

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

1. Natural rubber latex : Thai rubber latex corporation.
2. Methyl methacrylate monomer : Merck
3. Tert-butyl hydroperoxide : Fluka
4. Tetraethylene pentamine : Fluka
5. Oleic acid : Riedel-deHaen
6. Ammonia solution : Merck
7. Toluene : J.T. Baker
8. Isooctane : Fluka
9. Poly(vinyl chloride) resin : Thai Plastic & Chemical Co.,Ltd.
10. Ba-Zn heat stabilizer : Thai Plastic & Chemical Co.,Ltd.
11. DOP plasticizer : Thai Plastic & Chemical Co.,Ltd.
12. Epoxidized soybean oil : Thai Plastic & Chemical Co.,Ltd.
13. Sulfur : Petch Thai Chemical Industry Co., Ltd
14. Zinc oxide, Stearic acid : Petch Thai Chemical Industry Co., Ltd
15. TMTD, MBT, MBTS : Monsanto Chemical Industry Co., Ltd
16. Antioxidant : Kawaguchi Chemical Industry Co., Ltd
17. Light petroleum ether : Merck
18. Acetone : Merck
19. Acetic acid : J.T. Baker

Roles of raw materials

Natural Rubber Latex

Latex concentration is differentiated by the method of concentration and type of preservation used. Three methods of concentration are employed, centrifugation, evaporation and creaming; centrifugation is preferred method. The predominant latices are the HA and LA-TZ types. In this research, the latex concentration was the HA, which has 60% rubber content, 0.7% ammonia as preservative system.

Methyl methacrylate monomer

Methyl methacrylate was purified prior to use. The inhibitor (hydroquinone) from MMA was removed by washing it first with sodium hydroxide solution and then with distilled water to remove traces of alkali and was dried over anhydrous sodium sulphate (Na_2SO_4) and distilled under reduced pressure ($40^\circ\text{C}/20\text{ mm Hg}$)

tert-Butyl hydroperoxide/Tetraethylene pentamine system

This system is redox initiators which comprise two or more substances whose mutual interactions produce free radicals which are able to initiate polymerization. Tetraethylene pentamine is capable of decomposing tert-butyl hydroperoxide vigorously.

Vulcanization chemicals

These materials are necessary for vulcanization, since without the chemical crosslinking reactions involving these agents, no improvement in the physical properties of the rubber mixes can occur.

i) Sulfur. Although NR can also be crosslinked with peroxides, or high energy radiation, in practice, sulfur and accelerators are predominantly used. NR requires generally higher sulfur concentrations (2-3 phr), and lesser amounts of accelerator (0.2-1.0 phr). For lower sulfur concentrations, larger amounts of accelerator are required, in order to keep up the level of crosslink density. This

will, at the same time, reduce the sulfur rank of the crosslinks, which results in an improvement in the heat resistance and reversion resistance, and in compression set, but also worsens the notched tear and dynamic properties of the vulcanizate.

ii) Activator. Activators are substances which increase the the effect of accelerators. The two most widely used are zinc oxide and long-chain saturated fatty acid, e.g., stearic.

a) Metal oxides. Metal oxide are required in a compound to develop the full potential of accelerators. The main metal oxide is zinc oxide which has different grades such as ZnO white-seal (for general purpose rubber compound) and ZnO active (for transparent rubber compound). Therefore, only the ZnO active used in this research.

b) Long-chain fatty acid. Many accelerator systems require additional activators, like fatty acids, or salts of fatty acids, namely stearic acid, zinc soaps, or amine stearates. Therefore, only the stearic acid used in this research.

c) Accelerator (TMTM, MBT and MBTS). In combination with vulcanizing agents, these materials reduce the vulcanization time (cure time) by increasing the rate of vulcanization. Three types of accelerators were used.

-TMTM : Tetramethylthiuram monosulfide.

-MBT : 2-Mercaptobenzothiazole.

-MBTS : Benzothiazyl disulfide.

Poly(vinyl chloride)

PVC gained wide commercial acceptance because it could be mixed with organic liquids (plasticizers) to give a tough flexible material not unlike rubber in its properties and the way in which it could be processed. PVC when processed is always mixed with other materials to improve its heat stability or its processibility or to modify its properties. A suspension polymerized homopolymer PVC (TPC type102) having a K value of 58 was used in this study.

3.2 Glassware

- 2.1) 4-Necked bottom reactor 1000 cm³
- 2.2) Liebig condenser
- 2.3) Nitrogen gas tube
- 2.4) Other general laboratory glassware

3.3 Equipment

- 3.1) Two rolls mill, : Lab Tech Engineering.
- 3.2) Infrared Spectrophotometer (FTIR), : Perkin Elmer model 1600.
- 3.3) Thermal Gravimetric Analyzer (TGA), : Shimudzu model 50.
- 3.4) Rubber hardness Tester, : Wallace.
- 3.5) Differential Scanning Calorimeter : Rheometric Scientific.
(DSC)
- 3.6) Curing machine, : Monsanto model ODR2000.
- 3.7) Abrasion testing machine, : Teledyne Taber
model 5130 Abraser
- 3.8) Tensile testing machine, : Testometric medel50 kN
- 3.9) Hot press, : Lab Tech Engineering
model LP20
- 3.10) Prodex-Henschel high-intensity mixer, : Lab Tech Engineering
model LMX 10 DC
- 3.11) Scanning Electron Microscope, : JSM-5410LV

3.4 Preparation of Grafted Natural Rubber

The graft copolymer of methyl methacrylate onto natural rubber was prepared by graft emulsion polymerization.

The NR latex (60% DRC, 500 g) was charged to a reaction kettle equipped with stirrer, dropping funnel, reflux condenser and nitrogen inlet tube. The equipment setup is shown in Figure 3.1. The latex was diluted to 30% by adding 2% NH_4OH solution and was deoxygenated by bubbling nitrogen for at least 0.5 h through the diluted latex and the latex was still stable. The temperature was maintained at 30°C throughout the reaction period before the addition, dropwise over 60 min, of the methyl methacrylate monomer (20 phr, 60 g), the stabilizer at 0.5 wt % of dry rubber content (1.5 g) and the *tert*-butylhydroperoxide at 0.3 wt % of dry rubber content (0.9 g). After period of 15 min, the amine activator (3.50 g of a 10% w/v solution) was added. The reaction was then allowed to proceed for 6 hr. under continuous stirring to complete the polymerization. To form a sheet, the latex was cast at room temperature in open glass trays to give a final sheet thickness of ca. 1.5 mm. After drying, the sheet was removed from the tray and transferred to a vacuum oven (40°C) to remove any last traces of monomer that may be present. The dried sheet was then leached with distilled water to remove any water-soluble impurities. The sheet was then thoroughly dry in the vacuum oven.

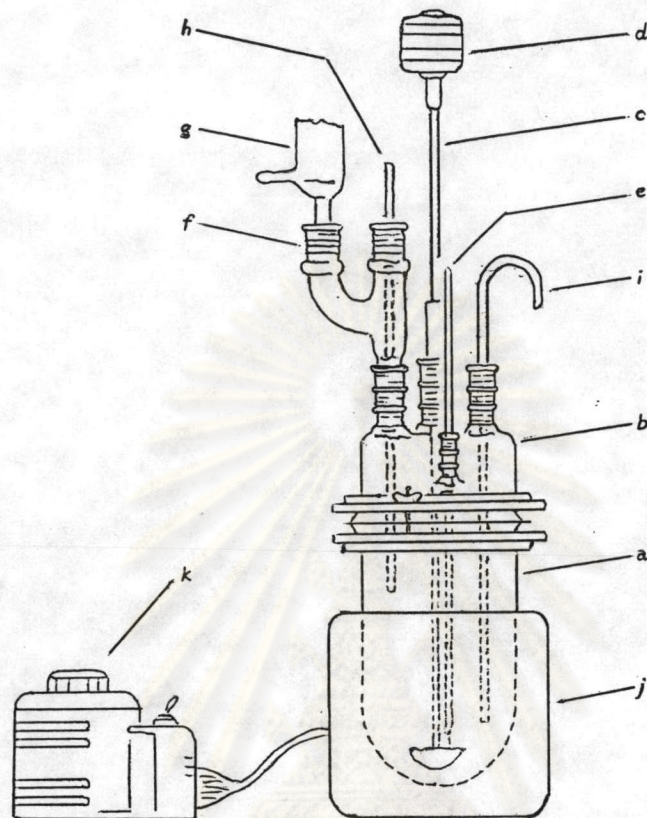


Figure 3.1 Apparatus for graft emulsion polymerization of MMA monomer onto NR latex.[35]

- | | |
|-----------------------------|-------------------------|
| (a) Reaction kettle bottom | (b) Reaction kettle top |
| (c) Stainless steel stirrer | (d) motor |
| (e) Thermometer | (f) Adapter |
| (g) Condenser | (h) Nitrogen-inlet tube |
| (i) Sampling | (j) Water bath |
| (k) Variable transformer | |

In order to find an appropriate condition for graft copolymerization, a series of experiments were performed by varying the ratio of MMA monomer to dry rubber content, NR latex concentration (or % dry rubber content), reaction temperature and reaction time as shown in Table 3.1. The procedure of preparation of graft natural rubber and the characterization are summarized in Figure 3.2.

Table 3.1 Graft copolymerization conditions used in this study.

Conditions	Value
MMA monomer (g/100 g rubber)	20, 40, 60, 80
Dry rubber content (%)	30, 40, 50
Reaction temperature ($^{\circ}\text{C}$)	30, 40, 50
Reaction time (hr)	2, 4, 6, 8

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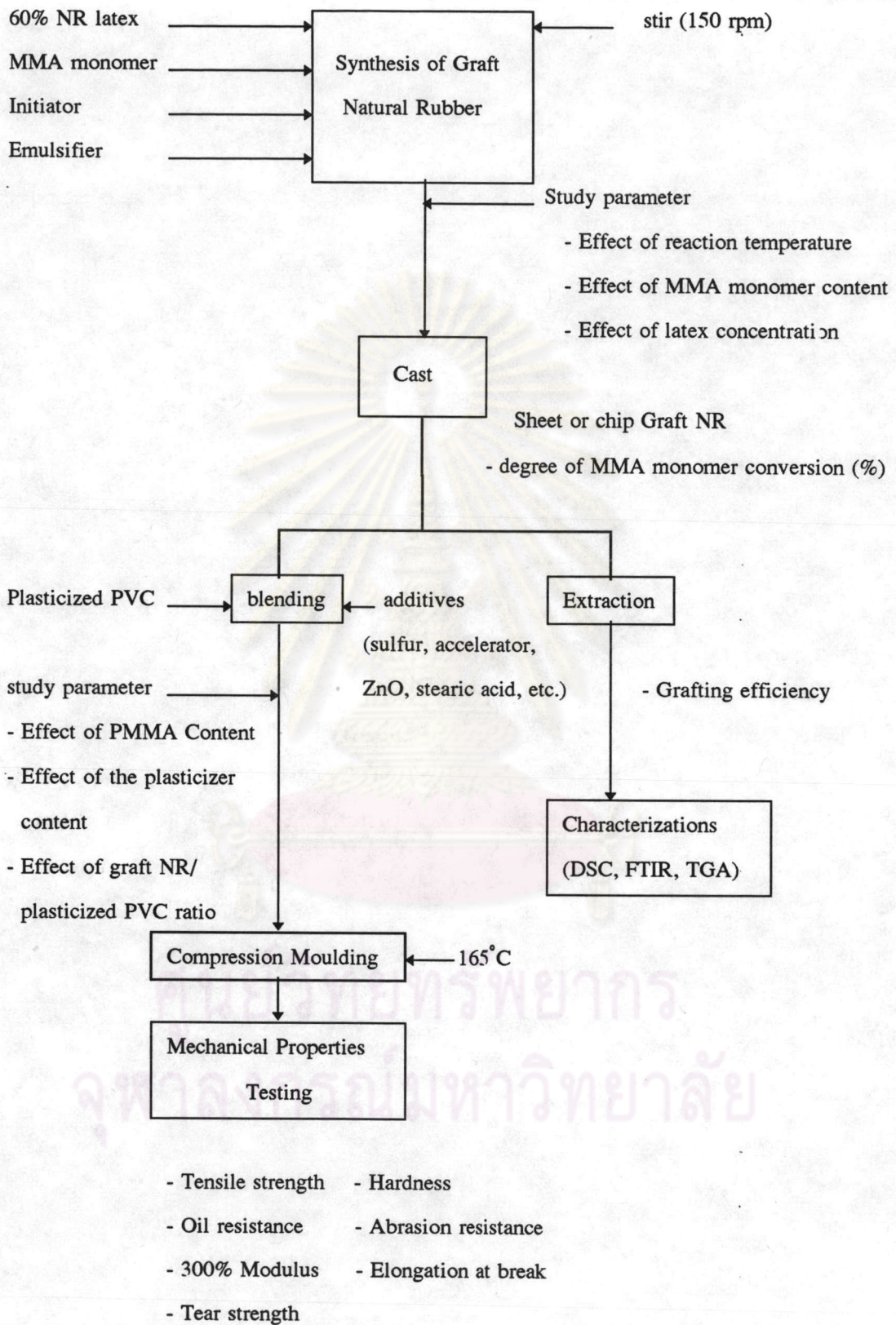


Figure 3.2 Summary of the research work plan

3.5 Characterization of the Grafted natural rubber

3.5.1) % conversion and % grafted natural rubber

% conversion

The grafted natural rubber latex was cast in a glass tray, dried at room temperature, leached in distilled water, dried again subsequently at room temperature and at 50°C, and, finally, dried under vacuum at room temperature and weighed. The degree of conversion was determined by the percentage increase of rubber weight. The details of all calculations are shown in the Appendix A.

% grafted natural rubber

The free poly(methyl methacrylate), free natural rubber and graft copolymer in the reaction products could be determined by the soxhlet extraction process. The free natural rubber was extracted by solvent extraction, using light-petroleum ether as solvent for 24 h while free poly(methyl methacrylate) was extracted by acetone for 24 h [36]. The graft copolymer content was determined by the residual weight after extraction of homopolymers. The degree of grafting was determined by the assumption that the unextracted PMMA is the grafted polymer. Data obtained from this step were used to calculate the grafted natural rubber. The details of all calculations are shown in the Appendix A.

3.5.2 Cure characteristics

The Monsanto Oscillating Disc Rheometer 2000 (ODR 2000) was used to measure the curing characteristics of compounded rubber samples in accordance with international testing standards. A sample was sealed in a temperature controlled die cavity (vulcanization chamber) and surrounded a rotor. This rotor

oscillated through a small arc at 1.66 Hz (100 cpm) and exerted a shear strain on a sample as that sample cured. The resulting output data were correlated to the degree of vulcanization as a function of cure time. In the ODR test determined the scorch time, cure time (vulcanization time), and cure rate index (CRI) were determined from the plot of the torque curve versus time. The scorch time was measured when the torque curve increased from the minimum torque at one unit (such as 1 lb-in). The cure time was measured when the torque curve increased from the minimum torque at 90 percent of the difference between maximum torque and minimum torque. The temperature was at 165°C. The typical ODR2000 was shown in Figure 3.3. The cure characteristics of rubber compounds are shown in Appendix B.



Figure 3.3 Typical ODR2000. [37]

3.5.3 Thermal Gravimetric Analyzer (TGA)

Thermogravimetry is a technique for measuring the changes in the mass of the sample during heating. The thermal stability of the grafted natural rubber samples was investigated by using a Shimadzu Thermogravimetric Analyzer model

TGA-50. The measurements were carried out over a temperature range of room temperature to 500°C with the heating rate of 10°C/min. and the oxygen flow rate of 10 ml/min.

3.5.4 Differential Scanning Calorimeter (DSC)

The thermal stability of the grafted natural rubber samples was also investigated by using a Rheometric Scientific DSC. The measurements were carried out over a temperature range of -100 to 150°C with the heating rate of 10°C/min. and the nitrogen flow rate of 10 ml/min.

3.5.5 Fourier Transform Infrared Spectrophotometer

Infrared (FTIR) Spectra of grafted polymer were determined by Perkin-Elmer Infrared Spectrophotometer model 1600. The grafted polymer films were made by dissolving the polymer in chloroform and casting on NaCl cell.

3.6 Preparation of Grafted Natural Rubber/PVC Blends

3.6.1 Preparation of compound

i) Dry blending of PVC compounds (first stage) :

Prodex-Henschel high-intensity mixer was used for blending. The raw materials were PVC resin, zinc stearate, stearic acid, Ba-Zn stabilizer, epoxidized soybean oil and DOP plasticizer.

First, PVC resin and other materials except DOP plasticizer were mixed together at motor speed of 2,000 rpm until the temperature of the mixer reached 80°C (the temperature slightly increased) for 5 min. Then, DOP plasticizer was mixed into the materials by the mixer. The temperature of mixer was controlled in

the range of 80-84°C, the mixing time was 3-5 minutes because the plasticizer was absorbed by PVC. After mixing of PVC compound, the temperature of PVC compound was decreased to room temperature by cooling water circulated around the mixer.

Recipe of PVC compounds

PVC resin	100	phr
DOP plasticizer	0, 20, 40	phr
Ba-Zn stabilizer	3	phr
Epoxidized soybean oil	3	phr
Zinc stearate	0.5	phr
Stearic acid	0.5	phr

ii) Grafted NR compounding (second atage)

The temperature for rubber compounding with ingredients of vulcanization system was lower than the plastic processing temperature. Thus, the temperature for rubber compounding was at 70°C. First, the rubber was charged into the two-roll mill. Then, the ZnO activator, Antage SP-P and stearic acid were added at the same time. Finally, the accelerators (TMTM, MBT, MBTS) were added.

Recipe of rubber compounding :

Grafted Natural rubber	100.0	phr
ZnO active	2.0	phr
Stearic acid	1.0	phr
TMTM	0.04	phr
MBT	0.08	phr
MBTS	1.20	phr
Sulfur	2.0	phr
Antage SP-P	1.0	phr

Note: The steps of rubber compounding are as follows:

- at 0 minute - Transfer the rubber to two roll mill.
- at 3rd minute - Add the ZnO activator.
- at 5th minute - Add the antioxidants (Antage sp-p).
- at 6th minute - Add stearic acid.
- at 7th minute - Add the accelerators (TMTM, MBT and MBTS).
- at 8th minute - Remove the compound from two roll mill.

iii) PVC and Modified NR Blends

First, the temperatures of the mixing rolls were maintained constant at 160°C for the front roll and at 150°C for back roll. The PVC and the grafted NR compounds were cut into small sheets. The PVC and grafted NR sheets were weighed (depending on the PVC and grafted NR blend composition). Then, the plasticized PVC was fed to the two roll mill for 3 minutes and the grafted NR sheets were added and blended for 5 minutes until the surface of blend was smooth. Finally, the sulfur was added and blended at 100°C for 2 minutes and a 2-mm thickness sheet was formed. The compositions of PVC and grafted NR blends are shown in Table 3.2.

3.6.2 Preparation of test specimen

The specimens were prepared in the compression molding. The milled sheets were cut into strips in the the mill direction and placed into a preheated mold. The mold was placed in a hot press at 165 °C and pressed at pressure of 120 kg/cm² for 5 min. After pressing, the mold was transferred to a water cooled press under pressure 80 kg/cm² for 5 min.

Table 3.2 PVC and grafted NR blend composition.

Code	% MMA	Plasticizer, phr	Composition
			GNR:PVC
NR/PVC-P00	0	0	90:10, 80:20, 60:40, 40:60
GNR20/PVC-P00	20	0	90:10, 80:20, 60:40, 40:60
GNR40/PVC-P00	40	0	90:10, 80:20, 60:40, 40:60
GNR60/PVC-P00	60	0	90:10, 80:20, 60:40, 40:60
			GNR:PVC-P20
NR/PVC-P20	0	20	90:10, 80:20, 60:40, 40:60
GNR20/PVC-P20	20	20	90:10, 80:20, 60:40, 40:60
GNR40/PVC-P20	40	20	90:10, 80:20, 60:40, 40:60
GNR60/PVC-P20	60	20	90:10, 80:20, 60:40, 40:60
			GNR:PVC-P40
NR/PVC-P40	0	40	90:10, 80:20, 60:40, 40:60
GNR20/PVC-P40	20	40	90:10, 80:20, 60:40, 40:60
GNR40/PVC-P40	40	40	90:10, 80:20, 60:40, 40:60
GNR60/PVC-P40	60	40	90:10, 80:20, 60:40, 40:60

3.7 Physical Properties Testing

The mechanical properties of the blends were determined according to the ASTM, ISO and B.S. test methods.

3.7.1 Hardness (ISO48)

The hardness property of the specimen was measured by using IRHD hardness tester (used for medium hard samples). The minimum thickness of

specimen was 6 mm. The indenter of durometer was pressed onto the flat specimen surface for 15 seconds and the hardness value was recorded.

3.7.2 Tensile properties (ASTM D412)

For determination of the tensile properties, the dumbbell specimen was used, die type 1 (115 mm long, 25 ± 1 mm, gauge length 25 mm, and gauge width 6 ± 0.4 mm.) as illustrated in Figure 3.4. The specimen were cut from a 2.0 mm thick sheet. The testing was performed on a universal testing machine with a crosshead speed of 500 mm/min. The test condition was at $27 \pm 2^\circ\text{C}$. An average of four specimens was considered as a representative value.

$$\text{Tensile strength} = F/A, \text{ N/mm}^2 \text{ or MPa} \quad (12)$$

where F = Tension force (N)

$$A = \text{Cross section area (mm}^2\text{)}$$

$$\text{Modulus at 300\% elongation} = F_1/A, \text{ N/mm}^2 \text{ or MPa} \quad (13)$$

where F_1 = Tensile force at 300% elongation (N)

$$A = \text{Cross section area (mm}^2\text{)}$$

3.7.3 Tear strength (ASTM D624)

Dimension and shape of specimen was angle shape cut followed to Figure 3.5. A crosshead speed of the universal testing machine at 500 ± 50 mm/min was used. The test temperature was at $27 \pm 2^\circ\text{C}$. An average of five specimens was considered as a representative value. The thickness of specimen was 2 mm.

Calculation of tear resistance is as follows:

$$T_s = F/d \quad (14)$$

where T_s = tear resistance (kN/m or N/mm)

$$F = \text{force (N)}$$

$$d = \text{specimen thickness (mm)}$$

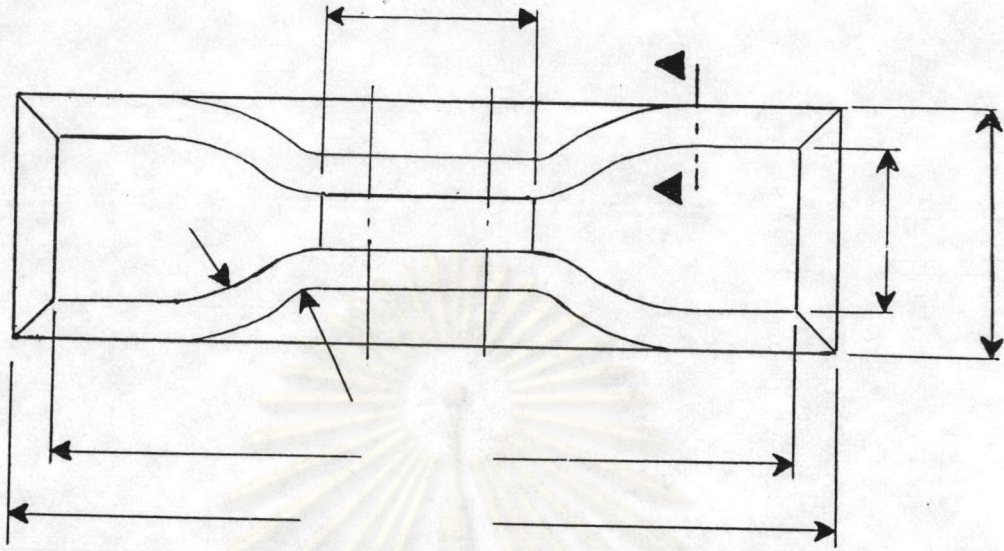


Figure 3.4 Tensile strength specimen, Die type C.

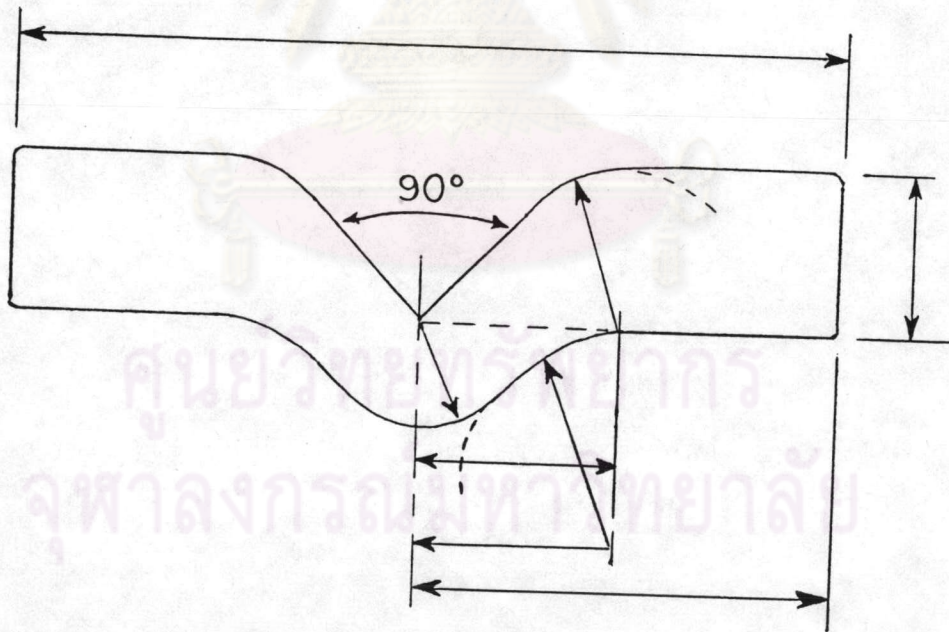


Figure 3.5 Tear strength specimen, Die C.

3.7.4 Oil resistance (ASTM D471)

This test method measured the comparative ability of rubber and rubber-like composites to withstand the effect of liquids.

The liquid type of this study was Reference Fuel C (isooctane 50% by volume and toluene 50% by volume) and the immersion period was 7 days (168 hours) at room temperature ($27\pm 2^{\circ}\text{C}$). Test specimen size was $2.0\times 1.5\times 0.2$ cm and an average of five specimens was considered as a representative value.

3.7.5 Abrasion resistance [38]

This test is used to measure resistance to abrasion during wear of surfaces of materials. It can be used to conduct abrasion test of various kinds of material by simply changing the weights and abrasive wheels. The H-18 abrasive wheel with 1000 gf load was used. Two abrasive wheels were arranged on the turntable. This test procedure according to this standard provides a measuring method for assessing the resistance of elastomers to wear by rubbing. The determination of the volume loss by rubbing with a test emery of defined abrasive power by this method is suitable for comparative testings, for checking the uniformity of specified products and for specifications.

The abrasion resistance is the volume loss (V in cm^3) determined under the conditions for this method of a cylindrical test.

The test specimen was cylindrical shape of 16 ± 0.2 mm diameter and at least 6 mm thickness. The abrasion resistance referred to Taber wear index was determined by calculating the milligram loss in weight per 2000 cycles of abrasion under test conditions selected by means of a precision balance before and after the test. The smaller the wear index of a material, the larger the resistance to wear.

3.7.6 Specific gravity Measurements (B.S.903, Part 14)

The specific gravimetric balance was used. The specific gravity can be calculated by the following equation.

$$\text{Specific gravity} = \frac{W_1}{W_1 - W_2} \quad (15)$$

where W_1 = weight of the test specimen in air.

W_2 = weight of the test specimen in water.

3.7.7 SEM Analysis

The scanning electron microscopic study of the GNR/PVC blends was done with a JSM-5410LV scanning electron microscope operated at 15 kV. The samples were mounted on a SEM stub using a double-sided tape. The samples were then coated with gold coating. The samples were then scanned at magnification of 5000 times.

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