

CHAPTER III

EXPERIMENTAL METHOD

3.1 Materials

- a) Concentrated latex (solids content: 60 wt.%) stabilized by a treatment with ammonia in a high concentration was from Rivertex.
- b) Pre-vulcanized latex (solids content: 60 wt.%) stabilized by a treatment with ammonia in a high concentration was from Rivertex.
- c) Polychloroprene latex (solid content: 60 wt.%) from Bamco.
- d) Nonionic surfactant (NP-9) from Rodia.
- e) Chemicals
 - Hydrochloric acid was from LAB SCAN.
 - Potassium permanganate was from ARSOM

3.2 Apparatus and instruments

- a) Thermogravimetry analyser (TGA); Mettler-Teledo/SDTA 851
- b) High Pressure Liquid Chromatography (HPLC); Waters 2690
- c) Scanning Electron Microscope (SEM); JOEL JSM-5800LV
- d) Ozone resistant tester; HAMPDEN Model 703
- e) Differential Scanning Calorimeter (DSC); NETSSCH DSC 200

f) Apparatus for chlorination

A 2 liter three neck round-bottomed flask was equipped with a mechanical stirrer and an alkali trap (A), which connected to the bubble flow meter. The chlorine gas was produced from the reaction of KMnO_4 and HCl which were in a 1 liter three neck round-bottomed flask (D) with magnetic bar and graduated separating funnel. The gas forming was checked by bubble of water (C).

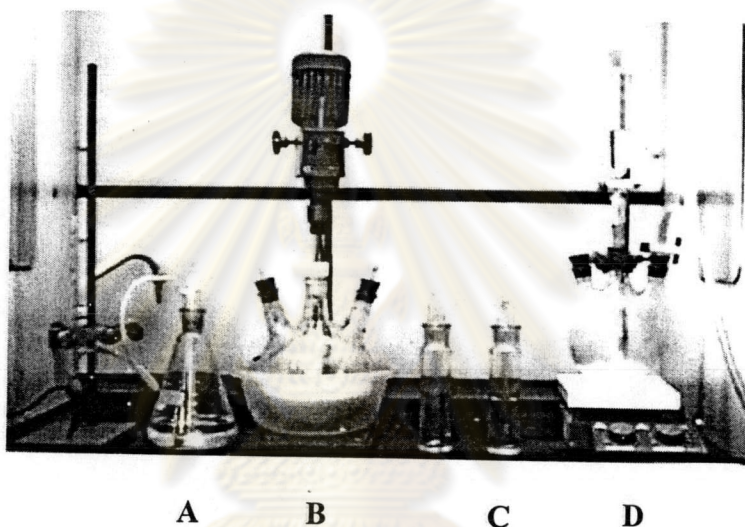


Figure 3.1 Chlorination apparatus for preparing chlorinated rubbers.

g) Apparatus for combustion [7]

The apparatus consisted of a hard glass tube of 16 mm internal diameter, covered with rolls of wire gauze at E and F. The porcelain boats were in the tube at position E and F.

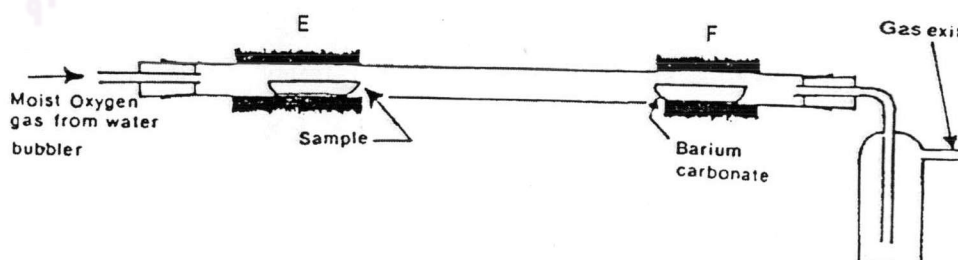


Figure 3.2 Combustion apparatus for determining chlorine content

3.3 Experimental methods

3.3.1 Preparation of chlorinated rubbers

The latex used was NH_3 stabilized concentrate NR latex which was diluted to 30 % DRC using equipment set-up as shown in Figure 3.1. About 300 g of the rubber latex was placed in the 2 litre three-neck round bottom flask. After the addition of 1 phr a nonionic surfactant, the latex was stirred continuously for 24 hours at room temperature.

From Figure 3.1, It was checked that the apparatus did not leak by maintaining a small steady nitrogen pressure into flask (D) (approx. $15 \text{ cm}^3/\text{min}$). It was confirmed that the rate of bubble formation (to prevent the escape of chlorine and absorb HCl liberated) in the monitor trap (C) and the alkali trap (A). When it was confirmed that the connections were sealed, (concentration) chlorine was generated in D by adding concentrated HCl (37%) dropwise at room temperature into excess of KMnO_4 with stirring (the amount of HCl added should have agreed with the chlorine uptake). The chlorine was passed in below the surface of the latex. The reaction was conducted at room temperature and continued for 4 hour.

Any unreacted chlorine and HCl was trapped by 5%w/v NaOH. The HCl removal from the chlorination was necessary because the chlorinated rubber without removal of HCl was poor in the stability properties. The removal of HCl could have been done by following nitrogen gas through the flask (B) 15 minutes after the reaction completed. The chlorinated rubber film was made by pouring the chlorinated rubber latex on the glass box with dimension to $180 \times 180 \times 5 \text{ mm}^3$ and dried it in air for 24 hours. Then, dried it in the oven at $50 \text{ }^\circ\text{C}$ for 24 hours. The chlorinated rubber film obtained became 2mm thickened. Chlorinated rubbers were prepared in different chlorine contents; 1 phr, 2 phr, 3 phr, 4 phr, 5 phr. The type of rubbers was varied by using pre-vulcanized latex and polychloroprene latex, respectively.

3.3.2 Measurement of chlorine content of chlorinated rubbers [7]

The simplest method of determining chlorine in polymers is the conversion of organic chlorine to chloride by combustion. The combustion apparatus is shown in Figure 3.2

The apparatus consisted of a hard glass tube of 10 mm internal diameter, covered with rolls of wire gauze at E and F. Oxygen was passed into the tube at the end at the rate of 5 ml/minute. The rubber film was contained in the porcelain boat E placed at a short distance from oxygen gas inlet, which was heated with a bunsen burner over the length of the wire gauze. The long porcelain boat F, which contained halogen-free barium carbonate was heated by a burner. Rubber bungs were used for connections at the ends and a guard bubble containing acidified silver nitrate solution was provided. Should the solution in this become turbid during combustion, the combustion had to be abandoned, since it showed that the hydrogen chloride gas formed had not all been absorbed by the barium carbonate. Burn slowly so that complete combustion took about 1 hour, after completion of combustion the tube was cooled in a stream of oxygen. When cooled, the boat of barium carbonate was withdrawn and its contents suspended in water in a porcelain boat. The chlorine content was determined by the ion chromatographic technique. The ion chromatography system was made by HPLC instrument and IC-PAK™ ANION HR column. It used sodium borate/gluconate as eluent and conductivity detector to determine chlorine content.

3.3.3 Solubility of chlorinated rubbers

0.1g the chlorinated rubbers were soluble in 10ml various solvents listed below.

Water	Ethanol
Toluene	Carbon tetrachloride
Xylene	Methylene chloride
Cyclohexene	Ethyl acetate
Methanol	

3.3.4 Ozone resistance (ISO 1431/1-1989 (E)) [13]

The ozone resistance was determined by using ozone resistant tester at the Rubber Research Instituted of Thailand. The test pieces consist of a strip of not less than 10mm width, thickness $2.0 \text{ mm} \pm 0.2 \text{ mm}$, and length not less than 40 mm between the grips before stretching. Strain the test pieces at 20 % elongation, condition them and examine the test chamber for the development of cracking.

3.3.5 Water and chemical resistance (ASTM D 471) [14]

Chlorinated rubber latex was prepared as thin films by casting on glass plate and dried in the oven at $50 \text{ }^\circ\text{C}$. Three film specimens, which had dimensions of 25 by 50 by $2.0 \pm 0.1 \text{ mm}$. Each specimen was weighed in air, M_1 . The specimens were placed in the appropriate reagents being used and immersed them in fresh reagent for 72 hours. To avoid any contact with the walls or bottom of the container, the specimens were suspended carefully. After that, the specimens were removed from the reagent, then dipped quickly into acetone, blot lightly with filter paper free of lint in a tared, stoppered weighing bottle, and determine the mass after the test, M_2 , of each specimen. The standard reagents of chlorinated rubber were as follow; 5%(v/v) hydrochloric acid, 5%(w/v) sodium hydroxide, water, vegetable oil and lubricating oil.

3.3.6 Thermal stability

The thermogravimetry (TG) of rubbers were determined by a TGA at the Technical Service: Rubber Technology Unit (Mahidol-MTEC). 7 mg of the sample was placed in the aluminum pan that was put on the sensor at room temperature along with an empty pan to assist output balance. Then they were rapidly heated at a rate of 10 °C/min to the required temperatures in nitrogen atmosphere.

3.3.7 Morphology

The morphology was determined by using a SEM at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. Specimens were prepared by placing the rubbers on an aluminum stub and mounted with the double-faced adhesive tape. Then it was coated under vacuum with a thin layer of gold.

3.3.8 Glass transition temperature

The glass transition temperature (T_g) of the rubbers was determined by a differential scanning calorimetry (DSC) at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. The analyses were performed at the heating rate at 10 °C/min. in the temperature range of -100 °C - 20 °C. The heating cycle was run twice. In the first scan, samples were heated and then cooled down to room temperature. In the second scan, samples were reheated at the same rate, only the second scan was recorded because the first scan was influenced by the mechanical and thermal history of samples.

3.3.9 Permanent set

Specimen $1 \times 6 \text{ cm}^2$ was cut into the films and marked to show a 2cm length. The specimens were clamped and stretched until the 2cm section reached 20cm and was held elongated for 10 minutes. The film was released and allowed to recover for 2 minutes and the new length measured and recorded. A further measure was made at 48 hours.



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