Chapter 2

Experimental

2.1 Preparation of palm oil based polyester ployols

2.1.1 Materials

Palm kernel oil and glycerol were kind gift from Cognis Oleochemical Sdn Bhd. Technical grade phthalic anhydride and fumaric acid was purchased from P.T.Prtrowidada, Indonesia. Potassium hydroxide was of analytical grade purchased from Sigma Aldrich. The palm kernel oil polyester polyol was synthesized. Diphenylmethane-4,4-diisocyanate (MDI) was purchased from Merck Sdn Bhd. Industrial grade butyl acetate was purchased from Supreme Chemical Sdn Bhd. Palm fiber mat was supplied by Ecofuture Bhd. Fine fiber was supplied by Sztech Engineering Sdn Bhd.

2.1.2 Equipment

(A) Oven: D06062 Model 600 Memmert
(B) Compress molding machine: Model KT-7014A, Kao Tieh Machinery Industry Co, LTD, Taiwan
(C) Power saw: Volout 14, Startrite, West Germany

2.1.3 Apparatus

Figure 2.0 represents the schematic setup of the apparatus, which was used for synthesized palm oil based polyester polyol.

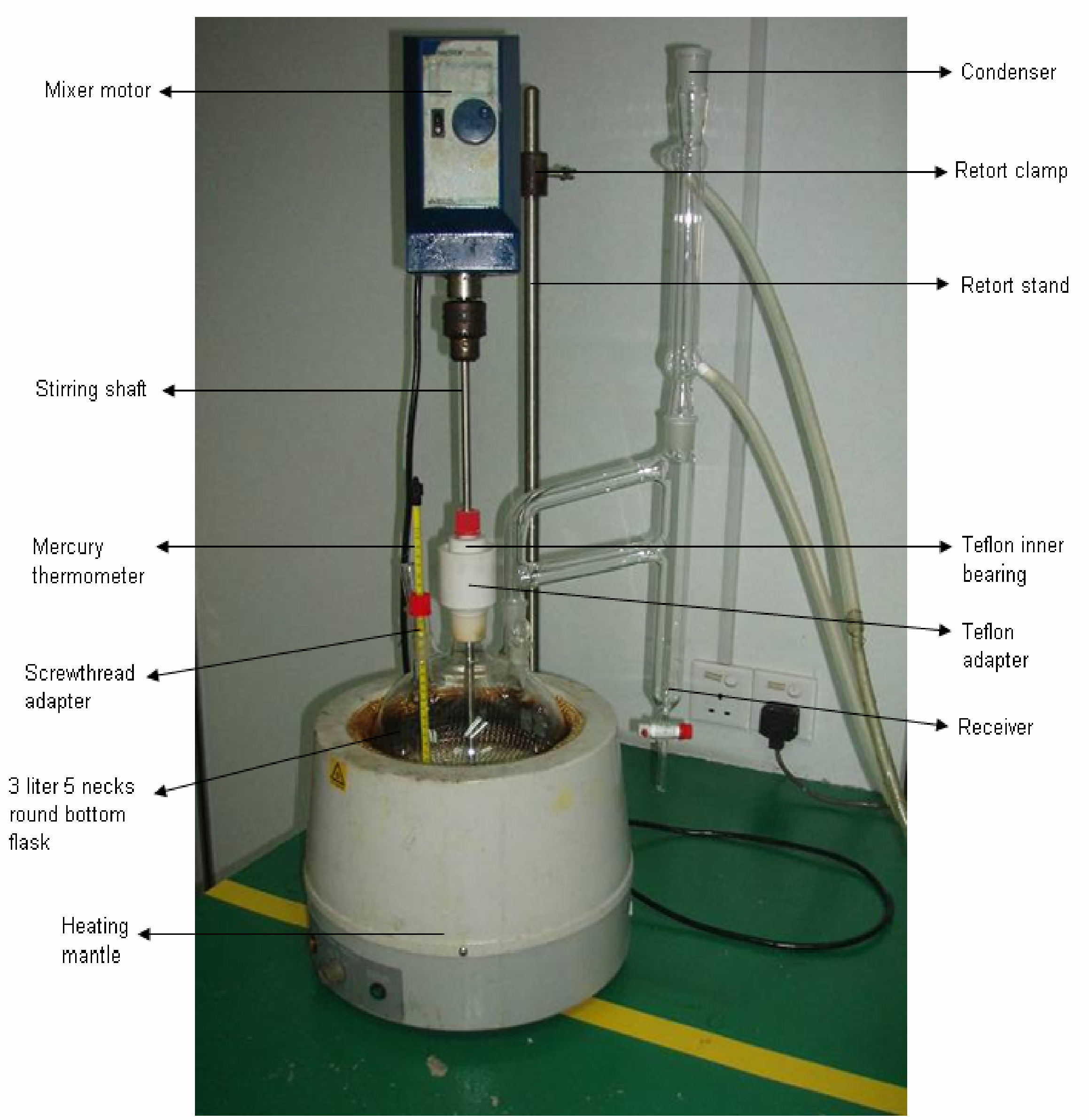

Figure 2.0: The setup for the preparation of palm oil based polyester polyol

2.1.4 Preparation of palm oil based polyester ployols

Table 2.0: Composition of the reaction mixtures for preparation of the palm oil based polyester polyol in weight (g)

Component	Weight (g)
Palm kernel oil	880.8
Glycerol	247.95
Pthalic anhydride	251.84
Fumaric acid	106.14
Potassium hydroxide	0.44 (dissolve in 5ml distilled water)

Table 2.0 shows the materials and the composition of the reaction mixtures. The required amount of palm kernel oil was weighed and poured into the reactor followed by glycerol. Potassium hydroxide was dissolved in 5 ml distilled water and was added into the mixture. The mixture was heated to 240°C for approximately 2 hours. When the mixture turned clear, 1 ml of sample was taken out and mixed with 4 ml of ethanol. If the mixture of sample and ethanol was clear, then the cracking oil was complete. The heater was turned off and the mixture was allowed to cool down below 140°C. Phthalic anhydride was weighed and added into the mixture together with fumaric acid. The mixture was heated slowly until 180°C and water of reaction was collected from the side arm of the condenser. The progress of the reaction was monitored by the water of reaction until the amount was close to the calculated value and the heater was turned off.

After the temperature has dropped to room temperature, the polyester polyol was packed into a container.

2.2 Preparation of fiberboard

2.2.1 Determination of total solid content of palm fiber mat and fine fiber

Empty petri dish was weighed (w_1). Around 5 g fiber was placed on it and weighed (w_2) and then dried in oven at 105°C for 3 hours. After that, sample was taken out to cool down to room temperature before it was weighed again (w_3). The weight loss was due to water evaporation. The % of dry fiber content of palm fiber mat can be calculated as in equation 2.0.

$$\text{\% of dry fiber content palm fiber mat} = \frac{w_3 - w_1}{w_2 - w_1} \qquad [2.0]$$

2.2.2 Formulation of preparation of polyurethane (PU) binder for making fiberboard

The average total solid content of palm fiber mat is 93.7%, while 6.3% is moisture.

In order to obtain 80 g of dry weight of palm fiber mat = $\frac{100}{93.7} x 80$

Weight of palm fiber mat = 85.4 g

Thus 85.4 g of palm fiber mat contained 80 g of dry weight of palm fiber mat

10% of 80 g palm fiber mat by dry weight of polyester polyol was used

Weight of the polyester polyol used = $\frac{10}{100}x80 = 8$ g

The amount of MDI can be calculated as equation [2.1].

Weight MDI = $[\sum_{\mathbf{MDI}} / \sum_{\mathbf{polyol}}]$ **x** $\mathbf{W}_{\mathbf{polyol}}$ [2.1]

$\sum_{\mathbf{MDI}}$ = equivalent weight of MDI

$\sum_{\mathbf{polyol}}$ = equivalent weight of polyester polyol

$\mathbf{W}_{\mathbf{polyol}}$ = weight of polyester polyol used, g

The equivalent weight of MDI = 133.3

$$\text{The equivalent weight of polyester polyol} = \frac{56100}{OHv}$$

$$= \frac{56100}{130}$$

$$= 431.54$$

OHv = hydroxyl value of polyester polyol

$$\text{The amount of MDI} = \frac{133.3}{431.54}x8$$

$$= 2.47 \text{ g}$$

Therefore 8 g of polyester polyol need 2.47 g of MDI to form PU binder where the NCO/OH ratio is 1.0

The total weight of PU binder = (8+2.47) g = 10.47 g

The percentage of PU binder to mold 80 g of dry weight of palm fiber mat into palm fiberboard is

$$\frac{10.47}{80}x100 = 13.08\%$$

Following the same calculation, the 15%, 20%, 25%, 30%, 35% and 40% of 80 g palm fiber by dry weight of polyester polyol were prepared to bind the palm fiber into boards. The palm fiber mat and fine palm fiber prepared used the same calculation as mentioned above and the same polyester polyol. The weights of various proportions used are summarized in Table 2.1. In this study, the NCO/OH ratio was kept constant at 1.0 except for the series with different NCO/OH ratio.

Table 2.1: The weight (g) of MDI, % of polyester polyol and % of PU binder of 80 g palm fiber mat and 80 g fine fiber by dry weight.

Weight of polyester polyol (g)	**Weight (g) of MDI**	**Weight (g) of PU binder**	**% of PU binder in the final board**
8.00	2.47	10.47	11.57
12.00	3.71	15.71	16.41
16.00	4.94	20.94	20.74
20.00	6.18	26.18	24.66
24.00	7.41	31.41	28.19
28.00	8.65	36.65	31.42
32.00	9.89	41.89	34.37

2.2.3 Procedure to calculate the standard deviation

Table 2.2 below shows the results on tensile strength of fiberboards made at 10% binder content and pressed at 7 MPa at 100°C for 25 minutes curing time.

Table 2.2: The results on tensile strength of fiberboard made at 10% binder content and pressed at 7 MPa at 100°C for 25 minutes curing time

Specimen	**Tensile strength (MPa), x_i**	**Deviation $(x_i - x)$**	**Square of deviation $(x_i - x)^2$**
1	1.05	0.01	0.0001
2	0.95	-0.09	0.009
3	0.92	-0.12	0.0144
4	1.01	-0.03	0.0009
5	1.29	0.25	0.0625
Total	5.22	0.02	0.0860

x_i is each value of tensile strength

x is the mean value of tensile strength

$$\text{The mean, } x = \frac{5.22}{5}$$

$$= 1.044$$

$$= 1.04$$

Deviation, $(x_i - x)$ for specimen 1 = $x_i - x$ (mean value)

= 1.05-1.04

= 0.01

The standard deviation, s can be calculated by equation

$$s = \left(\frac{\sum (x_i - x)^2}{n-1} \right)^{1/2}$$

$$= \left(\frac{0.086}{5-1} \right)^{1/2}$$

$$= 0.15$$

Thus, the best value for the tensile strength of fiberboard made at 10% binder content and pressed at 7 MPa at 100°C for 25 minutes curing time is 1.04±0.2 MPa.

2.2.4 Procedures to make fiberboard

Figure 2.1: Picture of palm fiber mat

Figure 2.1 shows the picture of palm fiber mat. Palm fiber mat was a kind gift from Ecofibre Technology Sdn Bhd. Palm fiber mat is a type of mulch made from palm fibers which is derived from empty fruit bunches. Palm fiber mat is environment friendly and fully biodegradable.

The palm fiber mat (Fig 2.1) was cut into the dimension of approximately 6 inches (width) x 6 inches (length), and then the fiber mat was put into oven to dry at 105°C for 3 hours. The required amounts of polyester polyol and MDI were weighed. Both were mixed in a polypropylene plastic cup and stirred until warm (approximately 2 minutes). The mixture of polyester polyol and MDI is called PU binder. The warm mixture was poured on the surface of the palm fiber mat. The fiber mat was put in between two metal plates and then the two metal plates were placed in between the platens of the compression moulding machine and pressed. The palm fiber mat was compressed under certain temperature and pressure. The fiber board was left to condition for more than 7 days at room temperature and then cut into required dimensions for testing of physical properties. The curing temperatures were varied from 60°C to 100°C. The curing time was varied from 5 to 30 minutes and applied curing pressure was fixed at 7 x 10^5 kg/ms^2. The same procedure was repeated for the 15% w/w, 20% w/w, 25% w/w, 30% w/w, 35% w/w and 40% w/w of polyol weight of dry weight of palm fiber mat used to mold the palm fiberboard. Two sets of palm fiberboard were prepared in order to compare the mechanical properties. The first set was prepared by using palm fiber mat and the second set was prepared from fine palm fiber. Figure 2.3 shows the procedure of making the board.

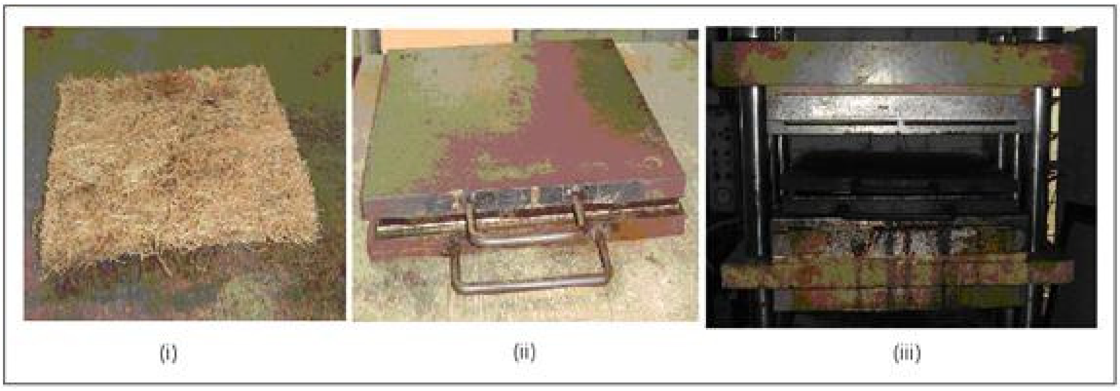

Figure 2.2: The procedure of making board: (i) PU binder was poured on fiber mat, (ii) the fiber mat was put in between two metal plates, (iii) then the two metal plates were placed in the platens of the compression moulding machine and pressed at the specified pressure and the set temperature for a specified time

2.3 Characterization of palm oil based polyester polyol

2.3.1 FTIR analysis

FTIR spectra were recorded on Perkin-Elmer FTIR 1000. The blank spectrum of sodium chloride cell was used as background for subtraction during the analysis. A drop of liquid sample was spread on the sodium chloride cell to form a thin film and was then positioned by using cell holder. The spectrum was recorded from 600 cm^{-1} to 4000 cm^{1}.

2.3.2 Thermogravimetric analysis

Palm oil based polyester polyol was analyzed by using Rheometric Scientific TGA 1000+ instrument to evaluate the thermal stability. About 5 to 10 mg of the sample was placed on the sample pan. The sample was scanned under nitrogen atmosphere from 50°C to 1000°C with a scan rate of 20°C min^{-1}.

2.3.3 Determination of water content by Karl Fischer Titrator

The water content in palm oil based polyester polyol was determined with the use of a Karl Fischer Titrator. Approximately 1 g to 2 g of sample was injected into the titration vessel through the small hole in the three-hole adapter by using a syringe without the needle. Hydrated di-sodium tartrate was used as the primary standard for the Karl Fischer titration whereas methanol serves as solvent.

2.3.4 Determination of acid value of palm oil based polyester polyol

This was done according to procedure recommended in ASTM D1639-90 with minor modifications. Reagents used were 95% ethanol, potassium acid phthalate, potassium hydroxide (0.1 N aqueous solution standardized) and phenolphthalein indicator (1 g in 100 ml of 95% ethanol).

The acid value is the number of mg of potassium hydroxide necessary to neutralize the free carboxylic groups in 1 g of sample. First of all, ethanolic KOH solutions was prepared and then titrated with potassium acid phthalate to obtain 0.1 normality. Sample was weighed (around 5 g) is dissolved in 50 ml of 95% ethanol in a 250 ml conical flask; if the sample did not dissolve readily, the mixture was boiled until sample dissolved. 3-4 drops of phenolphthalein indicator solution was added into the mixture. The mixture was titrated with standardized ethanolic KOH solutions. A minimum of 2 determinations were carried out and the average taken. The acid value can be calculated by the equation 2.2.

$$\text{Acid value} = \frac{V \times 56.1 \times N}{W} \qquad [2.2]$$

N = normality of the standardized ethanolic KOH solution

V = volume of the potassium hydroxide used in ml

W = weight of the test sample in gram

2.3.5 Determination of hydroxyl value of palm oil based polyester polyol

This was done according to ASTM D4274-88. Reagents used were pyridine (distilled from phthalic anhydride and collected at 114 ± 2°C), sodium hydroxide solution (0.5 N aqueous solution standardized), potassium acid phthalate, phenolphthalein indicator (1 g in 100 ml of pyridine). Four cleaned and dried bottles were prepared. Then, 5 ml of phthalic anhydride reagent was pipeted into two of the bottles, followed by the sample already weighed. Another two bottles were reserved for blank titration. The four bottles were capped and enclosed in the water bath and maintained at 98 ± 2°C for two hours. After two hours, the bottles were removed from the water bath and cooled to room temperature. 50 ml of redistilled pyridine and 0.5 ml of phenolphthalein indicator were added into each bottle. The bottles were then titrated with standard 0.5 N NaOH to a pink end point that persists for at least 15 seconds.

The hydroxyl value is defined as the amount (mg) of potassium hydroxide equivalent to the hydroxyl content of 1 g of the sample. It was used as a correction to the theoretical calculated OH value. A minimum of two determinations were determined for each polyol. The hydroxyl value can be calculated by equation 2.3.

$$\text{Hydroxyl value} = \frac{[(B - A) \times N \times 56.1]}{W} \qquad [2.3]$$

A = KOH required for the titration of the sample in ml

B = KOH required for the titration of blank in ml

N = normality of the KOH

W = weight of sample in gram

2.3.6 Gel permeation chromatography (GPC)

GPC is also known as Size Exclusion Chromatography (SEC). This technique is used to determine the molecular weight distribution of a polymer sample. Model of GPC use were Waters 1515 Isocratic HPLC Pumps and Water 2414 Refractive Index Detector in combination of μ-styrogel GPC column.

GPC functions by separating the polymer according to size or hydrodynamic radius. A small amount of polymer solution was injected into a set of columns that are packed with porous beads. Smaller molecules can penetrate through the pores and retained to a greater extent than the larger molecules which continue down the colums and elute faster.

The following are few equations that are important in interpreting the GPC curve. Number average molecular weight, M_n, is defined by equation 2.4.

$$M_n = (\Sigma n_i M_i)/\Sigma ni = \Sigma w_i/(\Sigma w_i/M_i) \qquad [2.4]$$

n_i = no of molecules with molecular weight M_n

w_i = weight of fraction with molecular weight M_i

Weight average molecular weight, M_w, which gives higher weightage to the large molecules, is defined by equation 2.5.

$$M_w = (\Sigma w_i M_i)/\ \Sigma w_i \qquad [2.5]$$

This kind of average is sensitive to component of high molecular weight

The polydispersity index, Q is defined as: $Q = M_w/ M_n$

2.4 Physical properties of palm fiberboard

2.4.1 Density

The fiberboard was cut into strips by using electrical band saw. The dimensions of the fiberboards were determined by measuring with caliper and the fiberboards were weighed by using analytical balance. The density of the palm fiberboards can be calculated by the mass of fiberboard in kg divided by the volume in m^3. Three specimens were tested for each sample.

$$\text{Density} = \frac{M}{V} \tag{2.6}$$

M = mass of the palm fiberboard in kg

V = volume of the palm fiberboard in m^3

2.4.2 Tensile test

This was done according to procedure recommended in ASTM D638-94b. The tensile strength of fiberboards were measured with an Instron Universal Testing Machine (model 4469). The palm fiberboards were cut into strips of 165x19x6 in mm by using electrical band saw. After that, the strips were cut into standard dumbbell shape by using spin machine (Tensike Kut, Siebdrg Industries WC, USA). The load cell use was 50 kN and the testing speed was 5 mm min^{-1}. The ultimate tensile strength and modulus of elasticity (MOE) were recorded. The tensile strength can be calculated by dividing the maximum load in newtons by the original cross-sectional area of the specimen in square meters. A minimum of five specimens were tested for each sample.

Tensile strength = maximum load/cross-sectional area of the specimen [2.7]

Maximum load = force in N

Cross-sectional area of the specimen = (length x width) in m^2

2.4.3 Flexural test

This was done according to procedure recommended in ASTM D790-92. The flexural strength of the fiberboards was measured with an Instron Universal Testing Machine (model 4469). The palm fiberboards were cut into rectangular beams of 130x13x6 in mm by using electrical band saw. A three point loading system was conducted to test the beams. The support span was 100 mm and the rate of cross-head motion was 2.8 mm min^{-1}. Maximum strain in the outer fiber beam was 5%. The flexural strength was equal to the maximum stress in the outer fiber at the moment of break. A minimun of five specimens were tested for each sample. The flexural strength is defined by equation 2.8.

$$\text{Flexural strength, } S = 3PL/\ 2bd^2 \qquad [2.8]$$

S = stress in the outer fiber at midspan in MPa

P = load at a given point at the load deflection curve in N

L = suport span in mm

b = width of beam tested in mm

d = thickness of beam tested in mm

2.4.4 Impact strength

This was done according to procedure recommended in ASTM D256-93a. The impact strength of the fiberboard was measured with Impact Tester [CSI, Subsidiary of Atlas Electric Device Co]. The palm fiberboards were cut into rectangular beams of 65x13x6 in mm by using electrical band saw. The single notched beam procedure was adopted. A minimum of ten specimens were tested for each sample. Impact strength can be calculated by equation 2.9.

$$\text{Impact strength, } I_s = (E_s - E_{TC}) / t$$

I_s = impact strength of specimen in J/m of width

E_s = dial reading breaking energy for a specimen in J

E_{TC} = total correction energy for the breaking energy (E_s) of a specimen in J

t = width of specimen or width of notch in m

2.4.5 Water absorption

This was done according to procedure recommended in ASTM D570-81 (reproved 1998). The fiberboards were cut into rectangular bars of 76.2x25.4x6 in mm by using electrical band saw. The specimen was dried in an oven at 50°C for 1 hour. After that, specimens were taken out and cooled in desicator. The specimens were weighed to the nearest 0.001 g. Then the specimens were placed into beakers containing distilled water to run the 2 hours immersion and 24 hours immersion. Three specimens were tested for each sample.

2.4.6 Optical microscope

The palm fiberboards and the fracture fiberboards were examined by using Dino Lite Digital Microscope (usb) Am 313.