# CHAPTER 3

# EXPERIMENTAL

## 3.1 Materials

Refined, bleached and deodorised (R.B.D) palm stearin and glycerol 99.5% were kind gifts from Emery Oleochemicals Malaysia Sendirian Berhad. Both of these materials were utilised without further purification while palm stearin was pre-heated to 60 °C to soften it prior to usage. ENR50 with 50 % mole of epoxidation was supplied by Rubber Research Institute of Malaysia (RRIM). Phthalic Anhydride (PA) was purchased from DC Chemical Corporate Limited, Korea. Maleic anhydride (MA), benzophenone and trimethylolpropane triacrylate (TMPTA) were obtained from Sigma Aldrich. All other chemicals such as potassium hydroxide (KOH), potassium hydrogen phthalate (KHP), toluene, ethanol, methanol, isopropanol and chloroform were purchased from Merck while calcium hydroxide ($Ca(OH)_2$) was purchased from HmbG Chemicals and they were used as commercially supplied.

## 3.2 Characterisation of palm stearin

### 3.2.1 Determination of acid value

Acid value is an indication on the amount of KOH (in mg) required to neutralise the free acids present in 1 g of sample. 1-3 g of palm stearin was weighed and dissolved in neutral solvent which is composed of equal parts by volume of isopropanol and toluene. Subsequently, the palm stearin was titrated with standardised KOH solution (concentration= 1 mol $dm^{-3}$) in the presence of phenolphthalein indicator. The titration was complete when pink color persists in the solution for 30 seconds and the volume of KOH solution required for the titration was recorded. The titration was done in duplicate and the acid value was calculated by taking the average of the two runs. Acid value of palm stearin was calculated using Eqn. 3.1.

$$\text{Acid value} = \frac{V \ \times K}{S \times N} \qquad \text{(Eqn 3.1)}$$

Where: V = volume of KOH solution required for titration, mL

K = concentration of KOH solution, mg KOH/ mL KOH solution

S = weight of sample used, g

N = Non-volatile content of sample, g

### 3.2.2 Determination of iodine value: ASTM D5768

Iodine value is a measurement of the amount of unsaturation in oils or fatty acids and it is usually expressed as number of centigrams (cg) of iodine absorbed by 1 g of sample. The test was carried out by back-titrating the excess reagent and comparing it with the blank determination. Palm stearin was heated to melt in an oven maintained at 60 °C. Subsequently, 1 g of palm stearin was weighed in a 250 mL Erlenmeyer flask and 20 mL of isooctane was added to dissolve the palm stearin.

The weight of palm stearin (1 g) used in this test was chosen after taking into account of the recommendation provided in the standard method (Table 3.1), where there should be an excess of 125 ± 25 % of Wijs solution in each test. It is noteworthy that the literature iodine value of palm stearin is in the range of 20 – 50 cg $I_2$ / g oil (Lin, 2011, pp. 25-32).

25 mL of Wijs solution was pipetted into the flask containing palm stearin and it was stoppered before kept in the dark for 1 hr. Two additional flasks were prepared for

the blank determination where 25 mL of Wijs solution was pipetted into each flask without any palm stearin and they were kept in the dark for the same period of time. After the storage time, 20 mL of potassium iodide (KI) solution followed by 100 mL of water was pipetted into each of the flask. All the flasks were titrated with standardised $Na_2S_2O_3$ solution in the presence of starch indicator solution. The calculation for the iodine value of palm stearin is shown in Eqn. 3.2.

$$\mathrm{I} = \frac{(\mathrm{B} - \mathrm{V})\ \mathrm{N}\ \ \mathrm{x}\ \ 12.69}{\mathrm{S}} \qquad (\mathrm{Eqn.}\ 3.2)$$

Where: I= Iodine value

V = $Na_2S_2O_3$ solution required for titration of palm stearin solution, mL

B = $Na_2S_2O_3$ solution required for titration of the blank, mL

N = normality of $Na_2S_2O_3$ solution

S = palm stearin used, g

Table 3.1: Recommended specimen weight for iodine value test based on estimated iodine value

| Iodine value / (cg $I_2$ /g oil) | Normal fatty acids, 100 - 150 % excess of Wjis solution / (g) |
|---|---|
| < 3 | 10 |
| 3 | 8.46 to 10.57 |
| 5 | 5.08 to 6.35 |
| 10 | 2.54 to 3.17 |
| 20 | 0.85 to 1.59 |
| 40 | 0.64 to 0.79 |
| 60 | 0.42 to 0.53 |
| 80 | 0.32 to 0.40 |
| 90 | 0.28 to 0.35 |
| 100 | 0.25 to 0.32 |
| 150 | 0.17 to 0.21 |
| 180 | 0.14 to 0.18 |

### 3.2.3 Determination of non-volatile content

10 g of palm stearin was heated in a vacuum oven at 60 °C and pressure 0.1 bar for 30 minutes. The sample was removed and cooled in a dessicator before measuring its final weight. The non-volatile content of palm stearin was calculated using Eqn. 3.3.

$$\text{Non} - \text{volatile conten } = \frac{F}{I} \times 100\ \% \qquad (\text{Eqn. } 3.3)$$

Where: F = weight of palm stearin after heating, g

I = weight of palm stearin before heating, g

### 3.2.4 Fourier transform infrared (FTIR) spectroscopy

Palm stearin was pre-heated to 60 °C in an air-circulating oven before applied as a thin film on KBr cell. The cast KBr containing palm stearin was left to cool down to room temperature and it was analysed using FTIR spectrometer (Perkin Elmer, Spectrum 400) from wavenumber of 400 to 4000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$.

### 3.2.5 Proton nuclear magnetic resonance ($^{1}$H-NMR) spectroscopy

Palm stearin was dissolved in deuterated chloroform with added tetramethylsilane (TMS) (99.8 % $CDCl_3$ + 0.03 % TMS). The palm stearin solution was analysed using JEOL JNM-GSX 270 NMR operating at 270 MHz for 16 scans. TMS served as the internal standard to lock the signal at 0 ppm.

## 3.3 Characterisation of ENR50

### 3.3.1 FTIR spectroscopy

ENR50 was dissolved in toluene before applied as a thin film on KBr cell. The solvent was removed using a hot air blower and the spectrum was recorded on Perkin Elmer Spectrum 400 FTIR spectrometer with 16 scans from 400 to 4000 $cm^{-1}$ at a resolution of 4 $cm^{-1}$.

### 3.3.2 $^1$H-NMR spectroscopy

ENR50 was dissolved in deuterated chloroform containing 99.8 % $CDCl_3$ and 0.03 % TMS as internal standard. The sample was analysed using JEOL JNM-GSX 270 Fourier Transform (FT) n.m.r spectrometer, with 16 scans at 270 MHz. The epoxy content of ENR50 was calculated based on the equation shown in Eqn. 3.4 (Burfield et al., 1984b).

$$Epoxy\ content\ of\ ENR\ 50 = \left(\frac{A_{2.70}}{A_{2.70} + A_{5.14}}\right) 100\ \% \qquad \text{(Eqn. 3.4)}$$

Where, A is intergrated area of the signals and subscript numbers represent chemical shift (ppm)

### 3.3.3 Differential Scanning Calorimetry (DSC)

The $T_g$ of ENR50 was determined using Mettler Toledo differential scanning calorimeter, (Model: DSC822e) equipped with a sub-ambient cooling accessory as shown in Figure 3.1. Calibration was carried out using high purity indium before each measurement to ensure the accuracy of the data obtained from the thermal analyser. Approximately 5-10 mg of sample was weighed and sealed in aluminium pan. The sample was analysed over the temperature range of -60 to 60 °C at a scanning rate of 20 °C/min and under nitrogen atmosphere. The analysis was repeated until two consecutive scans gave the same $T_g$ within experimental error (±1 °C). The $T_g$ was defined as the midpoint of the inflection in the DSC curves.

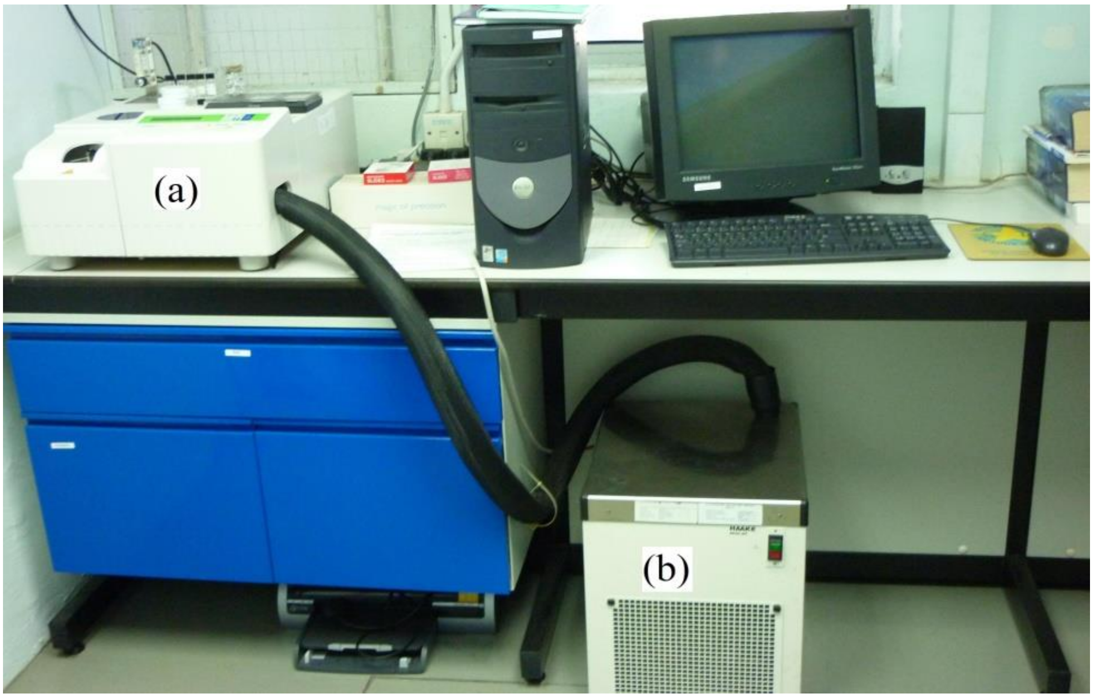

Figure 3.1: Mettler Toledo DSC (Model: DSC822e): (a) Temperature controller; (b) Intercooler

## 3.4 Alkyd synthesis

In this work, four types of alkyds with different –COOH content were synthesised. The synthesis began with the preparation of a control alkyd, AlkydCO, which was formulated with stoichiometric excess of hydroxyl groups. AlkydCO was then incorporated with different types and amounts of anhydrides to generate alkyds with higher –COOH content.

### 3.4.1 Theoretical design of AlkydCO formulation

AlkydCO formulation is designed according to the Patton's gel point calculation (Patton, 1962). Descriptions for the commonly used symbols in alkyd formulation are summarised in Table 3.2. Familiarisation with these symbols is important for a proper understanding of the theoretical derivations and calculations shown in the later sections.

Table 3.2: Descriptions of symbols used in alkyd formulation

| Symbols | Description | Unit |
|---|---|---|
| M | Molecular weight | g mol$^{-1}$ |
| m | Number of moles | Mol |
| $m_o$ | Total moles present at start of reaction | Mol |
| E | Equivalent weight | g mol$^{-1}$ |
| $e_o$ | Total equivalents present at start of reaction | Mol |
| $e_A$ | Number of acid equivalents | Mol |
| $e_B$ | Number of hydroxyl equivalents | Mol |
| F | Functionality | - |
| $F_{av}$ | Average functional groups per molecule | - |
| W | Weight | G |
| $W_{NV}$ | Non volatile weight | G |
| R | Ratio of total –OH groups to total –COOH groups | - |
| K | Total $m_o$/ Total $e_A$ | - |
| AN | Acid number | mg KOH /g alkyd |
| k | Number of functional groups that disappear for every one molecule that participate in the polyesterification | - |
| P | Percentage of reaction completed | - |

AlkydCO was synthesised from palm stearin, PA and glycerol. The theoretical design of AlkydCO formulation is shown in Table 3.3. Several parameters were pre-fixed in the formulation in order to ensure that no gelation occurs during the alkyd cooking process. Among the parameters include the alkyd constant, K was fixed at 1.1, and R value was fixed at 1.4.

Table 3.3: Theoretical design of AlkydCO formulation

| Components | $e_A$ | $e_B$ | F | $m_o$ |
|---|---|---|---|---|
| Palm stearin | $A_1$ | | 1 | $A_1$ |
| PA | $A_2$ | | 2 | $A_2/ 2$ |
| Glycerol | | B | 3 | B/3 |
| Total | $A_1 + A_2$ | B | | $A_1 + (A_2/ 2) + (B/3)$ |

*Source:* Patton, T. C. (1962). *Alkyd Resin Technology: Formulating Techniques and Allied Calculations.* New York: Interscience Publisher.

Generally, there are two basic equations which are frequently used in alkyd formulation. The first equation sets the sum of all equivalents taking part in an alkyd cook equal to unity while the other sets the ratio of total –OH groups to total –COOH groups equal to R. These equations are shown in Eqn 3.5 and 3.6.

$$1 = A_1 + A_2 + B \qquad (Eqn. 3.5)$$

$$R = \frac{\sum e_B}{\sum e_A} = \frac{B}{A_1 + A_2} \qquad (\text{Eqn. } 3.6)$$

Another expression for the theoretical alkyd constant, K (Eqn. 3.7) in terms of $A_1$, $A_2$ and B can also be derived by substituting the values of $m_o$ and $e_A$.

$$K = \frac{\sum m_o}{\sum e_A} = \frac{\left[\mathrm{A}_1 + \left(\frac{\mathrm{A}_2}{2}\right) + \left(\frac{\mathrm{B}}{3}\right)\right]}{[\mathrm{A}_1 + \mathrm{A}_2]} \qquad (\mathrm{Eqn.}\,3.7)$$

From these three independent equations (Eqn. 3.5-3.7), the values for $A_1$, $A_2$ and B can be calculated as follow:

$$A_1 = \frac{\left[2K - \left(\frac{2R}{3}\right) - 1\right]}{1 + R} \qquad (Eqn.\,3.8)$$

$$A_2 = \frac{\left[(-2K) + \left(\frac{2R}{3}\right) + 2\right]}{1 + R} \qquad (Eqn.\,3.9)$$

$$B = \frac{R}{1 + R} \qquad (Eqn.\,3.10)$$

From the calculation of $A_1$, $A_2$ and B, the values of $e_A$ and $e_B$ can be obtained and these values can be used to calculate several important parameters for formulating alkyd resins.

### (a) Initial acid value

Acid value is defined as the amount of KOH (in mg) required to neutralise the free –COOH groups in 1 g of the alkyd nonvolatile content. The calculation for the initial acid value is shown in Eqn. 3.11. Initial acid value of an alkyd cook was not measured experimentally but it is calculated based on the $e_A$ value of the dibasic acid introduced in the cook.

$$AN_{initial} = \frac{56100\, e_A}{W_{NV}} \qquad (Eqn.\,3.11)$$

Where: 56100 = Molecular weight of KOH in mg mol$^{-1}$

### (b) Excess –OH groups or equivalents

R value refers to the excess of –OH groups over the –COOH groups present in the alkyd cook. It can be defined as the ratio of $e_B$ to $e_A$ as shown in Eqn. 3.12.

$$R = \frac{total\ e_B}{total\ e_A} \qquad (Eqn. 3.12)$$

The percentage of excess –OH groups is given by Eqn. 3.13.

$$\%\ excess - OH\ groups = 100\ \%\ (R - 1) \qquad (Eqn. 3.13)$$

Since AlkydCO was formulated with excess of –OH groups to avoid premature gelation during the alkyd synthesis, the expected hydroxyl value in the finished alkyd can be calculated as given in Eqn. 3.14.

$$Expected - OH\ value = \frac{(\sum e_B - \sum e_A) \times 56100}{\sum W - W_{water}} \qquad (Eqn. 3.14)$$

The expected weight of water collected from the alkyd cook is calculated using Eqn. 3.15.

$$Expected\ weight\ of\ water = m_o(PA) \times 18\ g\ mol^{-1} \qquad (Eqn. 3.15)$$

### (c) Patton gel point

Patton gel point, K is defined as the point at which gelation is expected to occur. This theoretical constant is calculated using Eqn. 3.16. In practical formulation, this ratio is increased slightly > 1 to ensure that no gelation occur at 100 % extent of reaction.

$$K = \frac{m_o}{e_A} \qquad (Eqn. 3.16)$$

### 3.4.2 AlkydCO formulation

AlkydCO formulation is shown in Table 3.4. It served as the control alkyd and is expected to have the least amount of –COOH side chains along its alkyd chain.

Table 3.4: AlkydCO formulation

| | **CHARGE** | | | | **BREAKDOWN** | | | |
|---|---|---|---|---|---|---|---|---|
| | **W%** | **W** | **E** | **$e_o$** | **$e_A$** | **$e_B$** | **F** | **$m_o$** |
| Palm Stearin (PS) | 0.495 | 654.95 | 279 | 2.35 | | | | |
| Glycerol from PS | | | | | | 2.35 | 3 | 0.78 |
| Fatty Acid from PS | | | | | 2.35 | | 1 | 2.35 |
| PA | 0.304 | 402.26 | 74 | 5.44 | 5.44 | | 2 | 2.72 |
| Glycerol | 0.200 | 264.81 | 31 | 8.54 | | 8.54 | 3 | 2.85 |
| $Ca(OH)_2$ | | 0.89 | 37 | 0.02 | | 0.02 | | |
| TOTAL | | 1322.9 | | 16.35 | 7.78 | 10.91 | | 8.70 |

Details of AlkydCO cook are as follows:

i. Initial acid value $= \frac{5.44 \text{ mol} \times 56100 \text{ mg mol}^{-1}}{1322.92 \text{ g}}$

$= 230.\ 52$ mg KOH/ g alkyd

ii. R value $= \frac{10.91 \text{ mol}}{7.78 \text{ mol}}$

$= 1.4$

iii. Expected weight of water $= 2.72 \text{ mol x } 18 \text{ g mol}^{-1}$

$= 48.9$ g

iv. Expected –OH value $= \frac{[(10.91 \text{ mol} - 7.78 \text{ mol}) \text{ x } 56100 \text{ mg mol}^{-1}]}{(1322.92 \text{ g} - 48.9 \text{ g})}$

$= 137.84 \text{ mg KOH g}^{-1}$ alkyd

v. Patton gel point, K $= \frac{8.70 \text{ mol}}{7.78 \text{ mol}}$

$= 1.1171 \quad \approx 1.1$

vi. Oil length $= \frac{654.95 \text{ g}}{1322.92 \text{ g}} \times 100\ \%$

$= 49.5\ \%$

### 3.4.3 Theoretical design of modified alkyd formulation

All the modified alkyds (AlkydMA1, AlkydMA2 and AlkydPA1) in this work were synthesised via incorporation of MA or PA into AlkydCO. In designing the modified alkyd formulation, it is important to know beforehand the final acid value and hydroxyl value of AlkydCO. Both these values allow us to calculate the free –COOH and –OH groups present in AlkydCO as shown in Eqn 3.17 and Eqn. 3.18.

$$Amount\ of\ free - COOH\ groups = \frac{AN_{final}}{56100 \text{ mg mol}^{-1}} \qquad (Eqn. 3.17)$$

$$Amount\ of\ free - OH\ groups = \frac{Hydroxyl\ value}{56100 \text{ mg mol}^{-1}} \qquad (Eqn. 3.18)$$

AlkydCO has a final acid value of 16.71 mg KOH/ g alkyd and hydroxyl value of 155.6 mg KOH/ g alkyd. Based on these values, the amount of free –COOH groups present in AlkydCO is equivalent to 2.98 x $10^{-4}$ mol/ g while the amount of free –OH groups present is equivalent to 2.77 x $10^{-3}$ mol/ g. The amount of –OH groups present are in excess compared to the –COOH groups in which the ratio of –OH groups over –COOH groups, R is equal to 9.31. In the synthesis of modified alkyd, the R value was adjusted to be lowered than those of AlkydCO via incorporation of anhydride at controlled reaction temperature. The free –OH groups of AlkydCO was consumed during the half-ester formation with the incorporated anhydride and in the same time a free –COOH group was generated.

Theoretical design of modified alkyd formulation is shown in Table 3.5. Only portions of the synthesised AlkydCO were used in the synthesis of the modified alkyds and the weight of AlkydCO used is labeled as $W_1$. The weight of anhydride used, $W_2$ can be calculated by multiplying the equivalent weight, E of anhydride (MA = 49.03 g mol$^{-1}$ or PA = 74 g mol$^{-1}$) with its calculated $e_A$.

Table 3.5: Theoretical design of modified alkyd formulation

| Components | W | $e_A$ | $e_B$ |
|---|---|---|---|
| AlkydCO | $W_1$ | $2.98 \times 10^{-4}\, W_1$ | $2.77 \times 10^{-3}\, W_1$ |
| Anhydride | $W_2$ | $\frac{[2.77\times10^{-3}\, W_1]}{R} - [2.98 \times 10^{-4}\, W_1]$ | |

Two types of MA-modified alkyd were synthesised in this work namely, AlkydMA1 and AlkydMA2. In AlkydMA1, the R value was set to be equal to 2.0 while AlkydMA2 has R value = 1.1. Another type of PA-modified alkyd with R value = 2.0 was also synthesised in order to compare the reactivity of this alkyd with those modified with MA towards reaction with ENR50. Based on the formulation, several important parameters can be calculated to assist the alkyd cooking process.

### (a) Initial acid value

Calculation for the initial acid value of modified alkyd is shown in Eqn. 3.19. The initial acid value was not determined experimentally due to the inhomogeneity of the alkyd mixture at the early stage of the cook. Instead, it is calculated based on $e_A$ of the incorporated anhydride and final acid value of AlkydCO.

$$Initial\ acid\ value$$

$$= \left[\frac{e_A(Anhydride)\times 56100}{W_1 + W_2}\right] + \ 16.71\ mg\ KOH\ g^{-1}\ AlkydCO \qquad (Eqn. 3.19)$$

### (b) Expected final acid value

In order to preserve the –COOH groups generated, the modified alkyd cook was stopped when the final acid value of the alkyd has reached the point where $e_A$ of the anhydride incorporated has dropped to half of its initial. The expected final acid value is calculated using Eqn. 3.20.

$$Expected\ final\ acid\ value$$

$$= \frac{\left[\frac{e_A(Anhydride)}{2} + 2.98 \text{ x } 10^{-4}\ \mathrm{W}_1\right] \times 56100}{W_1 + W_2} \qquad (Eqn. 3.20)$$

### 3.4.4 AlkydMA1 formulation

AlkydMA1 formulation is shown in Table 3.6. AlkydMA1 was cooked by incorporating 14.6 g of MA into 273.8 g of AlkydCO to generate –OOC-C=C-COOH in the alkyd chains. Addition of MA into AlkydCO causes the R value of AlkydMA1 to decrease to 2.0.

Table 3.6: AlkydMA1 formulation

| Components | W | E | $e_A$ | $e_B$ |
|---|---|---|---|---|
| AlkydCO | 273.8 | | 0.082 | 0.759 |
| MA | 14.6 | 49.03 | 0.298 | |
| TOTAL | 288.4 | | 0.380 | 0.759 |

Details of AlkydMA1 cook are as follows:

i. Initial acid value = $\left(\frac{0.298\ \text{mol} \times 56100\ \text{mg mol}^{-1}}{288.4\ \text{g}}\right) + 16.71\ \text{mg KOH/g AlkydCO}$

= 74.68 mg KOH/ g AlkydMA1

ii. Expected final acid value $= \frac{\left[\frac{0.298}{2}\ \text{mol} + 0.082\ \text{mol}\right] \times 56100\ \text{mg mol}^{-1}}{288.4\ \text{g}}$

= 44.86 mg KOH/ g AlkydMA1

### 3.4.5 AlkydMA2 formulation

AlkydMA2 formulation is given in Table 3.7. The amount of MA incorporated in this alkyd was higher as compared to AlkydMA1 cook where 1.12 x $10^{-3}$ mol MA /g AlkydCO was used in the synthesis to make the R value equivalent to 1.1.

Table 3.7: AlkydMA2 formulation

| Components | W | E | $e_A$ | $e_B$ |
|---|---|---|---|---|
| AlkydCO | 275.2 | | 0.082 | 0.763 |
| MA | 30.0 | 49.03 | 0.612 | |
| TOTAL | 305.2 | | 0.694 | 0.763 |

Details of AlkydMA2 cook are as follows:

i. Initial acid value = $\left(\frac{0.612\ \text{mol} \times 56100\ \text{mg mol}^{-1}}{305.2\ \text{g}}\right) + 16.71\ \text{mg KOH/g AlkydCO}$

= 129.19 mg KOH/ g AlkydMA2

ii. Expected final acid value $= \frac{\left[\frac{0.612}{2}\ \text{mol} + 0.082\ \text{mol}\right] \times 56100\ \text{mg mol}^{-1}}{305.2\ \text{g}}$

= 71.30 mg KOH/ g AlkydMA2

### 3.4.6 AlkydPA1 formulation

AlkydPA1 was cooked by incorporating 22.8 g of PA into 282.4 g of AlkydCO to generate –OOC-Ph-COOH in the alkyd chains. AlkydPA1 formulation is given in Table 3.8. The R value was fixed at 2.0, similar to AlkydMA1.

Table 3.8: AlkydPA1 formulation

| Components | W | E | $e_A$ | $e_B$ |
|---|---|---|---|---|
| AlkydCO | 282.4 | | 0.084 | 0.783 |
| PA | 22.8 | 74 | 0.308 | |
| TOTAL | 315.2 | | 0.392 | 0.783 |

Details of AlkydPA1 cook are as follows:

i. Initial acid value = $\left(\frac{0.308\text{mol} \times 56100 \text{ mg mol}^{-1}}{315.2 \text{ g}}\right) + 16.71 \text{ mg KOH/g AlkydCO}$

= 73.24 mg KOH/ g AlkydPA1

ii. Expected final acid value $= \frac{\left[\frac{0.308}{2} \text{ mol} + 0.084 \text{ mol}\right] \times 56100 \text{ mg mol}^{-1}}{315.2 \text{ g}}$

= 43.73 mg KOH/ g AlkydPA1

### 3.4.7 Preparation of AlkydCO

AlkydCO was prepared based on the formulation given in Table 3.4. The synthesis is divided into two stages which started with an alcoholysis process and followed by esterification under fusion cook. In alcoholysis process, palm stearin was heated with glycerol and 0.08 % w/w of $Ca(OH)_2$ (over total weight of palm stearin used) in a 2 L reaction flask equipped with condenser, digital thermometer and mechanical stirrer (Figure 3.2(a)). The mixture was maintained at the temperature of 210-220 °C for 2 hours with active stirring at 220 rpm. The completion of the alcoholysis process was confirmed by dissolving one part of the reaction mixture with four parts of ethanol. The alcoholysis process was deemed complete when a clear solution was obtained upon dissolving the reaction mixture with ethanol.

The alcoholysis products obtained were then cooled to below 140 °C and custom-made glassware which resembles a Dean-Stark decanter was fitted to the reaction set-up as shown in Figure 3.2(b). PA was added slowly to the mixture before increasing the temperature to 220-230 °C. The time when water starts forming in the reaction was taken as the beginning of esterification reaction. Water generated was collected in the custom-made decanter and the volume collected was recorded. The reaction mixture was sampled at every 30 minutes interval from the beginning of esterification reaction and its acid value was determined. The same procedure explained in Section 3.2.1 was applied for the acid value determination. The reaction was stopped when the acid value of the reaction mixture has dropped to below 20 mg KOH/ g resin.

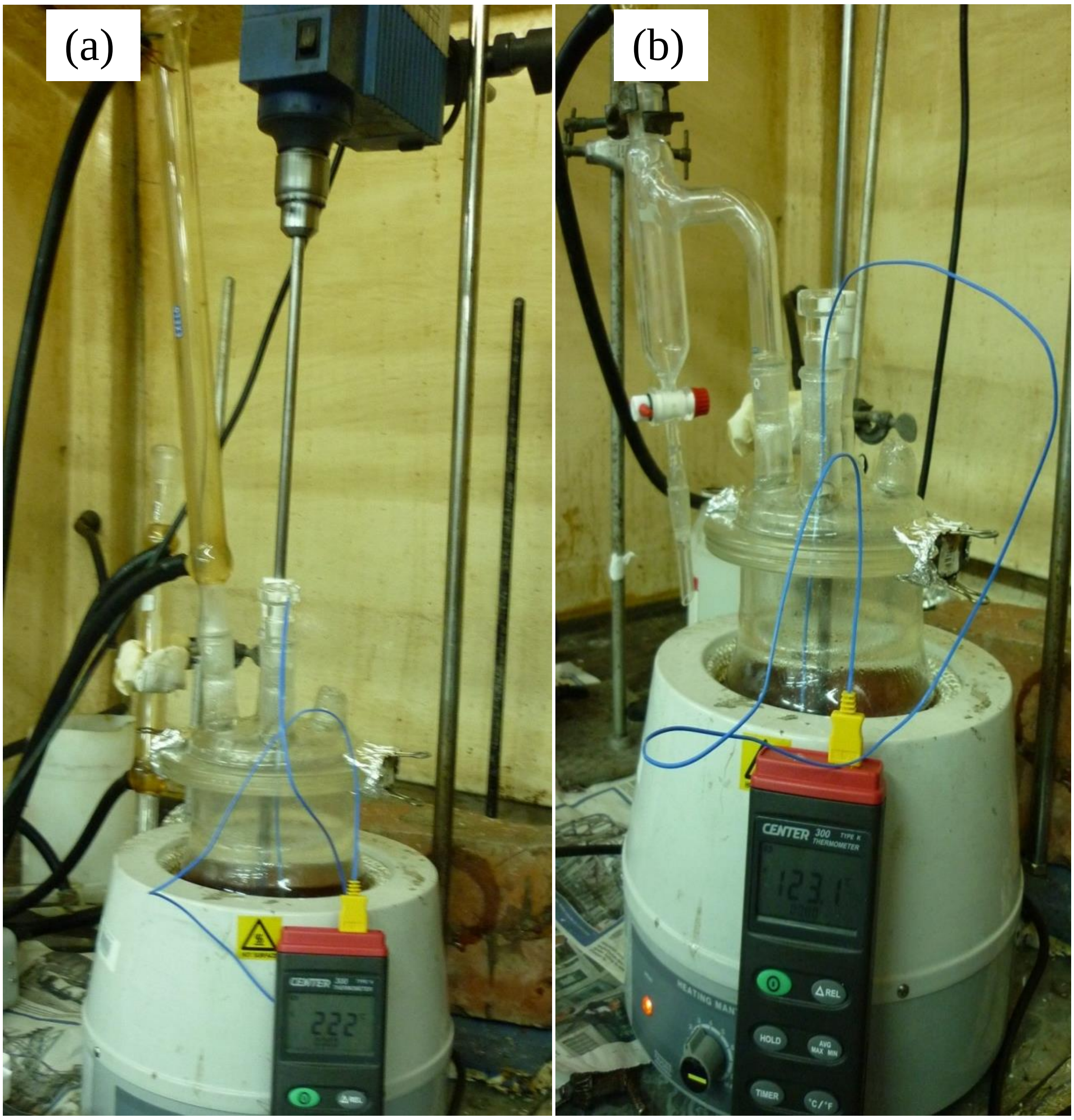

Figure 3.2: Apparatus set-up for (a) Alcoholysis process, and (b) Esterification process

### 3.4.8 Preparation of MA-modified alkyds, AlkydMA1 and AlkydMA2

MA-modified alkyds were prepared via incorporation of MA into AlkydCO. The composition of materials used in AlkydMA1 and AlkydMA2 cooks are given in Table 3.6 and Table 3.7 respectively. The reaction was carried out in the same reaction set-up as shown in Figure 3.2(b). An amount of AlkydCO was heated to melt at 60 °C in an air-circulating oven before being transferred into a 1 L reaction flask. The weight of AlkydCO transferred was measured and the amount of MA required for the synthesis was calculated based on the formulation given in Table 3.5. Subsequently, MA was gradually added into AlkydCO while maintaining the temperature at 120-130 °C with active stirring at 220 rpm. The alkyd synthesis was monitored by determining the acid value of the reaction mixture periodically. The reaction was stopped by allowing it to cool when the acid value of the reaction mixture has dropped to approximately half of its initial.

### 3.4.9 Preparation of PA-modified alkyd, AlkydPA1

AlkydPA1 was prepared by incorporating $5.47 \times 10^{-4}$ mol/ g of PA (over total weight of AlkydCO used) into a portion of the synthesised AlkydCO. An amount of AlkydCO was heated to melt at 60 °C in an air-circulating oven before being transferred into the reaction set-up as shown in Figure 3.2(b). The weight of AlkydCO transferred was measured and the amount of PA required for the synthesis was calculated and weighed. 30 ml of toluene (10% v/w of total ingredients charged) was employed as the azeotropic solvent. PA was added slowly into the AlkydCO solution and the temperature was maintained at 160-170 °C throughout the synthesis. Sampling was carried out periodically to determine the acid value of the reaction mixture. The reaction was allowed to continue until the acid value of the reaction mixture has dropped to approximately half of its initial. The final product (AlkydPA1) was air-dried at room temperature in fume hood before further dried under reduced pressure (0.1 bar) in a vacuum oven at 60 °C for 24 hours to facilitate the removal of toluene.

## 3.5 Characterisation of alkyds

### 3.5.1 Final acid value and amount of –COOH groups in alkyds

Final acid value of alkyd was determined according to the procedure explained in Section 3.2.1. Neutral solvent which composed of equal volume of isopropanol and toluene was used to dissolve the alkyd, followed by titration using standardised KOH solution, with phenolphthalein as the indicator. Note that the solvent was neutralised with KOH solution prior to dissolving the alkyd. This step is important to remove any neutralising effect from the species present in the solvent which might interfere with the acid value determination. The amount of –COOH groups in alkyd was calculated based on Eqn. 3.17.

### 3.5.2 Hydroxyl value

Hydroxyl value of alkyd was determined according to the standard procedure adopted from ASTM D4274-94, test method B. This test method comprised of two stages, where in the first stage, 25 mL of PA reagent (composition= 0.16 g PA/mL redistilled pyridine) was used to dissolve alkyd in a stoppered conical flask, and the solution was heated at 98 - 100 °C for 2 hr in water bath. The purpose of this reaction is to allow free hydroxyl groups in the alkyd to react with PA reagent to form ester group. In the second stage, the alkyd solution was allowed to cool down to room temperature and 50 mL of distilled pyridine was added to the flask before titrated with standardised KOH solution, using phenolphthalein as indicator. This step serves the purpose of neutralising the excess PA remaining in the alkyd solution. The volume of KOH required for the titration is recorded. A blank solution containing 25 mL of PA reagent in a stoppered conical flask was prepared and the solution was heated at 98 - 100 °C for 2 hr in water bath. The flask was then allowed to cool down to room temperature; 50 ml of distilled pyridine was added to the blank solution before titrated with standardised KOH solution, using phenolphthalein as indicator. The hydroxyl number of alkyd was determined using following equation:

$$Hydroxyl\ number = \frac{56\ 100 \times M \times (V_b - V)}{W} \qquad (Eqn. 3.21)$$

Where: V = Volume of KOH required for sample titration, mL

$V_b$ = Volume of KOH required for blank titration, mL

M = molarity of KOH solution, mol KOH/ mL KOH solution

W = weight of alkyd sample, g

56100 = molecular weight of KOH, mg KOH/ mol

### 3.5.3 FTIR analysis

Alkyd was thinned with toluene, followed by spreading into a thin film on a potassium bromide (KBr) cell. The toluene was removed by blowing with hot air before analysed with Perkin Elmer Spectrum 400 FTIR spectrometer, with 16 scans from 4000 cm$^{-1}$ to 400 cm$^{-1}$ and resolution of 4 cm$^{-1}$.

### 3.5.4 $^1$H-NMR analysis

Alkyd was dissolved in deuterated chloroform with added TMS (min. 99.8 % $CDCl_3$ + 0.03% TMS). The TMS serves to lock the signal at 0 ppm. $^1$H-NMR spectra of alkyd was recorded using JEOL JNM-GSX 270 Fourier Transform (FT) n.m.r spectrometer, with 16 scans at 270 MHz.

### 3.5.5 DSC analysis

5-10 mg of alkyd was encapsulated in an aluminium pan and sealed. The sample was analysed with Mettler Toledo DSC822e calorimeter by heating from -60 °C to 60 °C at a scan rate of 20 °C/min in nitrogen atmosphere. The thermal data was obtained based on the heating run.

## 3.6 Preparation of ENR and Alkyd solutions

### 3.6.1 Preparation of 10 % w/w ENR50 solution

An amount of ENR50 was mechanically masticated using a laboratory two roll miller with the nip setting of 4 mm for 6 times at room temperature. The rubber sheet was folded thrice before every passes into the miller to ensure homogeneities. The masticated rubber was then weighed in a covered glass bottle and toluene was added to make up the concentration equal to 10 % w/w. The solution was left to stir overnight using magnetic stirrer.

### 3.6.2 Preparation of 60 % w/w alkyd solution

An amount of alkyd was weighed in covered glass bottle before addition of toluene to make up the concentration equal to 60 % w/w. The alkyd solution was stirred overnight using magnetic stirrer.

## 3.7 Preparation of ENR50/Alkyd blend

Blending of ENR50 and alkyd was carried out via solvent casting technique using toluene. ENR50 and alkyd solutions were mixed in a covered glass bottle using magnetic stirrer until the desired blending time (5 minutes, 2 hours, 4 hours, 7 hours and 12 hours). At the end of the blending, the ENR50/Alkyd mixture was applied as thin film on glass panel followed by soaking in methanol to remove any unreacted alkyd. The trapped solvent was evaporated by keeping the blend in fume hood at room temperature for 24 hours before further drying in vacuum oven at 60 °C for 24 hours. Four types of blends were prepared, namely ENR50/AlkydCO, ENR50/AlkydPA1, ENR50/AlkydMA1 and ENR50/AlkydMA2 which denote the reaction products of ENR with AlkydCO, AlkydPA1, AlkydMA1 and AlkydMA2 respectively. Two parameters were investigated in this work and the procedures are explained in Section 3.7.1 and 3.7.2.

### 3.7.1 Effect of –COOH content in MA-modified alkyds on reaction between ENR50 and alkyd

The blend series of ENR50/AlkydCO, ENR50/AlkydMA1 and ENR50/AlkydMA2 which each composed of blends with different blending times (5 minutes, 2 hours, 4 hours, 7 hours and 12 hours) were prepared at a composition of 10 parts of alkyd per hundred parts of ENR50. The blending was performed via magnetic stirring at ambient temperature (30 °C).

### 3.7.2 Effect of type of anhydride modification in alkyd on reaction between ENR50 and alkyd: Comparison between AlkydPA1 and AlkydMA1

In this study, the composition of the blend was fixed at 10 parts of alkyd per hundred parts of ENR50 and blending was performed at ambient temperature. Two series of blends composed of different alkyds were prepared: (i) ENR50/AlkydPA1 and (ii) ENR50/AlkydMA1. In each of the series, a total of 5 blends with different blending times were prepared: (i) 5 minutes, (ii) 2 hours, (iii) 4 hours, (iv) 7 hours and (v) 12 hours.

## 3.8 Characterisation of ENR50/Alkyd blends

### 3.8.1 FTIR analysis

A layer of polymer film from the blend solution was cast onto KBr cell immediately after the specified reaction time and the toluene was removed by blowing with hot air. The spectrum was recorded on Perkin Elmer Spectrum 400 FTIR spectrometer, with 16 scans from 4000 $cm^{-1}$ to 400 $cm^{-1}$ and resolution of 4 $cm^{-1}$.

### 3.8.2 Determination of gel content

A known weight of dried blend sample, $W_0$ was enveloped in a nylon bag (dimension = 6 cm x 6 cm and 50 mesh size). Subsequently, the sealed nylon bag containing the blend sample was soaked in toluene for 24 hours at room temperature in a covered glass bottle. After the soaking period, the nylon bag containing the blend sample was filtered using a sieve (size = 20 Mesh**)** and was left to air-dry in fume hood for 24 hours before further dried in air-circulating oven at 100 °C until constant weight is achieved. The dry weight of the blend sample, $W_1$ was recorded and the gel content was calculated based on the equation shown in Eqn 3.22. It should be noted that the gel formed during immersion in toluene appeared to be sticky and jelly-like in nature. Therefore, a nylon bag was employed in this test as it entrapped the gel formed and eases the separation from the toluene soluble component.

$$Gel\ content = \frac{W_1}{W_0} \text{x}\ 100\ \% \qquad \text{(Eqn. 3.22)}$$

Where: $W_1$ = weight of dried blend sample after soaking in toluene

$W_0$ = weight of blend sample before soaking in toluene

### 3.8.3 DSC Analysis

Dried blend sample (5-10 mg) was encapsulated in aluminum sample pan and analysed using Mettler Toledo DSC822e calorimeter under $N_2$ atmosphere from -60 to 60 °C at a scan rate of 20 °C $\text{min}^{-1}$.

### 3.8.4 TGA analysis

The thermogravimetric analysis and derivative thermogravimetric analysis of the ENR50/Alkyd blend sample were carried out in a Perkin Elmer TGA 6 instrument (Figure 3.3). The sample was heated from 50 °C to 900 °C in $N_2$ atmosphere at heating rate of 10, 20, 25, 30 and 40 °C $\text{min}^{-1}$. The kinetics of degradation was studied by Kissinger method. The sample weight used in each analysis was between 5-10 mg.

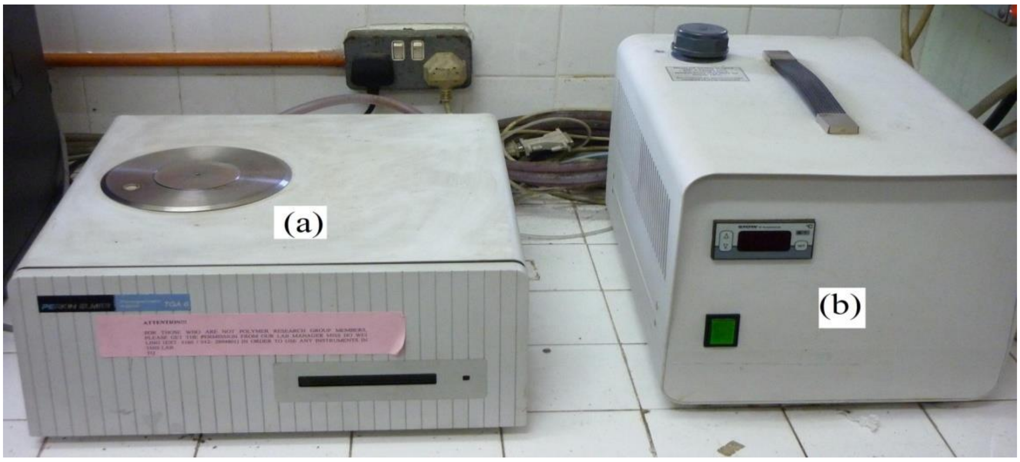

Figure 3.3: Perkin Elmer TGA 6 instrument: (a) Furnace (b) Intercooler

### 3.8.5 Gel Permeation Chromatography (GPC) analysis

GPC was performed at room temperature (30 °C) using a GPC setup consisting of a Water 600 controller, Water 717 Auto sampler, and Water 2414 Refractive Index detector. The chromatograph was fitted with a set of four styragel columns connected in series (dimension 4.6 x 300 mm). The column set was calibrated using monodispersed polystyrene standards. Tetrahydrofuran was used as the solvent at a flow rate of 1 mL min$^{-1}$. The chromatograms and integrated data were collected and processed using Empower software.

## 3.9 Development of UV-curable ENR50/Palm stearin alkyd blend

### 3.9.1 Preparation of UV-curable ENR50/Palm stearin alkyd blend

30 g of ENR50 solution (10 % w/w in toluene) was blended with 0.5 g of AlkydMA1 solution (60 % w/w in toluene) for 12 hours at ambient temperature (30 °C). The blend composition is equivalent to 10 parts of AlkydMA1 for every 100 parts of ENR50. After blending for 12 hours, benzophenone (UV photoinitiator) and TMPTA

(crosslinker) were added into the blend solution and it was stirred for another 1 hour to obtain a homogeneous solution. 5 blends with different proportions of benzophenone and TMPTA were prepared, and the compositions of all the blends are shown in Table 3.9. The blend mixture was applied as thin film on glass panels and left to dry in fume hood at room temperature for 48 hours. Subsequently, the dried films from the blend were irradiated with UV light for (i) 60 s, (ii) 120 s, (iii) 180 s, and (iv) 240 s. The source of UV light from this work is from a 400 W metal halide lamp which radiates UV light ($\lambda$= 365 nm) at intensity of 225 mW/cm$^2$ (Figure 3.4). The UV-cured blends were conditioned at room temperature for 24 hours prior to analysis.

Table 3.9: Compositions of UV-curable ENR50/Palm stearin alkyd blend

| Blends | Composition / g | | | |
|---|---|---|---|---|
| | ENR50 | Alkyd | Benzophenone | TMPTA |
| EA-B0T0 | 3.0 | 0.3 | 0 | 0 |
| EA-B5T0 | 3.0 | 0.3 | 0.17 | 0 |
| EA-B5T1 | 3.0 | 0.3 | 0.17 | 0.03 |
| EA-B5T3 | 3.0 | 0.3 | 0.17 | 0.10 |
| EA-B5T5 | 3.0 | 0.3 | 0.17 | 0.17 |

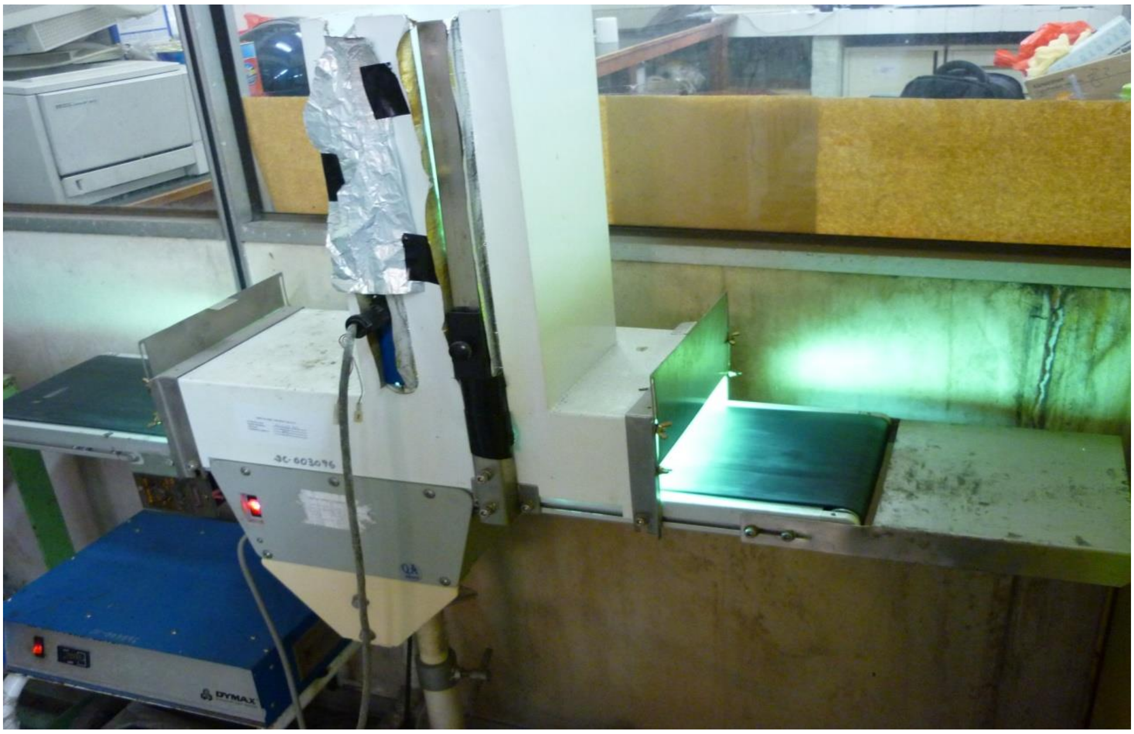

Figure 3.4: DYMAX Light Curing System 5000E (a) Power supply, (b) Roller belt and (c) Reflector housing with a 400W UV light bulb

### 3.9.2 Characterisation of UV-curable ENR50/Palm stearin alkyd blends

#### (a) FTIR analysis

Dried film from the UV-cured blend was analysed using Perkin Elmer Spectrum 400 FTIR spectrometer, with 16 scans from 4000 $cm^{-1}$ to 400 $cm^{-1}$ and resolution of 4 $cm^{-1}$.

#### (b) Thermal analysis

$T_g$ of the UV-cured blend was measured using Mettler Toledo DSC822e calorimeter. The sample was scanned under $N_2$ atmosphere from -60 to 60 °C at 20 °C $min^{-1}$ and $T_g$ was obtained from the heating cycle. Thermogravimetric analysis was carried out using Perkin Elmer TGA 4000 instrument. The sample was heated from 50

°C to 900 °C in $N_2$ atmosphere at heating rate of 20 °C $min^{-1}$. The sample weight used in each analysis was between 5-10 mg.

### (c) Swelling test and crosslink density calculation

A known weight of UV cured blend sample was immersed in toluene for 48 hours at room temperature in a covered glass bottle. After the soaking period, the swollen gel was filtered out using a sieve (50 mesh) and sandwiched between two pieces of filter papers. The weight of the swollen gel and filter papers was measured and recorded as $w_1$. Immediately after that, the swollen gel was removed from the filter papers and the weight of the wet filter papers was measured, $w_2$. The purpose of having the filter papers in the procedure was to remove the excess solvent on the surface of the samples. The swollen gel was left to dry in fume hood at room temperature for 24 hours before further dried in air-circulating oven at 100 °C until a constant dried gel weight, $w_3$ was obtained. The % of swelling of the UV-cured blend was calculated using Eqn. 3.23.

$$Percentage\ of\ swelling = \frac{(w_1 - w_2) - w_3}{w_3} \times 100\% \qquad (Eqn. 3.23)$$

Theoretically, crosslink density, $v$, can be calculated based on the mass measurement of polymer during equilibrium swelling (Mahomed et al., 2010) and is defined in Eqn. 3.24.

$$v = \frac{\rho}{M_c} \qquad (Eqn. 3.24)$$

where $\rho$ is the density of polymer and $M_c$ is the average molecular weight of the chains between crosslinks.

Besides, the same set of data obtained from swelling test can be used to calculate the volume fraction of polymer in its equilibrium swollen state, $\emptyset$ (Doty & Zable, 1946) as shown in Eqn. 3.25.

$$\emptyset = \frac{1}{1 + [\frac{(w_1 - w_2)\rho}{w_3\rho_1}] - (\frac{\rho}{\rho_1})} \qquad \text{(Eqn. 3.25)}$$

where $\rho$ and $\rho_1$ represent density of the blend and toluene respectively.

According to the theory of Flory and Rehner (1943), the change in the Gibbs function on mixing a liquid with a polymer, of density, $\rho$, is given in Eqn. 3.26.

$$\Delta G = RT\left[\log_e(1-\emptyset) + \emptyset + \chi\emptyset^2 + \left(\frac{\rho V_1}{M}\right)\left(\emptyset^{\frac{1}{3}} - \frac{\emptyset}{2}\right)\right] \qquad \text{(Eqn. 3.26)}$$

where $R$ in the equation above is the universal gas constant (8.314 $JK^{-1}mol^{-1}$), while $T$ is the absolute temperature (273.15K), $\emptyset$ is the volume fraction of rubber in its equilibrium swollen state, $\chi$ is the solvent polymer interaction parameter and $V_1$ is the volume occupied by one mole of liquid ($V_1$ for toluene is 107.4ml $mol^{-1}$).

$\Delta G$= 0 when a polymer is swell to a state in which it is in equilibrium with the liquid. A combination of Eqn. 3.24 and Eqn. 3.26, gives rise to the calculation of $v$ as shown in Eqn. 3.27.

$$v = -\frac{log_e(1-\emptyset) + \emptyset + \chi\emptyset^2}{V_1\left(\emptyset^{\frac{1}{3}} - \frac{\emptyset}{2}\right)} \qquad \text{(Eqn. 3.27)}$$

The solvent-polymer interaction parameter, $\chi$ was obtained using the Hildebrand’s solubility parameter theory (Zeng et al., 2007, pp. 289-304) as given in Eqn. 3.28.

$$\chi = 0.34 + \frac{(\delta_1 - \delta_2)^2 V_1}{RT} \qquad (Eqn. 3.28)$$

where $\delta_1$ and $\delta_2$ is the solubility parameter of toluene and blend respectively.

The solubility parameter of the blend was obtained using turbidimetric titration method (Ng & Chee, 1997). ENR50 and AlkydMA1 were dissolved separately in toluene ($\delta$= 18.1(J/ml)$^{1/2}$) to very dilute concentration of 0.3 % w/v. Subsequently, the ENR50 and AlkydMA1 solutions were titrated with two non solvents having high and low solubility parameter, at a rate of 0.25 ml/ minute until it reaches cloud point. The volume of non-solvent required to reach cloud point was recorded. The two non solvents that were used in the titration are acetonitrile [$\delta$= 24.1(J/ml)$^{1/2}$] and heptane [$\delta$= 15.0(J/ml)$^{1/2}$].

Based on the titration, the solubility parameter of polymer, $\delta'_p$ (ENR50 and AlkydMA1) can be calculated from the equation derived by Suh and Clarke (1967), as given in Eqn. 3.29-3.32.

$$\delta'_p = \frac{\sqrt{V_{12}}\delta_{12}+\sqrt{V_{13}}\delta_{13}}{\sqrt{V_{12}}+\sqrt{V_{13}}} \qquad (Eqn. 3.29)$$

where

$$V_{1i} = \frac{V_1 V_i}{\emptyset_1 V_i + \emptyset_i V_1}; i = 2,3 \qquad (Eqn. 3.30)$$

$$\delta_{1i} = \emptyset_1 \delta_1 + \emptyset_i \delta_i; i = 2,3 \qquad (Eqn. 3.31)$$

With

$$\emptyset_1 = 1 - \emptyset_i = \frac{\vartheta_1}{\vartheta_1 + \vartheta_i}; i = 2,3 \qquad (Eqn. 3.32)$$

$V$, $\emptyset$ and $\vartheta$ are the molar volume, volume fraction and volume at cloud point respectively. The subscripts 1, 2 and 3 correspond to the solvent and the two non solvents of different solubility parameter.

According to Oommen and Thomas (1997), solubility parameter of polymer blend can be calculated by knowing the weight fraction ($X_a$ and $X_b$) involved in blending and the solubility parameters ($\delta_a$ and $\delta_b$) of the individual polymers. Therefore, solubility parameter of ENR50/AlkydMA1 blend, $\delta_2$ can be calculated based on Eqn. 3.33.

$$\delta_2 = 0.91\delta_a + 0.09\delta_b \qquad (Eqn. 3.33)$$

where $\delta_a$ and $\delta_b$ are the solubility parameter of ENR50 and AlkydMA1 respectively.

Density of the blend, $\rho$ was determined experimentally using a pycnometer (Weight = $W_0$) which has been calibrated using distilled water to obtain volume of the pyncnometer, $V_0$. Dried film from the blend was cut into small pieces and was placed in a 100 ml beaker before being mixed with 25 ml of glycerol. An amount of methanol was then added gradually into the beaker and the glycerol/methanol mixture was stirred homogeneously using a magnetic stirrer. The mixture was left to stand still, without stirring, and the position of the small pieces of films from the blend was observed. If small pieces of films float in the solvent mixture, then methanol has to be added to the mixture. Conversely, if the films sink in the solvent mixture, glycerol has to be added to the mixture. Addition of either one of the solvents was continued until the films were observed to remain suspended in the methanol/glycerol mixture. The solvent mixture was transferred to the calibrated pycnometer and the weight was recorded as $W_f$. Density of the blend was determined as shown in Eqn 3.34:

$$Density\ of\ blend, \rho = \frac{W_f - W_0}{V_0} \qquad Eqn. 3.34$$