CHAPTER 2

METHODOLOGY

2.1 Materials

NR Latex was a kind gift from Malaysian Rubber Board (MRB). It was the centrifuged latex, concentrated and stabilized with ammonia containing 60% rubber. The natural rubber latex was used as received without any modification. Glycerol and Oleic acid was a kind gift from Cognis Oleochemicals (M) Sdn Bhd. These materials were used without any purification. Phthalic anhydride (PA) was purchased from P.T. Petrowidada Indonesia. Fumaric acid (FA), sodium lauryl sulphate (SLS), polyoxyetylene nonyl phenyl ether (NP40), potassium hydroxide (KOH), sodium hydroxide (NaOH), potassium hydrogen phthalate (KHP) and phenolphthalein (indicator) were chemicals of analytical grade from Merck. They were used as received. Toluene (R&M chemical grade) was distilled before used. The plastic backing–polypropylene film was a kind gift from Hong Leong Plastics and Packaging Sdn. Bhd.

2.2 Procedure of alkyd synthesis

The set up of fusion cook alkyds consisted of a 1 L round-bottomed flask reactor, equipped with a thermometer, a condenser, a stirrer motor and a heating mantle (Figure 2.1). Oleic acid and glycerol were loaded in the reaction flask and nitrogen was allowed to flow for 5 min. The mixture was heated up to a temperature 180^0C to 200^0C and maintained for 2 h. Water that was discharged at the side arm of condenser was collected. Heating rate was maintained until no water collected and mixture was allowed to cool to 100^0C. A moderate and continuous stirring rate of 130-140 rpm was chosen to ensure a uniform reaction.

Phthalic anhydride was added to the flask and reacted at temperature ranges from 140^0C to 180^0C for 1-2 h and allowed to cool to 100^0C. Fumaric acid was then added and temperature was increased to 180 - 210^0C and maintain for 3- 4 h. Another amount of water was collected and heating was turned off when the acid number had reached the desired value. Acid number was checked by titration with KOH solution against the alkyd sample. Three fusion cook alkyds with different oil length designated as Alk-45 (short oil length), Alk-47 (medium oil length) and Alk-65 (long oil length) were synthesized. The formulations of fusion cook alkyd were shown in Table 2.1 (Patton, 1962). The theoretical calculations for the formulation of alkyds are shown in Chapter 3. Furthermore, the determination of the dry rubber content and solid content of alkyd emulsion were shown in section 2.2.1 and 2.2.2 respectively.

Table 2.1: Formulation of fusion cooks alkyds

	Charge per 100 part yield			
Alkyd	**Oleic Acid**	**Glycerol**	**PA**	**FA**
Alk-45	43.16	33.68	16.84	6.32
Alk-47	44.12	26.47	21.01	8.40
Alk-65	64.00	17.60	13.60	4.80

2.2.1 Determination of dry rubber content

Firstly, the empty beaker was pre- weighed and label as (w0). Then, about 10ml of latex was pipette and dropped into pre-weighed beaker and weighed again and label as (w1). Next, the sample was dried in the oven at T= 60^0C and leave overnight. Later, the temperature was raised up to 100^0C and leave overnight. After that, the dried sample was cooled down in the desiccators and weighed. Finally, the sample was put back in the oven, and repeated drying for a few hours until no change in the weight of sample (wf).

$$\text{Dry rubber content of latex} = \frac{(w1\text{-}wf)}{(w1\text{-},w0)} \times 100\% \qquad [2.1]$$

2.2.2 Determination of dry solid content

Firstly, the empty beaker was pre- weighed and label as (w0). Then, about 10ml of emulsion was pipette and dropped into pre-weighed beaker and weighed again and label as (w1). Next, the sample was dried in the oven at T= 60^0C and leave overnight. Later, the temperature was raised up to 100^0C and leave overnight. After that, the dried sample was cooled down in the desiccators and weighed. Finally, the sample was put back in the oven, and repeated drying for a few hours until no change in the weight of sample (Wf).

$$\text{Dry solid content of emulsion} = \frac{(w1\text{-}wf)}{(w1\text{-}w0)} \times 100\ \% \qquad [2.2]$$

2.2.3 Procedure of determination of acid number

Progress of the alkyds reaction was monitored by periodically checking acid number, a procedure adapted from ASTM D1980-87. In this test, the acid number was determined from the amount of KOH (mg) needed to neutralize the free acids in 1 g sample. The first step was to prepare test reagents and standardize the ethanolic KOH solution for titration of the sample and blank

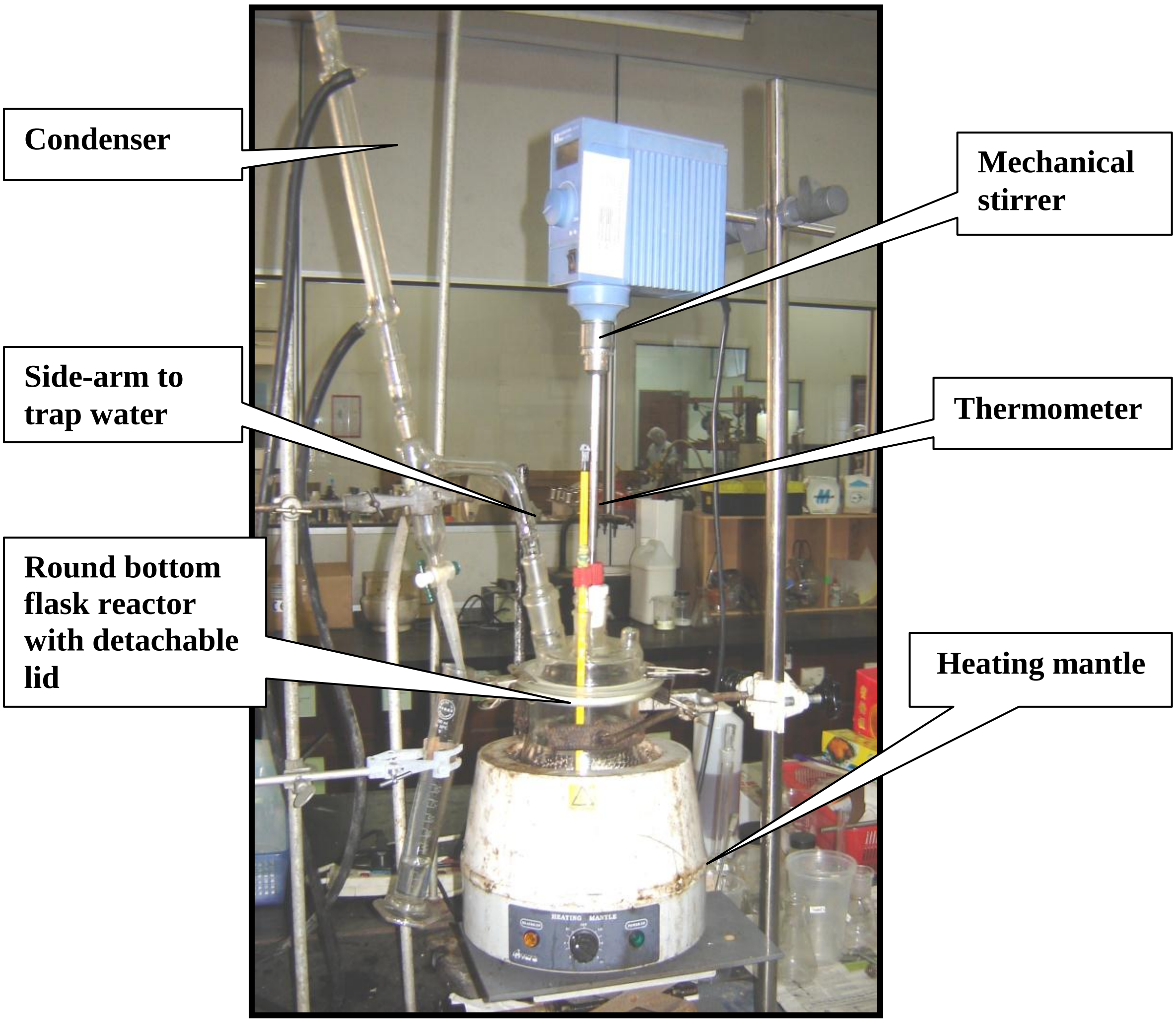


Figure 2.1: Apparatus set up for the synthesis of the alkyd resin

2.2.4 Standardization of Potassium Hydroxide

There are two reagents required for this test, normally KOH solution and phenolphthalein indicator solution. KOH solution is the standard solution with concentration of 0.05 M which was prepared by dissolving 0.7 g of KOH in 250 mL of ethanol. Phenolphthalein indicator solution (1% w/v) was prepared by dissolving 0.1 g of phenolphthalein in 10 mL of ethanol. The KOH solution was standardized by using potassium hydrogen phthalate ($KHC_8H_4O_4$). About 0.5 g of the dried KHP was dissolved in 50 mL of distilled water in a conical flask.

5 drops of phenolphthalein indicator was added into the flask and the mixture was then titrated with 0.05 M of ethanolic KOH solution until the first appearance of a permanent pink colour. The pink colour must persist for at least 10 s. The molarity of KOH solution was determined as follows:

$$\text{Molarity of KOH calculated as follow} = \frac{W_{KHP}}{0.2042 \times V_{KOH}} \qquad [2.3]$$

Where, W_{KHP} is weight of KHP in g and VKOH refers to the volume of KOH used for neutralizing of KHP.

2.2.5 Sample and blank titration

About 2-4 g of the sample was weighed into a conical flask, followed by addition 50 mL of solvent mixture which consists of ethanol and toluene in a ratio of 2:3 respectively. 50 mL of solvent mixture was pipetted into conical flasks with about 0.5 mL of phenolphthalein indicator added to each sample and blank solutions. The solutions were titrated with KOH solution until the first appearance of a permanent pink colour. Sample and blank titrations were carried out in triplicate and the acid number was reported by averaging the results. The acid number was calculated as follows:

$$\text{Acid Number} = \frac{56.1 \times M \times (V - V_{blank})}{W} \qquad [2.4]$$

where, M is the molarity of KOH solution, W is the weight of sample in g, V and V_{blank} refer to the volumes of KOH solution necessary to titrating sample and blank, respectively.

2.2.6 Hydroxyl number

This test was done according to the procedure from ASTM D4274-94, with test method B. Firstly, the sample was esterified with phthalic anhydride (PA) and then neutralized with KOH solution. The hydroxyl number was calculated from the difference in values of titration of the blank and sample. The process involves two stages, where the initial part is to prepare test reagents and standardize the standard KOH solution and the next step is to titrate blank and sample.

2.2.7 Preparation of test reagent

Four reagents are needed for this test namely redistilled pyridine, PA reagent, standard KOH solution and phenolphthalein solution. The reagents are prepared as follows:

a) Pyridine was re-distilled, collected at boiling point around 114-115 ^{0}C and stored in a brown glass bottle.

b) PA reagent was prepared using about 114 g in 700 mL of redistilled pyridine in a brown bottle and shook vigorously by using an orbital shaker until dissolved.

The prepared reagent was left to stand overnight at ambient temperature before use. The product should be colorless and must be discarded if it developed a colour.

c) Phenolphthalein indicator solution (1%w/v) was prepared by dissolving 0.1 g of phenolphthalein in 10 mL of redistilled pyridine.

d) Standard KOH solution with concentration 0.5 M was prepared by dissolving 5 g KOH in 250 mL of distilled water.

The KOH solution was standardized before use. About 10 g of KHP was dried in an oven at 110 ^{0}C for 2 h and cooled down in desiccators. About 4-5 g of the dried KHP was weighed accurately and about 200 mL of distilled water was added into the flask with nitrogen gas bubbled through for 5 min before the addition of 3-4 drops of phenolphthalein indicator. The mixture was titrated with 0.5 M KOH solution until the first appearance of permanent pink colour. Molarity of KOH solution was calculated as follows:

$$\text{Molarity of KOH} = \frac{W_{KHP}}{0.2042 \times V_{KOH}} \qquad [2.5]$$

where, W_{KHP} is the weight of KHP in g and V_{KOH} is the volume of KOH solution used for titration.

2.2.8 Sample and blank titration

Sample used for titration was first dried in an oven at 110^{0}C for 2 h to remove excess water in the sample. The amount of sample needed for the test was calculated as follows:

$$\text{Sample size} = \frac{561}{\text{Estimated hydroxyl number}} \qquad [2.6]$$

The calculated sample size was dissolved in 25 mL of PA reagent into a stoppered conical flask. A blank solution also prepared by transferring 25 mL of PA reagent into conical flask and stoppered. Both the sample and the blank were clamped in a water bath and heated to 98-100^{0}C for 2 h. Thereafter, the flasks were removed from water bath and cooled down to room temperature. About 50 mL of redistilled pyridine and 0.5 mL of phenolphthalein indicator were added to both the sample and the blank solutions.

The solutions were titrated against standardized KOH solution until the first appearance of a permanent pink color solution was observed. To achieve the result close to the estimated hydroxyl number, two requirements must be fulfill. First, in the blank titration, 25 mL of PA reagent should consume an amount of 0.5 M of the standard KOH solution in range of 95-100 mL volume. Second, the net titration of the blank minus sample should be between 18-22 mL. If both criteria are not fulfilled, the titration processes have to be repeated by adjusting the sample size. Sample and blank titrations were carried out in triplicates and the hydroxyl number was recorded by averaging the results. The hydroxyl number of the sample was calculated as follows:

$$\text{Hydroxyl number} = \frac{56.1 \times M \times (V_b - V)}{W} \quad [2.7]$$

where, M refers to the molarity of the KOH solution, W is the amount of sample (sample size) and V and V_b refer to the volumes of KOH solution needed to titrate sample and blank respectively.

2.3 Determination of moisture content

Karl Fischer titrator was used to quantify water content in polyesters. The presence of moisture in the bulk materials can alter the properties by reducing its glass transition temperature, inducing cracks or also by chemically reacting with the polymer, a process called hydrolysis. The principle of the determination is based on the Bunsen reaction between iodine and sulphur dioxide in methanol. In the reaction, water and iodine are consumed in a 1:1 ratio. Indictor electrode would detect voltametrically in the presence of excess iodine, once all the water present is consumed.

The amount of water present in the alkyds sample is calculated based on the concentration of iodine in the Karl Fischer titrating reagent and the amount of Karl Fischer reagent consumed in the titration process. First step is the calibration process of Karl Fischer reagent. After that, about 0.05 mg of sample was weighed and injected into the titration vessel. The water content of polyesters shown on Karl Fischer titrator (701 KF Titrino, Metrohm) was then recorded.

2.4 Alkyd resin characterization

The prepared fusion cook alkyds resin was characterized as described in the following parts.

2.4.1 Fourier transforms infrared (FTIR)

Infrared spectroscopy is an important analytical analysis where molecular vibrations are analyzed. Infrared radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample.

Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. FTIR analysis can provide few information such as it can identify unknown materials; determine the quality or consistency of a sample and the amount of components in a mixture. A thin layer of fusion cook alkyds (Alk 45, Alk 47 and Alk 65) were coated on the sodium chloride cell. The spectrum of sodium chloride was taken as reference using Perkin Elmer FTIR RX-1 spectrometer at room temperature, with wave number from 4000-600 cm^{-1} and a resolution of 4 cm^{-1}. Background effects due to atmospheric water, carbon dioxide and other volatiles were subtracted and tungsten-halogen as a source.

2.4.2 Nuclear magnetic resonance (NMR)

NMR spectroscopy is a research technique that exploits the magnetic properties of certain atomic nuclei to determine physical and chemical properties of atoms or the molecules in which they are contained. NMR is a powerful tool for non selective analytical which allows molecular structure characterization including relative configuration, absolute concentrations and even intermolecular interactions.

It relies on the phenomenon of nuclear magnetic resonance and can provide detailed information about the structure, dynamics, reaction state, and chemical environment of molecules. The impact of NMR spectroscopy on science has been substantial because of the range of information and the diversity of samples, including solutions and solids. About 10 mg mL^{-1} of sample was dissolved in deuterated chloroform, $CDCl_{3.}$ The ^1H NMR spectra for alkyds were recorded in a JOEL JNM-LA 400FT-NMR spectrometer, operating at 400 MHz. The chemical shifts were referenced against tetramethylsilane (TMS) as 0 ppm, which was used as an internal standard. The peak shown at 7.26 ppm is for the solvent.

2.4.3 Differential scanning calorimetry (DSC)

DSC is a technique used to investigate thermal transition or the changes that occurs in a polymer when they are heated. DSC measures the temperatures and heat flow associated with transitions in material, as a function of time and temperature. The basic principle underlying this technique is that when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature depending on whether the process is exothermic or endothermic. Heat of transition, heat capacities, and temperature dependent crystallinities can be established by DSC.

Rheometric Scientific Perkin Elmer Diamond DSC with hyper DSC was used to measure the glass transition temperature (T_g) of the alkyds. Hyper DSC means the ability to perform valid heat flow measurements while heating or cooling sample with fast linear controlled rates. Approximately 1-2 mg of the sample was weighed and placed into a sample pan kit along with a blank pan as a reference. Hyper DSC measurement was conducted over temperature range from -50 ^{0}C to 100 ^{0}C at the heating rate of 10 ^{0}C/ min.

2.4.4 Thermogravimetric analysis (TGA)

TGA is a type of testing performed on samples that determines changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can identify the point where weight loss is most apparent. The interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required.

TGA is commonly employed to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points, and solvent residues. In this work, TGA was performed using Rheometric Scientific thermal analyzer 1000 series to study thermal decomposition behaviors of the alkyds. Approximately 5-10 mg of the sample was weighed and placed into the sample crucible which was located in the furnace of thermal analyzer. Test was conducted over the temperature ranging from 40 ^{0}C to 950 ^{0}C at a heating rate of 20 ^{0}C under nitrogen gas atmosphere.

2.4.5 Gel permeation chromatography (GPC)

GPC is a type of size exclusion chromatography (SEC), that separates analytes based on the size or hydrodynamic volume (radius of gyration) of the analytes. The smaller analytes can enter the pores more easily and therefore spend more time in these pores, increasing their retention time. Conversely, larger analytes spend little if any time in the pores and are eluted quickly. This technique is often used for the characterization of polymers. When characterizing polymers, it is important to consider the polydispersity index (PDI) as well the molecular weight. GPC allows for the determination of PDI as well as M_v and based on other data, the M_n, M_w, and M_z can be determined. GPC was performed on WATERS equipment with refractive index detector, Waters TM 717 plus auto sampler and Waters TM 600 Controller. Tetrahydrofuran (THF) was used as the mobile phase. About 2% (w/v) of sample solution was injected into the column at 40 ^{0}C. The flow rate was set at 1 cm^3 min^{-1}. Polystyrene standards of various molecular weights were used to calibrate the column.

2.5 Preparation of alkyd emulsions

Emulsions, a subset of the subject of colloids, refer to a dispersion of particles or droplets through a liquid. Emulsions are quite different from hard particle dispersions. Most oils are less dense in water, and if oil and water are mixed then the oil will simply float to the surface. In emulsions, the oil is dispersed as liquid droplets through the continuous phase, but not necessarily water. This means that an emulsion is thermodynamically unstable, and those droplets want to combine together again. To prevent them from doing this, emulsions contain a surfactant which coats the surface of each drop and prevents the droplets from coalescing. In this study, alkyds emulsions were prepared from the fusion cook alkyds.

Emulsion Inversion Point (EIP) method with some modification was employed to prepare alkyd emulsion. 4% concentration of surfactant mixture solution was prepared as shown in Table 2.2

Table 2.2: Formulation of surfactant mixture solutions

No	**Mixing Ratio (wt %)**	
	SLS	**NP40**
S-2080	20	80
S-5050	50	50
S-8020	80	20

About 40 g of fusion cook alkyds were weighed and then heated on a hotplate at 60 ^{0}C -70 ^{0}C. After that, 7.5 ml of the surfactant mixture solution were added to the alkyd under continuous stirring. KOH solution (5 M) was added to adjust the pH in the range of 6-8. Distilled water was added slowly to the resin and stirred by glass rod to disperse the resin. The viscosity of W/O (water-in-oil) emulsion would increase as more water was added and reached the maximum at the inversion point. Once, more water was added, the unstable W/O emulsion would invert into O/W (oil-in-water) emulsion. The emulsion was finally homogenized at high speed with a homogenizer for 10-15 min. A stable alkyd emulsion was formed when no separation occurred and a creamy white in appearance was observed as the end product.

2.5.1 Rheology test

Two important properties of emulsions are their stability against creaming, and their flow properties, in other words their rheology. Stability against creaming relates to shelf life of the commercial products. The rheology is really important in the way a product is used. The rheological test was conducted to characterize the rheological properties of the alkyd emulsions using Brookfield R/S Rheometer 3000(RHEO 3000). RHEO 3000 was equipped with electronic unit and measuring drive integrated in one set, stand with working surface and AC adapter with the accessories such as coaxial cylinder measuring system and temperature measuring sensor.

The rheometer was a controlled stress (or controlled torque) instrument rather than a controlled rate (RPM) instrument. Controlled stress with R/S provides many benefits such as a very broad viscosity measurement range and the ability to measure flow properties of delicate high viscosity gels or liquids. About 3 ml of the sample was pipetted into the coaxial cylinder measuring system CC14. The measured sample was positioned in measuring gap between the stationary measuring cup and the rotating measuring bob (Searle – principle), between the rotating cone/plate and the stationary lower plate. The test was carried out at 30 °C. The properties of alkyd emulsion were measured.

2.6 Preparation of blends (NR latex and alkyd emulsions)

Fusion cook alkyds namely Alk-45, Alk-47and Alk-65, were blended with NR latex in the form of alkyd emulsions. Five different blends ratios were prepared by blending NR with each alkyd emulsions as shown in the Table 2.3. These blends were then homogenized with homogenizer for 10-15 min before coating them on the backing of polypropylene plastic to produce the adhesive tapes.

Table 2.3: Blend ratios of NR Latex and alkyd emulsion

No	**Mixing Ratio (wt %)**	
	Alkyd Emulsion	**NR Latex**
B-0-100	0	100
B-2080	20	80
B-4060	40	60
B-6040	60	40
B-8020	80	20
B-100-0	100	0

2.7 Preparation of pressure sensitive adhesive (PSA)

2.7.1 PSA plastic tapes

The blends were stirred homogenously before coating on the backing material to produce the adhesive tapes. PSA plastic tapes were prepared by coating the blends (NR latex and alkyd emulsions) onto a corona – treated polypropylene film of 12.2 ± 1.2 µm thickness. The blends were coated onto corona treated plastic film with wet adhesives thickness of 12.5 µm using the cheminstrument laboratory drawdown coater. After the coating process, the films were left to air dry for 2 h. This was followed by drying in an oven overnight at 100 ^{0}C before being tested for the peel and shear strength. The adhesive weight per unit area of the tape was eventually examined. Figure 2.2 showed a schematic process for making PSAs.

2.8 Adhesive test

Adhesive test for this study consisted of peel and shear tests which were done at room temperature. The adhesive properties of the commercial tapes were also characterized and the results were compared with the PSA tapes obtained in this study.

2.8.1 Peel test

Test was done in accordance to ASTM- D 3330-99, test method A, using the Instron Universal Testing Machine Model 2519-103. The peel test measures the force required to affect the peeling of the PSA tape. This was done with a constant load applied to the tape at an angle of 180^o. First a tape with 150.0 ± 0.5 mm length and 12.0± 0.5 mm width was prepared. Approximately 75.0 ± 0.5 mm portion of the tape was adhered onto a stainless steel panel. The size of panel was 50 mm by 125 mm and 2 mm thick. Peel test must be carried out within a minute after applying the tape onto the panel to avoid the increased of peel adhesion with dwell times. The test panel was clamped to the lower jaw, while the free end of the tape was doubled back and attached to the upper jaw of the machine. The tape was then peeled from the panel at angle of 180^o with the speed rate of 300 mm/min and 100 N load cells. The test was repeated five times for each sample, and average value was taken. Figure 2.3 showed the peel test set up using Instron Universal Testing Machine.

A typical measurement of peel strength was calculated according to following equations:

$$PL = \frac{PL_{max} + PL_{min}}{2} \qquad [2.8]$$

$$PS = \frac{PL}{d} \times 100 \qquad [2.9]$$

where, PL is the peeling load in (N) **,** PL $_{max}$ is the Maximum peeling load in (N)**,** PL $_{min}$ refer to Minimum peeling load in (N), PS refer to Peel strength in (N/mm) and d is the Width of the tape in (mm)**.**

2.8.2 Shear Test

Test was carried out in accordance to ASTM D 3654-90, procedure C. This test measures the duration of the PSA tape still remain adhered to the panel under constant load, which is applied in parallel with the surface of the tape. The test panel and the surface preparation method of the panels are similar as the peel test. The set-up of the shear test, comprise test panel, mass load and a stop clock. A tape with 150.0 ± 0.5 mm length and 12.0± 0.5 mm width was first prepared.

Approximately, 75.0 ± 0.5 mm portion of the tape was adhered to cover exactly the test panel with one end portion of the tape being free. The free end of the tape was gently clamped to a mass with standard load of 1 kg. The time elapsed for each tape to separate completely from test panel was recorded as shear strength. Each sample was repeated five times and average value was taken. The calculation of shear strength is shown as in Equation 2.10. Meanwhile, Figure 2.4 showed the apparatus set up for shear test.

$$SS = \text{antilog}_{10} \text{ of mean of } \log_{10} t \qquad [2.10]$$

Where, SS refer to Shear strength in (min), and T is the Time to failure in (min).

2.8.3 Determination of adhesive weight per unit area of tape

This test determines the quantity of the adhesive solids on a specific area of backing material in a solvent free condition. The test was done according to the ASTM D 898-99. Two commercial tapes namely Popular and Toyo were selected to investigate the adhesive weight per unit area of the tapes.

The same conditions and procedures were later conducted for the tape in this study. Firstly, a tape with the length approximately 300 mm was cut and weighed. It was then soaked in toluene and shaken overnight with an orbital shaker in order to separate adhesive from backing tape.

After that, the tape was removed from the solution and rinsed with ethanol. The tape was then rubbed with a scouring pad a few times to remove the adhesive completely from the backing material and dried in the oven to a constant weight. The adhesive weight per unit area of tape was then calculated. The test was repeated three times and average value was recorded. Figure 2.5 showed the tape underwent adhesive weight per unit area test.

The theoretical calculation is shown below.

$$D_1 = \frac{(W_2 - W_1) \times 10^{-3}\ \text{kg})}{(A \times 6.4516 \times 10^{-4}\ \text{m}^2)} \times 100 \qquad [2.11]$$

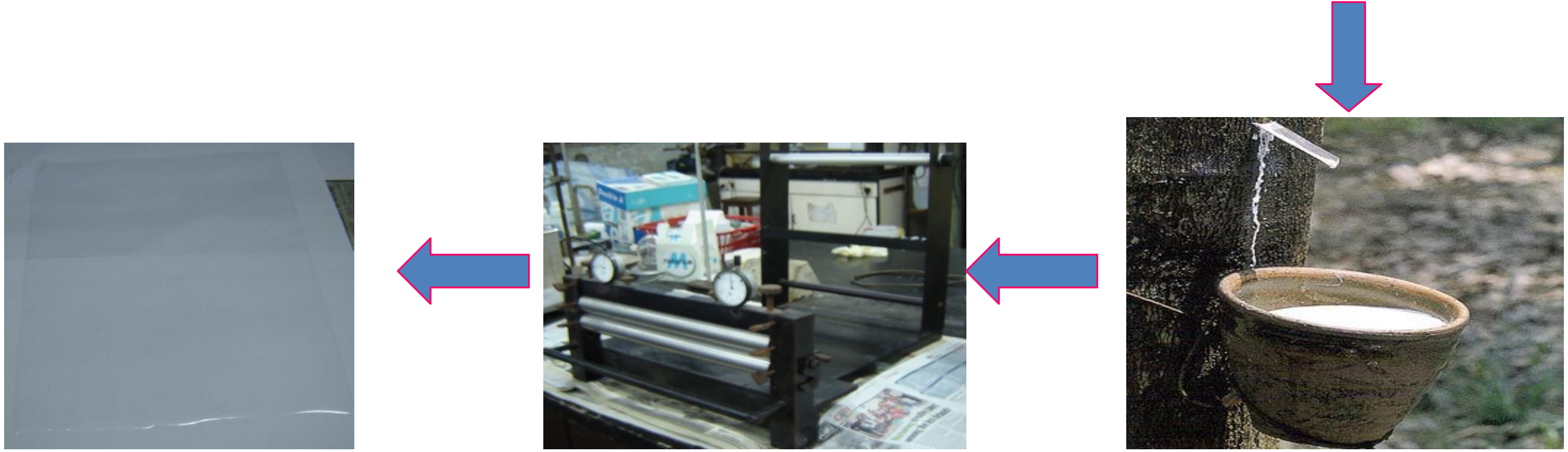
where D_1 is the weight of adhesive solids in kg /100 m^2, W_2 is the initial weight of tape in grams, W_1 refers to final weight of the tape after removal of adhesive in grams, A refers to the area of the tape in square inches, which equal to l x d (length and width of tape, in inches).

Figure 2.2: Instrument set up for peel strength test

Figure 2.3: Apparatus set up for shear strength test

Figure 2.4: Tape underwent adhesive weight per unit area test.

Synthesis of the alkyd resin **Alk-45, Alk-47, Alk-65** **Preparation of the alkyd emulsion**



Evaluation of the tape property **Preparation of the tape** **Blend with NR latex**

Figure 2.5: A schematic process for making PSAs