CHAPTER 3

RESULTS AND DISCUSSION

Development of environmental friendly product has gained importance as a result of global recognition of the harmful effects of volatile organic compounds (VOC). Thus, the use of vegetable oils derived from palm oil is to achieve this goal. In this work, oleic acid as one of the palm oil derivatives was used as raw material together with glycerol, phthalic anhydride and fumaric acid to produce alkyds (palm oil - based polyester resin).

Palm oil is classified as non drying oil because of its characteristic in which it has low iodine value. This makes palm oil not capable of forming coherent film by air oxidation. As such, the use palm oils alone in industry only a few for adhesive or surface coating applications. In some cases, it is necessary to mix with other oils to produce a workable application resin. Alkyds are tough resins derived from reaction of polyacids with polyols, in the presence of fatty acids as a major part of its compositions (Ataei et al. 2011).

The versatile resin forming reactions in alkyds have diversified the structural units connecting the ester groups. The properties of alkyds can be further modified either by physical or chemical blending with other polymers to produce end products with desirable characteristics. In this study, alkyds act as tackifying resins to NR in order to produce required balance of peel adhesion and resistance to shear in the application as PSA (Hofland, 2012).

3.1 Synthesis of palm oil based alkyds

Alkyds in this work were synthesized by fatty acid process in which using the whole oil (palm oleic) as the source of fatty acids. The presence of the fatty acid as a significant part of its composition distinguishes an alkyd from the other polyesters. In theory, alkyd resin is classified into different oil length (OL) based on oil (or fatty acid) in its formulation. In this work, three different oil length alkyds namely Alk-43 (short oil length), Alk-47 (medium oil length) and Alk-65 (long oil length) were formulated according to Patton's gel point calculation, which is an applicable formulation system to avoid gelation (Patton, 1962). Besides that, the synthesis process was carried out by employing fusion cook technique whereby no addition of solvents involved. The fatty acid process is often called the 'high polymer technique'. This is because it need to follow step by step addition of chemical in order to complete the polymerization process and obtained the desired product at the end of the synthesized process (Velayutham et al. 2009).

In addition, it also requires longer time as it involves heating and cooling processes before proceeding with the addition of other chemicals. In this work, the first part of reaction began when the mixture of oleic acid and glycerol were reacted together at temperature range from 180 ^{0}C to 220 ^{0}C and maintained for 2 h until the required degree of polymerization was reached. Generally, this was indicated by the soft clear viscous resin and amount of water collected as theoretical value. The next step involved addition of phthalic anhydride. Careful temperature control was needed as the phthalic is very reactive and easily sublimes inside the wall of reactor and condenser if temperature was raised drastically. It will cause loss of volatile products and effect end property of resin. At low temperature the anhydride half ring opening could occur and discharged some water (Uschanov, et al. 2008).

As the temperature was gradually increased the reaction would take place to complete the esterification and polymerization process. During synthesis, acid number of the reaction was measured periodically. Finally, the reaction with fumaric acid, another reactive material which needs carefully observation as there is high tendency for this material to form gelation.

The esterification reaction involves releasing of water molecule. Since the esterification reaction is reversible, the water of reaction must be removed once it is formed to prevent the occurrence of hydrolysis. Heating was stopped when the acid number had reached the final desired value and mixture was cooled to room temperature. Apart from that, to ensure the synthesis process was performed successfully the heat inducing cross linking or gelation during the alkyd cook has to be avoided. The reaction conditions and heating rates need to be controlled properly (Akintayo and Adebowale 2004).Thus, the chosen heating rate must be sufficiently high to permit the reaction to be carried out within reasonable time period, yet not too elevated to cause decomposition, discoloration and excessive loss of volatile material or even gelation. In addition, the rate of agitation might also affect the final alkyd resin product. Thus, it is necessary that the speed of stirrer motor be maintained at around 130 rpm, which was suitable to provide an intimate mixing of ingredients and to ensure smooth of reaction.(Philipp and Eschig 2012).

3.1.1 Synthesis of Alk-45

Alk-45 was prepared from oleic acid, glycerol, PA and FA. It was formulated according to Patton’s gel point calculation, which was a practical alkyd formulating system to calculate the ratios of functional groups and the extent of reaction that can be reached while avoiding gelation. The theoretical calculation is demonstrated in Table 3.1

Table 3.1: Theoretical calculation for the formulation of Alk-45

Material	**W(g)**	**E**	**e_A**	**e_B**	**F**	**m_0**
Oleic Acid (OA)	410	282	1.4539	-	1	1.4539
Glycerol	320	30.7	-	10.423	3	1.0811
Phthalic Anhydride	160	74	2.1622	-	2	0.5172
Fumaric Acid	60	58	1.0345	-	2	3.4745
Total	950	-	4.6506	10.423	-	6.5267

where, W is weight of the raw material used; E is the equivalent weight (total of molecular mass divided by functionality); e_A is value of acid equivalent; e_B is value of hydroxyl equivalent; F is functionality; m_0 is total moles present at the start of reaction. The formulation of $e_{A,}$ e_B and m_0 are calculated as follows:

$$e_A = \frac{\mathbf{W}_{\text{acid}}}{\mathbf{E}_{\text{ acid}}} \qquad e_B = \frac{\mathbf{W}_{\text{ hydroxyl compound}}}{\mathbf{E}_{\text{ hydroxyl compound}}} \qquad m_0 = \frac{e_A}{F} \text{ or } \frac{e_B}{F}$$

The most important concept in this Patton's gel point calculation is the constant K which refers to the extent of reaction when gelation might occur. The K is defined as follows:

$$\text{Patton's gel point constant } K = \frac{\sum m_0}{\sum e_A}$$

The K value should be larger than 1.00 so that the gelation would not occur at 100% reaction conversion. From Table 3.1, the K of Alk-45 was (6.5267/ 4.6506), or 1.40 and thus Alk-45 was expected to have no gelation at 100 percent of reaction.

Besides that, the excess of hydroxyl group in Alk-45 could be estimated by taking the ratio between e_A and $e_{B,}$ as follows:

$$\text{Excess of hydroxyl group} = \frac{\sum e_B - \sum e_A}{\sum e_A} \times 100 \quad = 124\%$$

This indicates that there was 124% of excess –OH groups available in the formulation. Since Alk-45 was formulated with excess of hydroxyl groups, the expected hydroxyl value in the finished alkyd could be further estimated as follows:

$$\text{Expected Hydroxyl value} = \frac{(\sum e_B - \sum e_A) \times 56100}{\sum W - \text{Water Loss}}$$

$$= \frac{(10.423 - 4.6506) \times 56100}{950 - 41.86}$$

$$= 356.6 \text{ mg KOH g}^{-1}$$

where water loss is total water loss for OA, PA and FA.

3.1.2 Synthesis of Alk-47

Alk-47 was synthesized with the same procedure as Alk-45. The theoretical formulation is tabulated in Table 3.2

Table 3.2: Theoretical calculation for the formulation of Alk-47

Material	**W(g)**	**E**	**e_A**	**e_B**	**F**	**m_0**
Oleic Acid (OA)	210	282	0.7447	-	1	0.7447
Glycerol	126	30.7	-	4.1042	3	1.3681
Phthalic Anhydride	100	74	1.3514	-	2	0.6757
Fumaric Acid	40	58	0.6897	-	2	0.3448
Total	476	-	2.7857	4.1042	-	3.1333

3.1.3 Synthesis of Alk-65

Alk-65 was prepared in the same way as Alk-45 and Alk-47. The theoretical formulation is tabulated in Table 3.3. Table 3.4 showed the properties and formula for alkyd resin calculation. Figure 3.1 shows a plausible reaction mechanism in the preparation of alkyds resin.

Table 3.3: Theoretical calculation for the formulation of Alk-65

Material	**W(g)**	**E**	**e_A**	**e_B**	**,F**	**m_0**
Oleic Acid (OA)	400	282	1.4184	-	1	1.4184
Glycerol	110	30.7	-	3.5831	3	0.5743
Phthalic Anhydride	85	74	1.1486	-	2	0.2586
Fumaric Acid	30	58	0.5172	-	2	1.1944
Total	625	-	3.0843	3.5831	-	3.1871

Table 3.4: Properties and formula for alkyd resin calculation

Symbol	Property	Formula
e_A	Number of acid equivalent	$\sum W / \sum$Equivalent W of acid
e_B	Number of hydroxyl equivalent	$\sum W / \sum$Equivalent W of hydroxyl
m_0	Total moles	e_A / F or e_B / F
OL	Oil Length	$[W(OA) / \sum W] \times 100$
K	Patton's gelation constant	$\sum m_0 / \sum e_A$
%OH	Hydroxyl excess number	$(\sum e_B - \sum e_A) / \sum e_A \times 100$
	Expected yield	$\sum W$ – water loss
OHN	Hydroxyl number	$\frac{\text{\% of excess OH} \times 56100}{\text{Expected yield}}$
EW	Equivalent weight	56100 / Expected OH number
MW	Molecular weight	Equivalent weight × 3

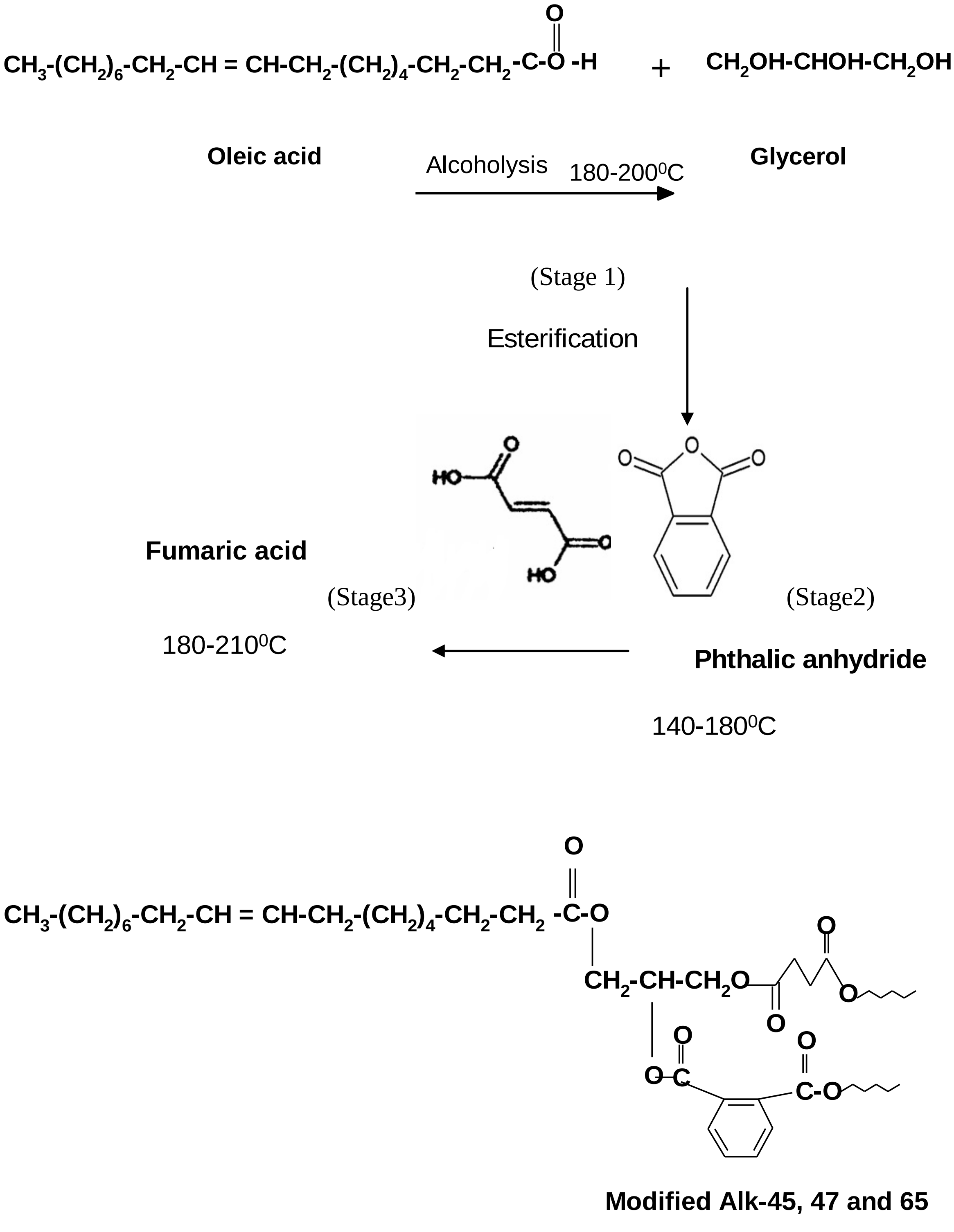


Figure 3.1: A plausible reaction mechanism in the synthesis of alkyds resin

3.1.4 Changes in acid numbers during synthesis of alkyds

Progress of the reaction during synthesis was observed by periodically checking the acid number of the reaction mixture. Determination of acid number during synthesis of alkyds follows equation [2.1] and [2.2] as mentioned in Chapter 2. A typical titration results for Alk-65 for 700 min are shown in Tables 3.5, 3.6 and 3.7 respectively.

Table 3.5: Titration results for standardization of KOH solution

No	First titration	Second titration	Third titration
Initial	0.00	0.00	0.00
Final	22.30	22.4	22.4
Average volume(ml)	22.40		

Standardization of KOH solution

$$M = W_a (V \times 0.2042)^{-1}$$

$$= 0.3893 (22.40 \times 0.2042)^{-1}$$

$$= \underline{0.0851N}$$

Table 3.6: Blank sample was titrated against of KOH solution

No	First Titration	Second titration	Third Titration
Initial	0.00	2.10	4.30
Final	2.10	4.30	6.50
Volume used (ml)	2.10	2.20	2.20
Average volume(ml)	2.20		

Table 3.7: Titration results of Alk-65 with standardized KOH solution at 700 min

No	**First Titration**	**Second titration**	**Third Titration**
Initial	0.00	10.0	21.0
Final	10.0	21.0	31.0
Volume used(ml)	10.0	11.0	10.0
Average volume(ml)	10.0		

Acid Number (AN) of Alk-65

$$AN = \frac{56.1 \times M \times (V - V_{blank})}{W_b}$$

$$AN = \frac{56.1 \times 0.0851N \times (10ml - 2.2ml)}{2.2315}$$

$$= \underline{16.68}$$

The value of acid numbers determined during synthesis of Alk-45, Alk-47 and Alk-65 are tabulated in Table 3.8, 3.9 and 3.10 respectively. The graph of changes in the acid number with increasing reaction time for different alkyd is shown in Figure 3.2

Table 3.8: Acid number during synthesis of Alk-45

Reaction time (min)	Acid number (mg KOH/g resin)
0	274.6
50	225.2
110	170.7
170	127.1
230	100.8
280	80.6
320	51.3
380	48.2
440	43.6
490	35.1
550	29.6
590	20.7
620	10.9
650	8.1

where, the initial acid number was calculated as $\frac{56100 \times e_A\,(\text{Total})}{\sum W}$ [3.1]

Table 3.9: Acid number during synthesis of Alk-47

Reaction time (min)	Acid number (mg KOH/g resin)
0	328.3
60	190.1
120	135.5
180	100.6
240	92.3
300	81.4
360	70.2
420	66.7
480	56.9
540	44.1
600	33.6
660	25.2
720	20.9
740	18.5

Table 3.10: Acid number during synthesis of Alk-65

Reaction time (min)	Acid number (mg KOH/g resin)
0	276.8
60	180.3
90	98.7
150	86.1
210	80.5
270	76.6
340	70.8
400	61.4
470	54.9
530	42.2
580	38.6
610	24.8
670	21.3
700	16.7

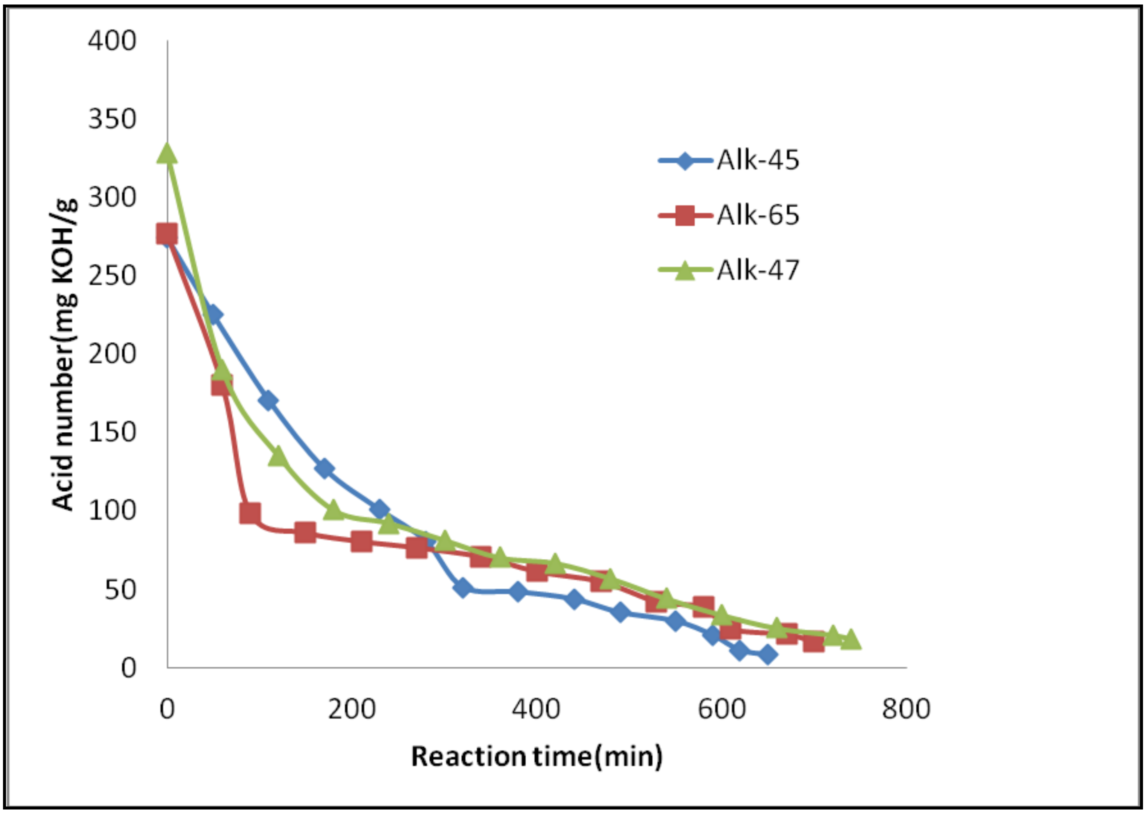


Figure 3.2: Plots of changes in acid number vs reaction time for alkyds

Figure 3.2 show the changes in acid number with reaction time. At the early stages of reaction the plots show rapid decrease in acid number for all three samples. These changes in acid number have been elucidated on the basis ratio of glycerol to acid in the alkyd formulation which may influence on the reduction rate of acid number. As, primary hydroxyl group is more reactive than secondary hydroxyl, thus rapid reduction of acid number occurs when primary group reacts followed by secondary group in later stages.

Therefore, the ratio of glycerol to acid in the alkyd formulation can influence the rate of reduction of acid number. Furthermore, as expected, the acid number decreases throughout the reaction process as PA and FA is incorporated into polyester backbone and could be related to the formation of branching between the chains or crosslink and consequently increase viscosity in the reaction. (Ikhuoria et al. 2007)

3.2 Characterization of synthesized alkyds

Three fusion cook alkyds Alk-45, Alk-47 and Alk-65 of oil lengths of 45, 47 and 65 respectively were synthesized. The general characteristics of these alkyds are summarized in Table 3.11.

Table 3.11: Characteristics of fusion cook alkyds

Property	**Alkyds**		
	Alk-45	Alk-47	Alk-65
Oil Length	45	47	65
Acid Number	8.10	18.52	16.68
Estimated Hydroxyl Number	356.62	164.04	46.85
Molecular weight	1455	4380	970
Moisture content (%)	0.18	0.25	0.12
Colour and physical appearance	Brownish viscous liquid	Brownish very viscous liquid	Light brownish
Stability	> 6 months	> 6 month	> 6 month

With reference to Table 3.11, the property of formulated alkyd resin depends on the chemical composition and their preparation processes. (Saravari and Praditvatanakit, 2013). Alkyd normally identify based on the proportion of oil length content such as 45 (short oil), 47 (medium oil) and 65 (long oil). Progress of the reaction, during synthesis was observed by periodically checking the acid number and the result shown that Alk-45 obtained acid value below than 10 as estimated value. On the other hand, Alk-47 and Alk-65 showed an excess of acid value and even prolong reaction process has no effect on reduction of acid number (Uschanov et al. 2008; Mańczyk 2002).

In addition, estimated hydroxyl number for Alk-45 showed much higher than Alk-47 and Alk-65 as in the formulation it consist more glycerol than others. Also, shown that the hydroxyl number decreases as the oil length of alkyds increases. The moisture content of alkyds resin was found to be below 0.5%. If more than that, it might affect the property of the PSA produced. Besides that, the viscosity and molecular weight of alkyds are normally related to each other.

Viscosity would increase as the molecular weight increases and oil length of polyester resin decreases (Abraham and Höfer, 2012). From the result, Alk-47 was observed to have higher molecular weight and viscosity as compared to Alk-45 and Alk-65. This is due to the formulation of Alk-47 (Table 2.1) in which has higher proportion of PA (presence of the aromatic ring) and FA as compared to Alk-45. Thus the structure is more compact and lead to higher molecular weight and viscosity as well (Aydin et al. 2004).

Generally alkyds cooked from fatty acid process are said to be more viscous with lighter colour than cooked by conventional method (Patton, 1962). However, as oleic acid is included, the end product, alkyds have a tinge of yellowness or brownish due to the nature of palm oil itself. Alk-65 colour is little bit light brownish than Alk-45 and Alk-47 due to higher percentage of fatty acid in the formulation of alkyds. At room temperature, Alk-47 was observed to be the most viscous, followed by Alk-45 and Alk-65(non viscous). Alk-47 has to be heated in the oven before it could be poured out from the bottle. Besides that, the synthesized alkyds resin had shown stability during storage for more than 6 month. (Philipp and Eschig, 2012).

3.2.1 Hydroxyl Number

In the hydroxyl number determination, the sample size of the alkyd must be determined first before the titration was carried out by substituting the expected hydroxyl number [3.2] into equation [2.6] as mentioned in Chapter 2.

$$\text{Estimated hydroxyl number} = \frac{(\sum e_B - \sum e_A) \times 56100}{\sum W - \text{Water loss}} \quad [3.2]$$

where water loss is [(e_AOA × 9) +(e_APA × 9) +(e_AFA × 9)]. So, the estimated hydroxyl value for Alk-65 was obtained as below:

$$\text{Estimated hydroxyl number} = \frac{(4.104-2.786) \times 56100}{476-25.26}$$

$$= 164.040 \text{ mg KOH g}^{-1}$$

Therefore, the sample size was (561/164.040); 3.42 g. For the hydroxyl number determination, free hydroxyl groups in the sample were first esterified with phthalic anhydride (PA). Then, the hydroxyl number was determined from the amount of KOH required to neutralize the unreacted PA remained in the sample. (Velayutham et al. 2009). The titration results for the standardization of KOH solution and the molarity of KOH solution calculated using the equation [2.3] is shown in Table 3.12. Meanwhile, the hydroxyl number for Alk-45 was calculated using equation [2.5] and the results is tabulated in Table 3.13. The titration result for Alk-47 and Alk-65 are tabulated in Tables 3.14 and 3.15 respectively.

Table 3.12: Standardization of KOH solution

No of titration	**1st titration**	**2nd titration**	**3rd titration**
Weight of KHP (g)	4.9853	4.9848	4.9840
KOH solution required (ml)	49.40	49.30	49.20
Molarity(M)	0.4942	0.4952	0.4961
Average Molarity(M)	0.4952		

Table 3.13: Titration result of Alk-45 with standardized KOH solution

No of titration	**1st titration**	**2nd titration**	**3rd titration**
Sample size (g)	1.5730	1.5791	1.5772
KOH solution required for titration of sample(ml)	75.30	75.65	75.21
KOH solution required for titration of blank (ml)	95.21	95.42	95.15
Hydroxyl number (mgKOH g^{-1})	351.63	347.81	351.22
Average hydroxyl number(mgKOH g^{-1})	350.22		
Estimated hydroxyl number	356.62		

Table 3.14: Titration result of Alk-47 with standardized KOH solution

No of titration	**1st titration**	**2nd titration**	**3rd titration**
Sample size (g)	3.4210	3.4204	3.4225
KOH solution required for titration of sample(ml)	75.40	75.50	75.55
KOH solution required for titration of blank (ml)	95.15	95.25	95.30
Hydroxyl number (mgKOH g^{-1})	160.38	160.41	160.31
Average hydroxyl number(mgKOH g^{-1})	160.37		
Estimated hydroxyl number	164.04		

Table 3.15: Titration result of Alk-65 with standardized KOH solution

No of titration	**1st titration**	**2nd titration**	**3rd titration**
Sample size (g)	11.98	12.00	11.85
KOH solution required for titration of sample(ml)	78.25	76.43	79.58
KOH solution required for titration of blank (ml)	95.35	95.20	95.45
Hydroxyl number (mgKOH g^{-1})	39.65	43.45	37.21
Average hydroxyl number(mgKOH g^{-1})	40.10		
Estimated hydroxyl number	46.85		

3.2.2 Fourier transforms infrared (FTIR) analysis of alkyds

FTIR is a common technique used to characterize the polymer structure by identifying the functional groups which vibrate and absorb typical frequencies within the infrared region. The assignments for FTIR spectra of the three fusion cook alkyds namely Alk-45, Alk 47 and Alk-65 are presented in Table 3.16 and the overlaid FTIR spectra are presented in Figure 3.3.

All the alkyds showed similar absorption peaks. These are as expected because all alkyds were prepared from the same material and only vary in the proportion. Peak that corresponding to the OH group is observed at 3400-3415 cm^{-1}. There is a broader peak observed for Alk-45 compared to Alk-47 and Alk-65. The peak is corresponding to OH group of the free glycerol. According to the reference, the amount of polyhydric alcohol used in the formulation of alkyd resin varies between 5 to 40% by weight. If the amount of polyhydric alcohol is greater than 40% by weight, the unreacted polyhydric alcohol in the alkyd system will show an excessive increase in absorption moisture (Uschanov et al. 2008).

Besides that, the presence of hydroxyl group in the alkyds is expected to enhance the adhesion of the blends of the adhesive. The C-H of the double bonds (sp^2) stretching is observed at 3005-3006 cm^{-1} while the C-H stretching of (sp^3) is observed at region 2800-2900 cm^{-1}. The appearance of the characteristic band of ester group of – C=O stretching at 1732-1733 cm^{-1} and band in the aromatic region at 741-773 cm^{-1}, confirmed the esterification reaction of the alkyd resins. The hydroxyls groups of the alkyds are expected to enhance the adhesion of the blends via hydrogen bonding across the interface of adhesives while the presence of the unsaturated C=C in both alkyds and NR allows further cross linking under certain conditions (Singh et al. 2013).

Table 3.16: Major absorption peaks of fusion cook alkyds

Wavenumber (cm^{-1})			Bonding
Alk-45	Alk-47	Alk65	
3400	3415	3400	O-H (Stretch)
3005	3006	3005	=C-H (Stretch)
2923	2924	2924	C-H (Stretch)
2854	2853	2854	C-H (Stretch)
1732	1733	1733	C=O (Stretch)
1456	1456	1456	C-C (Stretch)
1259	1258	1259	C-O (Stretch)
1072	1073	1071	C-O (Stretch)
773	771	771	Aromatic C-H (Bend)
741	743	742	Aromatic C-H (Bend)

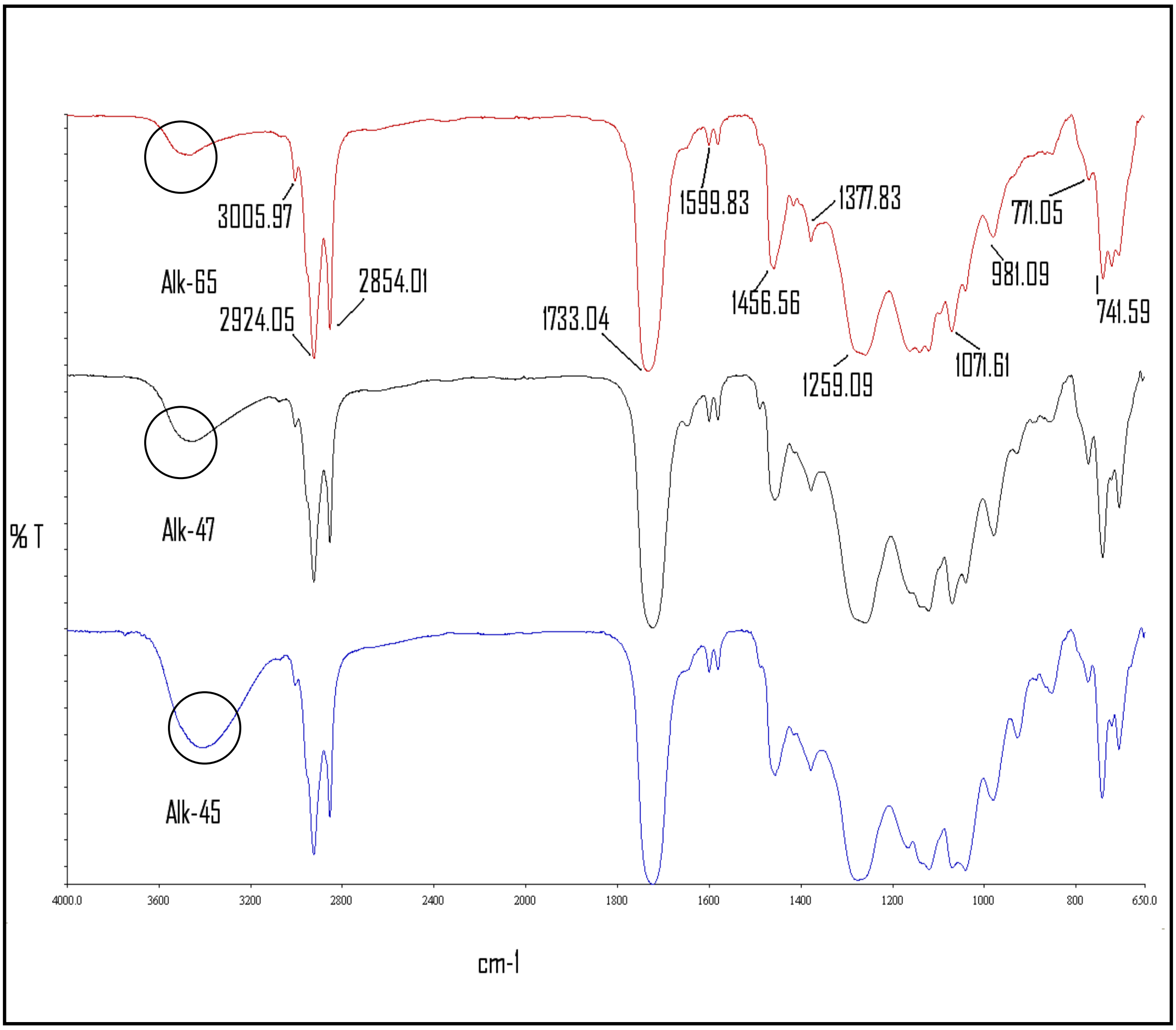


Figure 3.3: FTIR spectra of fusion cook alkyds

3.2.3 Nuclear magnetic resonance (NMR) analysis of alkyds

NMR is the spectroscopic method which also reveals the types of functional groups that present in a sample and gives information to support the IR analysis. The spectra of Alk-45, Alk-47 and Alk-65 as shown in Figure 3.4(b) show similar chemical shifts of the major peaks since they were prepared from similar material and only the proportion is different. The assignment of this alkyd is summarized in Table 3.17. A plausible molecular structure of synthesized alkyds is shown in Figure 3.4(a).

Generally, the alkyd resin has an ester structure with fatty acids of the oils as the integral part of its composition. The peak appearing at 0.80 ppm is assigned to the methyl protons in the chain end of the free fatty acid. The strong resonance at 1.24 ppm is due to the methylene protons secondary of the fatty acid and the weaker resonance at 1.5 ppm is assigned due to the methine protons attached to carbon in the long hydrocarbon chain. The peak at 1.90 ppm is due to the methylene proton next to C=C of the fatty acid chain. Peak attributed due to the methylene proton adjacent to carbonyl group appear at 2.3 ppm. (Akintayo and Adebowale, 2004).

Meanwhile, both methylene and methine protons on the glycerol unit that is attached to the oxygen of an ester group and fumaric acid are deshielded to form a broad peak at the lower field range between 3.5 - 4.5 ppm. Besides that, the peak which appears at 5.3 ppm is attributed to the vinylic proton of the unsaturated fatty acids. The strong peak which appears at 7.2 ppm is attributed to the $CHCl_3$ in the $CDCl_3$ solvent. On the other hand, the last two peaks appearing at 7.54 and 7.72 ppm represent the vinylic protons of aromatic ring of phthalate anhydride. (Thanamongkollit and Soucek, 2012)

Table 3.17:^{1}HNMR of fusion cook alkyds

Peak label	Chemical Shift (ppm)	Assignment
a	0.80	CH_3 - proton primary
b	1.20	CH_2 - proton secondary
d	1.50	CH - proton tertiary
c	1.90	CH_{-2} –CH_2-CH=CH-
e	2.30	$(CH_2)_6$ – C=0
f,g	3.50 - 4.50	-O-CH_2-CH-O-CH_2-O
h,i,j	5.30	-CH=CH-
L	7.26	-$CHCl_3$
k	7.54, 7.72	-CH of aromatic ring (phthalate anhydride unit)

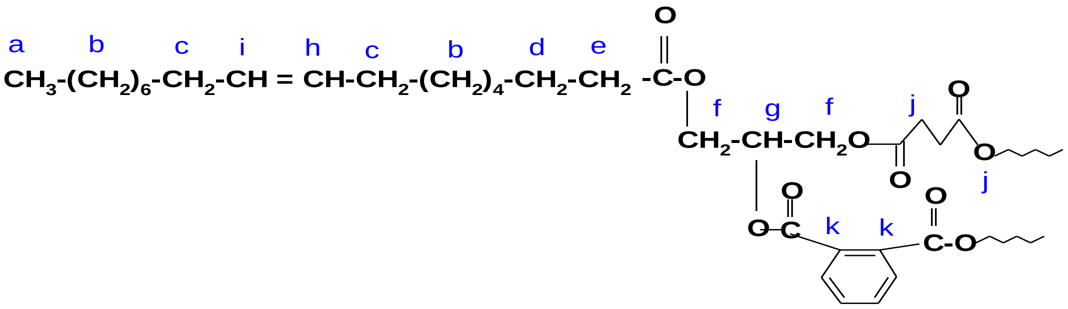


Figure 3.4(a): A plausible molecular structure of fusion cook alkyds

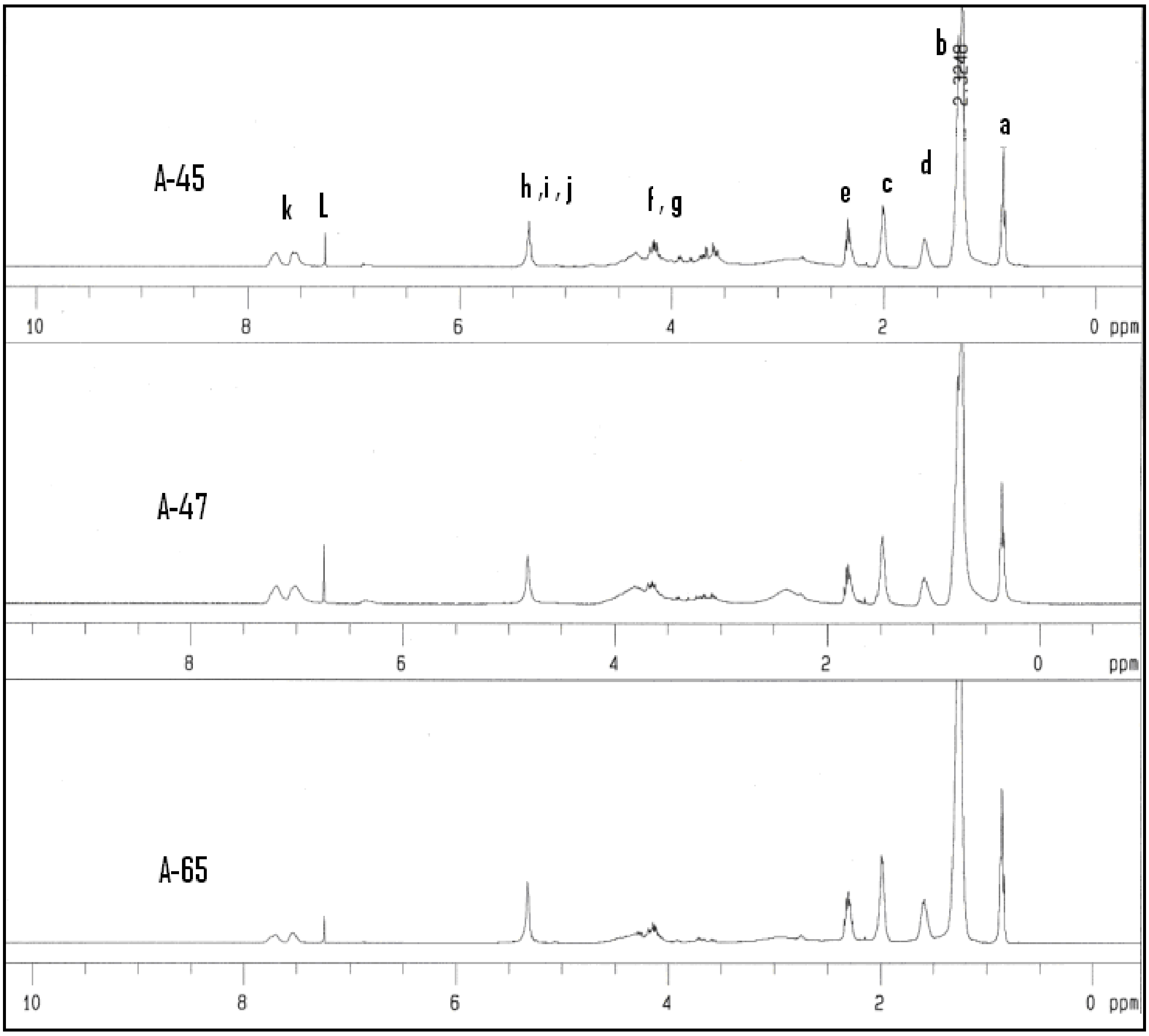


Figure 3.4(b): NMR spectra of fusion cook alkyds

3.2.4 Differential scanning calorimetry (DSC) analysis of alkyds

One of the most important characteristic of a polymer is its glass transition temperature. The glass transition temperature (T_g) is the state where the temperature of the polymer changes from a phase of a glassy state to an elastomeric state. When a sample is heated, the volume and energy of a polymer would increase gradually and reaches the T_g and become more rubbery. Below the glass transition temperature, polymer would not have enough energy to rotate and will stay in rigid states.

From the DSC curves as shown in Figure 3.5 and Table 3.18, Alk -65 has a T_g of -33.87 °C while Alk-47 and Alk-45 have T_g of -18.29 °C and -15.28 °C respectively. Between the fusion cook alkyds, Alk-65 had more fatty acid side chain in the polymer linkages and this makes the structure less compact and more flexible. Thus less energy required as compared to Alk-45 and Alk-47 whereby more heat energy is required to break the rigid state. (Robinson 1979; Philipp and Eschig, 2012).

Table 3.18: Thermal characteristics of DSC curves

DSC	
Alkyds	**T_g (°C)**
Alk-45	**-15.28**
Alk-47	**-18.29**
Alk-65	**-33.87**

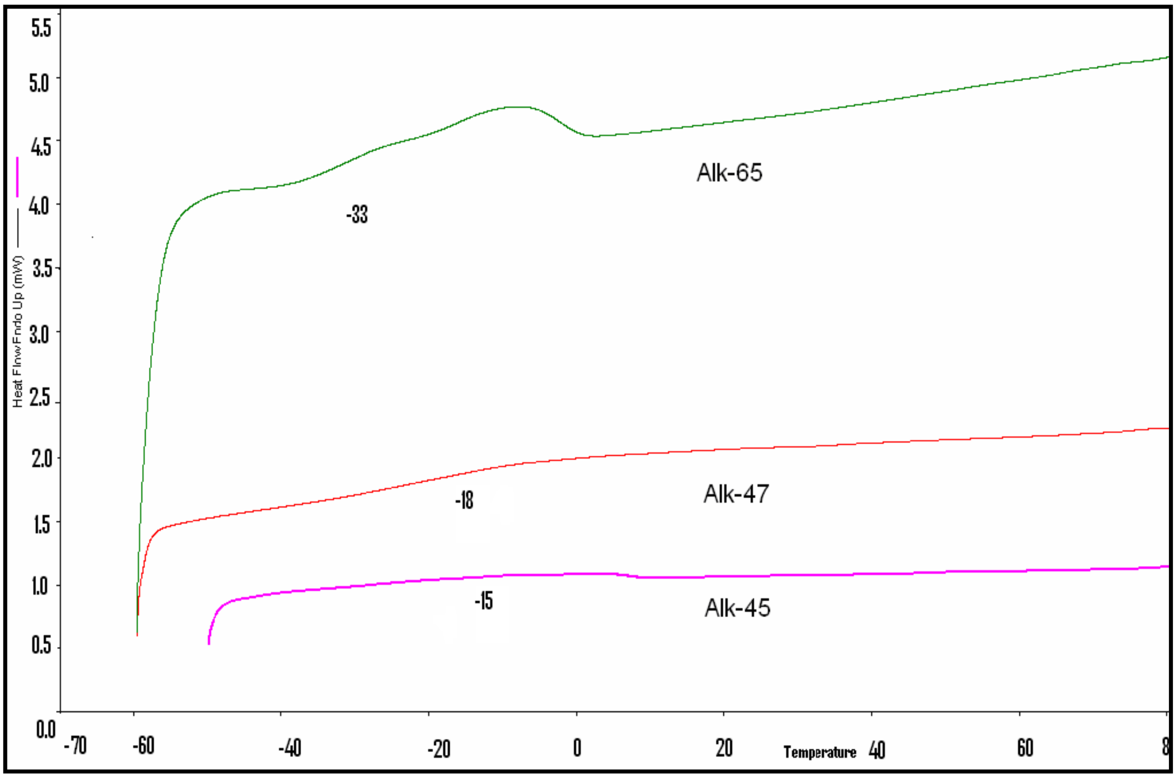


Figure 3.5: Overlay of DSC curves of fusion cook alkyds

3.2.5 Thermogravimetric analysis (TGA) of alkyds

Thermogravimetric analysis (TGA) is an important technique that used to study the thermal stability of alkyds. Table 3.19 shows the TGA thermograms of the fusion cook alkyds namely Alk-45, Alk-47 and Alk-65 at 10 wt%, 90 wt% and 100 wt% and overlaid curves are shown in Figure 3.6. There are three distinct stages of thermal degradation occurring at temperature above 160 °C. The first thermal degradation noted at 10 wt% of Alk-45, Alk-47 and Alk-65 at 160 °C and reaches the maximum between 306 to 332 °C with a weight loss between 5.92 to 8.75 %. The second weight loss is between 86.3 to 92.1 % occurring at a temperature of 332.3 °C and reaches the maximum between 447.3 to 461.9 °C. Meanwhile, the third thermal degradation starts at 461.9°C and reaches a maximum between 601.2 to 824.5^{0}C with a weight loss between 1.77 to 4.32 % (Boruah et al. 2012). Normally, low molecular weight organic molecules are stable only below a certain limiting temperature, usually from 100 to 200 ^{0}C. If the temperature is increased to certain temperature, organic molecules may vaporize or decompose into small fragment.

The results show that degradation of higher molecular weight polymer occurs at higher temperature whereas for the lower weight polymer, the degradation occurs at lower temperature. This is because the higher molecular weight polymer has the structure much more compact and less flexible as compared to lower molecular weight polymer (Güçlü and Orbay, 2009). The molecules are composed of atoms which linked together by covalent bond and thus lots of heat or temperature requires to break the rigid state and increase the kinetic movement between the atoms before the degradation can occurs. From the thermograms, it can be seen that Alk-47 has relatively higher thermal stability followed by Alk-45 and Alk-65. Generally, high molecular weight polymer would facilitate rapid drying during coating process while lower molecular weight fraction would act as plasticizer (Ikhuoria et al. 2007).

Table 3.19: Thermal characteristics of fusion cook alkyds

Alkyds	**Thermal Characteristics of TGA Curve**					
	$T_{10\text{ wt }\%}$ (^{0}C)	Wt Loss (%)	$T_{90\text{ wt }\%}$ (^{0}C)	Wt Loss (%)	$T_{100\text{ wt }\%}$ (^{0}C)	Wt Loss(%)
Alk-45	315.19	8.748	461.86	88.97	601.19	1.808
Alk-47	332.16	7.361	453.98	86.25	889.65	4.320
Alk-65	306.10	5.923	447.31	92.07	824.54	1.770

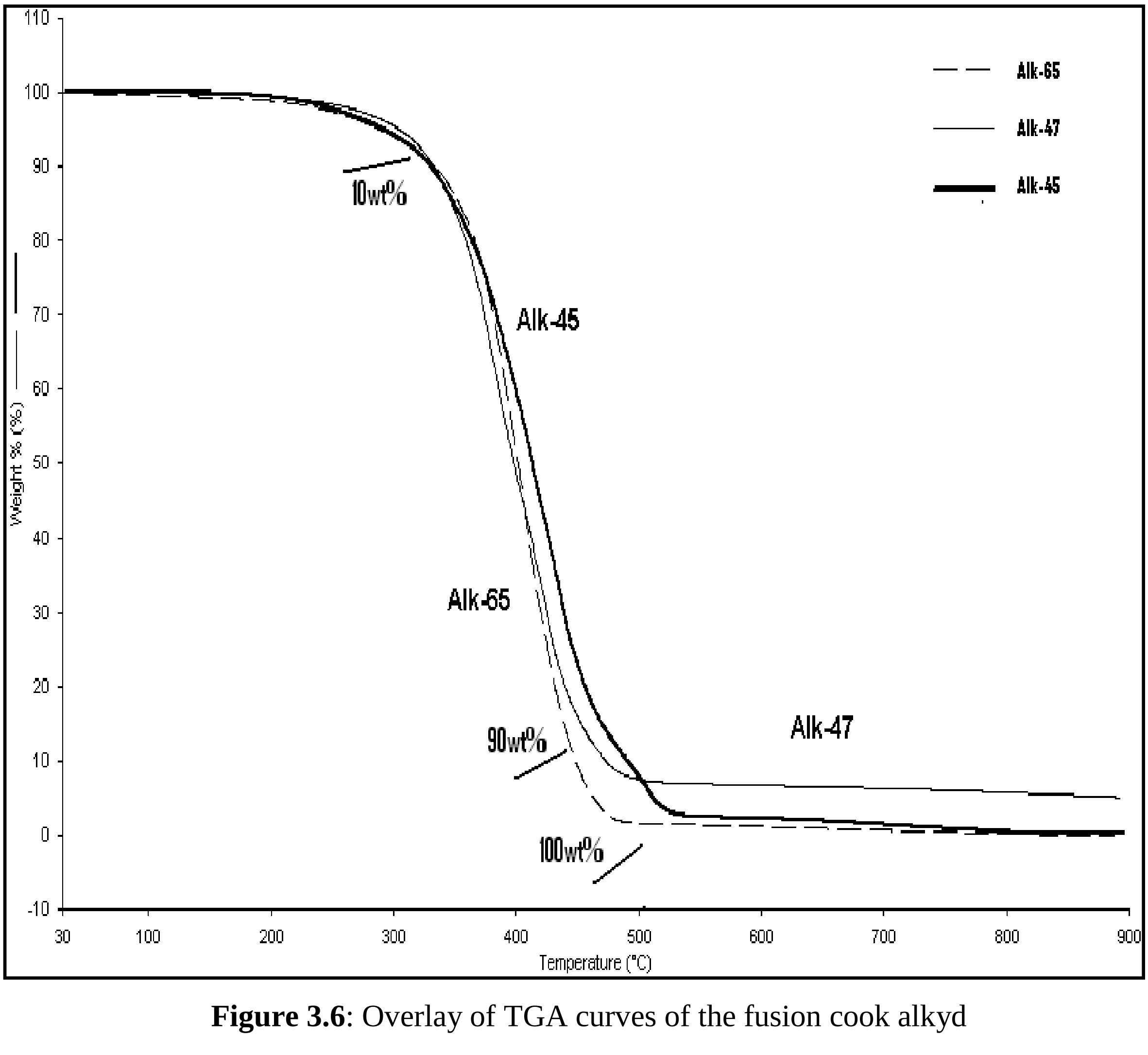


Figure 3.6: Overlay of TGA curves of the fusion cook alkyd

3.2.6 Gel permeation chromatography (GPC) analysis of alkyds

GPC is one of the most useful methods to determine the average molecular weight of polymers with high molecular weight. The GPC data for fusion cook alkyds are presented in Table 3.20 and the curves are shown Figure 3.7 (a), (b) and (c). The Mw and Mn of the Alk-47 are 14792 and 4380 respectively, and its polydispersity index (PDI) is 3.38. Polydispersity index (PDI), is a division of Mw by Mn and it is a measurement of the distribution of molecular weight in a polymer sample and indicates the distribution of an individual molecular weight in a batch of polymers (Vareckova et al. 2006).

Generally, the short oil length alkyd results in high molecular weight polymer since the molecules are more compact and rigid since it has less fatty acid side chain in the polymer linkages. However, for this analysis the medium oil length alkyd has higher molecular weight than short oil length alkyd (Kajtna, Golob et al. 2009). This might be due to the formulation of Alk-47 which has more Phthalic anhydride (aromatic ring) and fumaric acid ratio in the formulation as compared to Alk-45 and Alk-65. Thus, the molecular weight for that particular alkyd is higher. Besides that, due to higher molecular weight, Alk-47 observed has higher viscosity as compared to other alkyds (Güçlü and Orbay, 2009).

Table 3.20: GPC result of fusion cook alkyds

Alkyd	Mn	Mw	Mp	Mz	Mz +1	Polydispersity
Alk-45	1455	6857	1174	38905	88618	4.712432
Alk-47	4380	14792	2161	71246	206053	3.37686
Alk-65	970	3292	994	22338	53379	3.393290

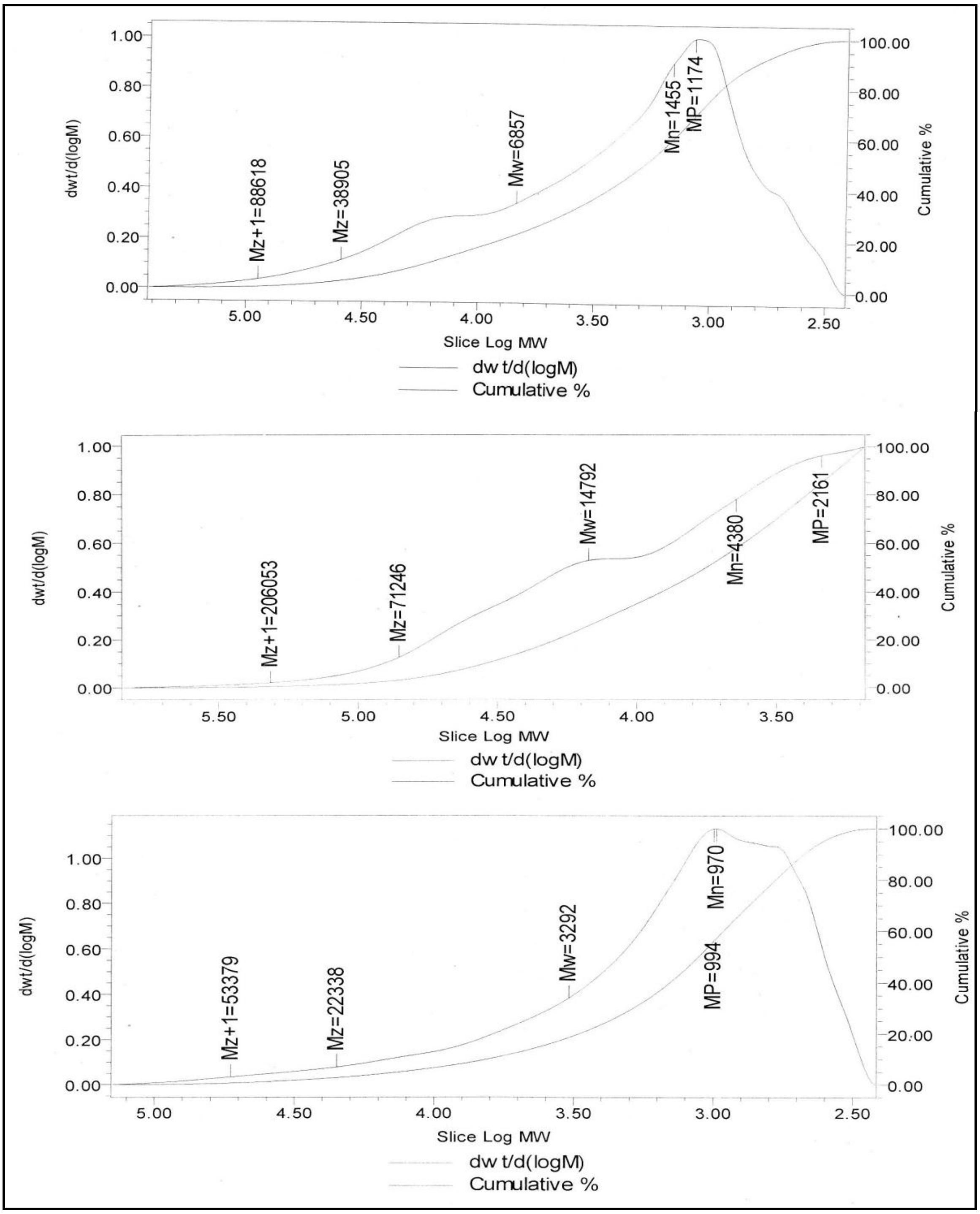


Figure 3.7: GPC trace for (a) Alk-45, (b) Alk-47 and (c) Alk-65

3.3 Formulation of Alkyd Emulsion

An emulsion is a mixture of two or more immiscible liquids. Emulsions are made up of a dispersed and a continuous phase in which the boundary between these phases is called the interface. It tends to have a cloudy appearance, because the many phase interfaces scatter light that passes through the emulsion. Energy input through shaking, stirring, homogenizing is needed to initially form an emulsion. (Elliott and Glass, 2000). Whether an emulsion turns into water - in - oil emulsion or oil- in- water emulsion depends on the volume fraction of both phases and on the type of emulsifier. Emulsions are unstable and thus do not form spontaneously. As such, in this study the fusion cook alkyds with different oil lengths were emulsified first in the form of oil in water (O/W) emulsion before being blended with the NR latex.(Philipp and Eschig, 2012). To form an emulsion, an emulsifier which stabilizes the emulsion by increasing its kinetic stability is added.(Holmberg, 2002) One class of emulsifiers is known as surface active substances or surfactants. Surfactants are molecules that have a hydrophobic (oil soluble) and an effective hydrophilic (water soluble) portion. They act by significantly lowering the interfacial tension and decreasing the coalescence of dispersed droplets, thus, providing the emulsion a lasting stability (Gooch, 2002). A mixture of ionic (SDS) and neutral surfactants (NP40) is normally chosen in order to prepare surfactant solution.

Owing to the fact that a mixture of both surfactants could greatly enhance the stability of emulsions compared to individual surfactant. During the emulsification, numerous small droplets were created from a large homogeneous oil phase through the use of surfactants to create a stable emulsion. (Weissenborn and Motiejauskaite, 2000).The stability of emulsion achieved through the mixtures of surfactants was explained from various points of view, including the concept of Hydrophile –Lipophile Balance (HLB). One of the earliest explanations was introduced by Griffin in 1949.

HLB expressed as the relative simultaneous attraction of the surfactant towards the water and the oil phase. In a research to determine the optimum HLB value, Tober and Autian discovered that although the emulsions were prepared using various mixtures of surfactants with similar HLB values, the stability of the emulsions was rather inconsistent. Also, Takamura *et al,* (1979) found that O/W emulsions, prepared with Tween 20-Span 80 mixtures, were unstable over the whole HLB range. Thus, it was found that the results on surfactant selection and emulsion stability that was predicted based on HLB were inconsistent (Tober 1958; Takamura 1979).

Shinoda introduced the concept of Phase Inversion Temperature (PIT), a more quantitative approach in evaluating surfactants in the emulsion systems. These methods make use of changing the spontaneous curvature of the surfactant. For non-ionic surfactants, this can be achieved by changing the temperature of the system, forcing a transition from an oil-in water (O/W) emulsion at low temperatures to a water-in-oil (W/O) emulsion at higher temperatures (transitional phase inversion). During cooling, the system crosses a point of zero spontaneous curvature and minimal surface tension, promoting the formation of finely dispersed oil droplets This method is referred as phase inversion temperature (PIT) method (Shinoda,1969).

Additionally, a transition in the spontaneous radius of curvature can be obtained by changing the water volume fraction (emulsion inversion point (EIP) method (Watson and Mackley 2002). By successively adding water into oil, initially water droplets are formed in a continuous oil phase. Increasing the water volume fraction changes the spontaneous curvature of the surfactant from initially stabilizing a W/O ‘emulsion to an O/W emulsion at the inversion locus. This process is well known for short-chain surfactants which form flexible monolayers at the oil–water interface, resulting in a bicontinuous microemulsion at the inversion point.

Also during this transition-referred to as catastrophic phase inversion minimal interfacial tension are achieved and reported to facilitate the formation of fine droplets (Jonsson 1998). In this work, alkyd resins of different oil lengths (Alk-45, Alk-47, and Alk-65) were emulsified successfully using Emulsion Inversion Point (EIP) method. Each alkyd emulsion was blended with natural rubber latex at four different ratios of 20% alkyd to 80% NR, 40% alkyd to 60% NR, 60% alkyd to 40% NR, 80% alkyd to 20% NR based on dry basis. The EIP is the point at which the emulsion composed of an oil, emulsifier and water changes from water in oil to oil in water system. During the emulsification process, the pH of alkyd emulsion was maintained within range 6-8 during the addition of the surfactant. Potassium hydroxide solution was added in order to adjust the pH of the emulsion. It was found that as more water content was added to the mixture, the viscosity of emulsion changed as well. Also as the emulsion reached the optimum value, the emulsion became creamy and white in color indicating formation of the O/W emulsion. (Gooch, 2002).

3.4 Rheology Test

Rheology is the study of the flow of matter mainly liquids but also soft solids or solids under conditions in which they flow rather than deform elastically. In order to study the rheological properties of the emulsion, Brookfield R/S Rheometer 3000(RHEO 3000) was utilized to conduct the rheological test. The shear rate dependent viscosities of the alkyd emulsions were determined as viscosities result would significantly relate to the storage stability of emulsion. Three different oil length alkyd emulsions were prepared from three different surfactant ratios as shown in Table 2.2 in Chapter 2. In this study, Alk 45, Alk-47 and Alk-65 were emulsified with surfactant mixtures S-2080, S-5050 and S-8020.

The shear rate dependent viscosity result for the Alk-45 was shown in Figure 3.8 whereas shear stress versus shear rate profile was displayed in Figure 3.9. Meanwhile, for Alk-47 and Alk-65, the figure for both result shear rate dependent viscosity and shear stress versus shear rate profile was shown in Appendix G. The tabulated data for the rheology test was shown in Table 3.21 and 3.22 respectively.

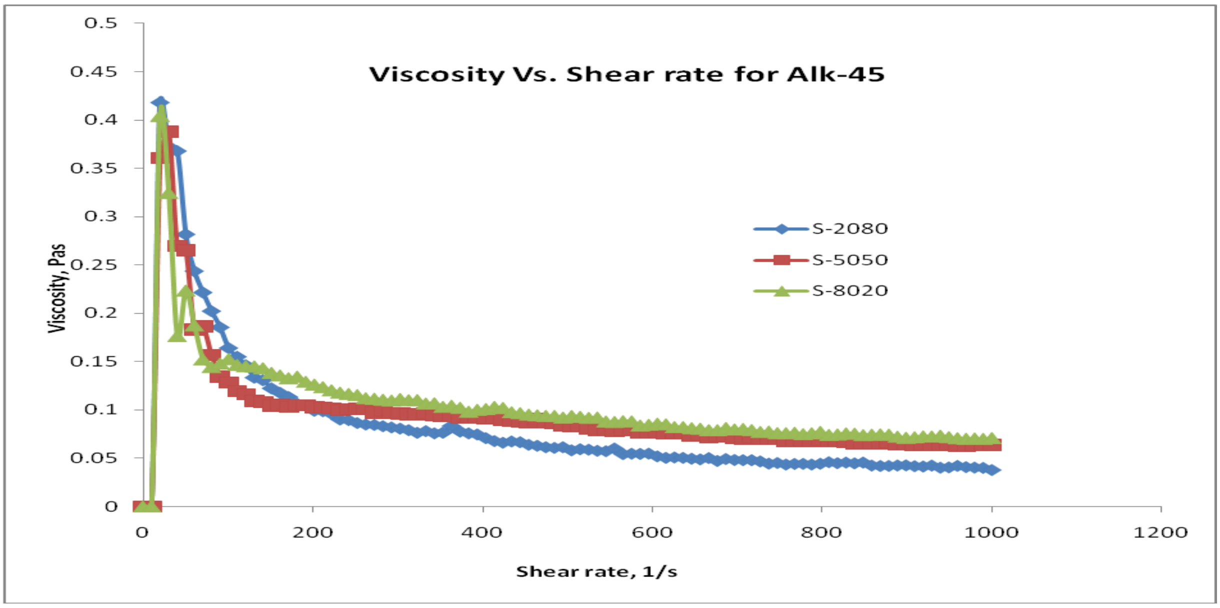


Figure 3.8: Viscosity Vs Shear rate for Alk-45 emulsion at different surfactant ratio

From the tabulated data in Table 3.21, it was found that both alkyds emulsion Alk-45, and Alk47 produced the most stable emulsion at the surfactant mixture ratio of S-8020. At this ratio the most stable emulsion was observed in which the emulsion was reached the highest viscosity of 0.4184 Pas and 1.2174 Pas for Alk-45 and Alk-47 respectively. This might be due to the higher SLS to NP40 ratio which allows the SLS to ionize and becomes more stable with Alk-45 and Alk-47 particles. On contrary, the shear rate dependent viscosity result for Alk-65 shows that the stable alkyd emulsion was achieved at the surfactant mixture of S-5050 which obtained the highest viscosity of 1.0850 Pas**.**

At the equal ratio, the surfactants might be significant to form a barrier in order to avoid penetration of SLS molecules into the oil droplets and allowing the SLS to ionize and then yield substantial negatively charged ions. Thus, it would lead to the formation of the stable alkyd emulsion. Furthermore, the shear rate dependent viscosity profile results showed the non-Newtonian behavior in which the flow properties are not described by a single constant value of viscosity.

Table 3.21: Tabulated data of Viscosity Vs. shear rate for synthesized alkyd resin

Alkyd	**Surfactant ratios**		
	S2080	**S5050**	**S8020**
Alk-45	0.4045	0.3608	0.4184
Alk-47	0.6586	0.8146	1.2174
Alk-65	0.8367	1.085	0.3968

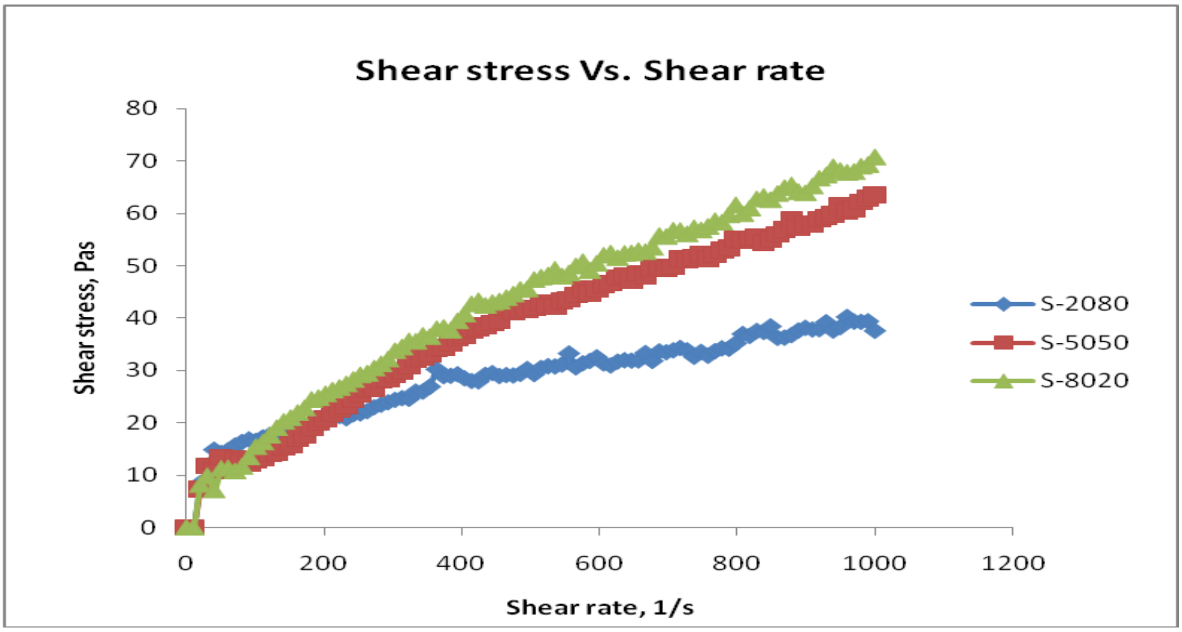


Figure 3.9: Shear stress Vs. Shear rate for Alk-45 emulsion at different surfactant ratio

The graph profiles correspond to the Bingham plastic behavior in which a viscoplastic material behaves as a rigid body at low stresses but flows as a viscous fluid at high stress. This means that the yield strength of viscous fluid must be exceeded before the fluid will flow. When an initial shear stress is applied to a fluid it will not begin to flow immediately. The slope angle, and therefore shear stress, must be increased until the yield strength of the fluid exceeded, after which flow will occur. This is contrary to a Newtonian fluid, which has zero yield strength and will flow on any slope. From the result of the shear stress dependent shear rate profile (Table 3.22) the Alk-45 and Alk-47 with surfactant mixture of S-8020 show higher yield stress than Alk-65. Both alkyds are predicted as a stable emulsion at that surfactant mixture. However, for the Alk-65, the result reveals that surfactant mixture at S-5050 showed higher yield stress of 228.601 Pas. Thus, it has produced a stable emulsion at that surfactant mixture. Among fusion cook alkyds, Alk-47 is observed to be the most stable emulsion during storage (Yu et al. 2006; Zhang et al. 2011).

Table 3.22: Tabulated data of Shear stress Vs. shear rate for synthesized alkyd resin

Alkyd	**Surfactant ratios**		
	S2080	**S5050**	**S8020**
Alk-45	40.313	63.469	70.757
Alk-47	343.981	330.329	377.032
Alk-65	129.74	228.601	101.689

3.5 Adhesive tests

Adhesives tests comprise of peel and shear strength measurements. Test describes the ability of the tape to resist against peeling force and could be characterized by peel test. Meanwhile, shear test describes the resistance of the tape towards creep force. Besides that, the adhesive weight per unit area test of the tape was carried out as well. In order to study the adhesive properties of sample, the selected commercial tapes were investigated as well with the same procedures applied for the both (tape under study and commercial tape). The entire test was carried out using ASTM method as mentioned in Chapter 2 and the result obtains from both sample and commercial tapes were compared in term of adhesive performance (Zhang and Wang, 2009).

3.5.1 Adhesive properties of the NR/Alk-45 emulsion tapes

The average values of peel and shear strength of the NR/Alk-45 tapes are tabulated in Table 3.23 while the plots of the peel and shear strength are shown in Figure 3.10 and 3.11 respectively. Meanwhile a typical peel test curve is shown in Figure 3.12 together with the calculation of the peel test as calculated using the equation [2.8] and [2.9] as mentioned in Chapter 2 is also given.

From the results, it is shown that the peel strength of the NR/Alk-45 blends at 80 weight % of alkyd emulsion gives the highest value of 31.44 N/mm and shear strength of 1.05 min. Moreover, it shows that the peel strength increases with the weight % of alkyd emulsion, indicating that satisfactory performance occurred when the percentage of alkyd emulsion in the blend was the dominant constituent. Besides that, it is shown that Alk-45 emulsion managed to improve the peel strength of NR/Alk-45 tapes giving a maximum value of 31.44 N/mm. Although not more than the commercial values, it is quiet close to the value of Loytape (Table 3.27) which has the peel strength is 35.48 N/mm.

Moreover, the peel and shear strength of pure NR are 16.21 N/mm and 8.00 min respectively. In contrary, it was found that pure Alk-45 emulsion did not have both the peel and shear strengths. In addition, the shear strength for NR/Alk-45 tapes did not perform satisfactorily since the tape was not sticky to the test panel and dropped down within a minute. This shows that Alk-45 did not perform very well to improve the shear strength of NR.

Table 3.23: Adhesive properties of the NR/Alk-45 tapes

Blending Ratio (wt %)		**Adhesive properties**	
Alkyd emulsion	**NR Latex**	**Peel Strength (N/mm)**	**Shear Strength (min)**
00	**100**	**16.21**	**8.00**
20	**80**	**11.73**	**1.00**
40	**60**	**17.13**	**1.00**
60	**40**	**20.81**	**1.00**
80	**20**	**31.44**	**1.05**
100	**00**	**0.00**	**0.00**

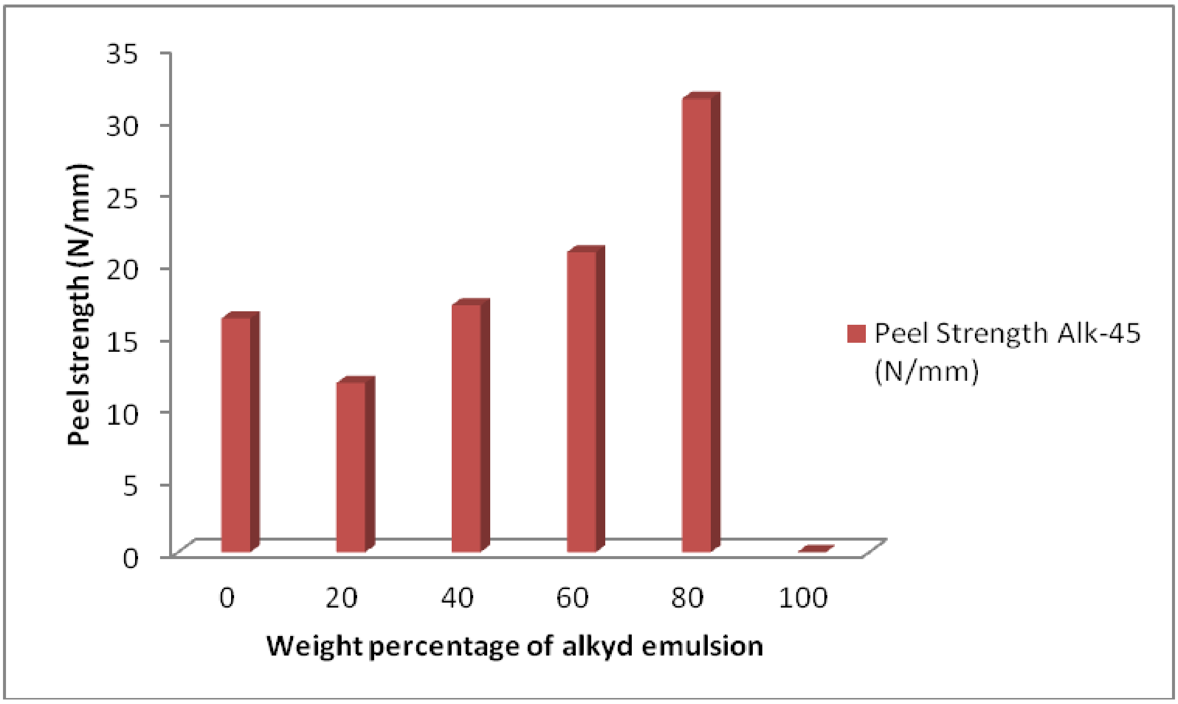


Figure 3.10: Peel strength vs. weight percentage of alkyd emulsion for NR/ Alk-45 blends

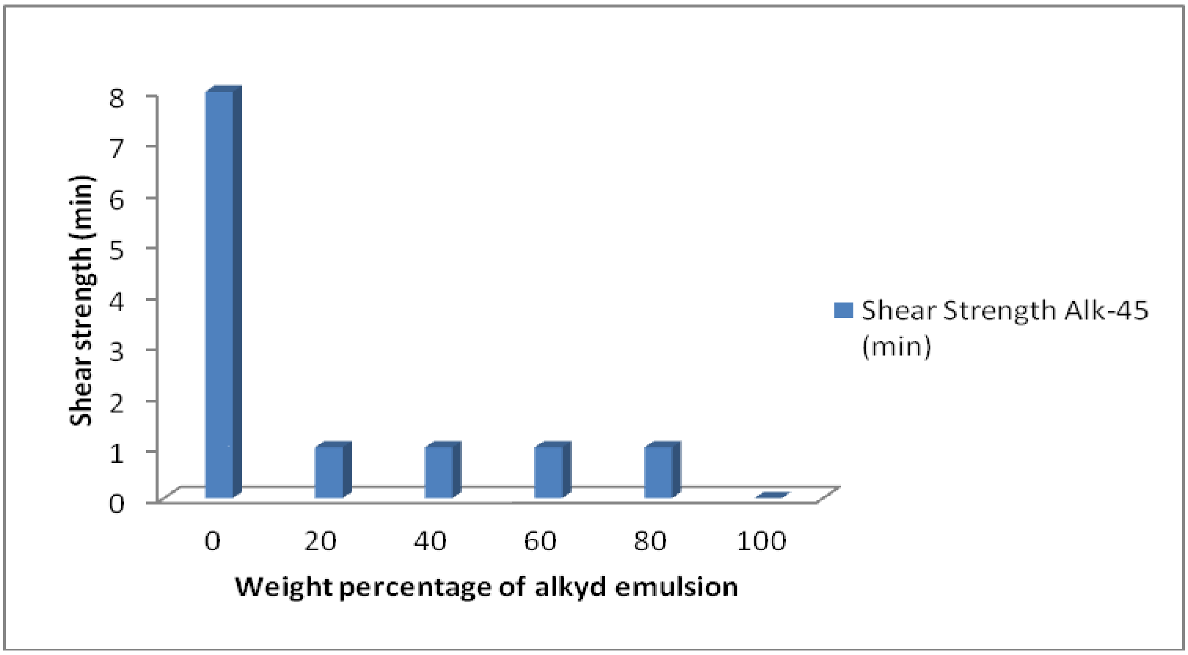


Figure 3.11: Shear strength vs. weight percentage of alkyd emulsion for NR/ Alk-45 blends

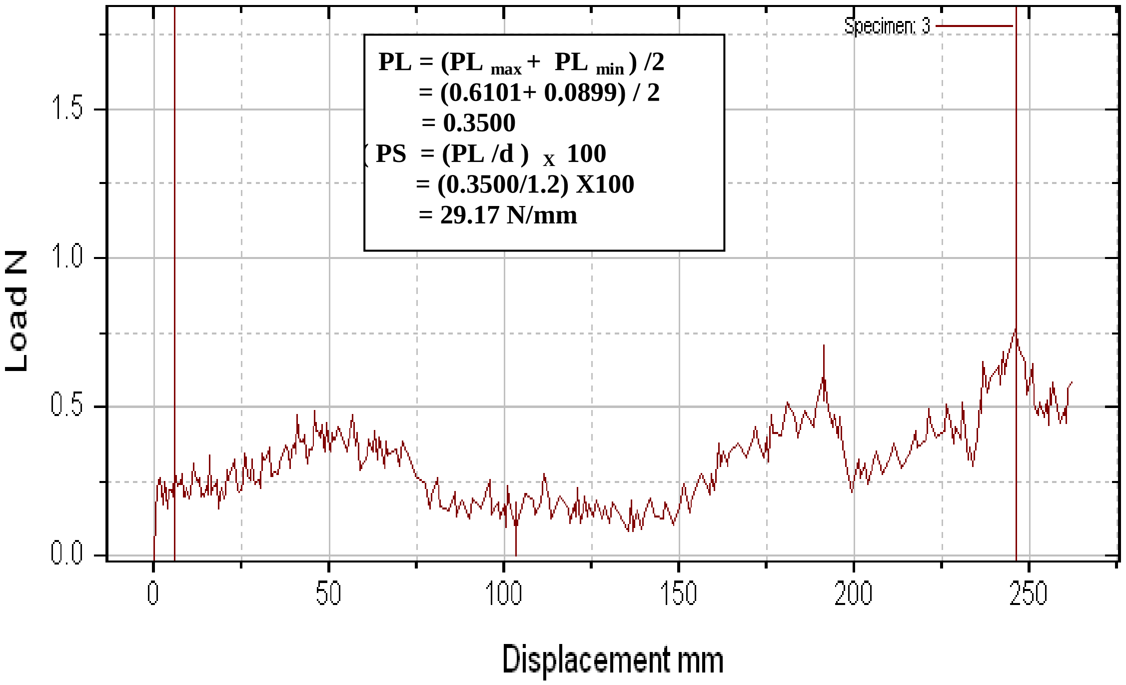


Figure 3.12: A peel test curve of NR/Alk-45 tape

3.5.2 Adhesive properties of the NR/Alk-47 emulsion tapes

The results for the peel test and shear strength of NR/ Alk-47 tapes are tabulated in Table 3.24 whiles the plots of the peel and shear strengths are shown in Figure 3.13 and 3.14 respectively. In addition, a typical peel test curve and calculation for the peel strength (inset) are shown in Figure 3.15. From the peel value, it is shown that the blend of NR/ Alk-47 at 80 weight % gives the highest value of peel strength of 84.27 N/mm as compared to other blend ratios. The result reveals that the peel strength increases with the weight percentage of alkyd emulsion, indicating that the optimum performance only occurs when the percentage of alkyd emulsion in the blend is higher. Moreover, the result shows that the NR/Alk-47 tapes tend to improve the peel strength of NR better than Alk-45. Overall, the NR/Alk-47 tape shows significantly higher value of peel strength than the selected commercial tapes (Table 3.27).

On the other hand, the shear strength also gives satisfactory result in which the highest value is 10.20 min at 80 weight % of NR. This shows that, the NR/Alk-47 tapes performed well when the NR ratio was dominant compared to the alkyd emulsion. Although, the shear values are lower compared to the shear strength of commercial tapes, Alk-47 manages to improve the shear strength of NR. Besides that, the peel and shear strengths for tape blends at 100 weight % of alkyds emulsion did not perform satisfactorily. The tape was non-sticky to stainless steel panel for peel test and the load was dropped down less than a minute for shear test. In addition, the peel and shear strengths of pure NR are 16.21 N/mm and 8.00 min respectively.

Table 3.24: Adhesive properties of the NR/Alk-47 tapes

Blending Ratio (wt %)		**Adhesive properties**	
Alkyd emulsion	**NR Latex**	**Peel Strength (N/mm)**	**Shear Strength (min)**
00	100	16.21	8.00
20	80	24.79	10.2
40	60	38.02	6.59
60	40	60.64	4.71
80	20	84.27	2.38
100	00	0.00	0.00

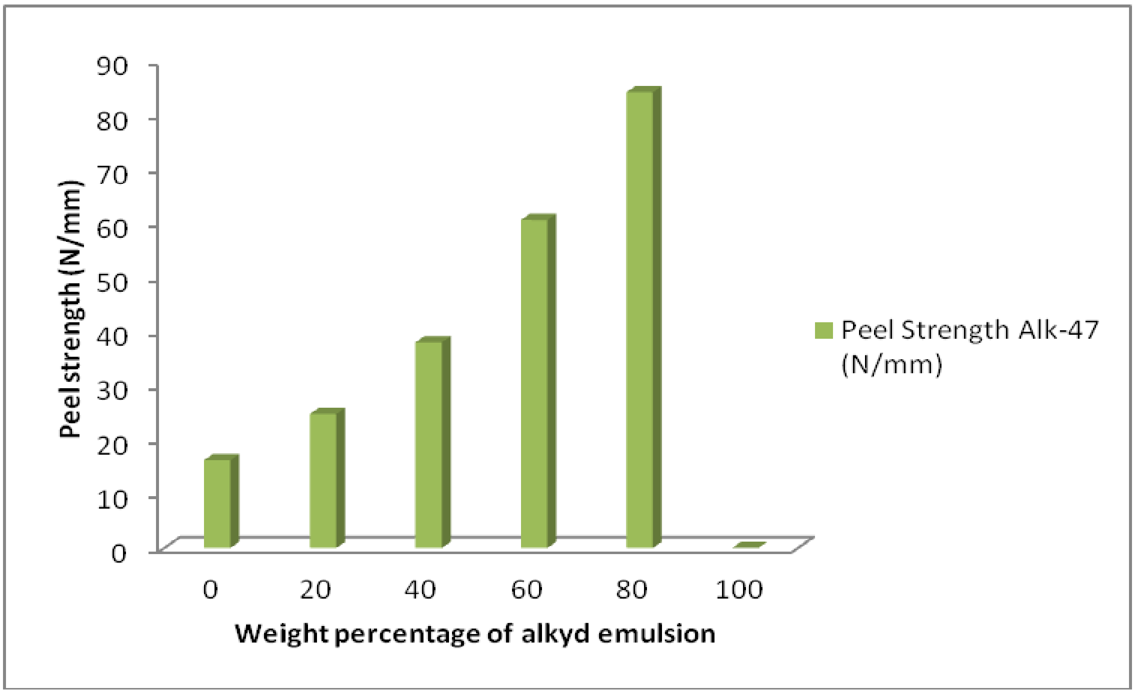


Figure 3.13: Peel strength vs. weight percentage of alkyd emulsion for NR/ Alk-47 blends

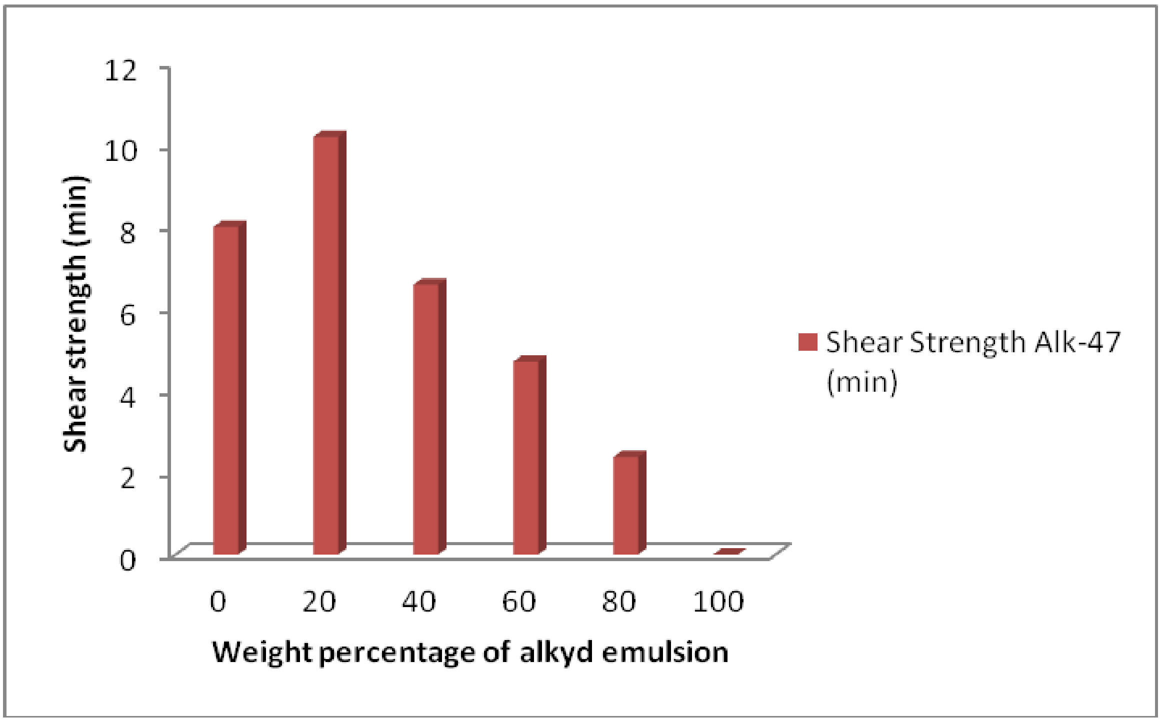


Figure 3.14: Shear strength vs. weight percentage of alkyd emulsion for NR/ Alk-47 blends

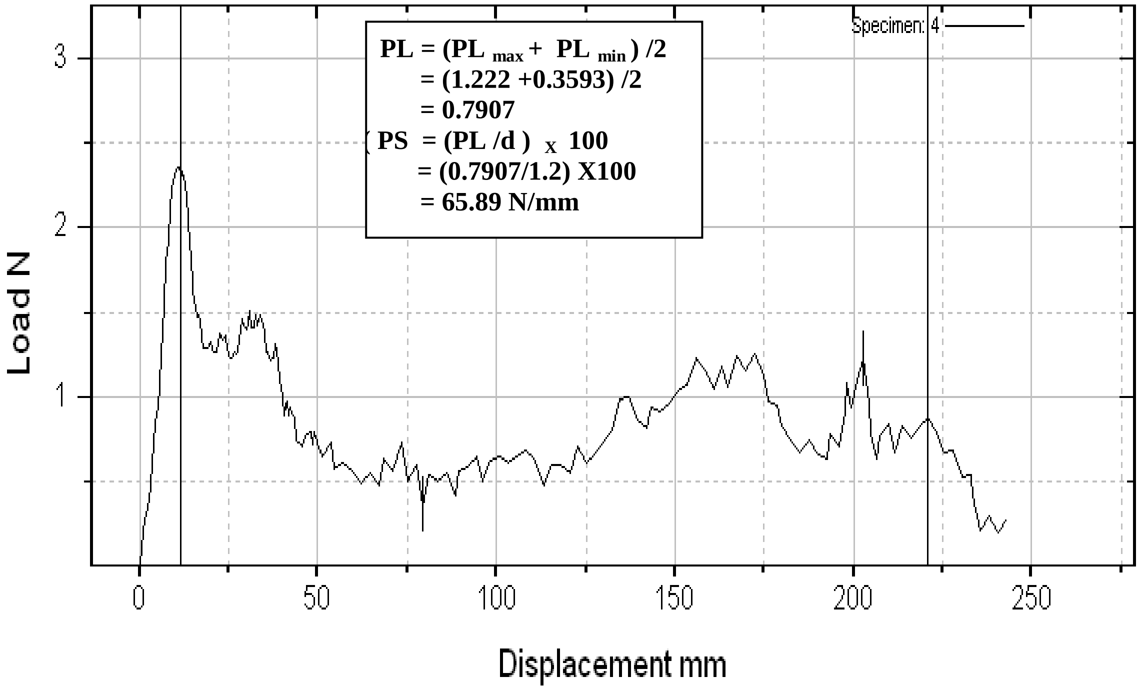


Figure 3.15: A peel test curve of NR/Alk-47 tape

3.5.3 Adhesive properties of the NR/Alk-65 emulsion tapes

Table 3.25 shows that the peel and shear strengths of pure NR are 16.21 N/mm and 8.00 min respectively. The plots of the peel and shear results are shown in Figure 3.16 and 3.17 respectively. In addition, a typical peel test curve and calculation for the peel strength (inset) are shown in Figure 3.18. For all blends, the results revealed that the peel strength increases with the weight percentage of alkyd emulsion, while the shear strength increases when the NR constituent is dominant for all blends. Besides that, the blend at the lowest NR ratio shows insignificant result for the shear strength as the load fell off within a few seconds after the test started. The highest peel strength result for NR/Alk-65 tapes is 15.68 N/mm at 80 weight % of alkyd emulsion. Meanwhile, the highest shear strength result for NR/Alk-65 tapes is 5.40 at 80 weight % of NR ratio. No satisfactory result in the shear test were shown as all blends did not manage to improve the shear strength of NR.

Furthermore, the results for the peel and shear strengths of pure alkyds emulsion were insignificant because the tape was non-sticky to stainless steel panel for peel test and the load was dropped down less than a minute for shear test. Even though no satisfactory results were obtained for all blends and that the values were lower than commercial tapes, the NR/Alk-65 tapes do show the property as adhesives from the result of peel and shear strengths.

Table 3.25: Adhesive properties of the NR/Alk-65 tapes

Blending Ratio (wt %)		**Adhesive properties**	
Alkyd emulsion	**NR Latex**	**Peel Strength (N/mm)**	**Shear Strength (min)**
0	100	16.21	8.00
20	80	3.318	5.40
40	60	9.340	3.18
60	40	12.52	1.50
80	20	15.68	0.00
100	0	0.00	0.00

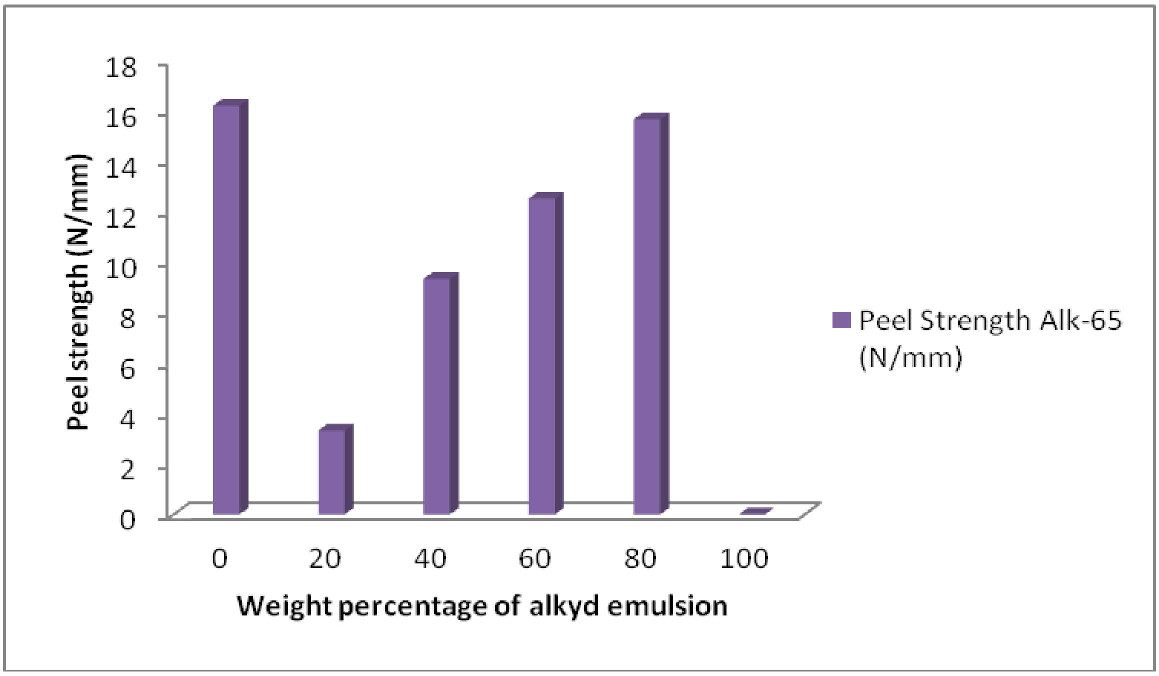


Figure 3.16: Peel strength vs. weight percentage of alkyd emulsion for NR/ Alk-65 blends

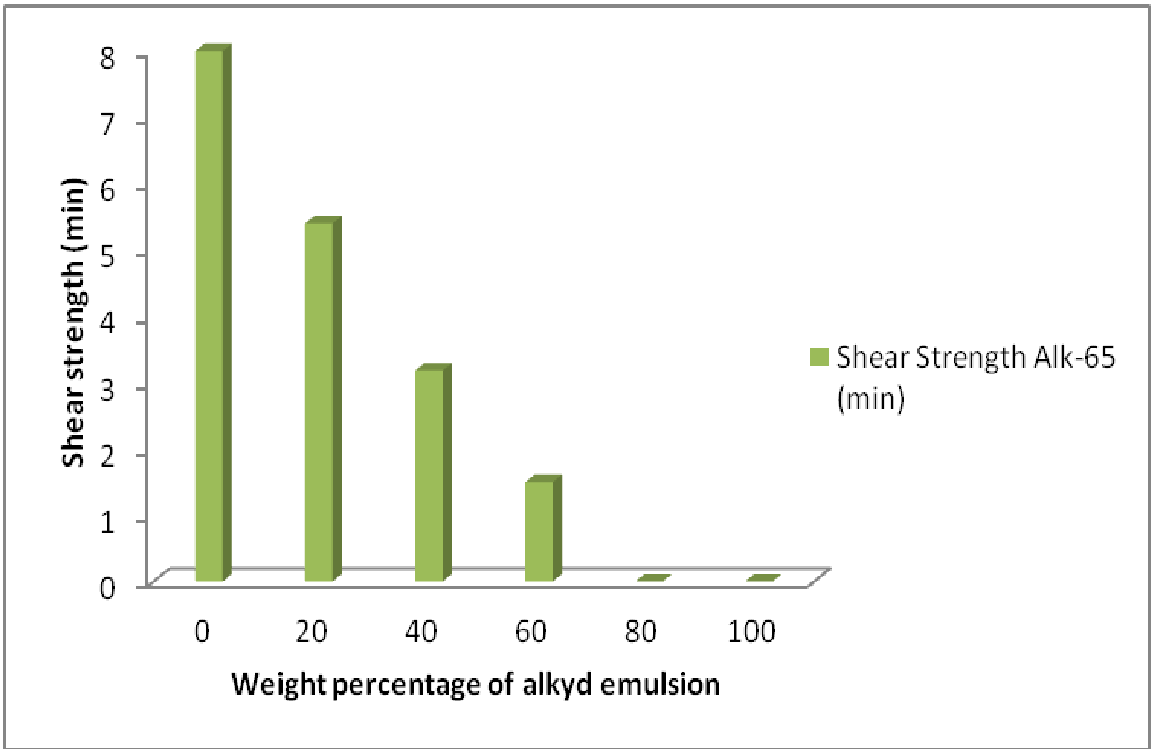


Figure 3.17: Shear strength vs. weight percentage of alkyd emulsion for NR/ Alk-65 blends

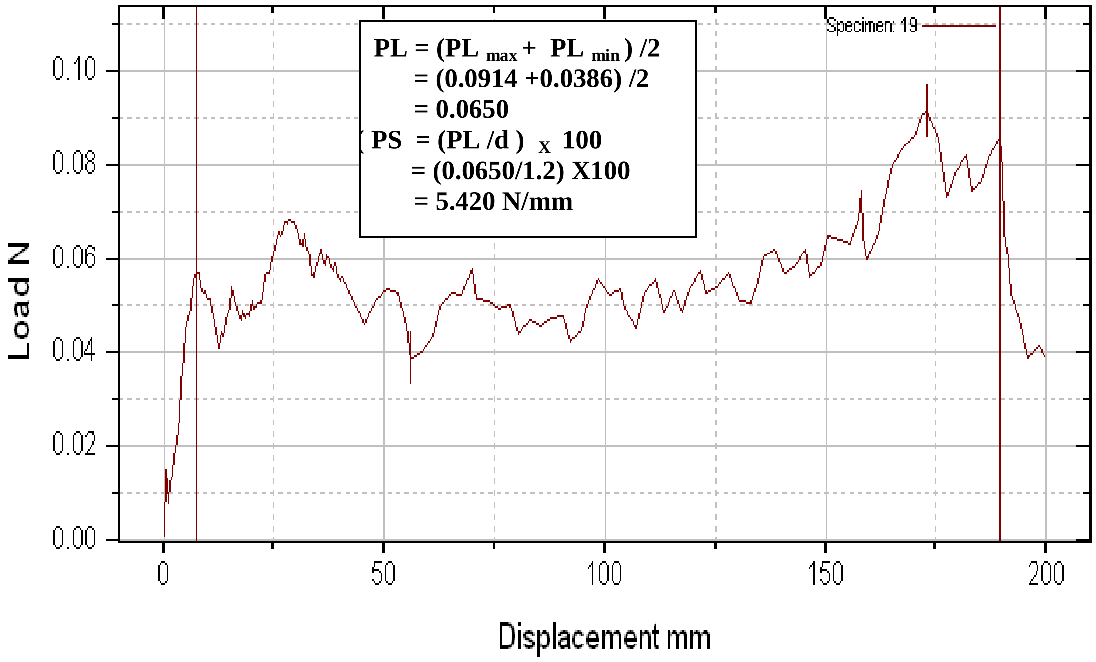


Figure 3.18: A peel test curve for NR/Alk-65 tape

Table 3.26: Adhesive properties of pure resin (without emulsification)

Type of alkyd	Peel Strength (N/mm)	Shear Strength (min)
Alk-45	11.33	3.74
Alk-47	22.95	8.62
Alk-65	5.19	1.50

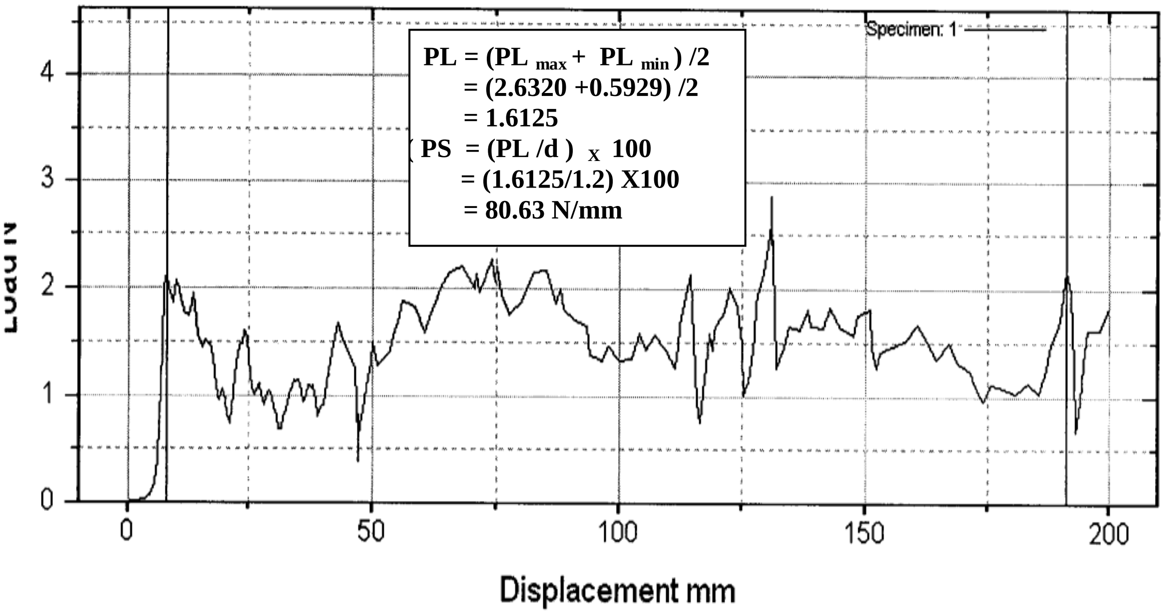
Table 3.27: Adhesive properties of commercial tapes

Type of tapes	Peel Strength (N/mm)	Shear Strength (min)
Toyo	80.63	50.21
ESI	56.29	40.50
Loytape	35.48	68.52
Popular	48.92	18.48

3.5.4 Adhesive properties of pure resin and commercial tapes

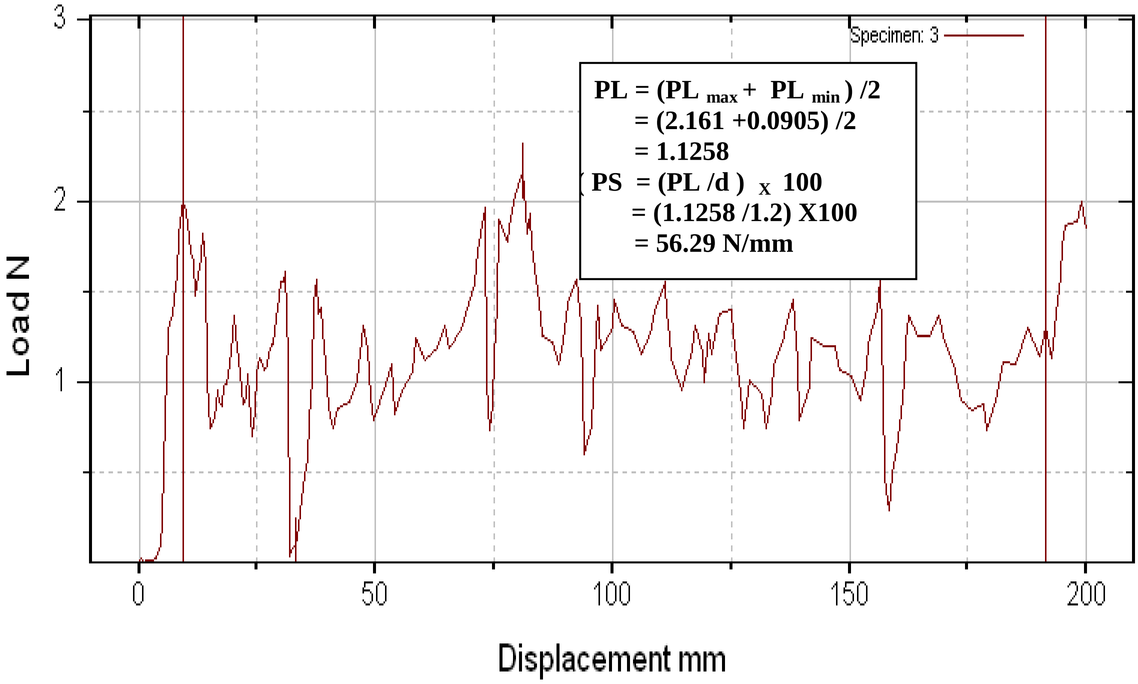
Thin films of pure alkyds were coated on plastic backing, allowed to air dry at room temperature and subsequently the peel and shear strength were measured. Pure alkyd 45, 47 and 65 without emulsification could form sticky film. The results in Table 3.26, show that pure Alk -47 shows stronger peel and shear strengths than Alk-45, Alk-65 and even pure NR (16.21 N/mm). In fact, the blend of Alk-47 with NR shows better adhesive property. The results in Table 3.24 show that Alk-47 blend with NR exhibits significant result for peel strength and also shear strength as compared to other Alkyd / NR blends. The result indicates that the peel strength increases with the increase in blend ratio of alkyds emulsion with NR. Thus, the optimum performance of the tapes is observed when the alkyds emulsion was dominant than NR. Meanwhile, Table 3.27 shows the result of peel and shear strengths for commercial tapes namely ESI, Loytape, Popular and Toyo brands. The peel test curves for commercial tapes namely Toyo and ESI are shown in Figure 3.19 and 3.20 respectively.

Meanwhile the plots of the peel and shear strengths for commercial tapes are shown in Figures 3.21 and 3.22 respectively. These tapes were widely used for several purposes such as packaging, bundling and masking. So, depending on the types of application and brands, the differences in performance can be observed. Thus, different brands of commercial tape might have different value of adhesive properties. In this study, highest peel strength of 80.63 N/mm is shown by Toyo tapes while the lowest is Loytape at 35.48 N/mm. In addition, the shear strength is highest for Loytape at 68.52 min and Popular has the lowest value of 18.48 min (Wool, 2013).



$$PL = (PL_{max} + PL_{min})/2$$
$$= (2.6320 + 0.5929)/2$$
$$= 1.6125$$
$$PS = (PL/d) \times 100$$
$$= (1.6125/1.2) X100$$
$$= 80.63\ N/mm$$

Figure 3.19: Peel test curve for commercial tape, Toyo



$$PL = (PL_{max} + PL_{min})/2$$
$$= (2.161 + 0.0905)/2$$
$$= 1.1258$$
$$PS = (PL/d) \times 100$$
$$= (1.1258/1.2) X100$$
$$= 56.29\ N/mm$$

Figure 3.20: Peel test curve for commercial tape, ESI

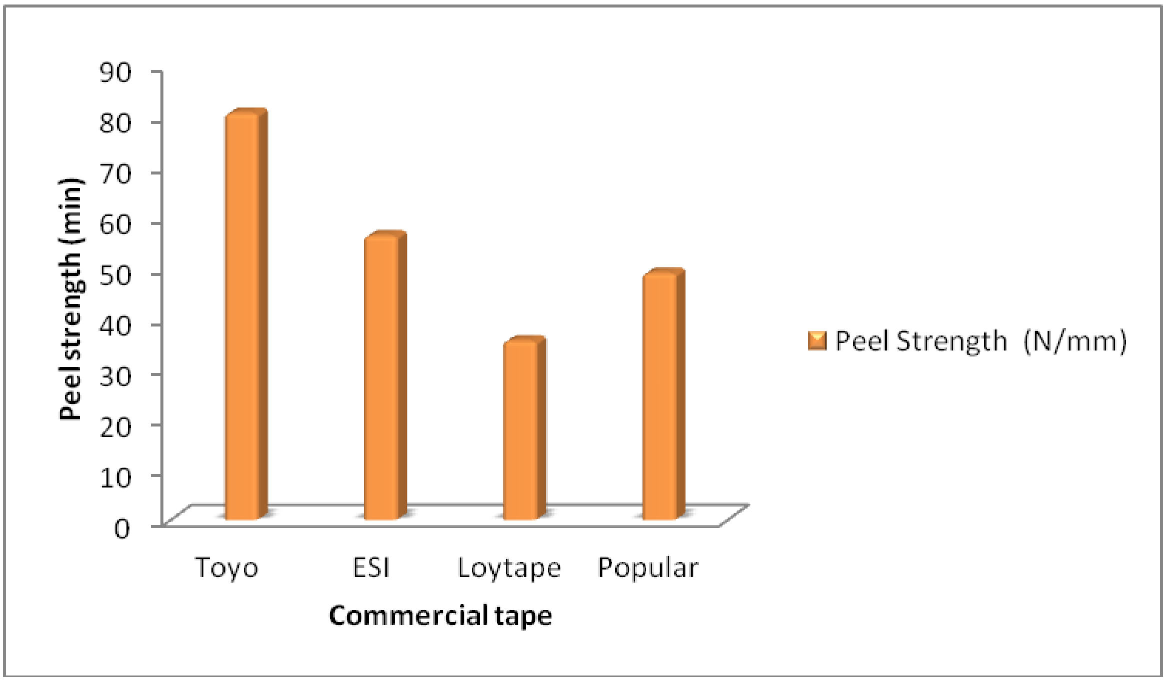


Figure 3.21: Peel strength for the commercial tapes

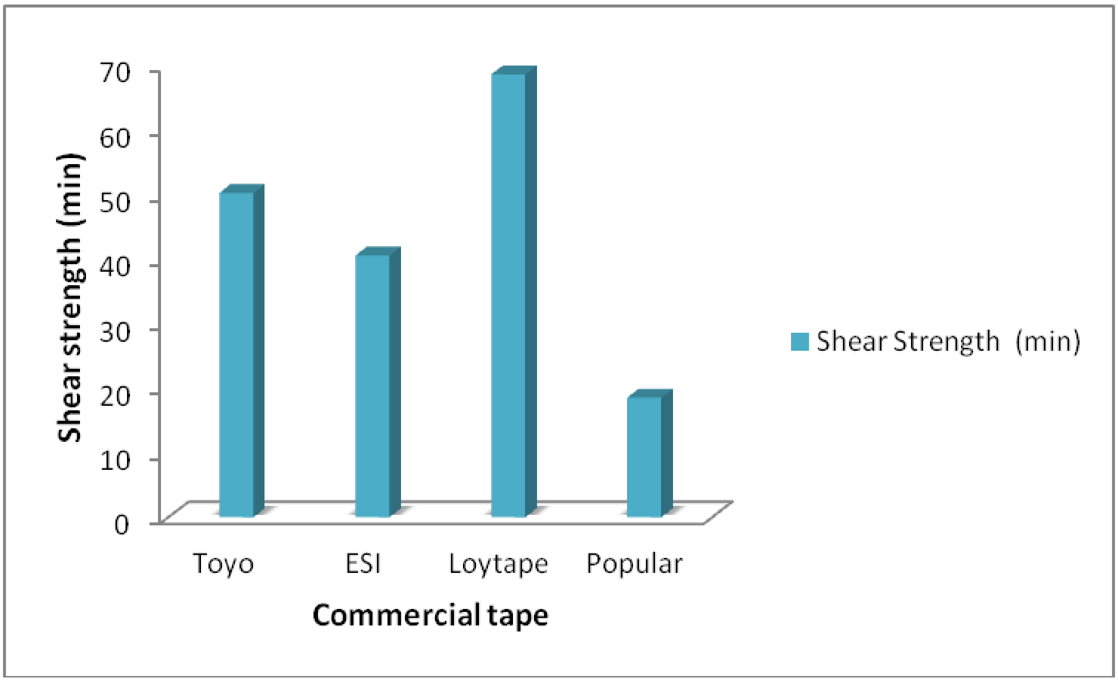


Figure 3.22: Shear strength for the commercial tapes

3.5.5 Adhesive weight per unit area of the adhesive tapes

The initial test was carried out on the commercial tapes to determine the amount of adhesive being applied on a specific area of the coating material which is the polypropylene (PP) film. The result for adhesive weight per unit area of the adhesives tapes and commercial tapes is tabulated in Table 3.28. For this purpose, three different brands of commercial tapes were selected and studied. It was found that the adhesive weight per unit area of the commercial tape was within 1.998 to 2.352 kg/100m^2. This result was used as a reference in order to prepare the PSA tape for the study and the value of the tape under the study was maintained within the range of commercial tapes. The results obtained show that the adhesive weight per unit area of the tapes in this study is within 1.980 to 2.345 kg/100m^2.

Table 3.28: Adhesive weight per unit area of the Alkyd emulsion adhesives tapes and the commercial tapes

Sample	Weight % of alkyd emulsion	D_1(kg/100m^2)
NR	0	2.175
Alk-45	100	1.980
NR/Alk-45	40	2.100
Alk-47	100	2.034
NR/Alk-47	60	2.307
Alk-65	100	1.995
NR/Alk-65	80	2.345
ESI	-	2.047
Loytape	-	1.998
Toyo	-	2.352

3.5.6 Adhesive properties of fusion cook alkyds

Figure 3.23 show that Alk-47 exhibits the highest values of peel strength amongst all the alkyds. Alk-45 has higher T_g than Alk-45 (Table 3.18) and would therefore becomes less sticky at room temperature. At room temperature, pure Alk-45 is observed to be stiff and thus causes an uneven stress distribution over the bonding area. This would result in lower peel strength of Alk-45 as compared to Alk-47. In contrary, Alk-47 was observed to be a viscous liquid at room temperature that enabled the distribution of peeling stress over a wider bonding area uniformly. This would result in higher peel strength due to the ability of Alk-47 to exhibit greater resistance towards the peeling force. Thus, Alk-47 has higher peel strength as compared to other alkyds.

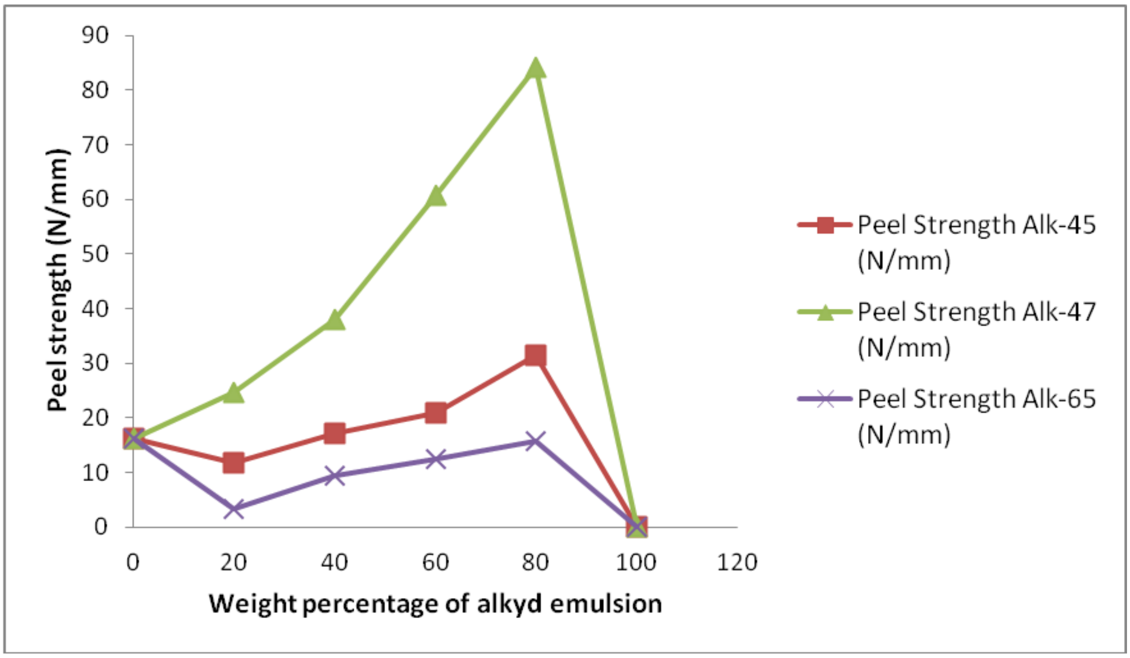


Figure 3.23: Peel strength Vs weight percentage of alkyd emulsion for NR/Alk tapes

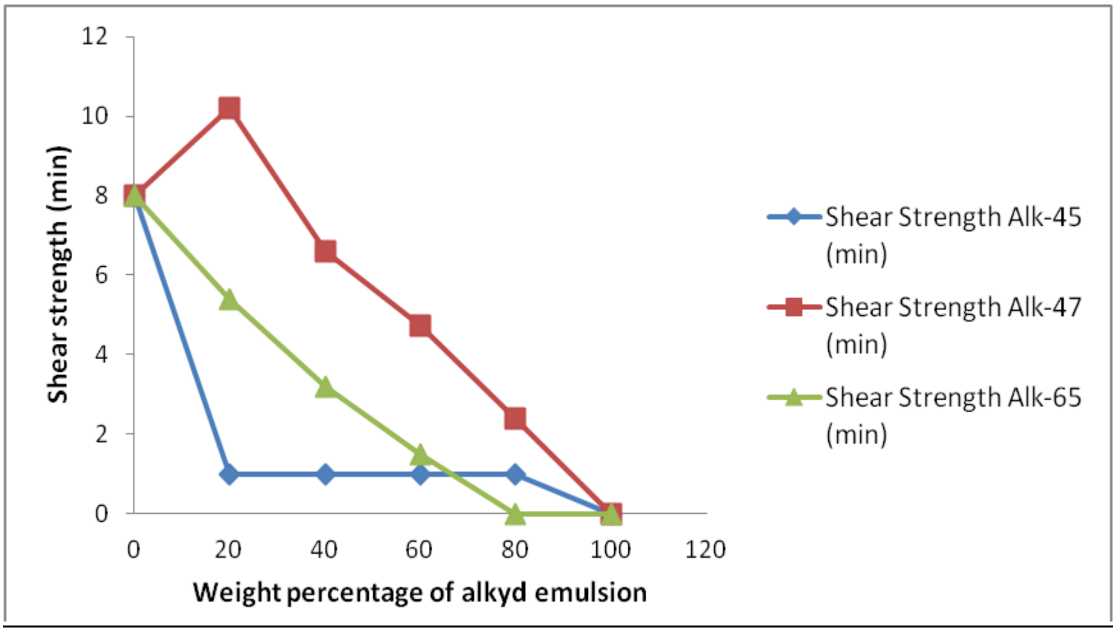


Figure 3.24: Shear strength Vs weight percentage of alkyd emulsion for NR/Alk tapes

Figure 3.24 show the plot of the shear strength for three fusion cook alkyds namely Alk-45, 47 and 65. Overall, Alk-47 shows higher shear value than other alkyds. Alk-47 manages to improve the shear strength of NR, although, the values are lower as compared to the commercial ones. There are a few main factors that have been identified as the main causes that might influence the result. Higher molecular weight and the degree of cross-linking are expected to cause a change in adhesive properties. It was shown that Alk-47 with the higher projected molecular weight (Table 3.11) as compared to Alk-65 improved the shear strength of NR more effectively. Besides that, Alk-65 with higher oil length would have more fatty acid side chains in the structure than other alkyd. This would cause Alk-65 be the most non-polar characteristic as compared to Alk-47 which would be more polar due to its shorter OL and higher hydroxyl number. As a comparison, Alk-47 would become more reactive and interacts with hydroxyl groups resulting in higher shear strength for Alk-47.(Singh et al. 2013).

From the results, it is also found that pure alkyds emulsion does not perform well for the peel and shear test. The emulsion is observed to be non sticky to the test panel for the peel test while the load was dropped down within a few seconds for the shear test. This might be due to the surfactants which could have effects on the adhesive properties. In this study, mixture of SLS and NP40 surfactants was used as the emulsifier in order to emulsify the synthesized alkyds. Even at low concentration, SLS can migrate rapidly to the surface of adhesive. In addition, NP- 40 did not form barrier towards the migration of SLS. As the water evaporated off, the surface rich in surfactant mixture would cause the loss of adhesive properties (Holmberg, 2002).

Besides that, overall pattern of the adhesive properties show that alkyd emulsion of the fusion cook alkyds have improved well in terms of the peel strength as compared to the shear strength of PSA tapes produced. This situation might be explained as due to the heating or thermal effect which would have affected the adhesive properties. Generally, the structures of NR latex have polyisoprene of higher molecular weight. So, it should have higher shear strength but lower peel strength (Sansatsadeekul et al. 2011).

However, the results show that the blends of alkyd emulsion with NR latex did not improve much in terms of shear strength. This could be because after the long heating duration (overnight) at 100-130 ^{0}C, the thermal degradation and chain scissor might have occurred in NR, causing a decrease in the molecular weight. Large amounts of low molecular weight fractions will be formed. Thus, would result in high peel strength and lower shear strength of NR/Alkyd emulsion PSA tape (Steward et al. 2000).

3.5.7 The properties of the water-based pressure sensitive adhesives (PSAs)

A PSA must flow under low pressures to wet a substrate while maintaining a certain degree of strength to provide a bond between two adherents. These properties tend to be at odds with each other, i.e., increasing the ability of an adhesive to flow and wet is accompanied by a reduction in strength. Water-based PSA tapes mean non chemical is involved as the solvent in formulation of the adhesives and water as the main solvent in this formulation. In order to make the PSA tapes, it involves a mixture of both viscous and elastic components which is driven by alkyd and NR latex. It should be stressed that NR has excellent formulability in which it can be depolymerized, detackified, repolymerized by cross linking, tackifier or plasticizers (Elliott and Glass, 2000). Since the alkyd emulsion cannot be made directly by polymerization process, hence we need to emulsify the alkyds through emulsion process.

All synthesized alkyd resins were successfully emulsified through the EIP method. In an aqueous adhesive mixture of alkyds emulsion and NR latex, each one is presented as single particles. Once the water has evaporated, these particles would come close together and mix on molecular basis during heating duration. Processing the adhesive as a water-based colloid provides many advantages, but the amphiphilic additives required to stabilize and coat the latex create a potential problem. These are retained in the adhesive and are likely free to migrate into adjacent phases. They influence the coalescence of latex particles and the interaction between adhesive and adjacent layers, and they provide for the rapid uptake of moisture. When water-based adhesives are dried, particles coalesce and surfactant segregates to interparticle domains that provide pathways for water to enter the adhesive film. Surfactant rich domains, which strongly interact with water, lead to dramatic differences between the wet and dry mechanical properties of adhesive films. (Weissenborn and Motiejauskaite, 2000)

However, the surfactant may protect the adhesive during exposure to lower temperature**.** Generally, high surfactant concentration lower the peel resistance and in many cases, the shear resistance. Besides that, the surfactant of the tackifier dispersion may be incompatible with polymer, although the tackifier is miscible with the polymer. An inherent advantage of the emulsion polymerization method is that crosslinking can be built into the polymer at the time of polymerization (Mahmood et al. 2001). Moreover, the emulsion polymerization does not impose viscosity/molecular weight restrictions, because the polymers are formed as discrete particles suspended in the medium. The high molecular weight achieved during emulsion polymerization provides suitable performance characteristics for a wide variety of PSA applications without necessitating further modification. In addition, the advantages of water-based formulation are evident; lower dry weight costs, easy clean-up, and environmental acceptance because no pollution, require reduced energy for drying, and the cost less than solvent types (Sun et al. 2013).

3.5.8 Palm oleic acid alkyds as tackifier

In this study the use of palm oleic acid in the form of alkyd emulsion would act as the tackifier in order to improve adhesive properties. Normally, NR alone will have very low level of attachment and adhesion to many types of surfaces. Thus, it is necessary to add tackifying resins to NR in order to produce the required balance of peel adhesion and resistance to shear in the application of PSA (Hintze-Brüning 1992). For water based adhesives formulation, tackifier is added to improve the adhesive wetting and coating properties. Hence, tackification is principally made to improve tack and peel resistance. Tackification can be related to the viscoelastic parameter of the polymer (Singh et al. 2012).

Suppose the tack and peel is bonding related and to improve it the adhesive must be softened and its modulus (the elastic component) must be reduced. Therefore, theoretically each additive that softens the adhesive and reduce the modulus, works like a tackifier. In this study, the synthesized alkyd resin (palm oleic acid-base polyester) acts as a tackifier by improving the peel strength of the PSA tapes produced (Sasaki et al. 2008). The chemistry of the structural unit connecting the ester groups allows the alkyd resin to have immense diversity and versatility such as temperature resistant performance materials. Tackification with resins depends on the elastomer or viscoelastomer to be tackified. Hooker and Creton (2002) studied SIS-based PSAs and elucidated the mechanism of how tackifiers improve adhesion. They determined that the highest adhesion values were observed when cohesive failure occurred, as opposed to interfacial failure or cavitation initiating at the interface.

This agrees with the general observation that misleadingly high peel values are usually observed for adhesives that exhibit cohesive failure rather than interfacial failure. The effect of a tackifier is to increase the soluble blend of the elastomer and the resin and to reduce the modulus at room temperature to improve tack and peel. This behavior quite similar to the results were obtained (Table 3.23 to Table 3.25) for the PSA tape produced from NR/Alkyds emulsion blends, where the alkyd resin act as tackifier and improved the adhesive properties. It is showed better performance of peel strength (adhesion value)when the amount of resin is dominant and low value observed for shear strength or cohesive value (Hooker and Creton, 2002).