

## CHAPTER III

### EXPERIMENTAL

#### Chemicals

1. Refined palm oil, iodine value 52, Lam Soon (Thailand) Co., Ltd.
2. Glacial acetic acid, AR grade, BDH.
3. Hydrogen peroxide solution, 50% commercial grade.
4. Sulfuric acid, 95-97% GR grade, Merk.
5. Hydrogen bromide, 48% RPE grade, Carlo Erba.
6. Iodine trichloride, Zur Synthese 97%, Merk.
7. Iodine resublimed, RPE grade 99.9%, Carlo Erba.
8. Sodium thiosulfate, GR grade 99.5%, Merk.
9. Potassium iodide, GR grade 99.5%, Merk.
10. Crystal violet, RPE grade, Carlo Erba.
11. Starch soluble, M & B.
12. Carbon tetrachloride, 99.8% GR grade Merk.
13. Benzene, 99.7% GR grade, Merk.
14. Hexane, Analyzed, Baker.
15. Sodium hydrogen carbonate, ACS 99.7%, Riedel de Haen.
16. Bis (2-ethyl hexyl) phthalate, Chemika, Fluka.
17. Epoxy D 81, Barostab, oxirane oxygen more than 6%, iodine value more than 3.
18. CWM 32, Barostab.
19. SK 6, Barostab.
20. PVC K66, TPC.

### Glassware

1. Four-necked flask, 500 ml, Pyrex.
2. Reflux condenser, Pyrex.
3. Additional funnel, Pyrex.
4. Thermometer 100°C.
5. Iodine flask, 500 ml, Kimax.
6. Erlenmeyer flask, 50 ml, Pyrex.
7. Buret, Witeg.
8. Pipet, Witeg.

### Equipment

1. Mechanical stirrer with a half moon-shaped teflon stirring blade, Baird & Tatlock, UK.
2. Water bath and rotavapor, Buchi 461, Switzerland.
3. Fourier Transform Infrared Spectrometer (FTIR), Biorad SPC 3200.
4. Proton NuclearMagneticResonance(HNMR), VarianEM-360L, Australia.
5. Universal Testing Machine, Instron 1026, USA.
6. Impact Tester, Yasuda, Japan.
7. Shore Durometer Hardness Type A-2, The Shore Instrument & MFG Co., Ltd., USA.
8. Two roll mill, Thropp, Germany.
9. Compression molding, Chaichareon Co., Ltd., Thailand.
10. QUV Accelerated Weathering Tester, The Q Panel Company, USA.
11. Extraction Set, Gerhardt, Germany.
12. Oven, maximum temperature 250°C, Memmert, Germany.
13. Thermal Analyzer, Setaram 92, France.
14. <sup>13</sup>CNMR Nuclear Magnetic Resonance

## Procedure

The in situ peracetic acid epoxidation with sulfuric acid catalyst was used to synthesize epoxidized palm oil. In order to get high epoxide contents, many reaction variables were tested.

### 1. Synthesis of epoxidized palm oil.

About 100 grams of the refined palm oil with an iodine value of 52, were mixed with 100% glacial acetic acid and hexane in a four necked flask fitted with a mechanical stirrer, a reflux condenser, a thermometer and an additional funnel. The mixture was heated in a water bath while agitation was provided by a teflon stirring blade at a speed of 200 revolutions per minute (rpm). At a desired temperature, of 50-55°C, 50% hydrogen peroxide solution mixed with sulfuric acid was added dropwise at a uniform rate over one hour. During adding hydrogen peroxide solution, the temperature increased gradually to 70°C. The reaction was stopped at the 8th hour. The mixture was poured into a 500-ml separatory funnel, the aqueous layer was separated and discarded. A portion of 200 ml of the saturated sodium bicarbonate solution was filled to the oil layer to neutralize the remaining acid and followed by adding each portion with 100ml of warm water until it was free from acids; then it was dissolved in ether and the water portion was discarded. Anhydrous magnesium sulfate was filled to absorb trace water that remained and filtered. Finally the ether and hexane were removed by vacuum evaporation (12,13). The product, the epoxidized palm oil, was analyzed for iodine value, oxirane oxygen and characterized by Fourier Transform Infrared Spectrometer (FTIR), Proton Nuclear Magnetic Resonance and Carbon Nuclear Magnetic Resonance (CNMR).

### 2. Study of Variable Effects on Epoxidation of Palm Oil

There were 7 variables i.e. the amount of 50% hydrogen peroxide, glacial acetic acid, concentrate sulfuric acid and solvent, and the reaction conditions:

temperature, agitation speed and reaction time involved with the extent and the amount of epoxidation. The steps to study the variables are as follows.

### 2.1 The 2<sup>4</sup> Factorial Design.

The correlation of hydrogen peroxide, acetic acid and solvent to yield the highest oxirane oxygen in epoxidized palm oil was studied by a 2<sup>4</sup> factorial design using two levels of chemical concentrations as, low and high. Duplication experiments were done for each level of the concentration (21). The amount of the chemicals was indicated in sections 2.1.1-2.1.4. The 2<sup>4</sup> factorial design experiments were carried out as in Table 3.1, the procedure of which was the same as Section 1.

2.1.1 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) was 0.7 and 1.8 mole per mole of the unsaturated double bonds in palm oil.

2.1.2 Acetic Acid (HOAc) was 0.15 and 0.8 mole per mole of the double bonds in palm oil.

2.1.3 Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) was 0.5 and 2% by weight of palm oil.

2.1.4 Hexane, as solvent (C<sub>6</sub>H<sub>14</sub>) was 15 and 30% by weight of palm oil.

Table 3.1 The<sup>24</sup> factorial design experiment.

Experiment number	The amount of chemicals			
	H <sub>2</sub> O <sub>2</sub> <sup>a</sup>	HOAc <sup>b</sup>	H <sub>2</sub> SO <sub>4</sub> <sup>c</sup>	C <sub>6</sub> H <sub>14</sub> <sup>d</sup>
1	0.7	0.15	0.5	5
2	0.7	0.15	0.5	30
3	0.7	0.15	2.0	5
4	0.7	0.15	2.0	30
5	0.7	0.8	0.5	5
6	0.7	0.8	0.5	30
7	0.7	0.8	2.0	5
8	0.7	0.8	2.0	30
9	1.5	0.15	0.5	5
10	1.5	0.15	0.5	30
11	1.5	0.15	2.0	5
12	1.5	0.15	2.0	30
13	1.5	0.8	0.5	5
14	1.5	0.8	0.5	30
15	1.5	0.8	2.0	5
16	1.5	0.8	2.0	30

<sup>a,b</sup> The quantity of H<sub>2</sub>O<sub>2</sub> and HOAc are mole per mole of the double bonds in palm oil.

<sup>c</sup> The quantity of H<sub>2</sub>SO<sub>4</sub> is % by weight of palm oil.

<sup>d</sup> The quantity of C<sub>6</sub>H<sub>14</sub> is % by weight of palm oil.

The results were calculated by the statistical method to determine the significant parameter(chemical) affecting theyield of oxirane oxygen. Consequently, the amounts of the influential parameter were investigated as shown in Table 3.2. The raction conditions were the same as in Section 1.

Table 3.2 Effect of chemical concentrations on oxirane oxygen content.

Chemical	The corresponding concentration			
H <sub>2</sub> O <sub>2</sub> <sup>a</sup>	0.8	1.0	1.3	1.5
HOAc <sup>a</sup>	0.3	0.5	0.6	0.8
H <sub>2</sub> SO <sub>4</sub> <sup>b</sup>	0.5	1.0	2.0	-

<sup>a</sup> The quantities of H<sub>2</sub>O<sub>2</sub> and HOAc are mole per mole of the double bonds in palm oil.

<sup>b</sup> The quantity of H<sub>2</sub>SO<sub>4</sub> is % by weight of palm oil.

The reaction conditions were also studied by following the additional parameters in Section 2.1.5 to 2.1.7.

2.1.5 The Temperature. The temperature was varied while fixing the other conditions as constant. The amount of H<sub>2</sub>O<sub>2</sub> is 1.5 mole per mole of the unsaturated in palm oil, HOAc is 0.8 mole per mole of the unsaturated and H<sub>2</sub>SO<sub>4</sub> is 2% by weight of palm. The range of the temperature was indicated in Table 3.3.

2.1.6 The Agitation Speed. The reaction conditions were the same as Section 2.1.5 except that the temperature range was 50-55°C, and agitation speed was varied as in Table 3.3.

2.1.7 The Reaction Time. The agitation speed of 200 rpm was used and the other conditions were the same as Section 2.1.6. The reaction time was varied as defined in Table 3.3. After adding hydrogen peroxide, the reaction mixture was removed each hour and was analyzed for iodine value and oxirane oxygen. At 10 hours of the reaction time, the iodine value decreased to 1-2, indicating completion of the reaction, then the reaction was ceased accordingly.

Table 3.3 The level of reaction condition.

Reaction parameters	Levels of the parameters									
	1	2	3	4	5	6	7	8	9	10
Temperature, °C	40-45	50-55	60-65	70-75	-	-	-	-	-	-
Agitation speed, rpm	200	300	500	-	-	-	-	-	-	-
Reaction time, hr	1	2	3	4	5	6	7	8	9	10

### 3. Determination of Oxirane Oxygen.

The oxirane oxygen content in epoxidized palm oil was determined in accordance with A.O.C.S. Method Cd 9-57 (22). The procedure was as follows: The epoxidized palm oil was weighed accurately to  $\pm 0.001$  gram in the range of 0.3-0.5 grams into a 50 ml Erlenmeyer flask. It was dissolved in 10 ml of benzene, and 0.1 ml of 0.1% crystal violet indicator in glacial acetic acid was added. The solution was stirred with a magnetic stirrer and titrated with the standard solution of 0.1 N hydrogen bromide in glacial acetic acid. The buret tip was inserted into a one-hole rubber stopper, which was attached to the flask just above the solution to avoid the loss of the hydrogen bromide. The colour of the end point was bluish-green that persisted for 30 minutes. The amount of oxirane oxygen in % was calculated by the following equation.

$$\text{Oxirane Oxygen, \%} = \frac{T \times N \times 1.60}{W} \quad (3.1)$$

where T = volume of hydrogen bromide in ml.

N = concentration of hydrogen bromide solution in normality.

W = weight of epoxidized palm oil in gram.

#### 4. Determination of Iodine Value by Wijs Method.

Wijs method was used to determine the iodine value of the epoxidized palm oil. This method was in accordance with the A.O.C.S. Official Method Tg 1-64 (23). The epoxidized palm oil was weighed accurately as recommended in Table 3.4, and dissolved in 10 ml of carbon tetrachloride in a 500 ml Iodine flask. 20 ml of Wijs solution was added, the flask was sealed with a glass stopper. The flask was kept for 30 min in a dark place. After that, 15 ml of 10% of potassium iodide solution and 100 ml of distilled water were added and the solution was titrated with the standardized 0.1 N sodium thiosulfate solution, starch indicator was added. The end point was a color change from blue to colourless. The blank was carried out in the same manner, without the epoxidized palm oil. Calculation of the iodine value is the following:

$$\text{Iodine Value} = \frac{(B-S) \times N \times 12.69}{W} \quad (3.2)$$

where B = The volume of sodium thiosulfate solution required for the blank in ml.

S = The volume of sodium thiosulfate solution required for the test in ml.

N = The concentration of sodium thiosulfate solution in normality.

W = The weight of epoxidized palm oil in gram.

Table 3.4 The recommended weight of sample for determining iodine value.

Iodine Value	Recommended weight, grams
0-10	2.0-2.5
20	1.0
30	0.65
40	0.50
50	0.40
60	0.34



#### 5. Characterization by FTIR.

The epoxidized palm oil was filled into a liquid cell of the FTIR. The spectrum was run from wavenumber of 4000 to 400  $\text{cm}^{-1}$  with a scan time 16 and resolution 8.

#### 6. Characterization by HNMR.

The epoxidized palm oil was dissolved in deuterium chloroform( $\text{CDCl}_3$ ) and run for HNMR spectrum at the temperature of  $25^\circ\text{C}$  and the frequency of 60 MHz.

#### 7. Characterization by CNMR.

The epoxidized palm oil was dissolved in deuterium chloroform( $\text{CDCl}_3$ ) and run for CNMR spectrum.

#### 8. Effect of Epoxidized Palm oil on PVC sheet.

The epoxidized palm oil was compounded with PVC resin K66 bis(2-ethylhexyl) phthalate (DOP) and barium-cadmium-zinc stearate. The properties of compounded PVC were performed.

##### 8.1 Experimental PVC Compounding.

PVC resin K66 was compounded with the epoxidized palm oil that is used as a secondary plasticizer, while DOP as a primary plasticizer and Ba-Cd-Zn stearate as stabilizer; the formula was shown in Table 3.5 (25).

Table 3.5 The formulation of PVC compound.

Ingredient	Amount, parts
PVC	100
DOP	30-60
EPO	2-3
Ba-Cd-Zn Stearate	2-2.5

The  $2^3$  factorial design was provided for the compounding as shown in Table 3.6. The process was: the PVC, DOP, EPO and stabilizer were mixed together and milled on a

two-roll mill at the temperature of 150°C for 15 minutes; the mixture was melted and a PVC sheet was obtained. The sheet was molded in a mold size of 150x150x3 mm<sup>3</sup> at the temperature of 170-175°C for 5 minutes without pressure and for 5 minutes with a pressure of 200 psi. The PVC sheet was then cooled (25).

Table 3.6 The 2<sup>3</sup> factorial design of PVC compound.

Formulation NO.	Amount of the ingredients, parts		
	DOP	EPO	Ba-Cd-Zn
1	30	2	2
2	30	2	2.5
3	30	3	2
4	30	3	2.5
5	60	2	2
6	60	2	2.5
7	60	3	2
8	60	3	2.5

The amount of the PVC was fixed at 100 parts.

## 8.2 Mechanical Properties of the PVC Sheet.

The compounded PVC sheets were tested for mechanical properties to find a correlation with the amount of the epoxidized palm oil incorporated.

8.2.1 Tensile properties. Tensile strength and elongation were performed according to ASTM D 638 (26). PVC sheet was cut into type IV specimen that has the narrow part of 6 mm wide, the minimum cross section area of the narrow part was measured. The gage length was 25 mm and the speed of the cross head motion of the universal testing machine was 50 mm/min. Tensile strength and elongation at yield and at breaking point were recorded. Seven specimens were tested and an average of tensile strength and elongation were calculated.

8.2.2 Hardness. The Shore Durometer Hardness type A was used for testing PVC hardness according to ASTM D 2240 (27). The PVC sheets were 6 mm thick. The ten measurements were carried out to obtain its average.

8.2.3 Izod impact strength. The test method was performed by following ASTM D 256 (28). The PVC sheet was cut to a specimen of 10.0 mm wide, 12.7 mm thick, and 60.3 mm long. The specimen was then notched to a Vshape. The impact property was tested by Yasuda impact tester with a hammer capacity of 2.7 joules. The seven specimens were tested and the average of the impact strength was calculated.

8.2.4 Flexural strength. A universal testing machine was provided for this test, which is conformed to ASTM D 790 method I (three-points loading system) (29). The PVC sheet was cut into 80 mm long, 25 mm wide, and 3.2 mm thick. The specimen was subjected on the support span of 50 mm. The rate of cross head motion was 1.3 mm/min. The results were recorded and calculated for the average.

### 8.3 Conventional PVC Compounding.

The epoxidized palm oil was compounded with PVC and additives by the same method in Section 8.1. The amount of ingredients was as shown in Table 3.7 (25). The commercial epoxidized soybean oil (Epoxy D 81) was also used to compound with PVC for comparison with the neat PVC compounding, i.e. without epoxidized oil.

Table 3.7 The conventional formulation of PVC compound.

Ingredient	The amount, parts
PVC K 66	100
DOP	40
Epoxidized oil	5
Ba-Cd-Zn Stearate	2

8.3.1 Mechanical Properties of the Conventional Formulation PVC Sheets. The mechanical properties of PVC sheets that were tested was the same as Section 8.2.

8.3.2 Transition Temperature. The Differential Scanning Calorimeter (DSC) was used to run the thermal transition from minus 100°C to 200°C, at a heating rate of 10°C/min using liquid nitrogen as a low temperature control.

8.3.3 Thermal Stability. Thermogravimetric Analyzer (TGA) of Setaram was used: for this purpose the PVC was heated from 20°C to 800°C on the TGA and the weight loss at each temperature was recorded. Additionally, ASTM D 4202 (30) was also used to find the time that PVC was degraded by heat. The tube containing the PVC sheet and connecting to congo red paper was heated to the temperature of 180°C. The time at which the colour of congo red paper changed to violet was recorded to indicate the heat stability of the PVC sheet.

8.3.4 Weathering stability. PVC sheets were tested for weathering and UV stabilities by the QUV accelerated weathering tester. The cycle of testing was a UV exposure at 60°C for 6 hours and followed by a condensation exposure for 4 hours(31). The aging times were 1, 2, 3, and 4 weeks; and the mechanical properties were tested to compare with the non-aging PVC sheet.

8.3.5 Plasticizer Migration. Two types of plasticizer migration were evaluated. The first type of the test is the plasticizer migration to solvent, The PVC sheet was extracted with hexane and the weight loss after 8 hours was determined. The second was method plasticizer migration by volatilisation. The PVC sheet was heated at the temperature of 80°C in an oven for 1, 2, 3 and 4 days and weight loss was calculated (3).