

# CHAPTER I

## INTRODUCTION

### 1.1 Statement of Problems

In rubber industry, besides carbon black, silica ( $\text{SiO}_2$ ) is the other reinforcing filler used to impart specific properties to rubber compounds. Silica offers a number of advantages on the vulcanizates such as good tear strength, good abrasion resistance and reduction in heat build-up. However, mechanical mixing between silica and rubber is somewhat a challenge due to the polar hydroxyl groups, silanol group ( $\text{Si-OH}$ ), on the silica surface. Its presence can result in a strong silica-silica interaction by hydrogen bonding. This can lead to aggregation of silica particles inside the rubber matrix and resulting in a poor dispersion of these particles and high viscosity during mixing. The silica can also adsorb curing agents on its surface which results in the reduction of curing efficiency [1]. Another important difficulty is the incompatibility of inorganic silica with the organic rubber.

These problems are partially overcome or minimized by adding specific additives such as coupling agent and mixing procedures [2-4]. As a method for overcoming these difficulties, a sol-gel process of tetraethoxysilane (TEOS) has been developed in order to generate silica inside the rubber matrix (*in situ* silica), instead of mechanical mixing them [5-7]. The parameters which influence the sol-gel reaction in each polymer is different. Therefore, the studies to find optimum condition which produces high silica content and good dispersion are widely investigated [8-13]. Those parameters are amount of organic and inorganic components, solvent type, the mole ratio of water to silica precursor, temperature, pH of the reaction, and so on [14].

To generate *in situ* silica, various matrices based upon rubber latex or solid rubber derived from synthetic or natural rubber, have been tried [5-6, 15-21]. Yoshikai *et al.* [21] studied *in situ* silica reinforcement for styrene butadiene rubber (SBR) latex and nitrile rubber (NBR) latex using the sol-gel reaction of TEOS. In this case, the advantages of the sol-gel reaction in latex were that organic solvents are not required and the reaction was faster than that of reaction in solid rubber. However, although, the *in situ* silica particles were uniformly dispersed in the rubbery matrix,

the *in situ* silica particle size was quite large (ca. 100 nm or less). The preparation of *in situ* silica for NR latex using TEOS had a long reaction time of about 10 days and the *in situ* silica generated in the NR latex was of low yield (19 phr) with large (100-500 nm) and extensively aggregated particles [17].

In order to improve the yield, the nanoparticle size and the dispersion of *in situ* silica in rubbery matrix, an alternative way is to generate *in situ* silica via solid rubber [19]. Some investigators have reported an effective catalyst for high *in situ* silica filling in uncured NR which attained a yield of about 71 phr with silica particle sizes of ca 46 nm [20]. However, considerable aggregation of the *in situ* silica particles was evident when the amount of *in situ* silica was greater than 50 phr, presumably due to the high nanoparticle surface area.

To solve this problem, the preparation of *in situ* silica via NR solution to obtain the optimum condition which produces high silica content in NR matrix was investigated in this study. Additionally, the effect of *in situ* silica content and the silane coupling agent on the curing characteristics, mechanical, and thermal properties was further reported compared with commercial silica.

## 1.2 Objectives

- 1 To develop the good dispersion of *in situ* silica particle in NR matrix by sol-gel technique via NR solution
- 2 To find the optimum condition which produces high *in situ* silica content in NR matrix
- 3 To study the mechanical properties of NR reinforced by *in situ* silica generated in rubber solution

## 1.3 Scope of the Investigation

- 1 Literature survey
- 2 Design and prepare experimental procedure
- 3 Generate the *in situ* silica in NR matrix via sol-gel technique by varying parameters as follows:
  - a) Types of solvent for sol-gel reaction: tetrahydrofuran (THF), chloroform (CHCl<sub>3</sub>) and carbontetrachloride (CCl<sub>4</sub>)

- b) Types of catalyst for sol-gel reaction: *n*-butylamine and *n*-hexylamine
  - c) Catalyst concentration of the aqueous catalyst solution for sol-gel reaction: 0.0640 - 0.1860 M
  - d) Mole ratio of TEOS to water in rubber solution: 1:1.8 to 1:3.0
  - e) Reaction temperature of sol-gel reaction: room temperature, 40, 45 and 50°C
  - f) Reaction times of sol-gel reaction 1 - 15 days
- 4 Determine the *in situ* silica content and study morphology of *in situ* silica in NR matrix by Thermogravimetry Analysis (TGA) and Scanning Electron Microscope (SEM), respectively.
  - 5 Prepare the rubber compounding using mechanical mixing
  - 6 Study the mechanical properties of *in situ* silica filled NR vulcanizates: tensile strength, hardness, compression set, and abrasion resistance
  - 7 Study the morphology of *in situ* silica filler NR vulcanizate by using Transmission Electron Microscope (TEM)
  - 8 Study the thermal properties and dynamic mechanical analysis (DMA) of *in situ* silica filled NR vulcanizates
  - 9 Study the effect of coupling agent on thermal and mechanical properties of *in situ* silica filled NR vulcanizates
  - 10 Compare the mechanical, morphology, and dynamic mechanical properties of *in situ* silica filled NR vulcanizates with commercial silica filled NR vulcanizates
  - 11 Summarize the results