

CHAPTER III

EXPERIMENTAL

3.1 Chemicals and instruments

3.1.1 Chemicals

Table 3.1 Chemicals used in this study

Chemicals	Commercial name	Supplier
1) NR	STR 5L	Teck Bee Hang Co., Ltd.
2) EPDM	Nordel IP 4640	Chemical Innovation Co., Ltd.
3) ZnO	Zinc oxide	Metoxide Thailand Ltd.
4) Stearic acid	Stearic acid	Pan-Century edible oil SSDN. BHD.
5) Dibenzothiazole disulfide	Rubator MBTS	Behn Meyer & Co., Ltd.
6) Tetramethyl thiuram disulphide	Rubator DTMT	Behn Meyer & Co., Ltd.
7) Homogenizing agent	Ultrablend 4000	Behn Meyer & Co., Ltd.
8) Sulfur	Sulfur	Siam Chemical Ltd.
9) Carbon black	HAF N-330	Thai Carbon Black Public Co., Ltd.
10) Silica	Ultrasil VN 3 Granulate	JJ-Degussa Chemicals Ltd.
11) Processing additive	Struktol EF44	JJ-Degussa Chemicals Ltd.
12) Poly(ethyleneglycol)	PEG 3350	Kijpaiboon Chemical Ltd.

The specifications of chemicals are given in Appendix A

3.1.2 Instruments

The Instruments used in this study are listed as below:

- 1) Two roll mill mixer 8"x20" Model R11-3FF (Kodaira, Seisakusho, Japan)
- 2) Internal mixer kneader (Farrell, UK, 3.5 l)
- 3) Vulcanizing press (Wabash, Charemnchai Karnchang factory, Thailand)
- 4) Mooney viscometer (Techpro, model Visctech, USA)
- 5) Rheometer (Techpro, Model Rheotech, USA)
- 6) Tensile testing machine (Lloyd LR5K, England)
- 7) Hardness tester (Shore A, Instron MFG, England)
- 8) Ozone test chamber (Hampden, England)
- 9) Ageing oven (Ueshima, Japan)
- 10) High resistance meter (Hewlett Packard, Model HP4339D, Japan)
- 11) High voltage tester (Hipotronics, Model HD100, USA)
- 12) Scanning electron microscope (JEOL JSM 5800LV, Japan).
- 13) Differential scanning calorimeter (DSC7, Perkin Elmer, England)
- 14) Advanced capillary extrusion rheometer (Rosand Precision, England)
- 15) Dynamic mechanical thermal analyzer (DMA 242, Netzsch, Germany)
- 16) Pulsed nuclear magnetic resonance (NMR) (PC20, Bruker, Germany)

3.2 Procedures

3.2.1 The control of rubber viscosity

Since Mooney viscosity of the NR is higher than that of EPDM, mastication of NR is necessary to reduce its Mooney viscosity to match that of EPDM. The NR was masticated on a two-roll mill for 0, 2, 4, 6 min and viscosity of the masticated NRs was

measured using Mooney viscometer. After mastication, the masticated NRs were set aside for 30 min and cut to give the NR specimens with a diameter of 44.5 mm. Then placed in a heated chamber under pressure and a disc-shaped rotor turning inside a cylindrical chamber. Shear stress was produced between surfaces of rubber and disc. The resulting torque obtained is a measured Mooney viscosity of the rubber. It is necessary to strictly control the rotor speed (normally within 2 ± 0.02 rpm) at the temperature of 373 ± 0.5 K. The specimens were warmed up for 1 min in the chamber before rotating the motor. A reading of viscosity was taken after 4 min. The typical Mooney viscosity is reported as ML1+4 (373 K). This test was performed according to ASTM D 1646-87.

3.2.2 Rubber compounding

In this study, a common mixing method was used by mixing 2 rubbers (NR/EPDM) in a homogenizing agent (Ultrablend 4000) and followed by an addition of ZnO, stearic acid, fillers and other curing agents e.g. accelerators and sulfur. The sequential addition and time schedule are as follows:

The NR was first masticated for 4 min by a two-roll mill. The masticated NR, EPDM and homogenizing agent were mixed together for 3 min in an internal mixer, with a capacity of 3.5 L. The temperature of this step was controlled between 373-393 K because the softening point of homogenizing agent is 368-383 K. Zinc oxide, stearic acid, and a half quantity of carbon black (N330) were added and mixed for 3 min. If the other filler, e.g. silica (1/3 quantity of silica) and the processing aid (PEG 3350) were required, it could be added at this step. The 2/3 quantity of the residual filler was then added and mixed for 3 min and the accelerators (MBTS and TMTD) were added and mixed for 2 min. The compounded rubber was removed from the internal mixer and it was mixed with sulfur on a two-roll mill at 363 K for 4 min. Compounded

rubbers were sheeted out and left for 24 hrs before vulcanization in a hot press. Figure 3.1 shows the rubber compounding sequences.

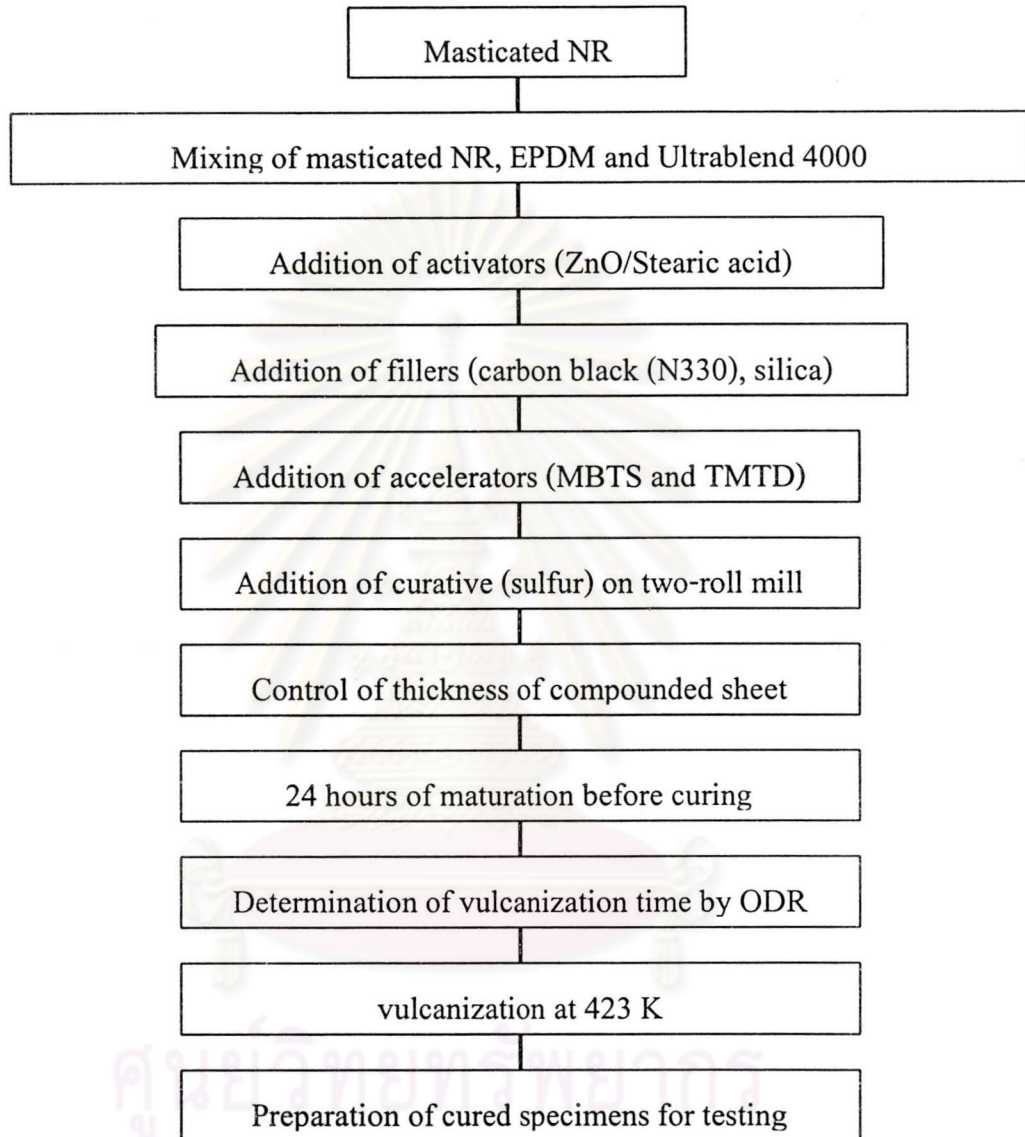


Figure 3.1 Flowchart of rubber compounding/composition

3.2.3 Determination of the vulcanization characteristics of compounded rubber

The oscillating disk rheometer (ODR) was utilized to determine the vulcanization time of compounded rubbers. The temperature was set at 423 K, the

testing time of 20 min and the rotational amplitude of 3° , according to ASTM D2084-95. The compounded rubbers were tested under pressure in the die cavity located in the electrically heated plates. The cavity was formed by a fixed lower die and a movable upper die. The ODR maintained a contact with the specimen till the cure reaction.

3.2.4 Preparation of blend compounds

The rubber masterbatch was compounded with the ingredients e.g. homogenizing agent, activators, fillers and accelerators using the internal mixer. The temperature of mixing was 363-393 K. Then curatives were added on a two-roll mill to protect scorch of the compound [23]. The important parameters under study are as follows:-

3.2.4.1 Effect of carbon black concentration on electrical properties of rubber compounds/blends.

This study concentrates on electrical conductivity of the rubber blends by the addition of carbon black. The formulations used are shown in Table 3.2.

3.2.4.2 Effect of homogenizing agent (Ultrablend 4000) concentration on the compatibility of NR/EPDM blends

The homogenizing agent (Ultrablend 4000) was used to improve the blend homogeneity. It is a low molecular-weight polymeric resin blends and has compatible components with aliphatic, naphthenic or aromatic parts of the rubber. Besides, Ultrablend 4000 can function as a processing aid, thus the effects of homogeneity and physical properties on the final products were studied. The formulation of NR/EPDM blends with Ultrablend 4000 concentration is given in Table 3.3.

Table 3.2 Recipe of rubber compounds/blends in the presence of carbon black (N330) in NR/EPDM blends

Compound ingredients (phr)	NEC0	NEC3	NEC5	NEC7	NEC10	NEC20	NEC30
NR	70	70	70	70	70	70	70
EPDM	30	30	30	30	30	30	30
Ultrablend 4000	5	5	5	5	5	5	5
ZnO	5	5	5	5	5	5	5
Stearic Acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Carbon Black (N330)	0	3	5	7	10	20	30
MBTS	1	1	1	1	1	1	1
TMTD	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Sulfur	2	2	2	2	2	2	2

Table 3.3 Recipe of NR/EPDM blends in the presence of Ultrablend 4000

Compound Ingredients (phr)	NEH0	NEH3	NEH5	NEH7
NR	70	70	70	70
EPDM	30	30	30	30
Ultrablend 4000	0	3	5	7
ZnO	5	5	5	5
Stearic Acid	1.5	1.5	1.5	1.5
Carbon Black (N330)	3	3	3	3
MBTS	1	1	1	1
TMTD	0.3	0.3	0.3	0.3
Sulfur	2	2	2	2

The result of tensile properties obtained from the recipes of NR/EPDM blend in Table 3.3 was not so satisfactorily because tensile strength decreased after ageing. Addition of reinforcing silica was thus necessary, as shown in Table 3.4.

Table 3.4 Recipes of NR/EPDM blends containing fillers (carbon black and silica)

Compound Ingredients (phr)	NEC3	NES30	NEC3S30
NR	70	70	70
EPDM	30	30	30
Ultrablend 4000	5	5	5
ZnO	5	5	5
Stearic Acid	1.5	1.5	1.5
Carbon Black (N330)	3	-	3
Silica	-	30	30
PEG	-	1	1
EF44	-	1	1
MBTS	1	1	1
TMTD	0.3	0.3	0.3
Sulfur	2	2	2

3.2.4.3 Effect of NR/EPDM ratios on ozone resistance

In order to study the effect of NR/EPDM blend ratios in the presence of Ultrablend 4000 and silica on properties required, Table 3.5 shows the varied concentrations of both NR/EPDM and Ultrablend 4000 in each formulation.

Table 3.5 Recipes of NR/EPDM blend ratios and Ultrablend 4000

Compound ingredients (phr)	NS	N8E2S	N7E3S	N6E4S	ES
NR	100	80	70	60	-
EPDM	-	20	30	40	100
Ultrablend 4000	0	5	5	5	0
ZnO	5	5	5	5	5
Stearic Acid	1.5	1.5	1.5	1.5	1.5
Carbon Black (N330)	3	3	3	3	3
Silica	30	30	30	30	30
PEG	1	1	1	1	3
EF44	1	1	1	1	1
MBTS	1	1	1	1	1
TMTD	0.3	0.3	0.3	0.3	0.3
Sulfur	2	2	2	2	2

3.3 Testing of electrical properties of the blends

3.3.1 Volume resistivity and surface resistivity

A standard size specimen, according to ASTM D 257-99, was placed between two electrodes. A voltage of 500 Volts is applied for 60 s and the resistance was measured. Surface or volume resistivity was then calculated. Surface resistivity is expressed in ohms (per square) and volume resistivity is expressed in ohms cm. The connection of volume and surface resistivity measurements is shown in Figure 3.2. Volume resistivity, that is electrical resistivity, was also measured by the method as described in ASTM D 991-89.

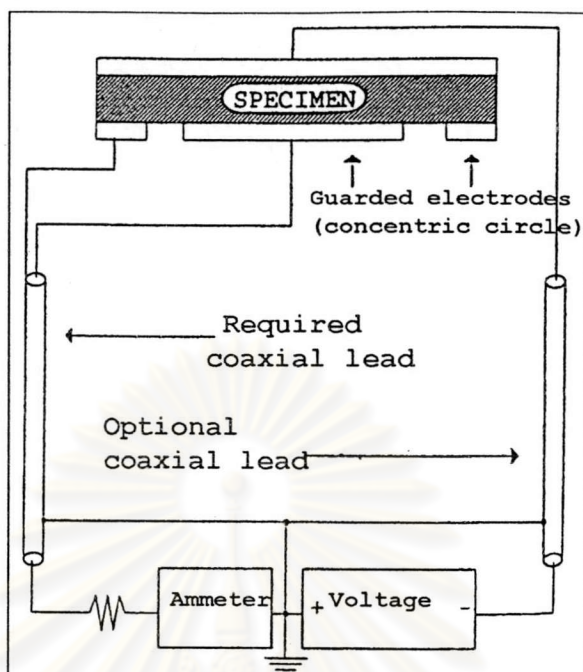


Figure 3.2 Connections to guarded electrodes for volume and surface resistivity measurements

3.3.2 Dielectric strength

In this study, the test method applied by the maximum voltage required is 10 kVac for 1 min. It is the TOT's specification [4]. The voltage was applied across the two electrodes and raised from 0 to 10 kVac at a uniform rate. A breakdown was observed when an electrical burn-through punctured the sample, or decomposition occurred in the specimen. If it did not cause any damage to the specimen, it implied that the specimen could withstand the voltage applied. The specimen size for this test was a 4-in plaque or somewhat larger. Although any specimen thickness could be used, the most common thickness used was usually between 0.8 to 3.2 mm (0.032 to 0.125 in), according to ASTM D 149-97.

3.4 Determination of the NR/EPDM compatibility

3.4.1 Thermal analysis by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA)

3.4.1.1 Differential scanning calorimetry (DSC)

A sample of 8 to 10 mg in an aluminum sample pan was placed into the differential scanning calorimeter. The sample was cooled at a controlled rate of 10 K min⁻¹ and the temperature from 173 to 273 K. A plot of heat flow versus temperature was produced. The resulting thermogram was then analyzed.

3.4.1.2 Dynamic mechanical thermal analysis (DMTA)

The sample size for the usual flexural test mode is 1 x 10 x 40 mm; slightly less sample is required in the parallel plate shear mode. The sample was cooled at a controlled rate of 5 K min⁻¹, frequencies from 1.66 to 3.33 Hz, and the temperature from 173 to 293 K. Thermograms are plotted to show elastic modulus, E', and tanδ versus temperature. The T_g of sample can discriminatory measure by the peak of the tanδ.

3.4.2 Scanning electron microscopy

A JSM-5800LV scanning electron microscope was used to observe blend morphology of vulcanized rubber in this study. The sample was prepared by staining with osmium tetroxide, which reacted with unsaturated carbon-carbon bonds. Then the sample was placed on the stub by double-sided sticky tape and was coated by sputtering of carbon or other conductive material such as gold to provide an electrically conductive layer, to suppress surface charges, to minimize radiation damage and to increase electron emission.

3.4.3 Capillary rheometry

The blend compatibility of NR/EPDM blends was studied through the capillary and dynamic flow of a Rosand single bore capillary rheometer. Testing conditions were carried out at a wide range of shear rates ($10\text{-}1500\text{ s}^{-1}$) at 373 K [24]. The capillary die used was 2 mm diameter and 32 mm length.

3.4.4 Pulsed nuclear magnetic resonance (Pulsed NMR)

Pulsed NMR equipment was manufactured by Bruker and the model was PC-20 (resonance frequency for proton being 20 MHz). The NMR measurement is done under the control of a microcomputer incorporating software. The sample (30-50 mg) was dissolved in solvent and transferred into an NMR sample tube. Then the sample tube was set in an NMR sample holder, and a real-time measurement was started. After the measurement, data were analyzed with a microcomputer by a nonlinear least squares fitting method.

A block diagram of a real-time pulsed NMR measurement system is given in Figure 3.3 [25]. The H signal of NMR was fed into the signal averager and averaged for certain times to increase the signal-to-noise ratio if necessary. The temporal changes of both the fraction and the spin-spin relaxation time T_2 signals from the solid echo and spin echo method were obtained. From this information, the degree of heterogeneity from the difference in mobility of polymer can be obtained.

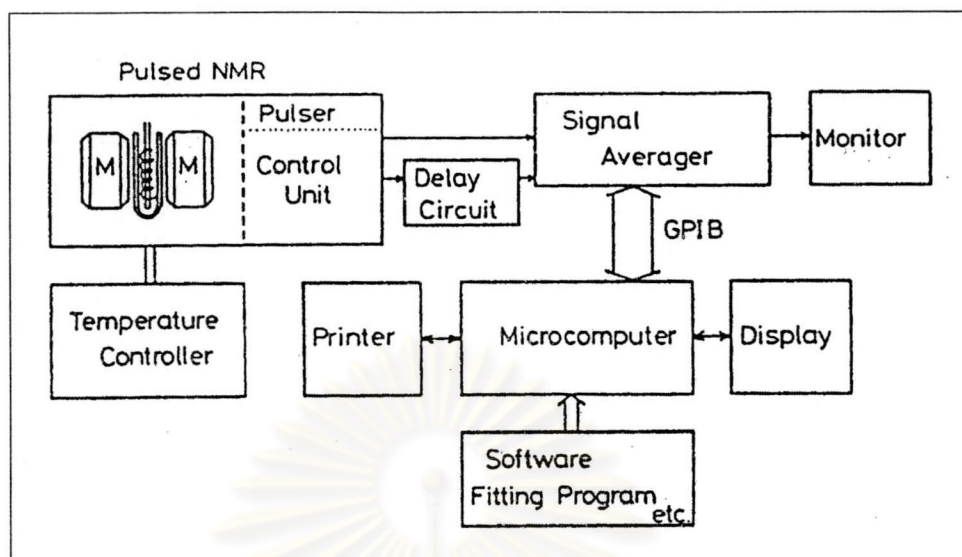


Figure 3.3 Block diagram of the real-time pulsed NMR measurement system controlled by a microcomputer

3.5 Mechanical testing

Mechanical properties of the vulcanized rubbers, i.e., tensile strength, hardness, tear resistance, before and after ageing were measured according to ASTM and ISO test methods.

3.5.1 Tensile properties

Tensile strength, tensile modulus and elongation at break of specimen were measured in a universal testing machine (Lloyd LR5K). Dumbbell specimen is required (die C) as shown in Figure 3.4, according to ASTM D 412-87. The specimens were placed in the grips at a specified grip separation and pulled until failure. Six specimens were required for each measurement. The test speed of 400 mm min^{-1} was for measuring strength and elongation, and 1 mm min^{-1} was for measuring modulus.

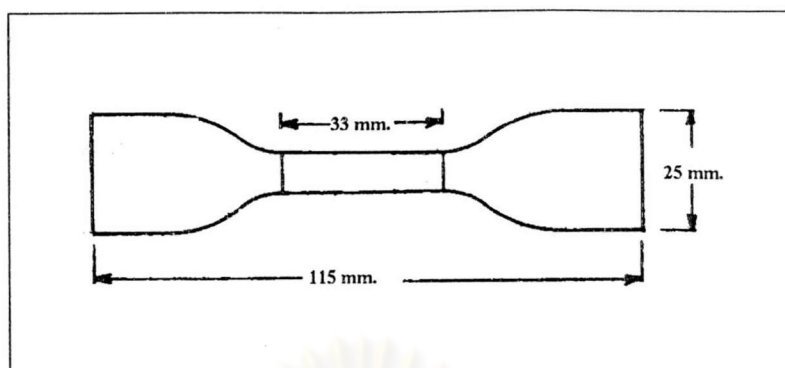


Figure 3.4 Dumbbell shape specimen for tensile property testing

3.5.2 Hardness measurement

A standard specimen of 6.4 mm (0.25 in) thickness was either molded or cut from a sheet, according to ASTM D 2240-97 with Shore A scale. A standard specimen was placed on the surface of the Rockwell Hardness tester. A minor load is applied and the gauge was set to zero. The major load was applied by tripping a lever. After 15 s, the major load was removed. The specimen was allowed to recover for 15 s and then the hardness was read off from the dial with the minor load was still applied.

3.5.3 Tear resistance

The specimen was die cut to the appropriate shape (Die C) from a sheet (see Figure 3.5), according to ASTM D 624-81. The specimen was then placed in the grips of the testing machine and pulled at a rate of 500 mm min^{-1} until rupture. The resistance was measured in Newtons.

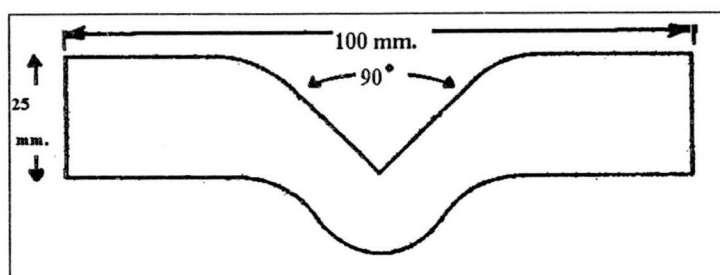


Figure 3.5 Angle shaped specimen for tear resistance testing

3.6 Ageing tests

3.6.1 Thermal ageing

In this study the specimen was tested in an air oven, at 373 K for 22 h, according to ISO 188 standard or ASTM D 573-99.

The results of the ageing test was expressed as a percentage of the change in each physical property and calculated as follows:

$$P = [(A-O)/O] \times 100$$

where P = percentage change in property,

O = original value,

A = value after ageing.

3.6.2. Ozone resistance test

The strip specimen size was 10x40x2 mm. Then the specimen was stretched up to 20% elongation and it was hung in a controlled chamber at 313 K, the ozone concentration at 50 ppm and was left for 72 h, according to ASTM D 1149-99. Crackings on the specimen surface were then examined.