SYNTHESIS AND CHARACTERIZATION OF EPOXIDIZED PALM OIL HYDROGEL

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…Special thanks to my beloved mak and engku, my family and friends

Thank you for the everlasting love, guidance, inspiration and support…

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ABSTRACT

A bio-based hydrogel (HPEPO) was synthesized from epoxidized palm oil (EPO) by using ring opening polymerization (ROP) in the presence of a fluoroantimonic acid hexahydrate ($HSbF_6 \cdot 6H_2O$) catalyst, followed by a chemical hydrolysis catalyzed with sodium hydroxide (NaOH). A response surface methodology (RSM) was adopted to optimize the reaction parameters, namely, concentration of NaOH solution, NaOH solution loading and reaction time used during the chemical hydrolysis. The successful ring opening of EPO was confirmed by the disappearance of the epoxy functional group at 833 cm^{-1} of the Fourier transform infrared and at 2.8 to 3.0 ppm of nuclear magnetic resonance spectra. The increase of melting points of HPEPO was observed in the temperature range between 45 °C to 60 °C, corresponded to the increase of crystalline phase in hydrogel as determined by differential scanning calorimetry. The thermal stability of hydrogel was improved up to 200 °C, as shown by thermogravimetric analysis. Apart from that, the swelling behavior that was largely influenced by the hydrophilic carboxyl group and the hydrophobic alkyl group of hydrogel showed some sensitiveness towards the temperature changes, ranging from 15 °C to 40 °C. Meanwhile, the RSM analysis showed that the optimum conditions for all reaction parameters were achieved at 0.33 M concentration of NaOH solution, 73 mL of NaOH solution loading and 25 hours of reaction time.

ABSTRAK

Hidrogel berasaskan bio (HPEPO) telah disintesis daripada minyak sawit terepoksida (EPO) dengan menggunakan pempolimeran pembukaan cincin (ROP) di dalam kehadiran asid fluoroantimonik heksahidrat ($HSbF_6.6H_2O$) sebagai pemangkin diikuti oleh hidrolisis kimia menggunakan natrium hidroksida (NaOH). Kaedah gerak balas permukaan (RSM) telah digunakan untuk mengoptimumkan parameter tindakbalas iaitu kepekatan larutan NaOH, kandungan larutan NaOH dan masa tindakbalas yang digunakan semasa hidrolisis kimia. Keberkesanan pembukaan cincin EPO telah dibuktikan dengan kehilangan kumpulan berfungsi epoksi masing-masing pada 833 cm^{-1} di dalam spektrum inframerah transformasi Fourier dan pada 2.8 ppm hingga 3.0 ppm di dalam resonans magnetik nuklear. Peningkatan takat lebur HPEPO yang berada di dalam julat suhu 45 °C ke 60 °C adalah disebabkan oleh peningkatan fasa kristal di dalam hidrogel seperti yang ditunjukkan oleh kalorimetri pengimbas pembezaan. Kestabilan terma hidrogel juga meningkat sehingga 200 °C seperti yang dipamerkan oleh analisis termogravimetrik. Sementara itu, sifat pembengkakan yang banyak dipengaruhi oleh kumpulan karboksil hidrofilik dan kumpulan alkil hidrofobik di dalam hidrogel telah menunjukkan sensitiviti terhadap perubahan suhu antara 15 °C hingga 40 °C. Manakala, analisis RSM telah menunjukkan keadaan optimum bagi parameter tindakbalas boleh dicapai pada kepekatan 0.33 M larutan NaOH, 73 mL kandungan larutan NaOH dan 25 jam masa tindak balas.

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LIST OF ABBREVIATIONS

ANOVA	-	Analysis of variance
ASTM	-	American Society of Testing and Materials
CCD	-	Central composite design
CV	-	Coefficient of variance
DSC	-	Different scanning analysis
DTG	-	Differential thermogravimetric
ECB	-	Epoxidized cocoa butter
EGDMA	-	Ethylene Glycol dimethacrylate
EPO	-	Epoxidized palm oil
EMO	-	Epoxidized methyloleate
ESO	-	Epoxidized soybean oil
EVO	-	Epoxidized vegetable oil
FTIR	-	Fourier transform infra-red
GPC	-	Gel permeation chromatography
HEC	-	Hydroxyethyl cellulose
HEMA	-	Hydroxyethylmethacrylate
HPC	-	Hydroxypropyl cellulose
HPEPO	-	Palm oil hydrogel
IPN	-	Interpenetrating network
KBr	-	Potassium bromide
LCST	-	Lower critical solution temperature
MDI	-	Methylene diphenyl diisocyanate
NMR	-	Nuclear magnetic resonance
OOC	-	Oxirane oxygen content
PB	-	Polybutadiene
PCL	-	Polycaprolactone

PEPO	-	Palm oil polyol
PLA	-	Polylactic acid
PNIPAAm	-	poly(N-isopropylacrylamide)
PVA	-	poly(vinyl alcohol)
PVC	-	Poly (vinyl chloride)
PVP-CMC	-	Polyvinylpyrrolidone-carboxymethyl cellulose
ROP	-	Ring opening polymerization
THF	-	Tetrahydrofuran
TGA	-	Thermogravimetric analysis
RSM	-	Response surface methodology
UCST	-	Upper critical solution temperature

LIST OF SYMBOLS

%	-	Percentage
β_0	-	Constant coefficient
β_i	-	Linear coefficient
β_{ii}	-	Bilinear coefficient
β_{ij}	-	Interaction coefficient
^oC	-	Degree celcius
g	-	gram
M	-	mol per litre
mg	-	miligram
mL	-	millilitre
H_0	-	Hammet acidity constant
Q	-	Degree of swelling
W_s	-	Mass of sample before drying
W_d	-	Mass of sample after drying

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Natural oils are considered to be the most vital class of renewable resources. They can be obtained from naturally occurring plants, such as sunflowers, soybean cotton, linseeds and palms. They consist mainly of triglycerides where the glycerol molecule is attached to three fatty acid chains of unsaturated and saturated fatty acids. The saturated fatty acids contain only a single bond between two carbon-carbon atoms while the unsaturated fatty acids contain many double or triple bonds between two carbon atoms (Seniha *et al.*, 2007).

Vegetable oil offers numerous advantages in many applications as regards to its non-toxicity and biodegradability. However, it does not naturally bear reactive functional groups; therefore several chemical modifications are adopted to functionalize the unsaturated sites in vegetable oil such as trans-amidation with diethanol amine, glycerolysis with gylcerol, microbial conversion and epoxidation reaction (Jamal *et al*., 2007; Lee and Lee, 2011; Yahaya *et al*., 2013). Among these significant reactions in organic synthesis, epoxidation has been widely used to increase the reactivity of vegetable oil since it is both cost-effective and safe (Silverajah *et al*., 2012; Li *et al*., 1997).

Many epoxidized natural oils have been synthesized, such as epoxidized soybean oil, epoxidized palm oil, epoxidized rapeseed oil, and epoxidized linseed oil (Vinay and Kundu, 2006). Due to the high reactivity of the oxirane ring, this imperative intermediate can be converted to various polyols by reacting with short chain polyhydric alcohols in the presence of catalysts. It acts as a raw material for the synthesis of a variety of chemicals such as alcohols (polyols), glycols, olefinic compounds, lubricants, plasticizer and a stabilizer for polymers.

Epoxidized palm oil (EPO) is a new reactive material that is chemically derived from palm oil. Similar to other epoxidized vegetable oils, as an alternative to fossil fuel derived products, it has been used as intermediate materials in many applications due to its non-toxicity and biodegradability in the automotive, textile, disposable packaging, food, and electric appliance industries (Al- Mulla *et al.*, 2014). Yahaya *et al. (*2013) had successfully reacted EPO with glycerol using the ring opening polymerization method to give a bio-based polyol. Meanwhile, Ang *et al*. (2013) had successfully synthesized polyol with a high molecular weight and low hydroxyl functionality with potential to be used in wood adhesive applications.

To assist the ring opening of oxirane ring, catalyst such as Lewis acid is a popular choice. Liu and Erhan (2010) have used boron trifluoride diethyl etherate (BF_3OEt_2), a Lewis acid in a methylene chloride medium to ring opening epoxidized soybean oil (ESO); to produce low molecule weight polyol with a high crosslink network and good thermal stability. Clark and Hoong, (2013) had derived macromonomer polyols from renewable epoxidized vegetable oils by using Lewis acid in tetrahydrofuran (THF) solvent.

Another potential application of epoxidized vegetable oil is used to synthesize hydrogel. Hydrogel is a hydrophilic, three-dimensional, cross linked polymer (network) which swells when placed in water or biological fluid (Peppas *et al*., 2006). It can be derived from many synthetic and natural polymers which possess high water absorption capacity and biocompatibility. These attractive properties makes hydrogel highly suitable to be used in many biological and medical applications such as in the tissue engineering, pharmaceutical, agriculture, food, cosmetic and biomedical fields (Hoare and Kohane, 2008; Ahearne *et al*., 2008). Currently, most hydrogels are made from synthetic polymers which are derived from petroleum based resources. There have been extensive studies done on the suitability of vegetable oil for hydrogel applications by researchers (Singh *et al*, 2013; Jamil *et al*., 2012; Liu and Erhan, 2010).

Based on the research done by Liu and Erhan (2010), a bio polymeric hydrogel produced from ESO was found to have similar properties as a commercial type of hydrogel. Singh *et al.* (2014) had used olive oil for thermo-reversible emulsion hydrogel for antimicrobials controlled delivery in the treatment of sexually transmitted diseases (STDs). Since EPO also has comparable potential to other vegetable oils, considerable efforts on using it as a starting material in many different chemical reactions need to be explored in order to expand palm oils commercial value in various industrial areas, particularly for hydrogel applications.

1.2 Problem Statement

Vegetable oil can be transformed into polyol by many methods but the most popular one is epoxidation-ring opening polymerization (ROP) combination as it is the safest and most economical method (Yahaya *et al.*, 2013; Silverajah *et al*., 2012; Rosli *et al.*, 2003). According to Liu and Erhan (2010), soy oil-based polyol can be converted into bio-based hydrogel by further chemical modification via hydrolysis. This study had adopted the same technique as Liu and Erhan (2010) but epoxidized palm oil was used instead of soy oil. Palm oil is a local product and abundant available in Malaysia.

A major problem with palm oil is it has less unsaturation sites to be converted into epoxides. This affects the reactivity of the polyol produced as the sites are important for many major reactions to take place. Compared to ESO that has higher epoxy functionality of 6.0 – 6.8 epoxy rings per triglyceride, palm oil only has the average 2.0 – 2.8 functionality. This drawback limits the use of palm oil polyol in the area that need longer molecular chain or higher molecular weight. However, the idea to introduce palm oil polyol with crosslinking network has brought the exploration of polyol into hydrogel.

A number of experimental works have been reported on the ROP of EPO (Ang *et al*., 2013; Clark and Hoong, 2013; Yahaya *et al*., 2013). However, to date, there was no comprehensive study has been made on the synthesis of hydrogel from EPO. Therefore, systematic study was conducted to synthesis hydrogel from EPO by adopting and manipulating the ESO system done by Liu and Erhan (2010). To achieve that, the catalyst type had been changed from BF_3OEt_2 to fluoroantimonic acid hexahydrate ($HSbF_6 \cdot 6H_2O$), an environmentally benign catalyst. This is due to the concerns regarding the toxicity of BF_3OEt_2 which limiting the polymers application in food and medicinal areas (Liu and Knetzer, 2013). Therefore, for a clean organic reaction, $HSbF_6 \cdot 6H_2O$ was chosen as catalyst for ROP of EPO.

Meanwhile to get more understanding, few reaction parameters of epoxidized palm oil hydrogel (HPEPO) had been optimized using response surface methodology (RSM) as a process optimization tool. RSM is capable of optimizing various reaction parameters, reducing the amount of time-consuming experimental-based works. The reaction parameters that optimized were concentration of NaOH solution (hydrolysis agent), NaOH solution loading and the reaction time to synthesis hydrogel from EPO.

1.3 Objectives of the Study

The followings are specific objectives that need to be achieved:

i. To study the effect of catalyst amounts in ROP on the yield and the hydroxyl value of palm oil polyol (PEPO).

ii. To synthesize palm oil hydrogel (HPEPO) from PEPO via chemical hydrolysis at various reaction parameters such as concentration of NaOH solution (hydrolysis agent), NaOH solution loading and reaction time, and optimization by using RSM.

iii. To verify the structure of EPO, PEPO and HPEPO with Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR).

iv. To study the effect of the reaction parameters involved in the chemical hydrolysis on melting temperature (T_m), thermal decomposition and swelling behavior of HPEPO.

1.4 Scopes of Study

Sample preparation started with ring opening polymerization of EPO followed by chemical hydrolysis.

i. Ring opening polymerization: EPO was mixed with methylene chloride at different amount of fluoroantimonic acid hexahydrate ($HSbF_6 \cdot 6H_2O$) as a catalyst which varied from 0.5% to 2.5% and the yield of PEPO was measured.

ii. Chemical hydrolysis: The PEPO with the highest percentage of yield was chosen and converted into HPEPO via hydrolysis using sodium hydroxide (NaOH) as a hydrolysis agent at concentrations varying from 0.2 to 0.5M and the solution amount ranging from 50 to 100 ml, at 18 to 30 hours reaction time.

iii. Process optimization: RSM was adopted in a chemical hydrolysis reaction to find the optimal values of the variable involved including NaOH solution concentration, NaOH solution loading and reaction time.

The following tests were carried out for properties measurement and characterization of polymers:

i. Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and hydroxyl value tests were conducted to verify the structure and reaction mechanism of EPO, PEPO and HPEPO.

ii. Thermogravimetric analysis (TGA) was used to investigate the thermal decomposition behaviour of HPEPO while the melting temperature (T_m) was examined by using a differential scanning calorimetry (DSC).

iii. Swelling test was done to study the swelling behavior and sensitivity of HPEPO towards temperature range from 15 °C to 40 °C.

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