



CHAPTER 3

APPARATUS AND EXPERIMENTAL METHOD

3.1 Reagent and materials

3.1.1 Poly(vinyl chloride)

(Thai Plastic & Chemical Co.,Ltd.)

PVC resin (Type 102)

K-value	58
Bulk density	0.54
% volatile matter	0.50 max.
Polymerization degree(P)	720

3.1.2 Acrylonitrile butadiene rubber in bale forms

(Japan Synthetic rubber Co.,Ltd.)

	N220SH	N220S
Bound Acrylonitrile(%)	40	40
Mooney Viscosity ML(1+4), 100°C	80	56
Polymerization temperature	Cold	Cold
Stabilizer	Non-staining	Non-staining
Specific gravity	1.00	1.00

3.1.3 Chemigum P83

(Goodyear Chemical Co.,Ltd.)

Typical properties

Acrylonitrile:	33 %
Mooney viscosity:	36 to 50
Crosslinked:	Yes
Polymerization temp.:	Cold
Volatiles,wt-%:	1.2
Base polymer:	Acrylonitrile butadiene copolymer
Physical form:	free flowing powder
Particle size:	98 % through 1 mm. screen
Partitioning agent:	PVC 9 phr.

3.1.4 Di(2-ethylhexyl) phthalate(DOP) plasticizer

(Thai Plastic & Chemical Co.,Ltd.)

3.1.5 Ba/Zn stabilizer

(Thai Plastic & Chemical Co.,Ltd.)

3.1.6 Lubricants and co-stabilizer Calcium stearate and stearic acid are used in PVC compounds

3.1.8 Vulcanizing agent Sulfur

3.1.9 Accelerators Three types of accelerators were used

(Monsanto Industrial Chemicals Co.)

- Thiuram sulphides: TMTM(Tetramethyl Thiuram Monosulphide)

- Thiazoles: MBTS(Dibenzthiazyl disulphide)
- Sulphenamides: CBS(N-Cyclohexylbenzthiazylsulphenamide)

3.1.10 Zinc active (Seido Chemical Industry Co., Ltd.)

3.1.11 BHT (3,5-Di-tert-butyl-hydroxy-toluene)
(Sumitomo Chemical Co.,Ltd.)

3.1.12 CaCO₃ (Surint Omyalite ZT)
(Surint Omya Chemicals (Thailand) Co., Ltd.)

Typical chemical analysis

CaCO ₃	98.50 %
and others(MgCO ₃ ,Al ₂ O ₃ ,SiO ₂ ,Fe ₂ O ₃)	1.50 %

Physical properties

Specific gravity	2.70
Moisture content	0.15 % max
Bulk density	1.20 g/cc.

Particle size distribution

Mean Particle size	2.50 micron
Specific surface area (BET method)	5.00 ± 0.5 m ² /g

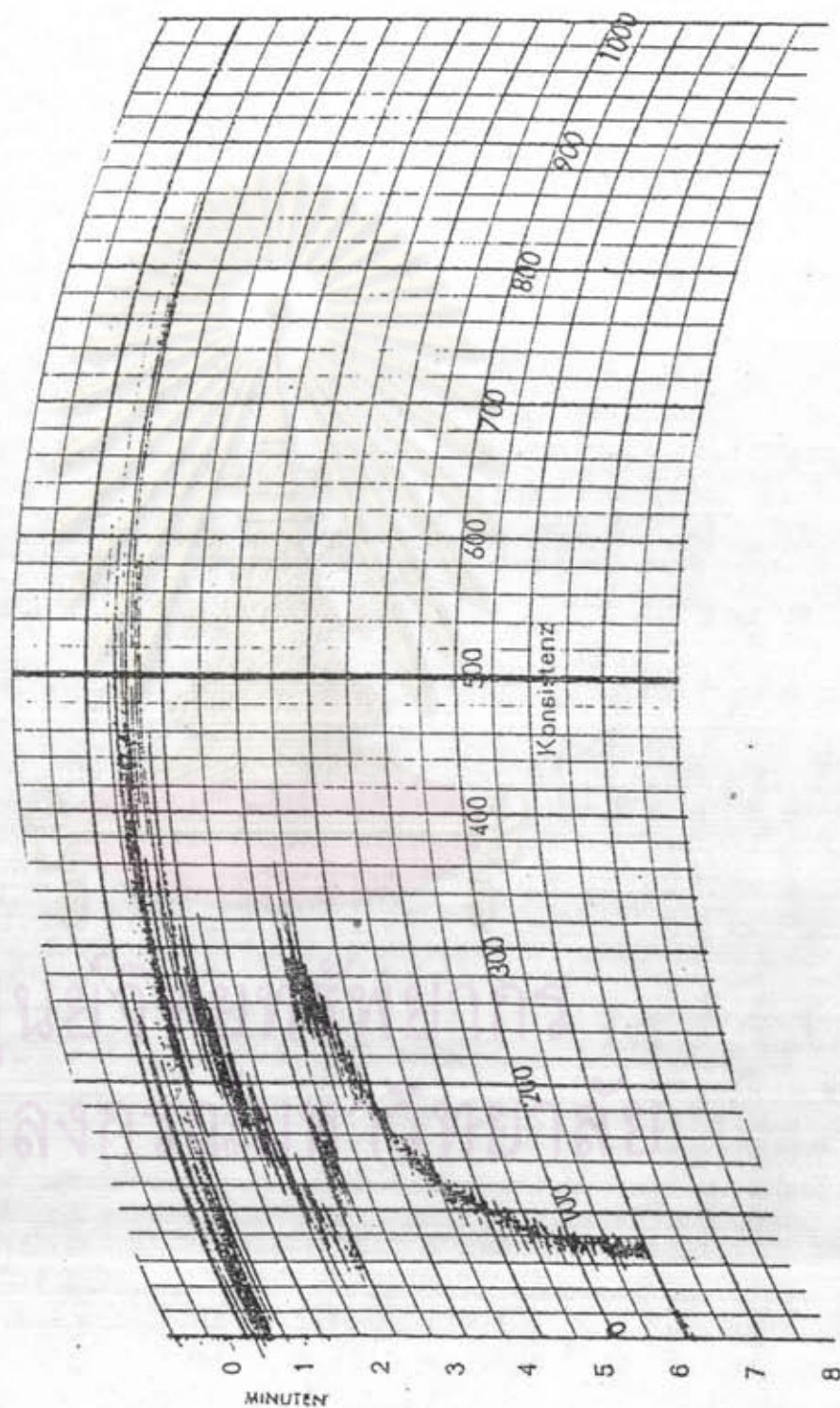


Figure 3.4 Torque curve of PVC/nitrile rubber blends mixed in Brabender Plasticorder.

3.1.13 Carbon black(N220, ISAF)

(Thai Carbon Black Co.,Ltd.)

Specific surface area	115 m ² /g
Range of particle size	20-25 nanometer[8]

3.1.14 Silica (Purosil UR grade)

(Pornpat Chemicals Co.,Ltd.)

SiO ₂ (%)	98
Fe ₂ O ₃ (%)	0.03
Na ₂ O (%)	1
Bulk density	0.22 ± 0.02
pH	6.5 ± 0.5
Specific surface area (BET method)	180 ± 20 m ² /g

3.1.15 Toluene Analytical grade3.1.16 Iso-octane Analytical grade3.2 Apparatus

- 3.2.1 Prodex-Henschel high-intensity mixer model LMX 10 DC of Lab Tech Engineering Co.,Ltd (as shown in Figure 2.4).
- 3.2.2 Two-rolls mill model-LRM110 of Lab Tech Engineering Co.,Ltd.
- 3.2.3 Brabender Plasticorder having the Cam Measuring Head from Duisburg in Germany (as shown in Figure 2.5(a),(b)).

- 3.2.4 Two-rolls mill diameter 12 inches of Stewart Bolling Co.
- 3.2.5 Hot compression model LP20 of Lab Tech Engineering Co.,Ltd.(as illustrated in Figure 3.1)
- 3.2.6 Micrometer
- 3.2.7 Tensile testing machine model S-100-C of Shimadzu Co., Ltd.
- 3.2.8 Oscillating disk rheometer(ODR.) of Monsanto Co., Ltd.
- 3.2.9 Durometer type A
- 3.2.10 Pycnometer 100 ml.
- 3.2.11 Abrasion tester(DIN 53 516) of Zwick Co.(as illustrated in Figure 3.2)
- 3.2.12 Transmission electron microscope model JEM-200 CX of Jeol Co.
- 3.2.13 Scanning electron microscope model JSM-35 CF of Jeol Co.
- 3.2.14 Polarized microscope model AFX 2 of Nikkon Co.,Ltd.
- 3.2.15 Differential scanning calorimeter model DSC 92 of Setaram Co.

3.3 Sample preparation

The samples were prepared by 4 main steps;

3.3.1) Dry blending of PVC compounds: Prodex-Henschel high-intensity mixer was used for blending. The raw materials were PVC resin, Calcium 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 increased to 80°C (the temperature slightly increased).

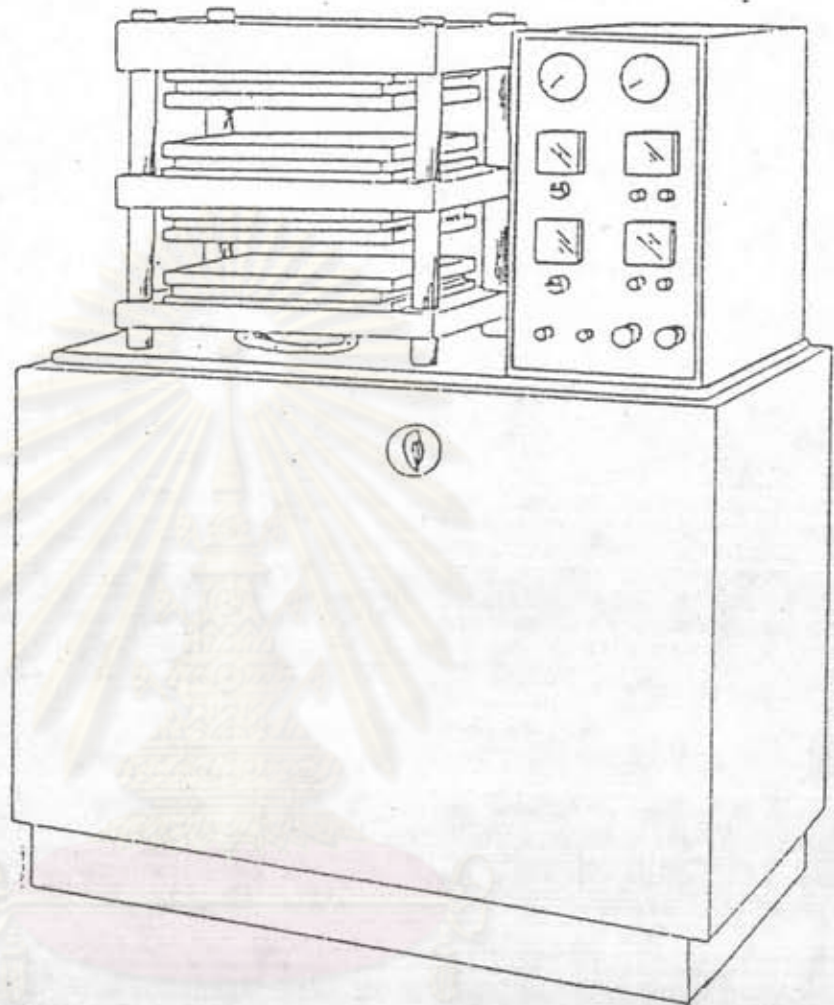


Figure 3.1 Hot compression model LP20.

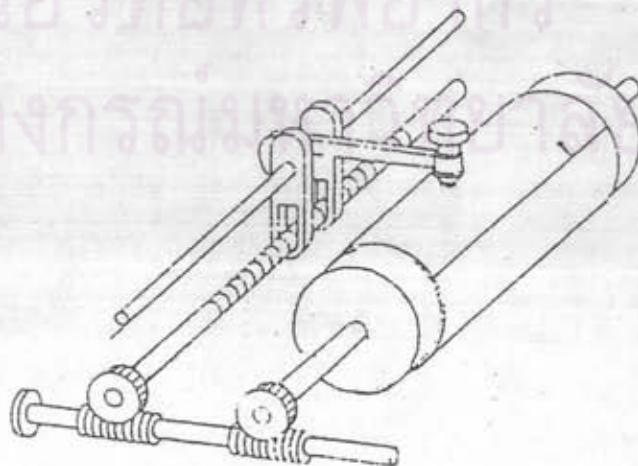


Figure 3.2 Abrasion tester.

Then, DOP plasticizer was mixed into the materials by the mixer. The temperature of mixer must be controlled in the range of 80-84°C (above the glass temperature but below the fusion temperature), the mixing time was 3-5 minutes because plasticizer was absorbed by PVC resin (all of compounded materials were not wet). After mixing 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
Ba-Zn stabilizer	3	phr
Epoxidized soybean oil	3	phr
Calcium stearate	0.5	phr
Stearic acid	0.5	phr
DOP plasticizer	40	phr

3.3.2) Two-rolls mill process: The PVC compound from dry blending (the first step) was melt and mixed on two-rolls mill at 150°C on front roll and back roll for 9 minutes of mixing time and the thickness of PVC sheet was controlled at 1 mm. The sheet was cooled down by an air blower or electric fan and was removed afterwards from the two-rolls mill.

3.3.3) The mixing in a Brabender Plasticorder: The steps of mixing are as follows:

A) Nitrile rubber compounding

The temperature for rubber compounding with ingredients of vulcanization system was lower than plastic processing temperature. Thus, the temperature for rubber compounding was at 100°C (If the temperature was too low, the torque curve would be too high). First, the rubber was charged into the Brabender chamber. Then, the activators (zinc active and stearic acid) and antioxidant(BHT) were added at the same time. Finally, the vulcanizing agent (sulphur) and accelerators (TMTM for recipe 1 or CBS, MBTS, TMTM for recipe 2) were added. The torque curve is illustrated in Figure 3.3

Recipes of rubber compounding:

Recipe 1

Nitrile rubber(grade N220S)	100.0	phr
Zinc active	5.0	phr
Stearic acid	1.0	phr
BHT	2.0	phr
TMTM	1.5	phr
Sulfur	1.5	phr

Recipe 2

Nitrile rubber(grade N220S)	100.0	phr
Zinc active	5.0	phr
Stearic acid	1.0	phr
BHT	2.0	phr
CBS	0.8	phr
MBTS	0.5	phr
TMTM	0.2	phr
Sulfur	1.2	phr

Note: Four steps of rubber compounding are as follows:

- at 0 minute - Transferred the rubber to Brabender chamber.
- at 3rd minute - Added the activators and antioxidants.
- at 6th minute - Added the vulcanizing agent and accelerators.
- at 8th minute - Removed the compounded rubber and transfer to a two-rolls mill to make a 1 mm thickness sheet.(Run 3 rounds of two-rolls mill)

B) PVC and nitrile rubber blends

First, the chamber of Brabender was heated to 160°C and maintained at this temperature. The PVC sheets from the two-rolls mill process were cut into small sheets (the size was about 1 x 2 inch). The nitrile rubber was masticated or compounded by Brabender Plasticorder, and formed sheets by the two-rolls mill. The nitrile rubber sheets were cut into small sheets as well. Then, the PVC sheets and the nitrile rubber sheets were weighed (depending on the PVC and nitrile rubber blends composition). Then, the PVC sheets

were fed to the Brabender with a rotor speed of 20 rpm for 2 minutes. Finally, the nitrile rubber sheets were added and blended at a rotor speed of 60 rpm for 4 minutes. The torque curve is illustrated in Figure 3.4.

Note: Steps of blending are as follows:

- at 0 minute - Transferred the PVC sheets to the Brabender chamber.
- at 2nd minute - Added the rubber sheets (either uncompounded rubber or compounded rubber)
- at 3rd minute - Added the filler (for 45 parts of fillers)
- at 6th minute - Removed the polymer blends from the mixer and transferred to the two-rolls mill for making a 1 mm thickness sheet (run 1 round of two-rolls mill)

PVC and nitrile rubber compositions in polymer blends were based on PVC resin and nitrile rubber. The compositions of polymer blends (no filler) were as follows:

PVC:NBR(N220SH)	80:20, 60:40, 40:60, 20:80
PVC:NBR(N220S)	80:20, 60:40, 40:60, 20:80
PVC:NBR(P83)	80:20, 60:40, 40:60, 20:80
PVC:NBR(Recipe1)	80:20, 60:40, 40:60, 20:80
PVC:NBR(Recipe2)	80:20, 60:40, 40:60, 20:80

For compositions of filler polymer blends, the filler was added 45 parts per hundred parts of polymer blends. Nitrile rubber used in this case was N220S type of compounded rubber (Recipe2).

PVC and NBR(N220S, Recipe2) ratios varied from 80:20, 60:40, 40:60 to 20:80. Polymer blend-to-filler ratio was constant at 100:45 and filler types were CaCO_3 , carbon black, silica and mixed fillers (mixed fillers were carbon black filler:silica filler = 30:15).

3.3.4) Hot compression: The molded specimens were prepared in the compression molding. The temperature, pressure and time were important. In this study, the temperature was 160°C and pressure depending on time was:

- at 0 minute - Preheated at 42.5 kg/cm^2
- at 2nd minute - Heated at 120.0 kg/cm^2
- at 8th minute - Cooled at 98.0 kg/cm^2 by cooling water
- at 12th minute - Removed the samples from the mould

3.4 Hardness test (ASTM D2240)

The hardness property of the specimen was measured by type A Shore durometer(used for the soft samples). The thickness of specimen was 6 mm minimum value. The indenter of durometer was pressed on sample surface for 3 seconds and read the hardness value.

3.5 Mechanical tests

3.5.1) Tensile test (ASTM D412)

Specimen was Die C as illustrated in Figure 3.5. The crosshead speed of universal testing machine at 100 mm/min was used. The test condition was at $27 \pm 2^\circ\text{C}$. An average of five specimens

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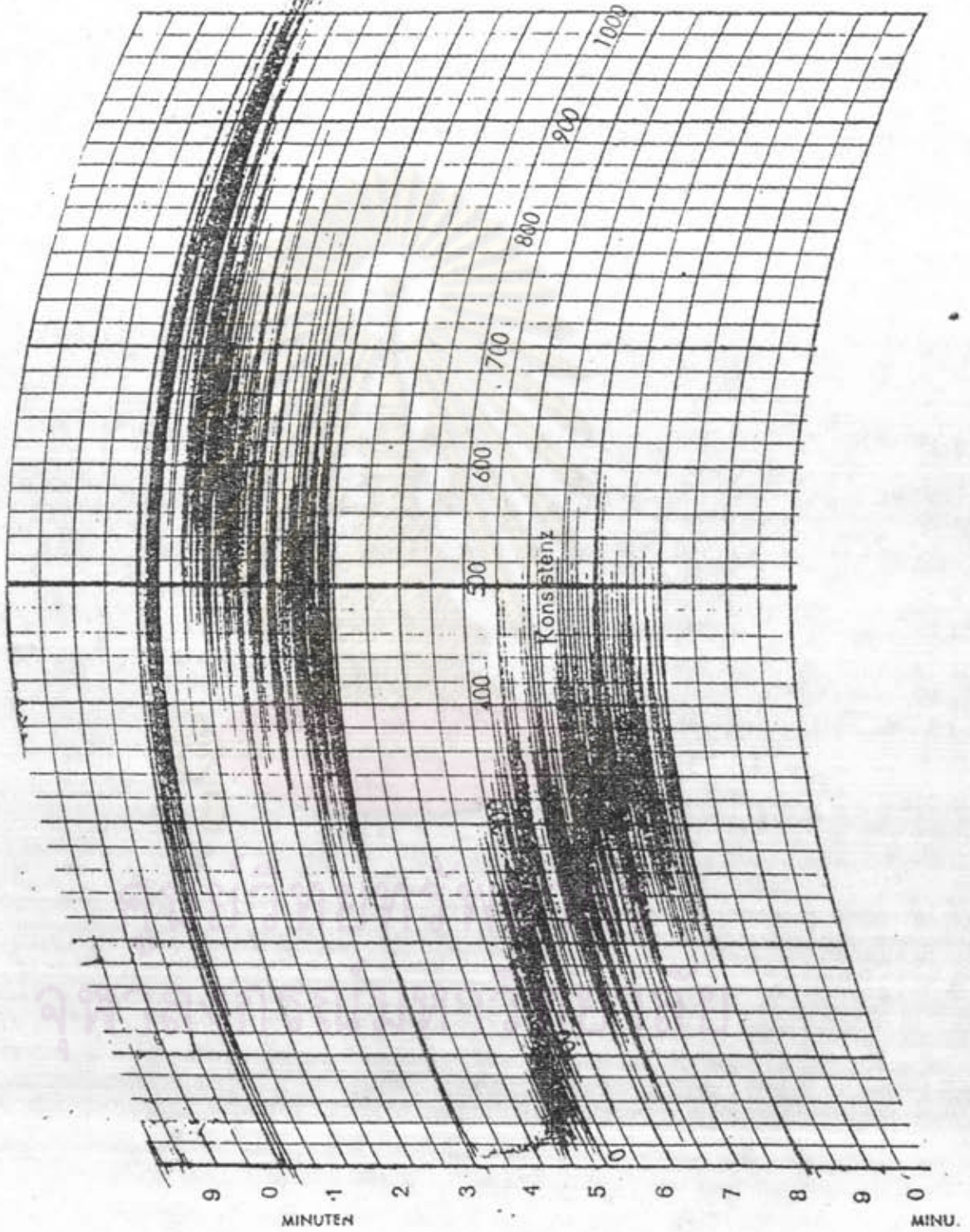


Figure 3.3 Torque curve of nitrile rubber compounding mixed in Brabender Plasticorder.

was considered as representative value. The gage length was 2.50 cm and the thickness of specimen was 2 mm.

$$\text{Tensile stress} = F/A$$

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

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

$$\text{Tensile stress} = \text{N/m}^2\text{(Pascal) or MPa(1 MPa = } 10^6 \text{ Pascal)}$$

Tensile at break is tensile stress at which the specimen ruptures.

$$\text{Modulus at 100 \% elongation} = F_1/A$$

$$\text{Modulus at 300 \% elongation} = F_3/A$$

$$F_1 = \text{Tensile force at 100 \% elongation (N)}$$

$$F_3 = \text{Tensile force at 300 \% elongation (N)}$$

3.5.2) Tear test (ASTM D624)

Dimension and shape of specimen was die C cut followed to Figure 3.6. A crosshead speed of the universal testing machine at 500 ± 50 mm/min was used. The test temperature was at 27 ± 2 °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:

$$T_s = F/d$$

$$T_s = \text{tear resistance (kN/m or N/mm)}$$

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

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

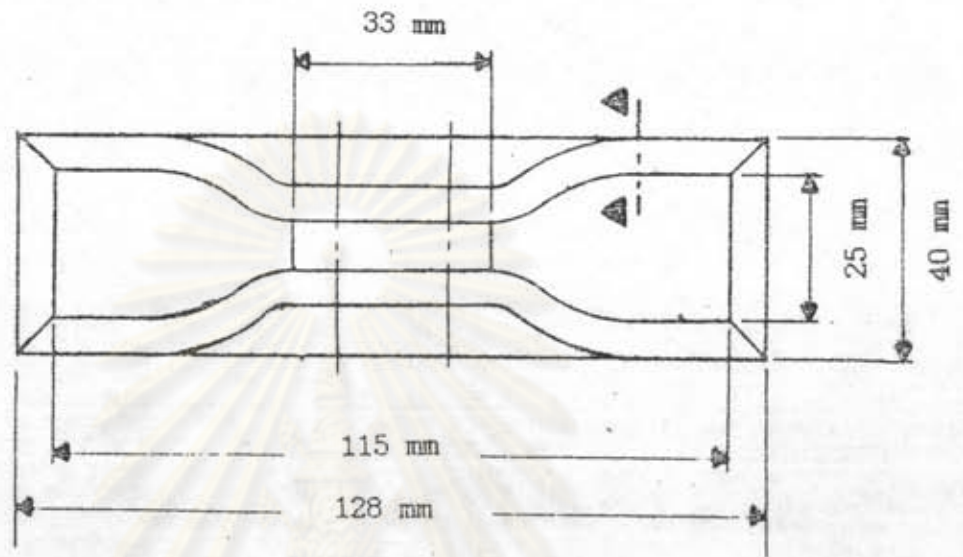


Figure 3.5 Tensile specimen Die C.

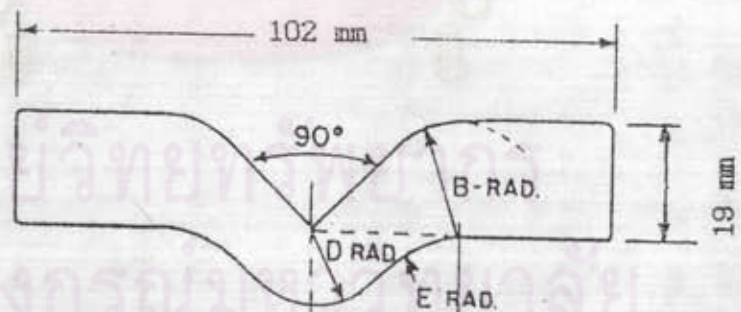


Figure 3.6 Tear specimen Die C.

3.6 Oil resistance test (ASTM D471)

This test method measured the comparative ability of rubber and rubber-like compositions 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 Abrasion resistance test (DIN 53516)

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 test is volume loss (V in mm^3) determined under the conditions for this method of a cylindrical test specimen drawn across a test emery paper of defined abrasive power and with a defined force of application and through a defined distance. The abrasive power S of a sheet of emery paper is the loss of mass in mg of a standardized test specimen of a comparative elastomer drawn across it under the test conditions.

The test specimens are cylindrical shape of 16 ± 0.2 mm

diameter and at least 6 mm thickness. A cylindrical test specimen is drawn across a test emery paper with corundum (diameter 150 ± 0.2 mm) of 60 grade at a constant application force of 10 N and at a constant speed of 0.33 m/sec and a rotational speed of 40 ± 1 rpm (Figure 3.2), the abrasion distance being 40 m or in a special case 20 m. An abrasive power in the range from 170 mg to 220 mg is allowable. The loss of mass of the test specimen in mg by weighing and its volume loss calculated on the basis of the specific gravity were determined.

The abrasion is referred to a nominal abrasive power of the test emery paper of 200 mg per 40 m abrasion distance and calculated as a loss of volume from the following equation:

$$V = \frac{m \cdot S_0}{\rho \cdot S}$$

Wherein

V = Abrasion (volume loss in mm^3)

m = Mass loss in mg

ρ = Density in mg/mm^3

S_0 = Value of nominal abrasive power (200 mg)

S = Average abrasive power in mg

3.8 Specific gravity measurements

The apparatus of this measurement is pycnometer (100 ml). The specific gravity can be measured by the following equation:

$$\text{Specific gravity of specimen} = M \times D / [W_1 - (W_2 - M)]$$

- M = mass of specimen (g)
- W1 = mass of pycnometer plus pure water
(volume of water=100 ml)
- W2 = mass of pycnometer plus pure water plus mass of specimen
(volume of water less than 100 ml because of the replacement of specimen volume)
- D = Density of pure water at room temperature (1 g/cm^3)

3.9 Oscillating disk rheometer test (ODR test)

The ODR test can determine the scorch time, cure time (or vulcanization time) and cure rate by plotting the torque curve versus time. The scorch time was measured when the torque curve increased from the minimum torque in two units (such as 2 lb-in). The cure time was measured when the torque curve increased from the minimum torque in 90 percent of the difference between maximum torque and minimum torque. The temperature was at 160°C .

3.10 Transmission electron microscopy (TEM)

A) TEM for PVC/nitrile rubber blends: the specimens were immersed into liquid nitrogen before cutting to ultrathin section. The thickness of thin layers was 100 nm. The thin layers were immersed into OsO_4 for one night and placed on the grid. The samples were viewed by TEM at x30,000 and x10,950 magnifications.

B) TEM for fillers: CaCO_3 filler, carbon black filler and silica filler were suspended in 95 % ethanol by ultrasonic machine for

10 minutes. Then, the samples were dropped on the grid and dried. They were viewed by TEM from x9,000 to x150,000 magnifications.

3.11 Scanning electron microscopy (SEM)

The specimen fracture surfaces were coated by gold and viewed by SEM at x1,000 and x1,500 magnifications.

3.12 Polarized microscopy

The specimens were compressed to thin layer (about 0.01 mm.) by hot compression. They were placed on slide glasses and viewed by polarized microscope at x100 magnifications.

3.13 Differential scanning calorimetry (DSC)

The samples were cooled down to -120°C by liquid nitrogen and heated up to 200°C . The heating rate was $10^{\circ}\text{C}/\text{min}$. The temperature, heat flow and differential heat flow were measured.

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