CHAPTER III
EXPERIMENTAL

3.1 Rubber Compounding

3.1.1 Materials

3.1.1.1 Concentrated Natural Rubber Latex (NRL)

NRL used in this study was received by Rubber Organization. Its properties are shown:

Total solid content (TSC)	62.11%
Dry rubber content (DRC)	60.71%
Mechanical stability time at 55% TSC	650 sec.
Volatile fatty acid number (VFA)	0.086
Potassium hydroxide number	0.80

3.1.1.2 Deproteinized Concentrated Natural Rubber Latex (DPNR)

DPNR used in this study was received by Sumitomo Rubber Industries, Malaysia. Its properties are shown:

Total solid content (TSC)	60.84%
Dry rubber content (DRC)	58.82%
Mechanical stability time at 55% TSC	141 sec.
Volatile fatty acid number (VFA)	0.0137
Potassium hydroxide number	0.52

3.1.1.3 10% Potassium Hydroxide (KOH)

Potassium hydroxide was purchased from Merck. This material is opaque pellet and used as stabilizer.

3.1.1.4 Vulcanizing Agents

Vulcanizing agents including 50% sulphur dispersion (S), 50% zinc diethyldithiocarbamate dispersion (ZDEC), and 50% zinc oxide dispersion (ZnO) were received from Rubber Research Institute of Thailand.

3.1.1.5 50% Wingstay-L dispersion (W-L)

50% Wingstay-L dispersion was used as antioxidant, received from Rubber Research Institute of Thailand.

3.1.1.6 50% Calcium Carbonate dispersion

50% Calcium carbonate dispersion was used as filler, received from Rubber Research Institute of Thailand.

3.1.1.7 10% Precipitated Silica dispersion

Precipitated silica HISIL 255 was used as reinforcing filler, received from PPA-Siam Silica Co., Ltd. HI-SIL 255 before dispersing was reported to have the BET surface area of 133 m^2/g with an average particle size of 27.4 μm. Density or specific gravity ~1.8-2 g/cm^3

3.1.1.8 10% Admicelled Silica dispersion

Modified silica HISIL 255 by styrene-isoprene (1:3 mole ratio) admicellar polymerization was used as reinforcing filler. Admicelled silica before dispersing was reported to have the BET surface area of 87 m^2/g with an average particle size of 61.99 μm., received from the Petroleum and Petrochemical College's research.

3.1.1.9 35% Coagulant Solution of Calcium Nitrate

Calcium nitrate was received from Rubber Research Institute of Thailand.

3.1.1.10 SI-69

SI-69 was used as silane coupling agent. It was reported to have surface area 240 $Å^2$ with the molecular weight of 539, supported from JJ. Degussa, Thailand.

3.1.1.11 Dispersing Agents

Dispersing agents including Valtamol and Bentonite were received from Rubber Research Institute of Thailand.

3.1.1.12 Toluene

Toluene was used as rubber solvent for swelling test, received from Merck.

3.1.1.13 Powder

Fine powder was used for releasing rubber film from the former

3.1.2 Procedure

3.1.2.1 Preparation of chemical dispersion

All chemical was obtained in the form of dispersions from The Rubber Research Institute of Thailand. Except for precipitated silica was prepared in the form of dispersion by ball milling (U.S. Stoneware OH 44413) the five part (from theoretical calculation) of SI-69 into the precipitated silica for fifteen minutes before dispersion and followed by ball milling with one part of the dispersing agent (valtamol and bentonite) for three days. The dispersion with a total solid content (TSC) of 10% and pH of 9 (adjusted by KOH solution) was prepared.

3.1.2.2 Preparation of Samples

There were two types of samples: vulcanized natural rubber latex films and vulcanized deproteinized natural rubber latex films

Both of them were prepared by throughly mixing in beaker with NRL, DPNR and the variety of the other additives which were varied the amount of three types of filler.

(a) Calcium Carbonate

50% Calcium carbonate dispersion was mixed in beaker, as indicated in Table 3.1 there were eight samples: DRD 1, DRD 2, DRD 3, DRD 4, DRD 5, DRD 6, DRD 7 and DRD 8.

Table 3.1 Formulation for vulcanized rubber film with calcium carbonate

MATERIAL	COMPOUND, Dry weight(phr)							
	DRD 1	DRD 2	DRD 3	DRD 4	DRD 5	DRD 6	DRD 7	DRD 8
60%NRL	100	0	100	0	100	0	100	0
60%DPNR	0	100	0	100	0	100	0	100
10%KOH	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
50%$CaCO_3$	**0**	**0**	**25**	**25**	**35**	**35**	**45**	**45**
50%S	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
50%W-L	1	1	1	1	1	1	1	1
50%ZDEC	1	1	1	1	1	1	1	1
50%ZnO	1	1	1	1	1	1	1	1
Distilled Water	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC

(b) Admicelled Silica

10% Admicelled silica dispersion was mixed in beaker, as indicated in Table 3.2 there were ten samples: DRD 9, DRD 10, DRD 11, DRD 12, DRD 13, DRD 14, DRD 15, and DRD 16.

Table 3.2 Formulation for vulcanized rubber film with Admicelled silica

MATERIAL	COMPOUND Dry weight (phr)							
	DRD 9	DRD 10	DRD 11	DRD 12	DRD 13	DRD 14	DRD 15	DRD 16
60%NRL	100	0	100	0	100	0	100	0
60%DPNR	0	100	0	100	0	100	0	100
10%KOH	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
10%Adm.Sil.	**1**	**1**	**3**	**3**	**5**	**5**	**10**	**10**
50%S	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
50%W-L	1	1	1	1	1	1	1	1
50%ZDEC	1	1	1	1	1	1	1	1
50%ZnO	1	1	1	1	1	1	1	1
Distilled Water	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC

(b) Precipitated Silica

10% Precipitated silica dispersion was mixed in beaker, as indicated in Table 3.3 there were eight samples: DRD 17, DRD 18, DRD 19, DRD 20, DRD 21, DRD 22, DRD 23, and DRD 24.

Table 3.3 Formulation for vulcanized rubber film with Precipitated silica

MATERIAL	COMPOUND Dry weight (phr)							
	DRD 17	DRD 18	DRD 19	DRD 20	DRD 21	DRD 22	DRD 23	DRD 24
60%NRL	100	0	100	0	100	0	100	0
60%DPNR	0	100	0	100	0	100	0	100
10%KOH	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
10%Pre.Sil.	**1**	**1**	**3**	**3**	**5**	**5**	**10**	**10**
50%S	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
50%W-L	1	1	1	1	1	1	1	1
50%ZDEC	1	1	1	1	1	1	1	1
50%ZnO	1	1	1	1	1	1	1	1
Distilled Water	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC	Add to 40% TSC

All compounded latex was matured at room temperature until getting 80-90% of degree of vulcanization by swelling test in toluene. It was also checked the viscosity by Brookfield viscometer to get viscosity around 5-6 cp at shear rate 233 1/sec which was proper viscosity for dipping film. The maturing time takes around three days. The duplicated experimental were carried out for each sample. Dipped films were constructed by the following chart:

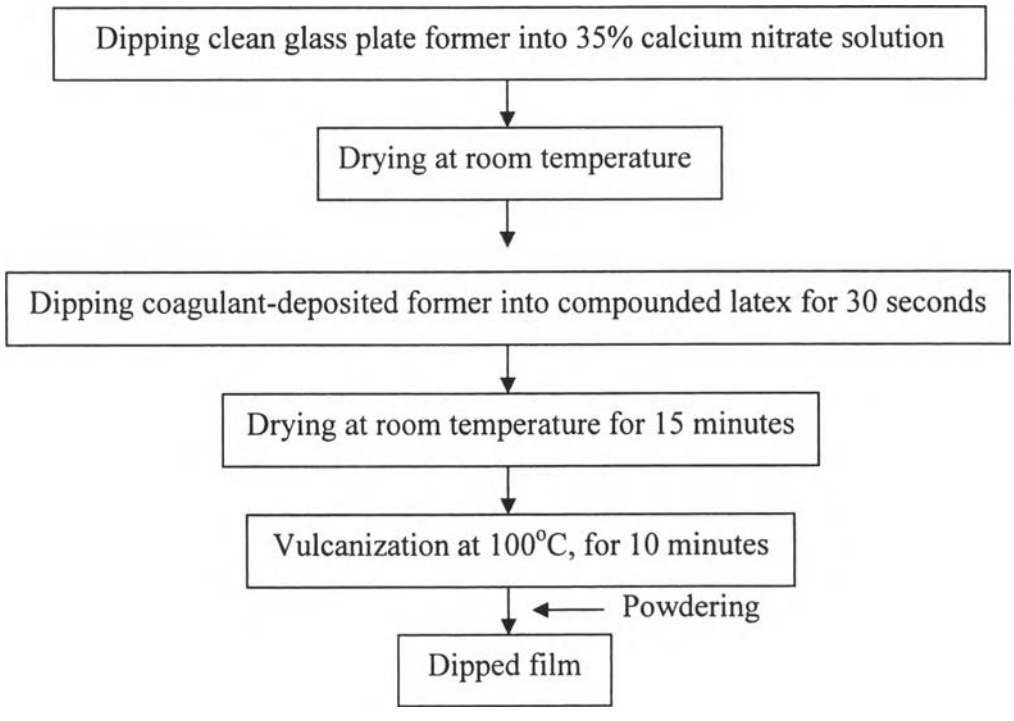

Figure 3.1 Flow diagram of vulcanized rubber film.

3.2 Characterization

3.2.1 Materials

Dipped films were used for mechanical studies with an average thickness 0.2 mm. They were cut base on the international standard specimens of each testing as shown in the following Figures.

3.2.1.1 Tensile Test

Dipped film was cut in dumbbell specimen by the die cutter type II of ISO 37 as shown in Figure 3.2

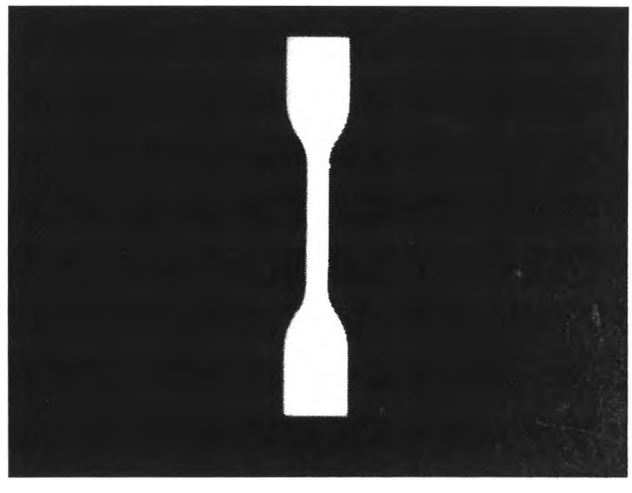

Figure 3.2 Dumbbell specimen for tensile test.

3.2.1.2 Tearing Test

Dipped film was cut to an un-nicked test piece by the die C of ASTM D624 as shown in Figure 3.3.

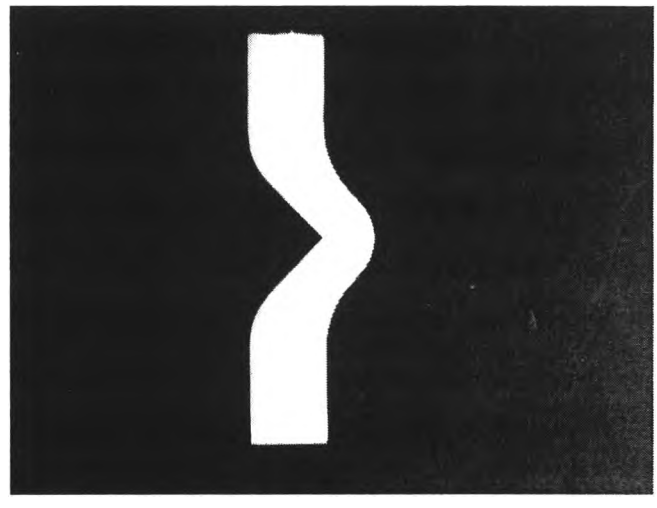

Figure 3.3 An un-nicked test piece for tearing test.

3.2.1.3 Hardness Test

Test specimens were prepared according to ASTM D2240.

3.2.1.4 Contact Angle Measurement and Friction Test

Dipped film for these two testing procedure must not be powdered because powder may cause the water absorption in contact angle measurement and reduce friction in friction test.

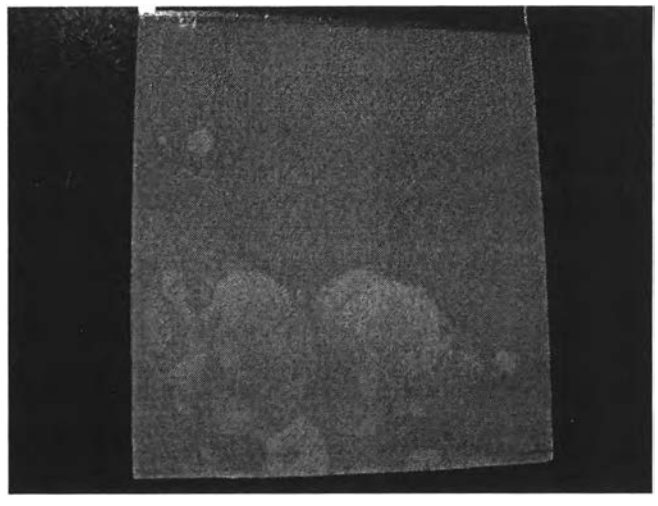

Figure 3.4 Unpowdered films for contact angle measurement and friction test.

3.2.2 Instruments

3.2.2.1 Universal Testing Machine (LLOYD LRX)

LLOYD LRX with load cell 500 N was used to determine tensile strength, elongation at break and tear strength.

3.2.2.2 Shore Durometer (ZWICK 3100)

ZWICK 3100 was used to check vulcanized film hardness.

3.1.2.3 Contact Angel Measurements (KRUSS DSA 10-Mk2)

A drop of distilled water on the surface of rubber films with 50% calcium carbonate dispersion was photographed by drop shape analyzer after 3 minutes of contact.

3.1.2.4 Friction Test (DAVENPORT FRICTION TESTER)

Only the rubber films with 50% calcium carbonate dispersion were tested by Davenport friction tester.

3.1.2.5 Water-Extractable Protein Concentration Test

Modified Lowry method was used to test the concentration of total water-extractable protein per gram for only the rubber film with 10% precipitate silica dispersion.

3.1.2.6 Brookfield Viscometer (DV-III)

Brookfield viscometer model DV-III was used to check the proper viscosity of latex compound for dipping process at room temperature.

3.2.3 Procedure

3.2.3.1 Tensile and Elongation at break Test

Tensile and elongation at break test were performed on a LLOYD LR5K. It incorporated these features, i.e., load cell 500 N, crosshead speed 500 mm/min. At least five pieces of a sample were carried out for average value.

3.2.3.2 Tear Strength Test

Tear strength were determined by LLOYD LR5K. It incorporated these features, i.e., load cell 500 N, crosshead speed 500 mm/min and gauge length 25 mm. At least five pieces of a sample were carried out for average value.

3.2.3.3 Hardness test

Hardness of vulcanized rubber film was determined by ZWICK 3100. At least three pieces of a sample were carried out for average value.

3.2.3.4 Contact Angle Measurement

Distilled water of 20 micro liters was dropped on horizontal surface of the sample placed on platen state. The contact angles at both sides of drop were measured after 3 minutes of contact. Average values for six drops were taken as representative of a sample surface.

3.1.2.4 Friction Test

The rubber film in calcium carbonate system was attached to the 200 g of sled cut approximately 120 mm square. During the slip test on the same sample surface must take note of the initial static force had to be taken immediately from the digital monitor. This reading is used to calculate the coefficient of static friction (coefficient of static friction = static force/weight of sample). At least three pieces of a sample were carried out for average value.

3.1.2.5 Water-Extractable Protein Concentration Test

The rubber film in precipitated silica system was tested of total water-extractable protein per gram by extracting protein from rubber film by water

and measuring the concentration of protein by UV spectroscopy at 750 nm. This method was tested by The Rubber Research Institute of Thailand. At least three pieces of a sample were carried out for average value.

3.1.2.6 Viscosity test

The compounded latex of 10 ml of each sample were poured into Brookfield cup and checked viscosity by using spindle no. 21 with shear rate 233 1/sec at room temperature.

3.1.2.7 Swelling test

White-gray paper was cut to a convenient size of 1.5 x 3.0 inches and then dipped into compounded latex to get a film of the latex. The film was dried for five minutes and punched a 1-centimeter diameter sample and immersed into toluene solvent for half an hour. The swollen film was calculated the percentage swell using the equation:

$$\text{percentage swell} = \frac{(\text{average swollen diameter} - \text{unswollen diameter})}{\text{unswollen diameter}} \times 100$$

The variation in percentage swell with crosslink density (degree of vulcanization), for natural rubber in toluene, was broadly as given below:

unvulcanized	160%
lightly vulcanized	100 – 160%
moderately vulcanized	80 – 100%
fully vulcanized	75%

3.2.4 Aging Condition

Both vulcanized natural rubber and vulcanized deproteinized natural rubber film samples were heated at 70°C for 7 days in hot air oven. Then these samples were characterized for tensile strength, elongation at break as in 3.2.3.1 and for tear strength as in 3.2.3.2.