

# CHAPTER III

## EXPERIMENTAL

### 3.1 Experimental Scope

The influence of carbon black type and loading on reversion behavior and thermal aging properties of natural rubber (NR) were studied. Five types of carbon black were used including; N330, N550, N776, N990 and graphitized N330. For each carbon black, a series of five NR compounds containing 10 to 50 phr of carbon black was prepared using an internal mixer. Reversion behavior defined as a cure characteristic of rubber at the prolonged cure stage was studied using a moving die rheometer (MDR). Thermal aging properties were indicated by the relative tensile properties of the aged specimens with respect to the unaged specimens. The change of network during reversion and aging processes was followed by the degree of crosslink and the sulfur crosslink distribution. The overview of experiment procedure is given as a flow chart in Figure 3.1.

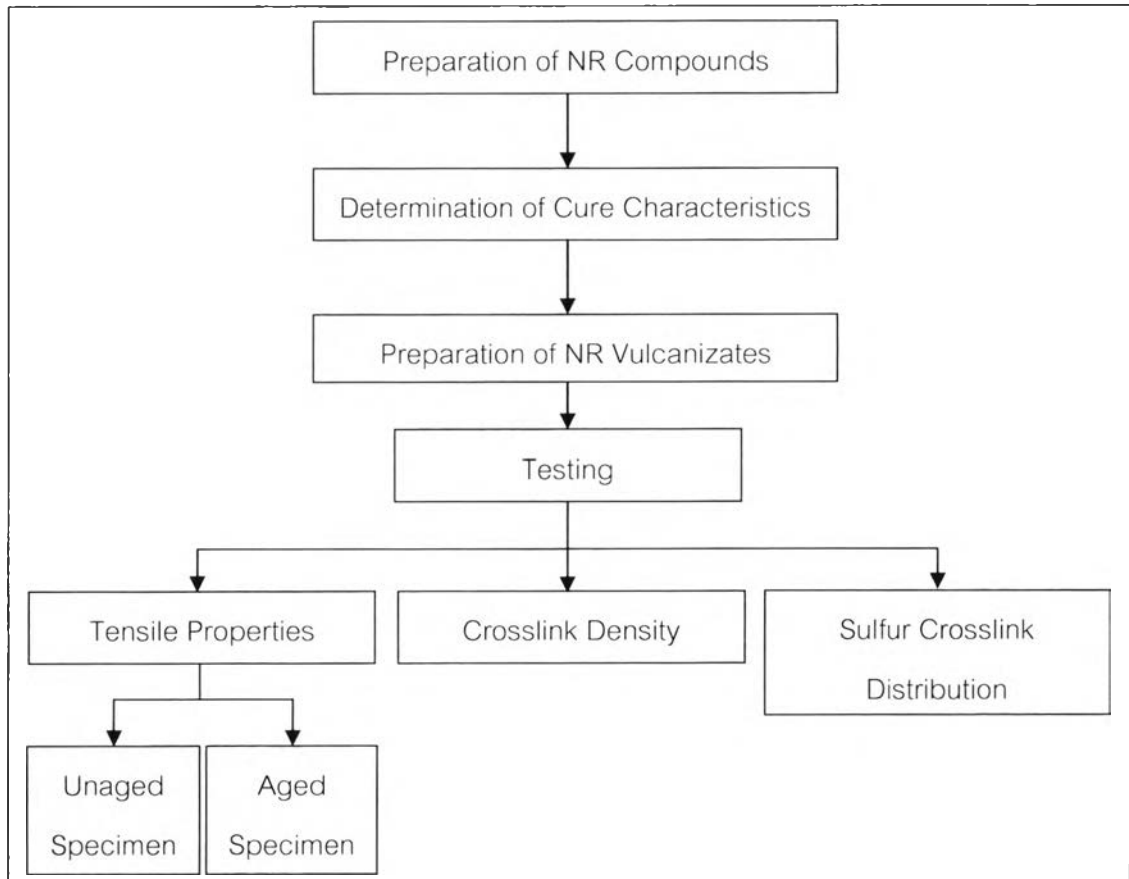


Figure 3.1 Flow chart of experimental procedure

### 3.2 Materials and Chemical Agents

A list of materials and chemical agents used in this present study is given in Table 3.1. The physical properties of carbon black used here including particle size, surface area indicated by BET N<sub>2</sub> adsorption value and filler structure indicated by di-butyl phthalate (DBP) absorption value are shown in Table 3.2.

**Table 3.1** Materials and Chemical Agents

Materials / Chemical Agents	Trade name/ Grade	Manufacturer / Distributor
Natural rubber (NR)	STR 5L	Sakdaroongreungkij Co.,Ltd., Thailand
Carbon black (CB)	N330	Sakdaroongreungkij Co.,Ltd., Thailand
	N550	Sakdaroongreungkij Co.,Ltd., Thailand
	N776	Thai Carbon Product Co.Ltd.,Thailand
	N990	Cancarb Co.Ltd.,Canada
Zinc oxide (ZnO)	Commercial	Sakdaroongreungkij Co.,Ltd., Thailand
Stearic acid	Commercial	Sakdaroongreungkij Co.,Ltd., Thailand
1,2-dihydro-2,2,4-trimethylquinoline (TMQ)	Commercial	Sakdaroongreungkij Co.,Ltd., Thailand
N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene diamine (6PPD)	Commercial	Sakdaroongreungkij Co.,Ltd., Thailand
N, N-dicyclohexyl-2-benzothiazole sulfenamide (DCBS)	Commercial	Sakdaroongreungkij Co.,Ltd., Thailand
Sulfur	Commercial	Sakdaroongreungkij Co.,Ltd., Thailand
Toluene	AR grade	RCI Labscan Limited

The physical properties of various carbon black types are given in Table 3.2, which BET N<sub>2</sub> adsorption value and di-butyl phthalate (DBP) absorption value were used to characterize the surface area and the filler structure, respectively.

**Table 3.2** Physical properties of different types of carbon black [53-55]

Carbon black	Particle size (nm)	BET (m <sup>2</sup> /g)	DBP adsorption(ml/100 g)
N330	26-30	76-80	102
N550	40-48	39-41	121
N776	61-100	28-32	72
N990	201-500	7-12	44

### 3.3 Instruments

All instruments used here are summarized in Table 3.3 with respect to these functions.

**Table 3.3** List of instruments used in the present study

Rubber compounder and shaper		
Instrument	Model	Manufacture / Location
Internal Mixer	MX500-D75L90	CHAREON TUT CO.,LTD
Laboratory Two-Roll Mill	LRM-S-110	Labtech
Compression Molding Machine	LP-S-50	Labtech
Cure characteristic tester		
Instrument	Model	Manufacture / Location
Moving Die Rheometer	A022S	CG ENGINEERING, LTD

Table 3.3 (continued)

Mechanical tester		
Instrument	Model	Manufacture / Location
Universal Testing Machine	5843	Labtech
Structure tester		
Instrument	Model	Manufacture / Location
X-ray Absorption Near Edge Structure Spectroscopy	Siam photon BL8	Synchrotron Light Research Institute (Public Organization)
Miscellaneous		
Instrument	Model	Manufacture / Location
Ageing Oven	UM 200	UNION TSL, LTD
X-ray Diffractometer	Philips PW 3710	Chulalongkorn University
Furnace	Haimaruchi 5000	Takado Electric

### 3.4 Formulation of NR Compounds

Formulation of NR compounds is given in Table 3.4. All compounds contained a common base composition of 100 phr NR, 8 phr ZnO, 1 phr stearic acid, TMQ and 6PPD, 2.25 phr DCBS and 2.63 phr sulfur. Carbon black including N330, N550, N776, N990 and gN330 (stand for graphitized N330) were used in this study. Carbon black loading was varied from 10 to 50 phr with the increment of 10 phr.

Table 3.4 Formulation of NR compounds

Materials	Part by weight (phr)
STR 5L	100
ZnO	8
Stearic acid	1
TMQ	1
6PPD	1
Carbon black	0,10, 20, 30, 40 and 50
DCBS	2.25
Sulfur	2.63

### 3.5 Mixing Procedure

NR compounds were prepared in a laboratory-size internal mixer as shown in Figure 3.2.



Figure 3.2 CHAREON TUT MX500-D75L90 Internal mixer

The mixing was divided into two steps. At first step, NR was first masticated for one minute. All ingredients, except the curatives, were mixed with NR in an internal mixer at a set temperature of 50°C with a rotor speed of 40 rpm and a fill factor of 0.7. The mixing sequence of these is shown in Table 3.4. The total mixing time was seven minutes. After discharging, the mixed NR compound was left at the room temperature until its temperature was equilibrated with the room temperature.

At second step, the mixed NR compound was loaded back into an internal mixer again and one minute later, the curatives (DCBS and sulfur) were added and mixed for three minutes. The mixing sequence of the second step is given in Table 3.5. Then the compound was taken out and placed onto a nip of a two roll mill as shown in Figure 3.3. Then, five end-roll passes were made before sheeting off. The rubber sheet was kept at least 24 hours at room temperature before the cure characterization step.

**Table 3.5** The mixing sequence in internal mixer

**Step I**

Step	Procedure	Time (min)
1	Load NR	0
2	Add ZnO, stearic acid, TMQ, 6PPD, carbon black	1-7
3	Dump	7

**Step II**

Step	Procedure	Time (min)
1	Load mixed NR compound	0
2	Add sulfur and DCBS	1-4
3	Dump	4



Figure 3.3 Labtech LRM-S-110 Two-roll mill

### 3.6 Determination of Cure Characteristics

The cure characteristics of NR compounds were determined at different temperatures of 130, 140, 150, 160, 170 and 180°C using a moving die rheometer (MDR) as shown in Figure 3.4 in according with ASTM D5289-95.



Figure 3.4 TECH PRO A022S Moving die rheometer

About 5 grams of uncured compound was placed between the heated parallel plates. The change in stiffness of rubber was measured by applied oscillating force. Figure 3.5 shows general feature of cure curve. The following parameters such as minimum torque ( $M_L$ ), maximum torque ( $M_H$ ), scorch time ( $ts_2$ ), 90% cure time ( $tc_{90}$ ) and 100% cure time ( $tc_{100}$ ) were recorded. The scorch time ( $ts_2$ ) was defined as the time in which the rheometer torque reaches two units from the minimum torque. The 90% of cure time ( $tc_{90}$ ) was defined as the time to reach 90% cure. The 100% of cure time ( $tc_{100}$ ) was defined as the time to reach maximum torque. Cure rate index (CRI), which is a measure of cure reaction rate [56], is given by:

$$CRI = \frac{100}{tc_{90} - ts_2} \quad (3.1)$$

The reversion behavior of NR can be observed from cure curve when torque decreases after reaching maximum. The characteristics of reversion behavior were described by two terms as shown in Figure 3.5. The first one was the region at which torque stayed constant after reaching maximum termed here as 'plateau region'. The second one was the slope of cure curve after torque started to decrease termed here as 'reversion rate'.

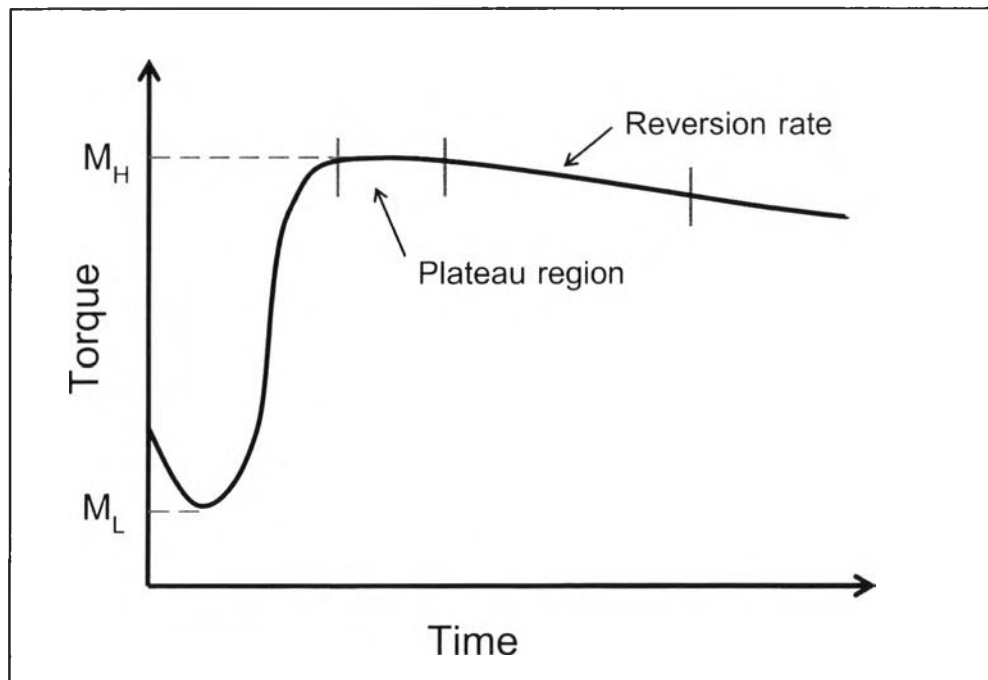


Figure 3.5 General feature of cure curve of NR



### 3.7 Preparation of NR Vulcanizates

The 2 mm thick NR vulcanizates were prepared at 160°C using a compression molding machine as shown in Figure 3.6 under pressure 50 Bar. To study the effect of reversion on the properties of NR vulcanizates, NR compounds were compressed with three different cure times including  $t_{c_{90}}$ ,  $t_{c_{100}}$  and  $t_{c_{100}}$  plus 20 minutes (defined as  $t_{c_{100+20 \text{ min}}}$ ). After compression, vulcanized rubber sheets were left at room temperature for 16 to 24 hours before testing.

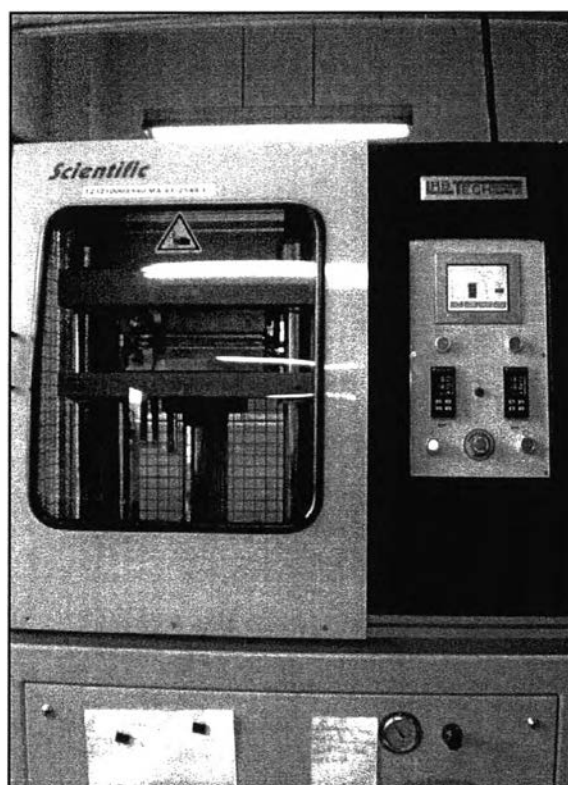


Figure 3.6 Labtech LP-S-50 Compression molding machine

### 3.8 Determination of Tensile Properties

Tensile properties of NR vulcanizates were measured according to ISO 37 using an Instron universal testing machine model 5843 at a crosshead speed of 500 mm/min with the load of 1 kN. Tensile dumb-bell specimens were cut from vulcanized rubber sheets using the type II die with the dimensions as shown in Figure 3.7. Thickness of specimens was measured. At least five specimens were tested and the average values were reported.



### 3.9 Determination of Thermal Aging Properties

To study the aging properties of rubber vulcanizates, dumb-bell specimens as shown in Figure 3.7 were placed in air circulating oven at 100°C for 72 hours. Then, the aged specimens were removed from the oven and cooled at ambient temperature for at least 16 hours before tensile testing. The tensile properties of the aged specimen were determined using the same condition as the unaged ones. At least five specimens for each compound were tested.

Relative tensile properties were calculated and used as an indicator for thermal aging resistance. Relative tensile properties including relative 100% modulus (relative M100), relative tensile strength (relative TS) and relative percent elongation at break (relative EB) were determined using the following equation:

$$\text{Relative M100} = \frac{M100_a}{M100_u} \quad (3.4)$$

where  $M100_a$  = 100% modulus of aged sample (MPa)

$M100_u$  = 100% modulus of unaged sample (MPa)

$$\text{Relative TS} = \frac{TS_a}{TS_u} \quad (3.5)$$

where  $TS_a$  = tensile strength of aged sample (MPa)

$TS_u$  = tensile strength of unaged sample (MPa)

$$\text{Relative EB} = \frac{EB_a}{EB_u} \quad (3.6)$$

where  $EB_a$  = elongation at break of aged sample (MPa)

$EB_u$  = elongation at break of unaged sample (MPa)

### 3.10 Determination of Network Structure of NR Vulcanizates

#### 3.10.1 Crosslink Density

The crosslink density can be determined from swelling measurement. The NR vulcanizates of 2 mm thickness, weighing approximately 0.2 g, were immersed in 50 ml of toluene. The samples were kept in the dark for 7 days at room temperature. After that the swollen samples were taken out. The samples were blotted with a paper and then transferred quickly to the weighing bottle to determine the weight. Swollen samples were air dried to constant weight at room temperature. The weight of dried sample was determined. At least three samples for each compound were measured. The crosslink density was calculated using the Flory and Rehner equation [58-59] as shown in equation 3.7:

$$-\ln(1 - V_r) - V_r - \chi V_r^2 = 2V_r \eta_{\text{swell}} V_t^{1/3} - \frac{2V_r}{f} \quad (3.7)$$

when

$$V_r = \frac{\left[ \frac{W_d}{\rho_d} - \frac{W_f}{\rho_f} \right]}{\left[ \frac{W_d}{\rho_d} - \frac{W_f}{\rho_f} \right] + \left[ \frac{W_s - W_d}{\rho_t} \right]}$$

- where
- $\rho_d$  = density of rubber ( $\text{g/cm}^3$ )
  - $\rho_f$  = density of carbon black  
( $1.8 \text{ g/cm}^3$  for N330, N550 and N774,  
 $1.7 \text{ g/cm}^3$  for N990)
  - $\rho_t$  = density of toluene ( $0.862 \text{ g/cm}^3$ )
  - $W_d$  = weight of dried sample (g)
  - $W_f$  = weight of carbon black in sample (g)
  - $W_s$  = weight of swollen sample (g)
  - $V_r$  = volume fraction of rubber in the swollen gel
  - $V_t$  = molar volume of toluene ( $106.2 \text{ cm}^3/\text{mol}$ )

- $\chi$  = rubber-solvent interaction parameter  
(0.39 for gun NR-toluene [60],  
0.42 for black filled NR-toluene [61])
- f = function of crosslink with sulfur  
vulcanization (4)
- $\eta_{\text{swell}}$  = number of moles of crosslink per unit  
volume ( $\text{mol}/\text{cm}^3$ )

### 3.10.2 Sulfur Crosslink Distribution

Figure 3.8 showed the Siam photon BL8 station. The sulfur crosslink distribution of unfilled and N330 filled NR vulcanizates was determined using X-ray absorption near edge structure (XANES) spectroscopic at the sulfur *K*-edge with synchrotron radiation by beamline 8 at Synchrotron Light Research Institute (Public Organization).

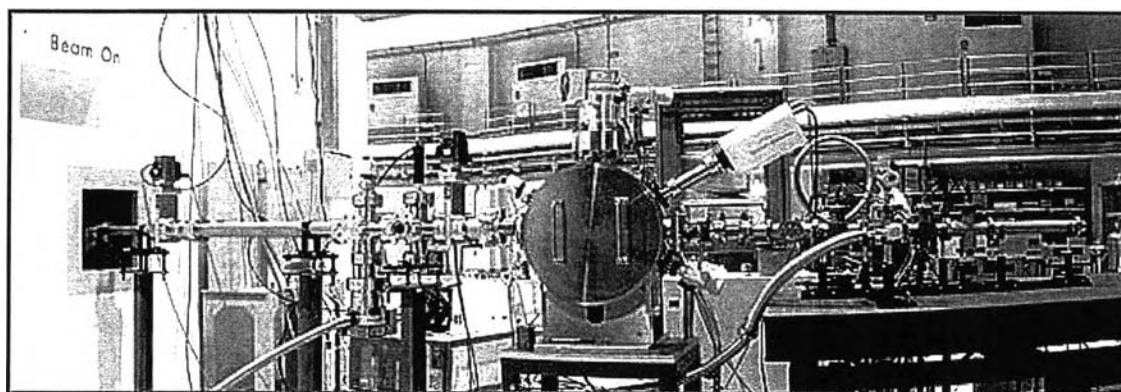


Figure 3.8 Siam photon BL8 X-ray absorption near edge structure spectroscopy

To prepare sample, NR compounds were compression molded at  $160^{\circ}\text{C}$  into NR films about  $200\ \mu\text{m}$  thick with different cure time as follow  $t_{c_{50}}$ ,  $t_{c_{60}}$ ,  $t_{c_{70}}$ ,  $t_{c_{80}}$ ,  $t_{c_{90}}$ ,  $t_{c_{100}}$  and  $t_{c_{100+20\ \text{min}}}$ .

Before XANES measurement, the residual sulfur/accelerator containing molecules on the samples were removed using 100 ml of chloroform for 24 hours. Afterwards, the treated sample was taken out and rinsed off with fresh chloroform two times. The treated sample was left at the room temperature until it completely dried. In

order to avoid any degradation that may influence on XANES spectrum around *K*-edge of sulfur due to the lack of antidegradant, the treated sample was freshly prepared no more than two days before the X-ray absorption measurement.

Each of samples was stuck to the sample holder which was 12 x 10 mm. Si(111) double crystal monochromator was selected for generating the photon energy. All XANES spectra around *K*-edge of sulfur were taken using two ionization chambers which were placed before and left-hand side of the sample. The first ionization chamber placing before the sample was filled with 37 mbar N<sub>2</sub> gas for the sulfur *K*-edge measurements. The sample chamber was filled with He gas and separated from the first ionization chamber using the polypropylene window. The second ionization chamber is Lytle detector or 5 Grid ionization detector which was placed on the left hand side of the sample. The white line of ferrous sulfate (FeSO<sub>4</sub>) was used for the calibration around sulfur *K*-edge absorption. Measurements were performed in Fluorescence mode. All of XANES spectra were averaged and normalized using IFEFFIT software version 1.2.11 [62].

### 3.11 Preparation of Graphitized Carbon Black

To study effect of surface activity of carbon black on reversion behavior, all functional groups at the carbon black surface were removed using high-temperature treatment (graphitization). N330 was treated at 1700°C under nitrogen atmosphere for 10 hours.

The change in crystallinity of carbon black after graphitization was characterized using a X-ray diffractometer (XRD) as shown in Figure 3.9. X-ray diffractometer was performed using a PW 3710 Philips diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 0.1542 \text{ nm}$ ) in a sealed tube operated at 40 kV and 30 mA. The diffraction curves were obtained from 5 to 30°, in steps of 0.01°. The scan speed was 0.5 sec/step.

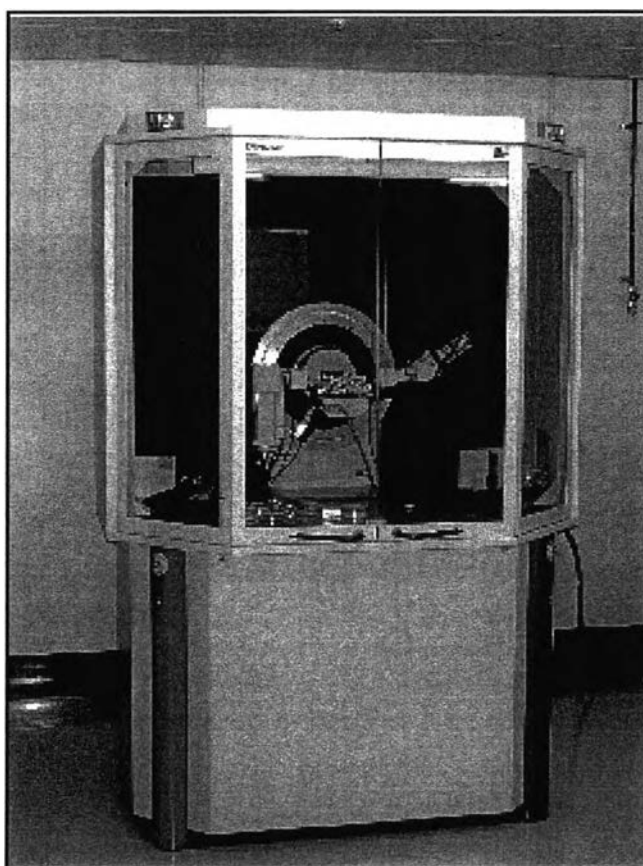


Figure 3.9 Philips PW 3710 X-ray diffractometer