mass of sample,g}} \qquad \text{Eq. (2)}$$

3.4.2 Acid Value Test

Acid value test was described as the amount of KOH in milligram required to neutralize the organic acids exist in 5 gram of fats. It is also measure the free fatty acids presence in acrylated epoxidized soybean oil follows ASTM D8032-16. The acid value test was determined by using titration process. 5g of fatty acid were titrated with potassium hydroxide solution (KOH) in the presence of phenolphthalein indicator until pink coloration can be observed which persist for 30s. The volume of KOH titrant used has been observed and acid value test was calculated according to the Equation (3).

$$\text{Acid value} = \frac{\text{VKOH x 5.61}}{\text{W}} \qquad \text{Eq. (3)}$$

Where, V_{KOH}= volume of KOH solution titrant used [mL]

W = weight of sample [g]

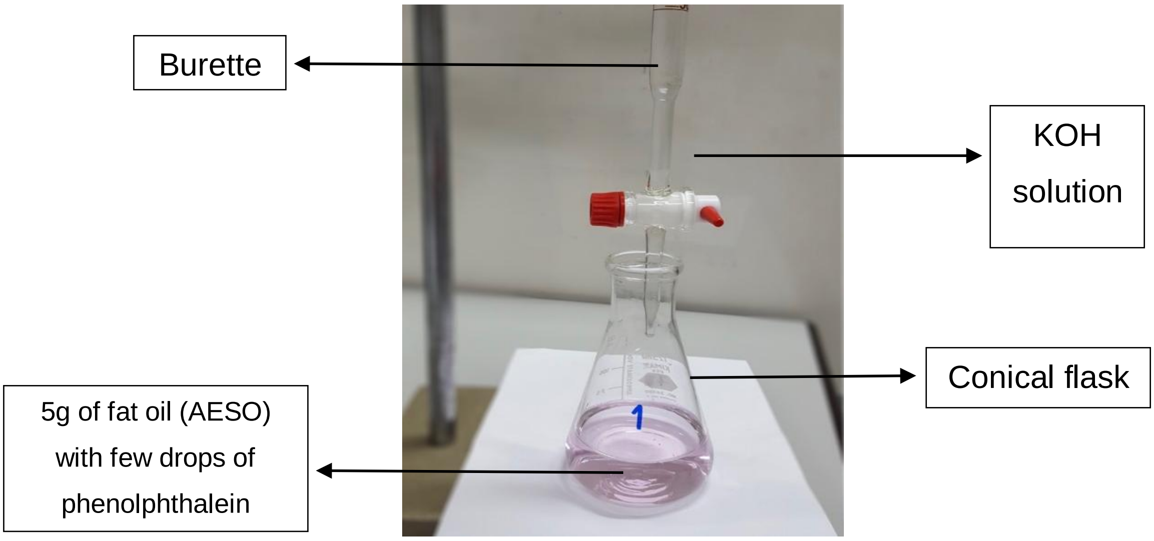


Figure 3.2 Titration process for acid value test

3.4.3 Viscosity Test

The viscosity test for acrylated epoxidized soybean oil was carried out by using Brookfield digital viscometer with a spindle number 3 and small sample adapter. The standard method for this test was referred to ASTM D2196. The viscosity values were depended on the molecular weight distribution. Results on the viscosity value were observed every 1 minute. The unit for viscosity in cP (mPa·s). High molecular weight of acrylated epoxidized fatty acid was produced high viscosity value. This test was conducted to identify the differences of viscous behavior between ESO and AESO.

Figure 3.3 Brookfield digital viscometer used in viscosity test

3.4.4 Fourier Transform Infra-Red Spectroscopy (FTIR) Test

In this study, structural properties of epoxidized soybean oil and AESO were characterized using Fourier Transform Infra-Red Spectroscopy (FTIR). The standard method was followed ASTM D7588. A drop of oil sample was placed on windows and spread evenly on their surface using sharp steel to push the sample until initial peak appeared. Spectra were recorded by 32 scans. The film samples were tested by using KBr plate technique. The result obtained presented in dependence of transmittance, T

(%) and wave number (cm^{-1}). By using Perkin-Elmer FTIR equipped at cold room temperature scanning range. Therefore, the result of functional group in AESO can be concluded based on the range number of peaks obtained. Resolution from $4000cm^{-1}$ to $500cm^{-1}$ was acquired spectra to analyze the structural properties.

3.4.5 Volatile Organic Compound (VOC) Test

Volatile organic compound (VOC) test was carried out in accordance to ASTM D2369 on the acrylated soybean oil film coating. It was used to measure volatile matters which was not fully consumed in the film coating and might harms the atmosphere when exposed under tropical environments. The volatile content were removed by heating process and left only non-volatile content in the film. The weight percent of volatile content of the sample was determined by heating at 120°C in the oven for 2 hours with 5g of fatty acid. Then, the sample from oven was placed in the desiccators and was let cooled. Desiccators was used to avoid the sample absorbed the surrounding moisture. After cooling was done, the heated sample (m_1) was weighed. The percentage of solid content stayed in the sample after the heating process was calculated by using formula as shown in Equation (4):

$$\text{VOC, \%} = \frac{m2-m1}{m2} \text{ x } 100 \qquad \text{Eq. (4)}$$

3.4.6 Pencil Hardness Test

Pencil hardness test have been used to determine the scratch hardness of particular coated film. It is simplest testing but the result was varying due to the equipment used for the test. The pencil hardness has been tested from the softest lead which is 6B to hardest which is 9H. Previously, film from polyester and polycarbonate fall in range B to 4H. The techniques used must be correct and the effort use is more. ASTM D3363 is the standardized test for pencil hardness. The procedure started with placed the film on the testing surface usually on glass plate. Then, the pencils were in sharp condition then placed the pencil at 45° to the testing surface and released it. Record the result for every type of pencil's lead used. If the result shows there are no scratch at both surfaces and sides of film, the film passes to commercialize.

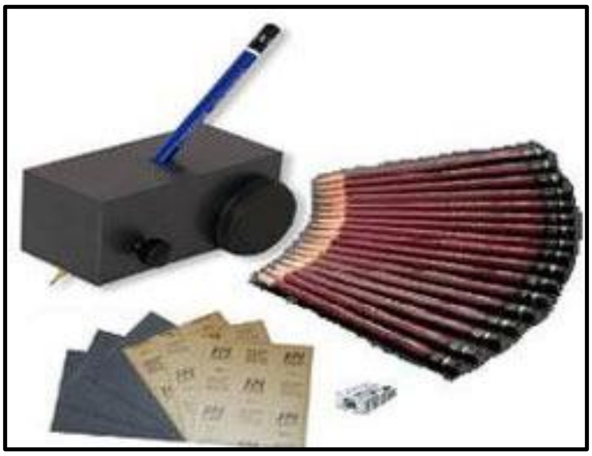


Figure 3.4 Equipment used to test the pencil hardness.

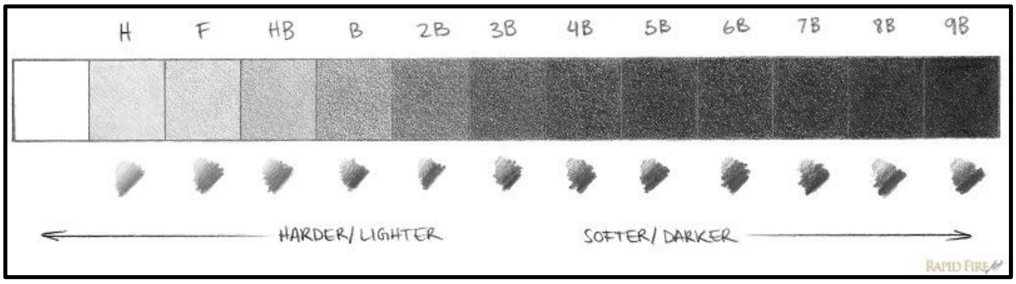


Figure 3.5 Different types of pencil's lead used in testing.

3.5 Flow Chart

Figure 3.6 below shows the methodology process starting from preparation of Epoxidized Soybean Oil (ESO) until characterization of Acrylated Epoxidized Soybean Oil (AESO) by conducted few tests which are acid value test, Oxirane Oxygen Content (OOC) test, viscosity test, FTIR test and the characterization for AESO film such as gel content, volatile organic compound test and pencil hardness test.

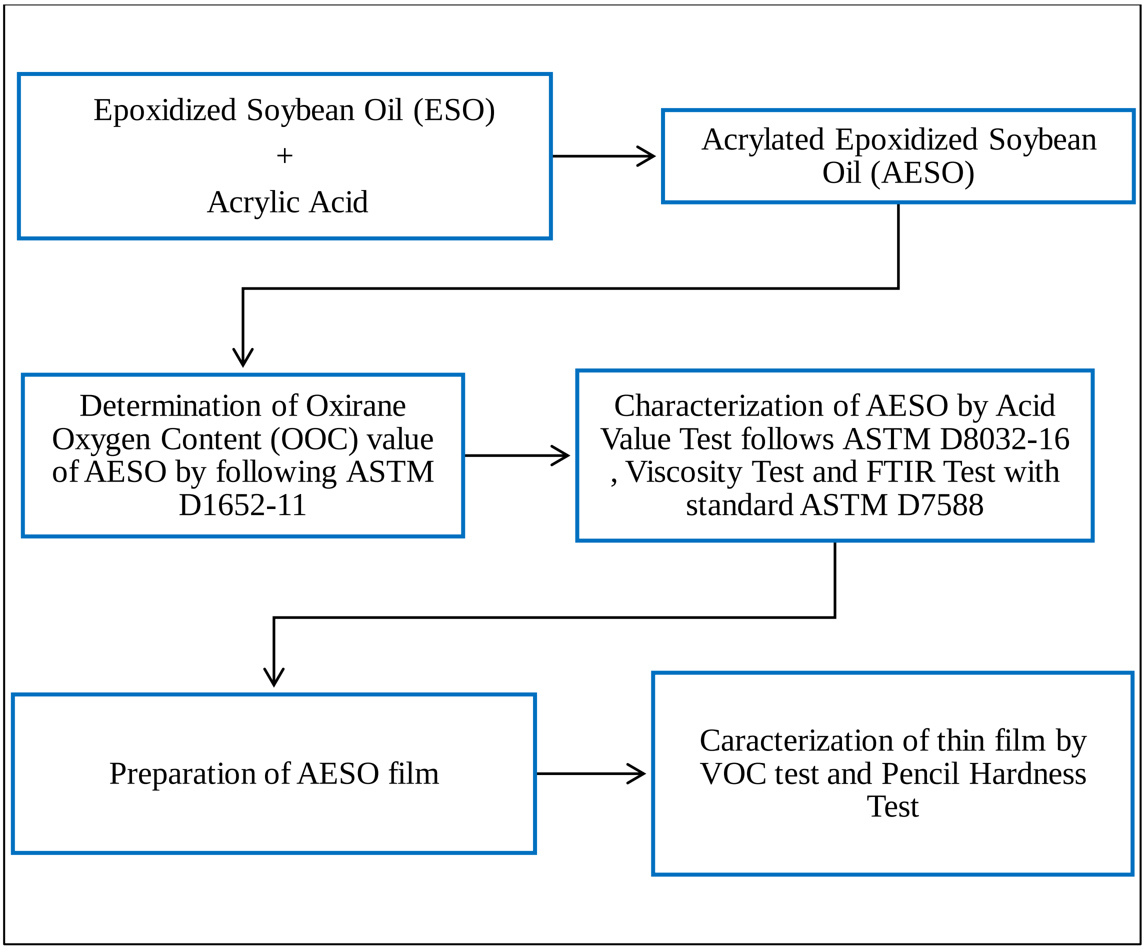


Figure 3.6 Flowchart of the methodology process

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

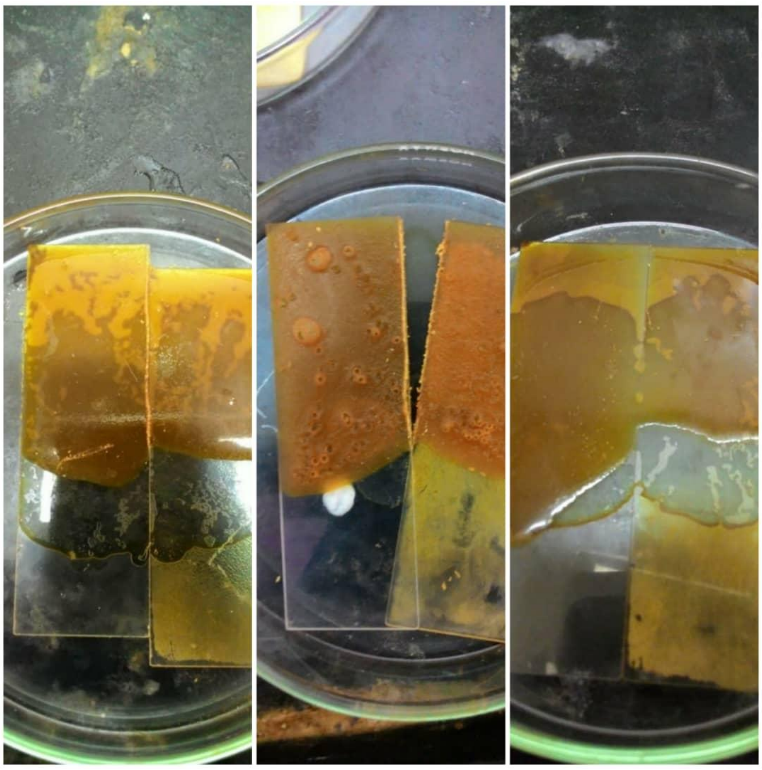
Acrylated epoxidized soybean oil (AESO) was produced by reaction of pure epoxidized soybean oil with acrylic acid with the incorporation of inhibitor. AESO widely used in industry because of its viscosity is not too viscous. Therefore, reactive diluents are not essential to use in order to reduce viscosity of AESO (Behera and Banthia, 2008).

The synthesis process was conducted in the paraffin oil bath in order to stabilize the temperature during reaction. The esterification reaction takes place to form additional polymeric hydroxyl ester by epoxy group reacts with carboxyl ionic group. The acrylate group was bonded to the opened epoxides ring and the acrylate was produced by the ring opening of oxirane oxygen group in the epoxidised soybean oil (Rahman, *et al*, 2015). The epoxy functional groups interact with carboxylic acid group to form AESO.

The pure ESO was put into reaction vessel that was immersed in the paraffin oil followed by the addition of acrylic acid for 45 minutes by dropwise to make it well dispersed, followed by the addition of 2g hydroquinone. The reaction take place for 4 hours to complete until the synthesize process was done and the color of oil turn likes caramel.

Next, film coating were prepared by the addition of trimethylolpropane triacrylate to lower the volatility of coating and 3-(Triethoxysilyl)-propylamine. The ratios of monomers used were 30:70, 50:50 and 70:30 respectively with 5g of AESO. Then the solutions were spread on the glass slide about 2mm thickness was cured in oven at 150°C for 24 hours.

The AESO coating films was shown in Figure 4.1. The AESO dark in color because the degradation of vinyl group during esterification was occurred. Nitrogen purge was crucial to minimize contact with oxygen and reduce the darker color.



(a) 70:30 (b) 50:50 (c)

Figure 4.1 AESO film coating for different formulations.

4.2 Influence of acrylic acid on Oxirane Oxygen Content and Acid Value of AESO

During acrylation, OOC test was done to measure the amount of epoxy group remaining on the triglyceride bone. The sample was added in the conical flask and shook well with 10ml glacial acetic acid and small amount of crystal violet as an indicator. The samples then undergo titration process with HBr acid until turned into green color (reach end-point). The values of OOC were taken for each 30 minutes from starting reaction until the reaction completed.

Range mass of AESO used for each OOC test were 0.3g to 0.5g. Before OOC test, the normality for AESO is 0.9N where it does not exceed 1N in order to obtain accurate results.

Based on the result, it shows that the percentage of oxirane oxygen content decreased with increasing time of synthesis. The amount of HBr consumed also decreased. Therefore, the number of oxirane group in double bonds reduced when the time consumed until 4 hours. The lower the OOC value means the acrylic acid was reacted.

The OOC graph was illustrated in Figure 4.3. OOC value steadily drops for 4 hours where the value were from 3.46% to 1.84%. Therefore, the value reduced about 1.62% along the synthesize process. The OOC value for ESO before the acrylation process started, it showed 5.9%. An OOC value seems to decrease continually with time indicating the attachment of acrylic acid to the opening ring of triglyceride backbone. Further reaction time was needed to reach almost zero OOC value for completing the ring opening process. Temperature was controlled not more than 90°C throughout the reaction.

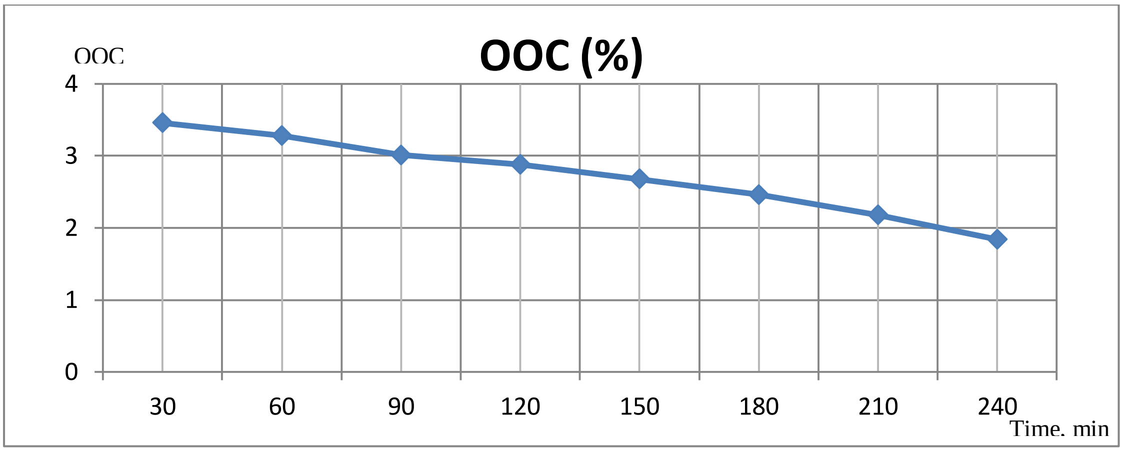


Figure 4.2 The graph of OOC value versus reaction times (minutes) for AESO.

The chemical reaction of acrylation was shown in Figure 4.4. From the reaction, the epoxy ring is in the triglyceride chain. The acrylic acid was reacted with epoxy ring and the acrylate group was attached to the opening ring bond of epoxy. The OOC value is 1.84% indicated that there is still remaining of epoxy ring residue attached to the chain. The reducing of OOC value was assisted by using high temperature and it help to reacting the epoxy ring more faster and also can prevent polymerization from occur besides adding inhibitor. During the reaction process, the inhibitor (hydroquinone) was added to prevent the sample from being polymerized very quickly. If it was polymerized faster, the gelations will occurred and if it's continually, the sample tend to become harden and damaged.

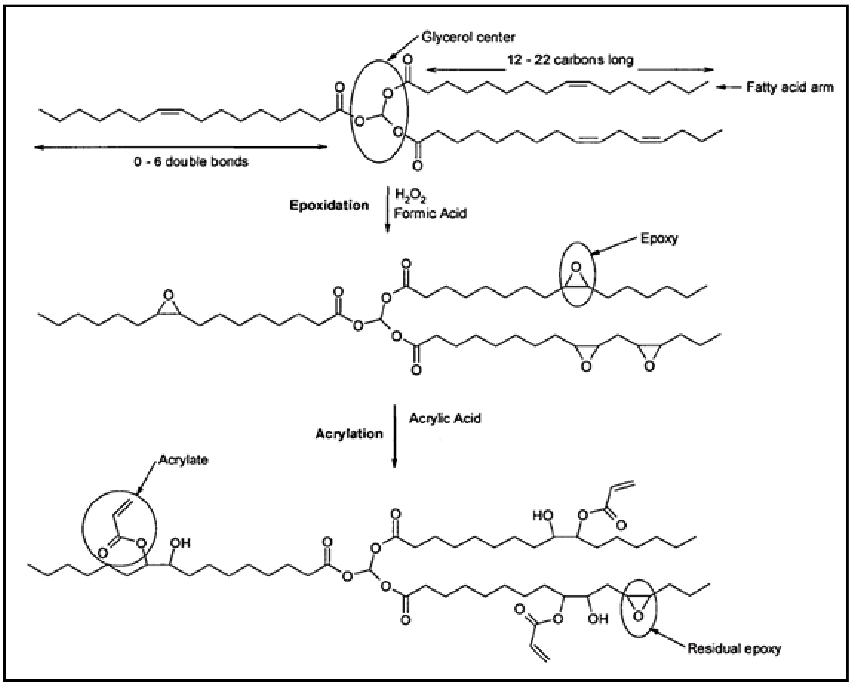


Figure 4.3 Schematic diagram of epoxidation process and acrylation of triglycerides process (**Scala** *et al.*, 2005).

Acid value was obtained in every 30 minutes of reaction. The KOH solution was used to determine the value by titration method. The solution turns to pink from colorless because the acid reacted with the phenolphthalein where to indicate the end-point of measurement.

The acid value for pure ESO is 130 mgKOH/gm and after acrylation, the acid value decreased to 5.53 mgKOH/gm. This happen due to the unreacted acrylic acid content in AESO increased the acid value. The change happened in the acid value with the reaction time because of the higher concentration of reactive sites and greater possibility of acid and epoxide groups association. In initial reaction, the acid value is high and decreased at prolonged reaction duration. The trend decreased is due to the reduction of free acid content in the mixture resulted in high of acid functionality group in the triglyceride backbone (Ibrahim, *et al*, 2005).

From the Figure 4.5, the value increased at initial reaction was high and shows the decreasing pattern when reaction time increased. The declination trend indicates that the occurrence of esterification process.

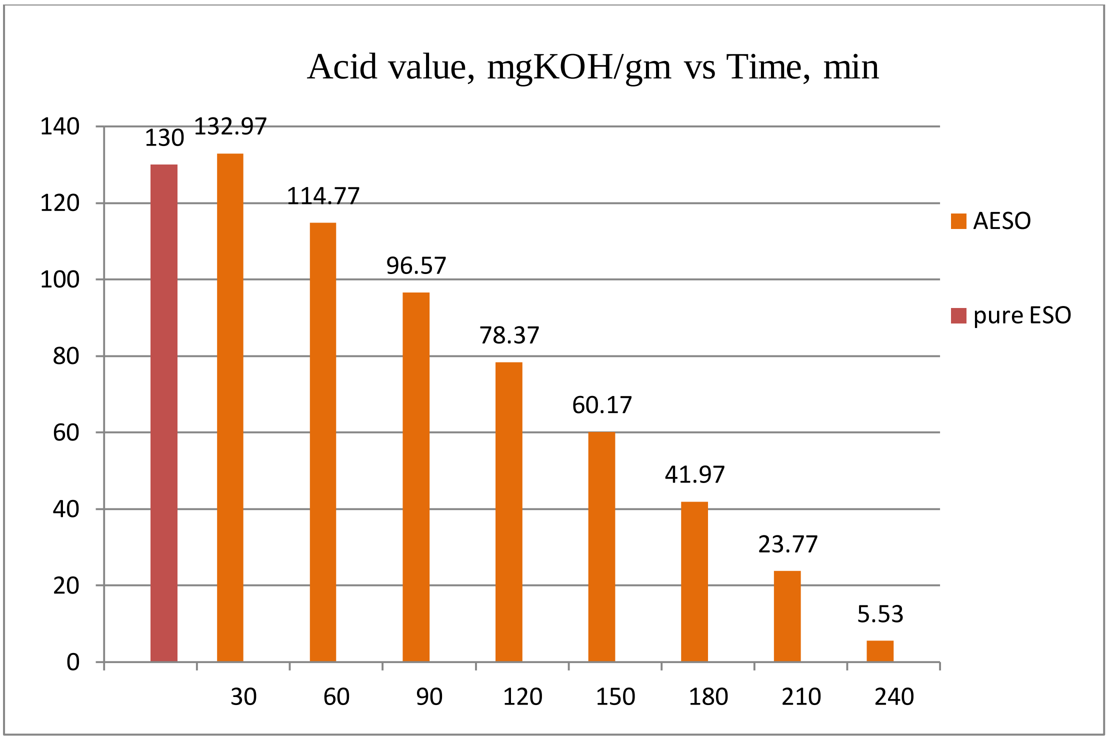


Figure 4.4 The acid value monitoring graph for AESO for 4 hours

4.3 Viscosity Test

Viscosity test was conducted to determine the viscosity of samples by using Brookfield viscometer. It functioned by spinning the spindle number 3 in the beaker filled with sample at specific speed. The spindle caused friction occur where the spindle spin through the sample layer by layer. High forces needed to shear the samples.

The color of the pure ESO is light yellow while AESO is caramel color. The appearance of color is affected by temperature and addition of chemical into ESO that lead to contribute the increased in viscosity. Other than that, it was stickier compared to ESO and the odor was strong due to the presence of excess diethyl ether.

The effect of grafting of acid value on ESO on the viscosity is shown in Table 4.1. The viscosity of AESO showed higher value than ESO which was 835.96 cP than 329.62 cP. Therefore, the differences between this two soybean oil were 43.44%. The increased in viscosity might due to the increased of molecular weight caused by the formation of acrylate group during reaction (Lu, *et al*, 2005).

Table 4.1 Viscometer reading (cP) every one minute

Time, min Sample	1	2	3	4	5	Average
Epoxidized Soybean Oil (ESO)	338.3	331.1	331.1	323.7	323.9	329.62
Acrylated Epoxidized Soybean Oil (AESO)	839.8	839.8	837.4	832.6	830.2	835.96

4.4 Fourier Transform Infra-Red spectroscopy

FTIR test was done to determine the chemical structure of pure ESO and AESO including the different ratio of monomers used to form AESO thin film. From the result of FTIR, the functional groups that exist in each sample were determined. Figure 4.3 shows the FTIR result of ESO and AESO. List of functional group exists in both ESO and AESO were presented in Table 4.6.

Based on FTIR spectra result of ESO, O-H group was showed at peak 3321.6 cm^{-1}, peak at 2925.64 cm^{-1} belongs to the stretching of CH_2 group and the peak at 1693.2 cm^{-1} corresponds to the C=O stretching. Then, 1110.4 cm^{-1} is the peak for C-O stretching. The most important peaks that could be observed in the FTIR result were at 928.98 cm^{-1} which belongs to epoxy ring.

Then, for the FTIR spectra result of AESO, there is a new peak at 3618 cm^{-1} which confirmed that there in an opening of epoxy ring that allow the formation of OH functional group on the sample. CH_2 peak appear at 2927.42 cm^{-1} and C-H peak appear at 2848 cm^{-1}. It could be seen at peak 1653.2 cm^{-1} is an ester C=O functional group while peak at 1547.77 cm^{-1} is C=C functional group. The acrylic has react and attach at the opening of epoxy ring and result in vinyl peak at 983.26 cm-^{1} and it form more broadened ester group at 1653 cm-^{1} Then, there is C-O functional group at peak 1056.88 cm^{-1}. However, there is peak of epoxy group at 816.72 cm^{-1} which was still remaining indicates that functional epoxy group have not being converted into acrylate.

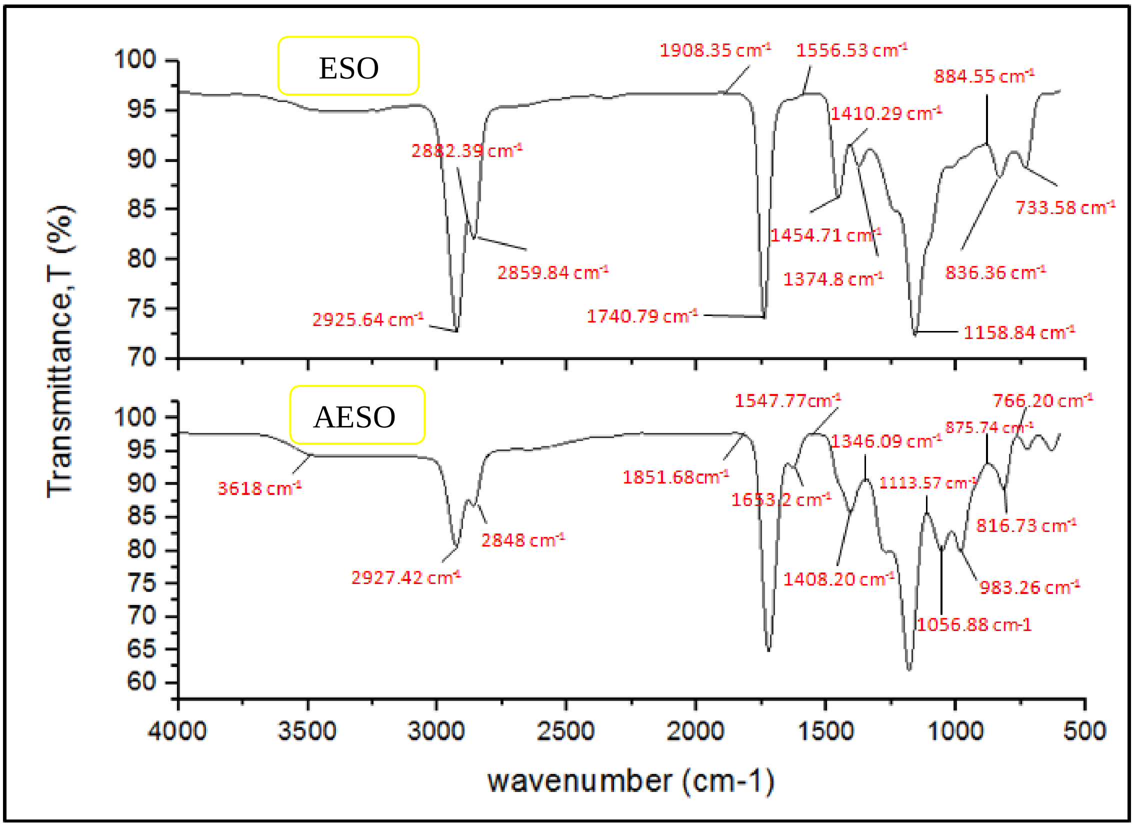


Figure 4.5 FTIR spectra for ESO and AESO

For cured thin film FTIR results based on different ratio applied were showed in Figure 4.7. The varying ratio of trimethylolpropane triacrylate (TMPTTA) to 3-(Triethoxysilyl)-propylamine were 30:70, 50:50 and 70:30. Trimethylolpropane triacrylate acted as monomer sources while proplyamine as curing agent. Good coating properties showed at ratio 30:70 solutions and it has good adhesion toward plywood.

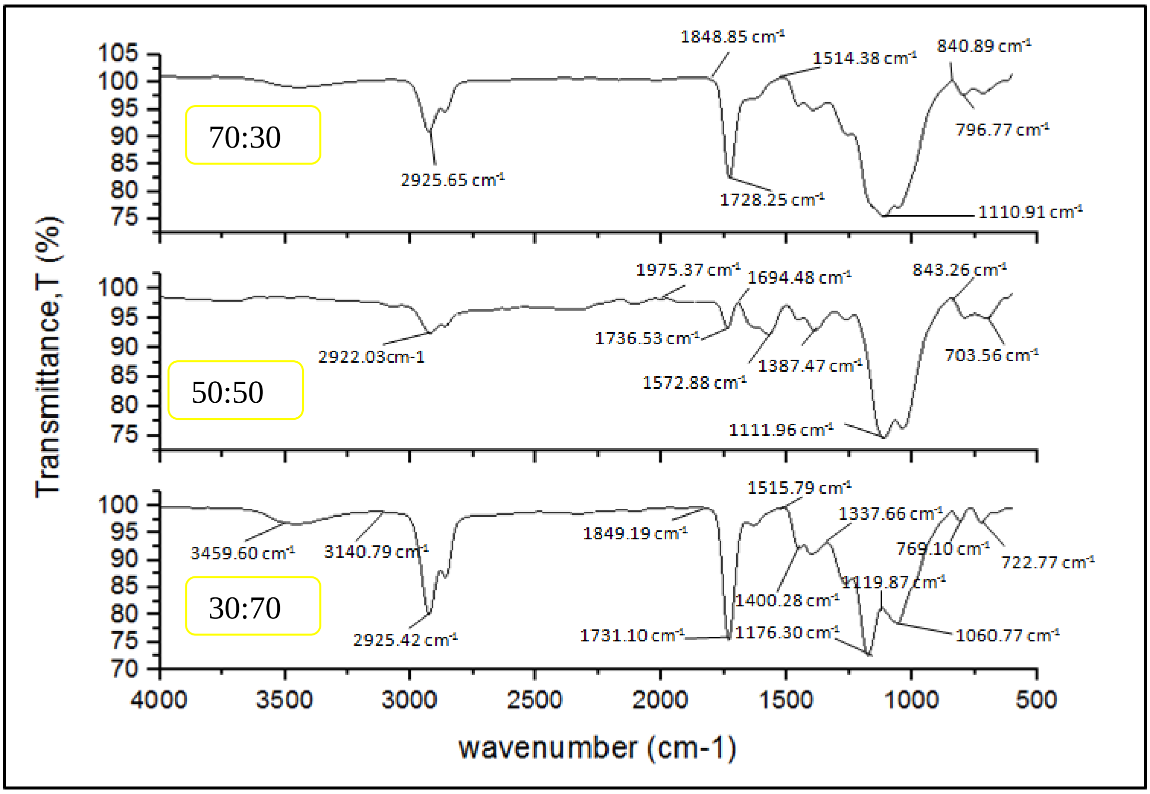


Figure 4.6 FTIR spectra for different ratio of trimethylolpropane triacrylate and 3-(triethoxysilyl)-polyamine.

Table 4.2 Functional group exist in the different formulation of film coating

Ratio of trimethylolpropane triacrylate to 3-(triethoxysilyl)-polyamine	O-H	C-H	C=O	C=C Alkene (vinyl)	C=C-H
70:30	-	2925	1728	-	-
50:50	-	2922	1736	-	3140
30:70	3459.6	2925	1731	1400	-

Due to the addition of trimethylolpropane triacrylate, wavenumber of the functional group presented in the resin shifted to the higher wavenumber. For example, in AESO, the C=O bond at 1653 cm-^{1} was shifted earlier into 1728 – 1731 cm-^{1}. The shift in wavenumber of functional group presents in AESO-TMPTA film coatings showed that there was interaction between AESO and TMPTA as more carbonyl functionality from copolymer added into the mixture.

Sample with ratio 30:70 show better properties since the present of hydrogen bonding at 3459 cm-^{1}. This result is in agreement with the study by Xu, et al (2017).

Table 4.3 The functional groups exist in the ESO and AESO with wavenumber

	Functional Group	Waveumber (cm-1)
ESO	O-H	2925.64
	CH_2	2925.64
	C=O	1693.2
AESO	OH	3618
	CH_2	2927.42
	C-H	2848
	C=O	1653.2
	C=C	1547.77

	C-O	1056.88
	C-O-C	816.72

4.5 Determination of Volatile Organic Content (VOC) for film coatings

VOC released into environment as the paint or coating dried. It is in solvents condition. Coating used in the furniture application and it has high amount of VOC. Hence, by replacing the harmful materials to bio-based materials helps to reduction of VOC. The result obtained after doing this testing showed that the amount of VOC in AESO solution was 4%. This means that the VOC was higher in AESO film. It because of the ether content higher due to it does not evaporated completely. Table 4.4 shows the VOC value for different ratio of film coatings.

Table 4.4 Ratio used for film coating and the amount of VOC

Sample	Before baking (g)	After baking (g)	VOC (%)
70:30	1.88	1.72	8.5
50:50	1.63	1.51	7.36
30:70	1.7	1.49	12.35

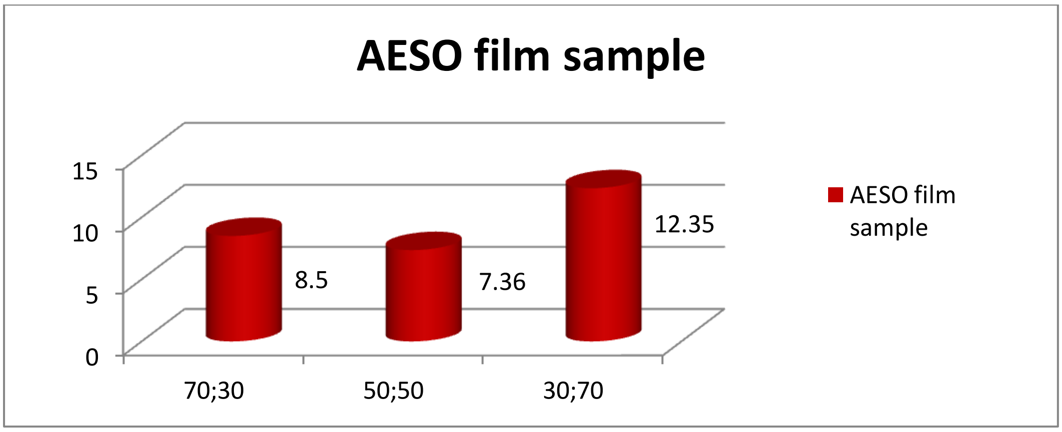


Figure 4.7 Graph plotted for VOC of film coating with different ratios

Coating samples have high VOC which is more than 7% means that high percentage of coating mixture loss during the testing. Based on the result, high VOC resin may contribute to environments pollution as greenhouse effect. Sample 30:70 shows the highest VOC. This happened due to the amount of curing agent used in the film. Based on the VOC of AESO, it does not give adverse effect on human health even the VOC value is 4%. High solid content observed on the coating sample might be due to the solvent component in the AESO that was not fully evaporated.

4.6 Pencil Hardness

Pencil hardness testing was conducted to determine the scratch hardness of AESO film coating that applied to the surfaces of object in order to give protection, provide safety and avoid from corrosion of surface occurred. The AESO films were tested by holding the pencil at 45° angle to the film surface. The edge of blunted lead pressed on the film and scratch with very low forces. The testing was started by using hardest grade to softest grade. Table 4.5 shows the result of scratches on the sample films.

Table 4.5 Results of pencil hardness test for AESO film.

Sample	Pencil Hardness
70:30	5B
50:50	2B
30:70	2H

Based on the result shown in Table 4.5, the hardness of the pencil increase with increased of TMPTA. The grade of pencil for AESO sample with ratio 30:70 of TMPTA: 3-(Triethoxysilyl)-propylamine was 2H where it has highest hardness. This is due to the forming of scratch on the film surface used the hardest grade of pencil lead. Moreover, ratio at 50:50 was 2B and it was harder than the first sample. Then, the AESO film sample with ratio of 70:30 was 5B and the hardness was lowest between other samples. This indicates that the film resulted lowest scratch resistance among others.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In the final analysis, acrylated epoxidized soybean oil (AESO) was successfully synthesized from ESO with acrylic acid without using catalyst to produce film. The thin film well cured with good coating behavior. AESO had higher viscosity compared to ESO. This is because the molecular weight increased that lead to increase in viscosity. Other than that, the OOC value decreased gradually which indicate that the reaction take place was ring opening. The constant of OOC value achieved was 1.84% after 4hours synthesized.

The spectra of ESO indicate typical characteristics of absorption peaks for common triglyceride. The important peaks exist were stretching of O-H and C=O groups at frequencies 2925.64 cm^{-1} and 1693.2 cm^{-1} respectively. While in AESO, new peak can be seen at 3618 cm^{-1} indicates that there was an opening of epoxy ring that allow the formation of OH functional group. Furthermore, C=C functional group appear at 1547.77 $cm-^{1}$ and there was an epoxy group at peak 816.72 cm^{-1} which remain in the AESO.

AESO film coating shows high VOC content compared to AESO in fluid was 4%. The VOC increased due to incorporation of monomer and curing agent. This means that the higher amount of curing agent, the VOC also high. In addition, sample with ratio of 70:30 shows the highest hardness compared with sample in ratio of 50:50 and 30:70.

This can be conclude that the sample with ratio of 70:30 was good to use as coating to achieve better results. This can be proven by the results obtained in the testing mentioned.

5.2 Recommendation

There are a few improvements that can be done to improve the synthesis of AESO from ESO. Nitrogen gas should be used to control the reactions occur in reaction vessel. It is act as blanket to protect the process. Crystal violet used must be in liquid form while in this study, the crystal violet was in powder and it gives difficulties to predict the amount used. Digital thermometer must be included in carrying this experiment because it will maintain the temperature and also the mechanical stirrer rotation speed. Decomposition of epoxy and hydroxyl groups will occur due to high temperature throughout the reactions.

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