

# CHAPTER I

## INTRODUCTION

### 1.1 Statement of Problems

Silica has been used as an important reinforcing agent in the rubber composite for years. It has a number of hydroxyl groups on the surface, which results in strong filler-filler interactions and adsorption of polar materials by hydrogen bonds. Since intermolecular hydrogen bonds between hydroxyl groups on the surface of silica are very strong, it can aggregate tightly [1]. This property can cause a poor dispersion of silica in a rubber composite which bring about aggregation of silica particles in the rubber matrix. Thus, the composite has adverse mechanical properties. The adsorption of curing activators and accelerators by silica results in delay of both scorch time and cure time and reduction of the delta torque (difference between maximum and minimum torques) of a rubber-silica compound.

In general, silane coupling agents such as bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT) is used in order to improve the filler dispersion and prevent adsorption of curing activators and accelerators on the silica surface. Silane coupling agent functions as a bridge between silica and rubber and enhances the rubber-silica interaction due to the two functionally active end groups, an alkoxy group and an organosilane group. The alkoxy group is capable of reacting with silanol group on silica surface whilst the organosilane group, generally having sulfur atoms in its molecule, is compatible with rubber and can participate in sulfur vulcanization leading to a strong chemical linkage between the silane coupling agent and rubber molecule. Some silane coupling agent such as TESPT is working not only as a coupling agent but also as a co-curing agent for sulfur vulcanization [2]. The coexistence of silane coupling agent during the sol-gel reaction resulted in the decreasing size of the particles produced. Thus, the degree of reinforcement is therefore greatly increased in the presence of silane coupling agent [3].

Mechanical mixing is a usual processing technique to prepare silica-rubber composites. Other than the conventional mixing, the *in situ* silica filling using the sol-gel reaction of tetraethoxysilane (TEOS) has been focused as a novel technique to reinforce the rubber vulcanizates. In the field of rubber science, Kohjiya et al. carried out the *in situ* silica filling for styrene-butadiene rubber (SBR) [2, 4, 5], butadiene rubber (BR) [6], acrylonitrile-butadiene rubber (NBR) [7] and epoxidized natural rubber (ENR) [8]. In these cases, the reinforcement effect of *in situ* silica was considerable for rubber vulcanizates. They found that the sol-gel reaction of TEOS produced the fine and well-dispersed *in situ* silica in the rubber matrix. Thus, the silica introduced by the sol-gel technique had a better reinforcing efficiency than the silica introduced by the conventional method. The disadvantage of the prepared *in situ* silica in rubber vulcanizate is the limited thickness of the samples to a few millimeters for swelling TEOS and aqueous solution of a catalyst. Until recently, the sol-gel reaction of TEOS synthesized silica in latex for compounding rubber and silica. The advantage of this procedure is that no organic solvent is used, since the system consists of the emulsified rubber, TEOS, water, and catalyst [9, 10].

As mentioned earlier, in order to achieve excellent reinforcement, it is important to incorporate very fine silica particles and to disperse them well in the rubber matrix. Therefore, it was hypothesized here that by performing the sol-gel process of combined TEOS and TESPT in natural rubber (NR) latex, the reinforcement of NR would be achieved in the most effective fashion.

## 1.2 Objective

The aim of this project was to generate modified silica particles inside rubber matrix in order to prepare silica-reinforced NR vulcanizates. The *in situ* modified silica was generated by the sol-gel process of two silane precursors, tetraethoxysilane (TEOS) and bis-(3-triethoxysilylpropyl)tetrasulfide (TESPT), in ammonium-added NR latex. The effects of TEOS and TESPT contents on the composites morphology and mechanical properties were evaluated.

### 1.3 Scope of the Investigation

The stepwise investigation was carried out as follows:

1. Literature review for methods to prepare *in situ* silica-NR composites.
2. Optimization of gelation time by selecting the gelation time that was long enough to complete the sol-gel process of the silane in latex
3. Study of the effects of TEOS, TESPT and ammonia (NH<sub>3</sub>) contents on the mechanical properties of NR vulcanizates. In this step the experiment was set according to a “two-level factorial design” concept.
4. Characterization of the reinforced NR vulcanizates for
  - morphology of the composites by SEM and TEM.
  - curing behavior by Monsanto rheometer.
  - spectroscopic evidences of modified silica in the rubber matrix by <sup>29</sup>Si-CPMAS NMR.
5. Summarizing the results and writing the thesis.