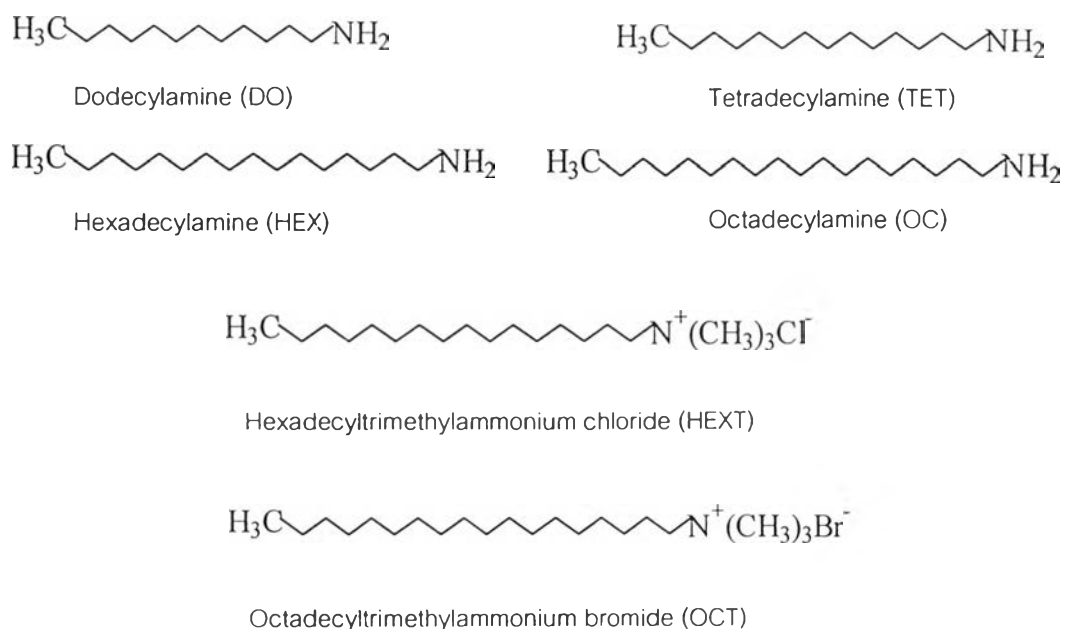


## CHAPTER III EXPERIMENTAL SECTION

### 3.1 Materials

The STR 5L NR was received from Rayong Bangkok Rubber Co., Ltd. Sodium montmorillonite (Na-MMT) with cationic exchange capacity (CEC) of 119 meq /100 g was obtained from Kunimine Industrial Co., Ltd., Japan. All of primary alkylamines and quaternary ammonium salts were purchased from Fluka Chemical, Switzerland. Curing agents, ZnO, stearic acid, MBTS, and sulfur, were available from Rubber Research Institute of Thailand. AR-grade toluene and HCl were purchased from J.T.Baker. All of chemicals were used without further purification. The chemical structures of primary alkylamines and quaternary ammonium salts, used as modifying agents, were shown in Figure 3.1.



**Figure 3.1** Chemical structures of modifying agents.

## 3.2 Equipment

### 3.2.1 Atomic Absorption Spectroscopy (AAS)

A Varian SpectrAA-300 was applied to determine Na<sup>+</sup>-exchanged percentage, using acetylene as fuel and air as supported gas. The sodium-hollow cathode lamp with 5 mA was chosen to produce the wavelength at 589.0 nm. All of standard solutions were prepared by dilution technique from the 1000-ppm-concentrated NaCl solution, and the standard curve was created for Na<sup>+</sup> determination.

### 3.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were obtained from a VECTOR 3.0 BRUKER spectrometer with 32 scans at a resolution of 2 cm<sup>-1</sup>. A deuterated triglycinesulfate detector (DTGS) with a specific detectivity, D\*, of 1×10<sup>9</sup> cm ×Hz<sup>1/2</sup> ×W<sup>-1</sup> was used to measure intensities within the frequency range of 4000-400 cm<sup>-1</sup>. KBr pellet technique was applied in the preparation of samples.

### 3.2.3 Thermogravimetric analysis (TGA)

A Dupont TGA was employed to observe thermal degradation temperature of materials used. Inside the analyzer, the chamber was continuously flushed with nitrogen at the flow rate of 20 ml/min and for balance the chamber, it was set at 30 ml/min. The temperature program was between 40 °C and 750 °C, and the heating rate was set at 10 °C/min.

### 3.2.4 X-ray Diffractometer (XRD)

XRD spectra were recorded by using a D/MAX-2000 series of Rigaku/X-ray Diffractometer that provides X-ray of Cu K-alpha at 40 kV/30 mA. The standard sample holders were applied to both ground samples and composite films. The experiment was operated in the 2θ range of 2-30 degree at the scan speed 5 degree/min with the 0.02-degree 2θ-stepwise increment.

### 3.2.5 Two-roll Mill

Raw NR was masticated at room temperature by using a Lab Tech LRM 110 two-roll mill.

### 3.2.6 Rheometer

Cure characteristics of the resulting gum composite were measured with a Rheo Tech rheometer, model TPD 1498, at 155 °C in accordance with ASTM D2084-95.

### 3.2.7 Compression Molding Machine

Gum composites were vulcanized at 155 °C by utilizing a Wabash V50H compression machine. The pressure acting on the mold was set at 10 tons. A picture-frame-shape mold made from stainless steel coated with chromium was used. The thickness of mold cavity was about 2 mm.

### 3.2.8 Tensile Properties

Tensile properties were determined on an Instron Universal Testing Machine, model 1011. The test was operated according to an ASTM 412-98 test procedure. The crosshead speed was set at 500 mm/min. The test for hardness was carried out using a Shore-type-A Lever Loader, model 716, following ASTM D2240. All tests were conducted at room temperature (25 °C).

## 3.3 Methodology

### 3.3.1 Preparation of Organically Modified Montmorillonite

Na-montmorillonite (Na-MMT) was organically modified by means of ion-exchange reaction between Na<sup>+</sup> and alkylammonium ion, protonated form of alkylamine. The ion exchange reaction could be done by stirring 10 g of Na-MMT overnight in 300 ml of distilled water. The resulting swollen clay and the separated 100 ml of 1.5 equivalent alkylamine

in excess amount of HCl solution were, in the same time, heated at 80 °C for half an hour. Then, the alkylammonium solution was gradually added into the Na-MMT suspension, and temperature was kept at 80 °C for another 2 hr with vigorous stirring. The sediment of organically modified MMT was collected by filtering and washing with 2 L of hot distilled water. After that, the collected sediment was dried overnight at 100 °C, and it was then ground with mortar and kept in a bottle.

### 3.3.2 Preparation of NR/Clay Nanocomposite

NR-clay nanocomposites were prepared through two methods: melt and solution techniques.

#### 3.3.2.1 *Melt Technique*

In melt technique, a Brabender Plasticorder was used as an internal mixer. In this method, raw NR was first masticated at room temperature for 10 min by using a two-roll mill. The mixing process taking place in a Brabender Plasticorder was operated at room temperature with a rotor speed of 40 rpm. The sequence of adding was shown below. After that the cure time of gum composite was determined at 155 °C, using a Rheo Tech rheometer. Finally, vulcanization of the gum composite at 155 °C was carried out by employing a Wabash compression machine.

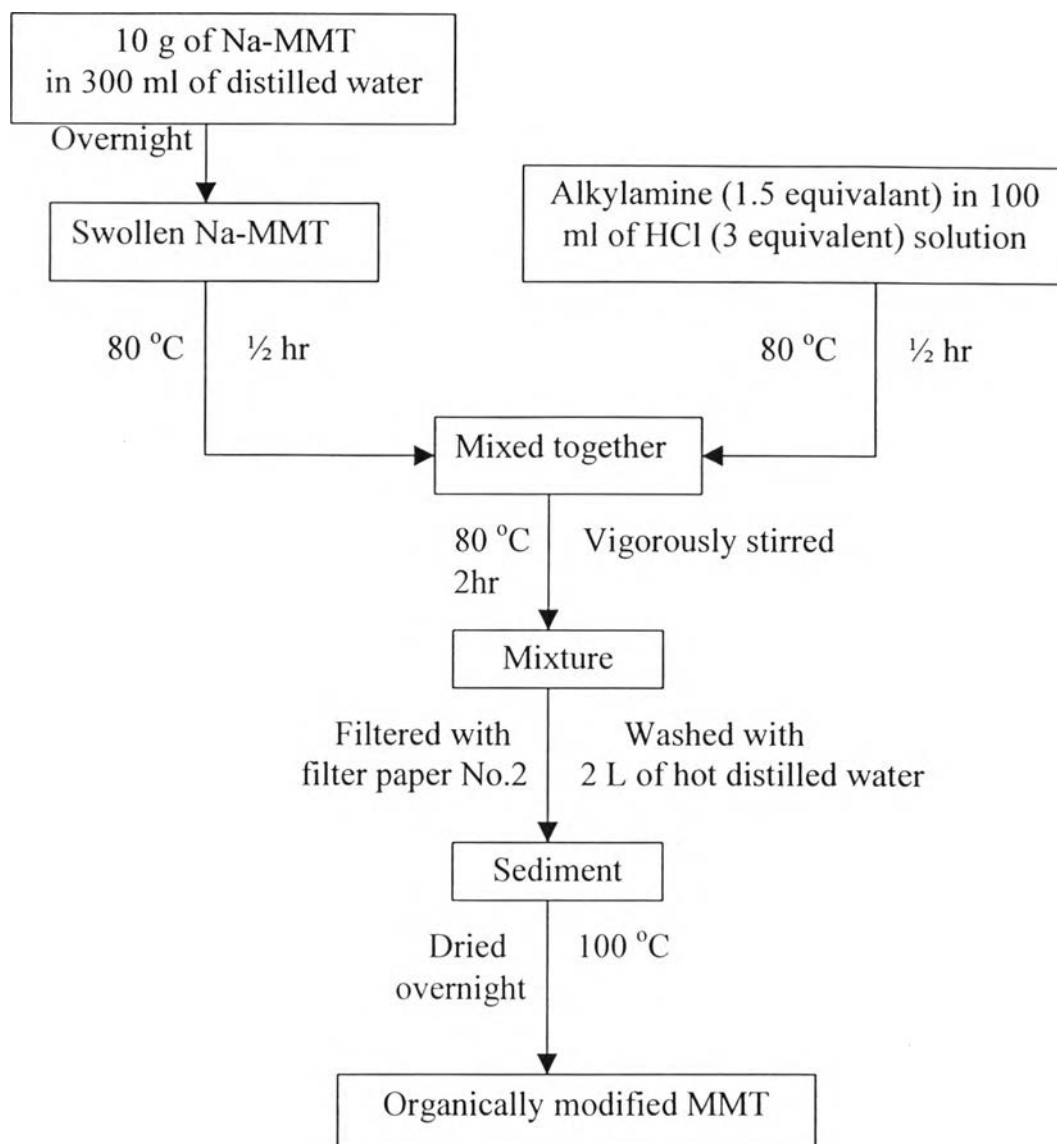
#### Sequence of adding

0-2 <sup>nd</sup> min : NR	5 <sup>th</sup> -6 <sup>th</sup> min : MBTS (1.8phr)
2 <sup>nd</sup> -3 <sup>rd</sup> min : modified MMT	6 <sup>th</sup> -7 <sup>th</sup> min : sulfur (3phr)
3 <sup>rd</sup> -4 <sup>th</sup> min : ZnO (5phr)	7 <sup>th</sup> -9 <sup>th</sup> min : continued mixing
4 <sup>th</sup> -5 <sup>th</sup> min : stearic acid (2phr)	

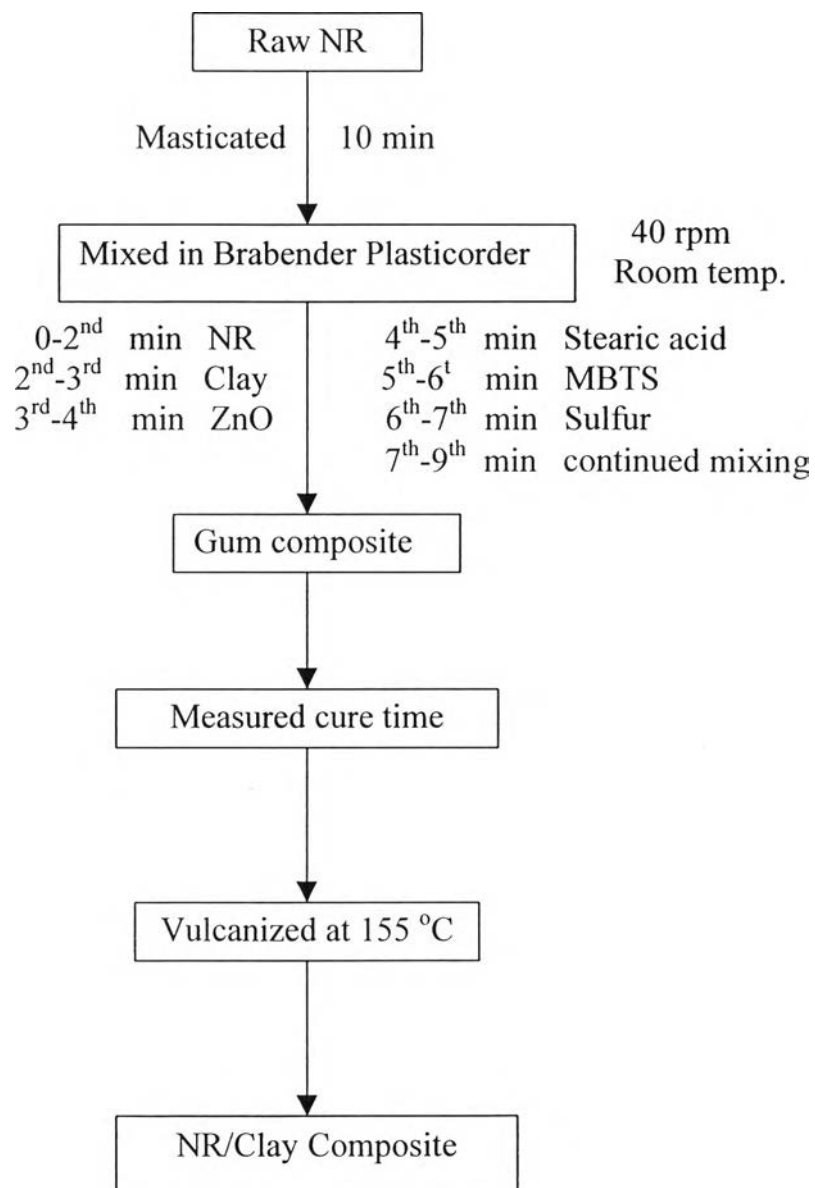
#### 3.3.2.2 *Solution Technique*

In solution method, 10-min masticated NR was first dissolved in toluene at the concentration of 10 wt/vol. % before it was heated at 70 °C for 1 hr with vigorous stirring. Then, swollen modified MMT in toluene was added into NR solution. The temperature was kept at 70 °C for

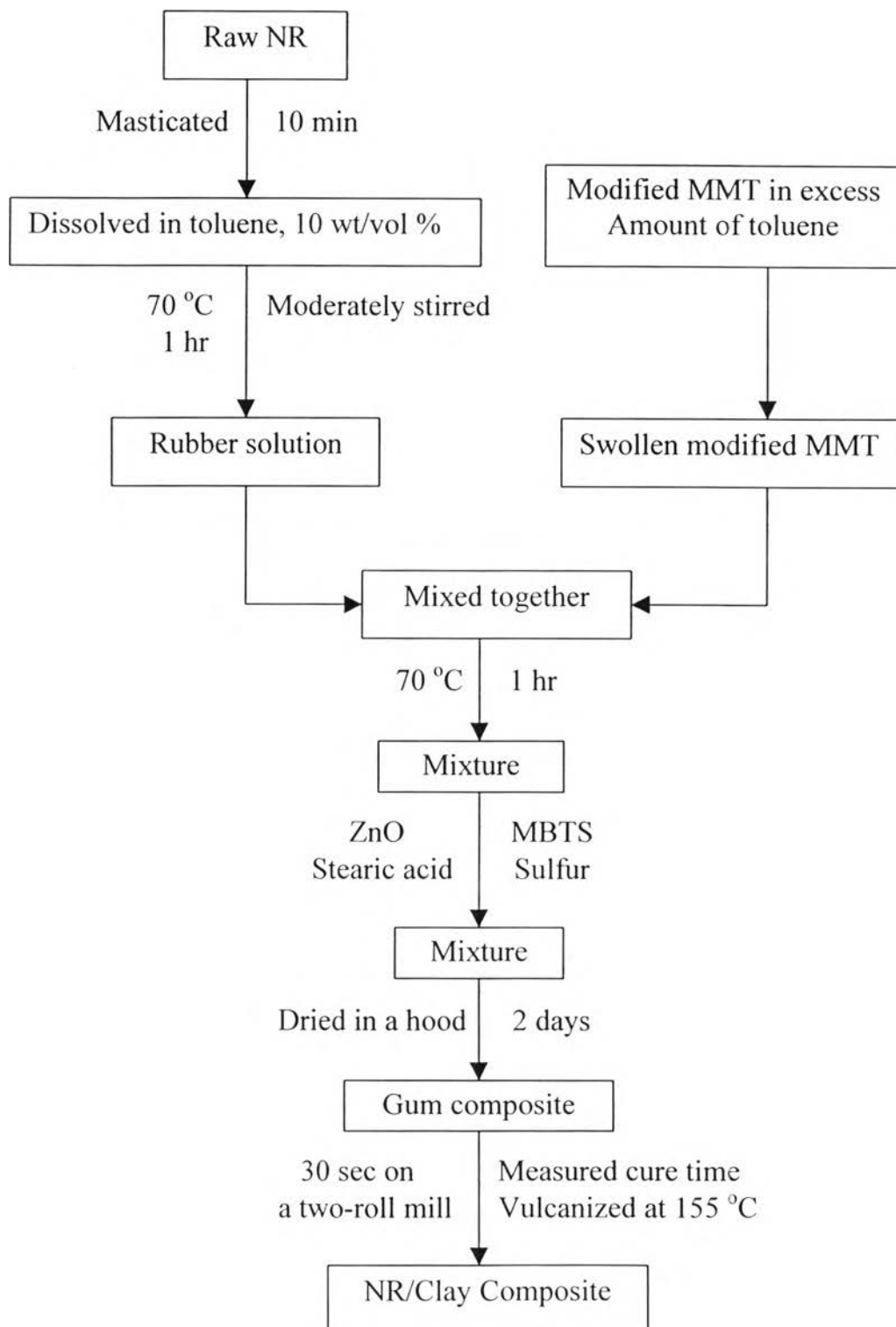
another 1 hr. Then, curing agents, ZnO, stearic, MBTS, and sulfur were sequentially added into the mixture at the same concentrations used in the melt technique. The mixture was subsequently poured into a stainless tray and then left in a hood for two days to allow toluene evaporating out. Before the cure time was measured, the dried gum composite was put onto a two-roll mill for 30 sec in order to make ZnO homogeneously dispersed. Finally, vulcanization of that gum composite was done in the same way as in the melt technique.



**Figure 3.2** Flow diagram of organically-modified-MMT preparation.



**Figure 3.3** Flow diagram of NR/clay composite prepared by the melt technique.



**Figure 3.4** Flow diagram of NR/clay composite prepared by the solution technique.