CHAPTER III

EXPERIMENTAL METHODS

3.1 Materials and Chemicals

3.1.1 Cashew Nut Shell Liquid : no. 4

(CNSL (Thailand) Co.,Ltd.)

Viscosity, 25°C (cps)	600
Specific Gravity , 30/30°C	0.94-0.98
Moisture (w/w, %)	1
Iodine Value (Wijs ,%)	220

3.1.2 Compounded Natural Rubber (Union Commercial Development Co., Ltd.)

Cured time, 153°C (min)	10
Mooney Viscosity (ML1' + 4' 100°C)	36.00
Specific Gravity, 25°C	1.13
Hardness (Shore A)	57
Tensile Strength (kg/cm^2)	97.00
Elongation (%)	360.00
Modulus at 300% (kg/cm^2)	70.00
Tear Strength (kg/cm)	36.40

3.1.3 Nylon-6 Chafer Fabric (Formosa Taffeta Co., Ltd.)

	Warp	Weft
Fabric Density (End/cm)	11.1	9.0
Tensile Strength (kg/cm)	146	102
Elongation at Break (%)	27.3	47.4
Heat Shrinkage at 150 CX 1/2 hr (%)	5.4	
Gauge (mm)	0.805	
Unit Weight (g/M^2)	441.3	
Adhesion Force (kg/in)	34.2	
After Aging 100°C for 4 days (kg/cm)	145	100
After Immersion in Water at 70°C for 4 days (kg/cm)	134	92

3.1.4 Plywood

Thickness 0.3 cm

Moisture 10 %

3.1.5 Others

n-Butyraldehyde (AR grade)

37% w/w Formalin (commercial grade)

Hexamethylenetetramine (commercial grade)

Linseed oil

Oxalic acid dihydrated (AR grade)

Resorcinol (AR grade)

Sodium hydroxide (commercial grade)

Stannous octoate (Union Carbide)

Toluene (commercial grade)

3.2 Equipments

1-L Reaction kettle with four-socket/flat flange lids

Heating mantle (1000 ml, Electrothermal)

Power regulator (Electrothermal)

Thermometer (-10 to 360°C)

150-ml Addition funnel

Mechanical stirrer

Condenser

Dean stark

3.3 Instruments

Hot-press machine

Brookfiled digital viscometer (model DV-1)

Scanning electron microscope (JEOL JSM-T220A)

Tensile testing machine (Lloyd 500, Lloyd Instruments PLC.)

3.4 Preparation of Adhesive

3.4.1 Resol Adhesive from CNSL

There were two procedures to prepare adhesive from CNSL. In one procedure, the adhesive was dehydrated and the other was not dehydrated in order to compare their shear strength.

3.4.1.1 Non-Dehydrated Adhesive

CNSL 200 g and 37% formalin 40 g were mixed together in the reaction kettle, which was equipped with a dean stark and refluxing condenser, a thermometer and a mechanical stirrer (Figure 3.1). The sodium hydroxide solution

(2 g NaOH in 10 ml of water, mole NaOH/mole anacardic = 0.1) was then added. The mixture had been stirred at ambient temperature for 10 minutes with agitation rate of 850 rpm before it was heat up to refluxing temperature at 97-99^{O}C for several minutes, as shown in Table 3.1 (total time of heat-up was 20 minutes). Then, toluene 100 ml was poured into the kettle before it was cooled by cold water. The product was red-brown viscous liquid.

The quantities of formalin was varied from 40 to 70 g and refluxing time was varied from 10 to 40 minutes, as illustrated in Table 3.1.

The solid content, viscosity, dry-to-touch time and shear strength, bonding of wood to wood, were determined. In addition, adhesive batch no.35/10 was used as an adhesive for bonding of nylon-6 fabric to natural rubber compound and the peel strength was evaluated.

3.4.1.2 Dehydrated Adhesive

The preparation of adhesive was carried out by the same manner as mentioned in section 3.4.1.1 but after refluxing, toluene 250 ml was poured into the kettle. The adhesive was dehydrated by azeotropic distillation. The water was collected by the dean stark. After the water had been removed, the product was a black viscous liquid.

The quantities of formalin and refluxing time were shown in Table 3.1 (batch no. D20/40 and D35/10).

The adhesive was checked for solid content, viscosity, and dry-to-touch time. The D20/40 and D35/10

were applied to bond wood to wood by dry-laminating and cold pressing and dry-laminating and hot pressing, respectively.

Table 3.1 Quantities of formalin and refluxing time

Undehydrating (batch)	Formalin (%)	CH_2O/Anacardic mole/mole	Refluxing Time (min)	Dehydrating (batch)
20/10	20	1.04	10	–
20/20	20	1.04	20	–
20/30	20	1.04	30	–
20/40	20	1.04	40	D20/40
25/10	25	1.30	10	–
25/20	25	1.30	20	–
25/30	25	1.30	30	–
25/40	25	1.30	40	–
30/10	30	1.56	10	-
30/20	30	1.56	20	-
30/30	30	1.56	30	-
30/40	30	1.56	40	-
35/10	35	1.81	10	D35/10
35/20	35	1.81	20	-
35/30	35	1.81	30	-
35/40	35	1.81	40	-

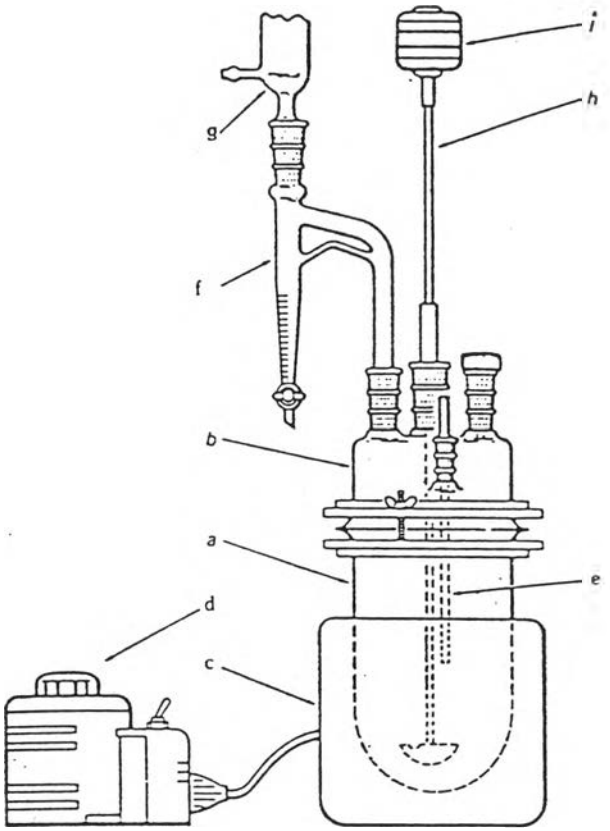


Figure 3.1 Polyesterification apparatus for resol adhesive from CNSL (a) reaction kettle, (b) 4-socket/flat flange lids (c) heating mantle, (d) power regulator, (e) thermometer, (f) dean stark, (g) condenser, (h) stainless steel stirrer and (i) air motor

3.4.2 Resorcinol-Formaldehyde Adhesive for Bonding Nylon-6 Fabric to Compounded Natural Rubber

Resorcinol (113.6 g, 1.03 mole) and n-butyraldehyde (14.1 g, 0.20 mole) (0.19 mole butyraldehyde per mole resorcinol) were added to the reaction kettle. The apparatus was setted as shown in Figure 3.2. The charge was heated to 80°C, when the reactants were liquefied, agitation was begun.

The kettle contents were refluxed at 107°C (total time of heating was up to 30 minutes) and the solution of oxalic acid dihydrated (0.7 g) in 4.2 g of water was added during eight minutes. The resulting exothermic reaction increased the refluxing temperature to 140°C. After 23 minutes of reaction time, the refluxing temperature had fallen to 125°C. Then formalin (32.6 g of 37%) (0.39 mole formaldehyde per mole resorcinol) was added slowly over a period of 45 minutes. During this addition, the refluxing temperature of the reaction decreased to 103°C and the mixture was refluxed for one hour.

The resin was cooled and the pH of the solution was adjusted to 7.1 by 50% aqueos solution of NaOH.

Solid content, viscosity, dry-to-touch time and peel strength, for bonding nylon-6 fabric and natural rubber compound, were evaluated.

The resulting resorcinol-formaldehyde adhesive was novolak type, therefore, hexamethylenetetramine was employed as the source of formaldehyde in curing step. It had been mixed with the resin before using it to bond nylon-6 fabric to compounded natural rubber . Its concentration was varies from 0 to 15 % by weight base on weight of adhesive.

3.5 Effect of Linseed Oil on Properties of The Adhesive Batch No.20/40

Linseed oil was added from 5 to 15% by weight to adhesive. The physical properties such as solid content,

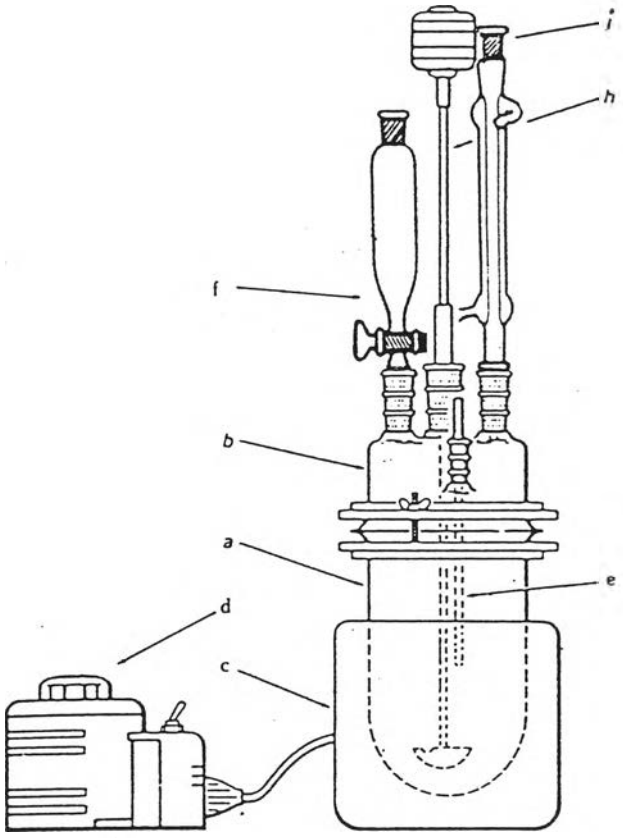


Figure 3.2 Polyesterification apparatus for resorcinol-formaldehyde adhesive (a) reaction kettle, (b) four-socket/flat flange lids, (c) heating mantle, (d) power regulator, (e) thermometer, (f) addition funnel, (g) condenser, (h) stainless steel stirrer and (i) air motor

viscosity, dry-to-touch time and shear strength were determined. The test specimens for shear strength test were prepared by dry-laminating and cold pressing with pressing time was 10 minutes.

3.6 Effect of Stannous Octoate on Properties of The Adhesive

3.6.1 Adhesive, Batch No.20/40

Stannous octoate was employed at different concentrations, 0.1, 0.2, 0.3, 0.4 and 0.5 percent by weight to weight of adhesive batch no. 20/40. Then, solid content, dry-to-touch time and shear strength were checked. For shear strength test, the test specimens assembly was dry-laminating and cold pressing with 10 minutes pressing time.

3.6.2 Adhesive, Batch No.35/10

Stannous octoate was employed at different concentrations, viz., 0.1, 02, 0.3,..., 1.0 per cent by weight respectively, to the weight of adhesive batch no.35/10. The physical properties, dry-to-touch time and peel strength were determined.

3.7 Test for Some Physical Properties of An Adhesive

3.7.1 Solid Content (Percent Nonvolatile, ASTM D4426-84)

About 0.5 g of an adhesive was put in the heat-treated aluminum foil dish and it was quickly weighed to minimize loss by evaporation. The dish was placed in an electric oven at 125±1°C for exactly 1:45 hr, then removed from the oven, cooled in a desiccator and reweighed as rapidly as posible.

The heat-treated dish was prepared by heating an aluminum foid dish in a furnace at 270°C for 15 s to flash off thin coating of oil, then put it in a desiccator to cool for at least 5 min before weighing.

$$\text{Solid Content} = (A/B) \times 100 \qquad (3.1)$$

A = net weight of dried residue (g)

B = net weight of adhesive before dried (g)

3.7.2 Viscosity At 25°C (ASTM D2556-69)

A 200 ml well-stirred adhesive was transferred to a 250 ml beaker and kept at 25°C for at least 1 hr. The viscosity was determined on a Brookfield Synchro-Lectice Viscometer.

3.7.3 Dry-To-Touch Time (ASTM D1640-83)

An adhesive was applied on a plywood with an area of 2.5x2.5 cm^2. The amount of the adhesive was 0.02 g (solid)/cm^2 (not involved volatile matter) as shown in Figure 3.3 (a).

The film was considered dry when it no longer adhere to the finger and did not rub up appreciably when the finger was lightly rubbed across the surface.

3.7.4 Shear Strength Properties of Adhesives by Tension Loading (Plywood-To-Plywood) (UDC 668.395: 778.632.652)

3.7.4.1 Preparation of Test Specimens

Two pieces of plywoods (2.5x8.5x0.3 cm^3, 10% moisture content) were used to conform the test specimens for measuring the shear strength of an adhesive. The adhesive was applied in the area of 2.5x2.5 cm^2 across the end of each wood

pieces (double spreading), assembled in pairs. The amount of the adhesive for each pieces was 0.02 g (solid)/cm^2 (Figure 3.3)

Adhesive curing was investigated in 5 different ways of test specimens assembly as shown below:

1. Wet-laminating and non-pressing
2. Dry-laminating and non-pressing
3. Wet-laminating and cold pressing
4. Dry-laminating and cold pressing
5. Dry-laminating and hot pressing

Wet-Laminating and Non-Pressing After an adhesive had already applied to woods, the test specimen was immediately conformed to the form with the grain direction of the two pieces being parallel (Figure 3.3 b). It was allowed to stand at room temperature for 6 days before testing.

Dry-Laminating and Non-Pressing After an adhesive was applied to woods, it was allowed to dry at room temperature until it reached dry-to-touch point, test specimen was conformed to the form as shown in Figure 3.3 (b).It was allowed to stand at room temperature for 6 days before testing.

Wet-Laminating and Cold Pressing Test specimens were prepared as same as *wet-laminating and non-pressing* but they were kept at room temperature for about 2 hours before pressing. They were pressed at ambient temperature with pressure of 20 bar for 10,

20 and 30 min, respectively. They were allowed to stand at room temperature for 6 days before testing.

Dry-Laminating and Cold Pressing Test specimens were prepared similar to that of *dry-laminating and non-pressing* and pressing conditions were followed as described in *wet-laminating and cold pressing.*

Dry-Laminating and Hot Pressing Test specimens and pressing conditions were followed as described in *dry-laminating and cold pressing*, but they were pressed at 120°C and kept at room temperature for a day before testing.

3.7.4.2 Procedure

Shear strength measurements were carried out on tensile testing machine (Lloyd 500). The test specimen was placed in the grips of the testing machine so that the applied load coincides with the long axis of the specimen. The conditions were follwed as shown below:

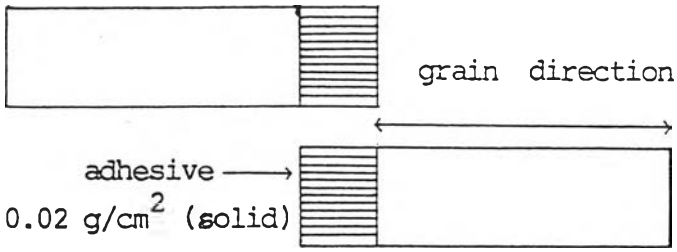
Gauge length	25 mm
Load cell	1 kN
Cross-head speed	9.00 mm/min
Temperature	27 ± 2 °C

shear strength (kg/cm^2) was recorded as a maximum load per shear area.

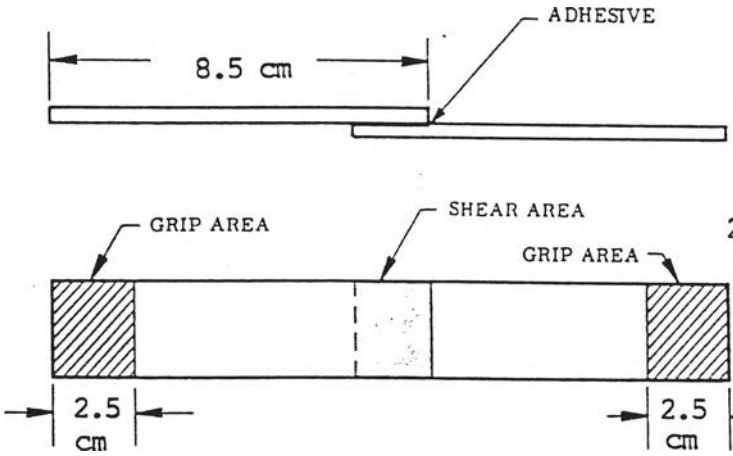
$$\text{Shear Strength} = F/A \qquad (3.2)$$

F = maximum load (kg)

A = shear area (cm^2)



(a)



(b)

Figure 3.3 (a) Dimension and adhesive-applied area of plywoods

(b) Test specimen (single-lab-joint)

3.7.5 Resistance to water

Test specimen preparation was carried out according to section 3.7.4.1. Each specimen was submerged in $30\pm2^{o}C$ water for 3 days. The shear strength was immediately measured as soon as it was picked up from water.

3.7.6 Determination of The Adhesion Strength of Nylon-6 Fabric to Compounded Natural Rubber by T-peel Test [ISO/R 36-1969 (E)]

T-peel test was primarily intended to determine the relative peel resistance of adhesive bonded between the flexible adherends, for example natural rubber to nylon-6.

Because of the best shear strength as the hot-setting adhesive, the batch no.35/10 was used to investigate bonding between nylon-6 fabrics and compounded natural rubber. The peel strength was compared with resorcinol-formaldehyde adhesive.

3.7.6.1 Preparation of The Test Panels and Test Specimens

Laminated test panels, consisted of a nylon-6 fabrics and compounded natural rubber as adherends were 12.5 cm wide by 14.5 cm long but they were bonded only over approximately 12 cm of their length (Figure 3.4). The adhesive was only applied to nylon-6 fabrics with the amount of 0.04 g (solid)/cm^2 by single spreading. It was allowed to dry at room temperature before assembly in pairs with compounded natural rubber to form the test panel.

The adhesion characteristics of nylon-6 fabric to compounded natural rubber using adhesive were evaluated at various conditions and compared to the ones without adhesive, as shown in Table 3.2 and 3.3 for the batch no. 35/10 and resorcinol-formaldehyde adhesive, respectively. Drying time,

the period of time for which an adhesive on an adherend was allowed to dry without the application of heat or pressure [12, 13], was studied at 2 hours for the batch no.35/10 and 24 hours for resorcinol-formaldehyde adhesive. The heat setting of the batch no.35/10 of the test panels was investigated at 150°C for 30, 40, 50 and 60 minutes, respectively, at 40 bar pressure. Whereas, the resorcinol-formaldehyde adhesive was conducted at 150°C for 20 minutes and the pressure was 40 bar. Hot-pressed test panels were kept at room temperature for 24 hours and cut into 2.5 cm wide test specimens (Figure 3.4).

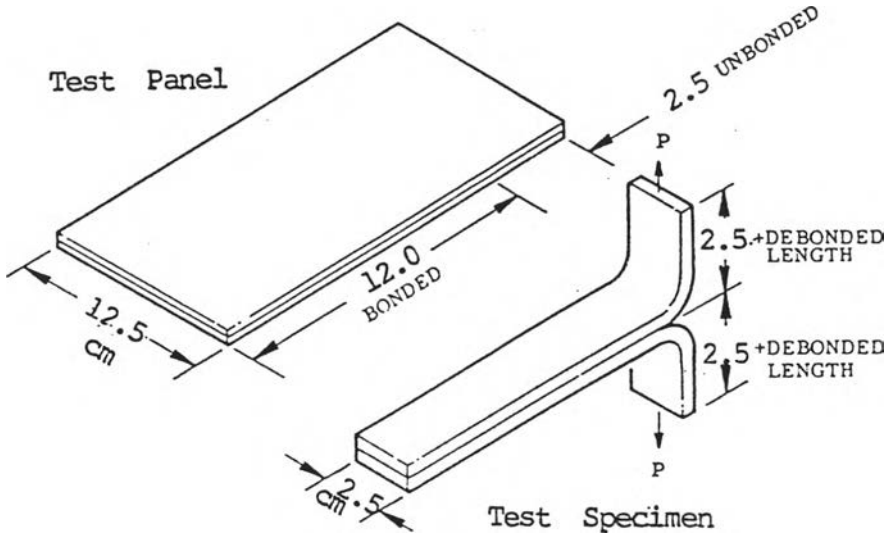


Figure 3.4 Test panel and test specimen

3.7.6.2 Procedure

The 2.5 cm long unbonded ends were bent apart perpendicular to the adhesive line and clamped in the grips of the tensile testing machine with the conditions as shown below:

Gauge length	25	mm
Load cell	1	kN
Cross-head speed	25.00	mm/min
Temperature	27±2	^{o}C

T-peel strength or adhesion strength, was expressed as the average load per unit width of bond line required to produce progressive separation of two bonded (3.3).

$$\text{T-Peel Strength} = F/L \qquad (3.3)$$

F = average load (kg)

L = adhesive line width (cm)

3.7.7 Storage Life

Storage life was defined as the time period for which an adhesive remained usable when stored under specified temperature conditions [13].

The adhesive batch no.20/40 was stored in the sealed container and keptat 25^{o}C. The time that the adhesive became solid was defined as the storage life.

3.7.8 Pot life (BS 5350 : Part B4 : 1976)

The adhesives, especially, those consisting of two components that had to be mixed together before use, were liable to undergo relatively rapid chemical or physical changes and to become unusable within a relatively short time.

Table 3.2 Conditions for preparing the test panels for CNSL adhesive.

Adhesive (batch)	Sn Octoate (%)	Drying Time (hr)	Press Temperature (^{o}C)	Presstime (min)
-	-	-	150	30-60
D35/10	-	2	150	30-60
D35/10	0.5	2	150	30-60

Sn Octoate = Stannous Octoate

Table 3.3 Conditions for preparing the test panels for resorcinol-formaldehyde adhesive

Hexamine (%)	Drying Time (hr)	Press Temperature (^{o}C)	Press Time (min)
0	24	150	20
5	24	150	20
10	24	150	20
15	24	150	20

The adhesive batch no.20/40 that was modified by 0.2% stannous octoate was kept in small container. It was at least three-quarters full. Pot life of an adhesive was the time for which an adhesive remained usable when kept at the normal application.

3.8 Scanning Electron Microscope (JEOL JSM-T220A)

The scanning electron microscope was employed to investigate the morphology of adhesive and surface of substrate.