

CHAPTER II

LITERATURE SURVEY

Nowadays, rubber compound is widely used in the industries owing to its advantages on morphological properties and the variation approaches to improve the end products. The term “rubber” is defined by ASTM D 1566-88b, Standard Terminology Relating to Rubber (Barlow, 1993), as follows:

Rubber - a material that is capable of recovering from large deformations quickly and forcibly, and can be, or already is, modified to a state in which it is essentially insoluble (but can swell) in boiling solvent, such as benzene, methyl ethyl ketone, and ethanoltoluene azeotrope. A rubber in this modified state, free of diluents, retracts within one minute to less than 1.5 times its original length after being stretched at room temperature (18 to 20 °C) to twice its length and held for one minute before release.

2.1 Natural Rubber

Natural Rubber is cis-1,4-polyisoprene (as shown in Figure 2.1) with isoprene repeating unit (C₅H₈). The density is 0.93 at 20 °C for average.

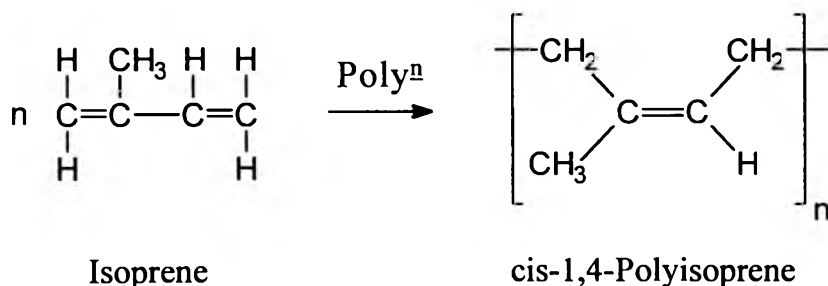


Figure 2.1 Chemical structure of natural rubber (cis-1,4-polyisoprene).

The natural rubber consists largely of cis-1,4-polyisoprene with linear, long flexible chains where the molecules can slide past each other. The glass transition state of rubber (-70°C) is far below the room temperature (Rodriguez, 1989). As a result, rubber is soft and can be melted by heating. On the contrary, it will be rigid and brittle at low temperatures. For this reason, the natural rubber can be utilized in a narrow temperature range. To improve thermal properties of natural rubber, vulcanizing with sulfur to form stable, insoluble, and three dimension network is known for decades (Figure 2.2).

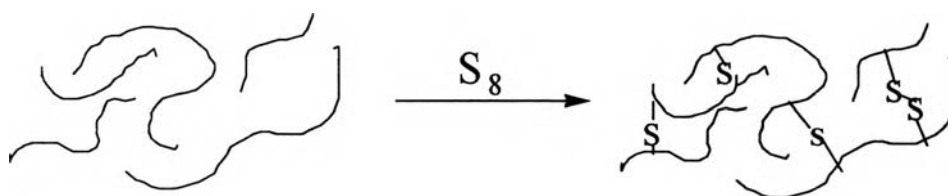


Figure 2.2 Improvement of rubber properties by vulcanization.

Although the vulcanized rubber has advantages such as high impact strength, low glass transition temperature (T_g), and flexibility, it also has many shortcomings, for example, low heat/ abrasion/ tear resistance, high heat build up, low hardness, stiffness, and modulus (Waddell *et al.*, 1995 and Wagner, 1976). To overcome these disadvantages, the addition of filler to improve the composite properties has been proposed.

Two types of fillers are known for rubber industries, i.e., nonblack filler and black filler. Carbon black, one of the black filler, is the major choice for rubber reinforcement because of the cost performance and the compatibility to various polymers. However, the black color of the product limits the applications.

The way to increase the value added rubber product is to reinforce the rubber with nonblack filler such as silica (Plueddemann, 1982), clay or calcium

carbonate to achieve the color controllable product. A popular nonblack filler is silica. Silica is frequently used for reinforcing white or light color compound such as non-marking solid industrial tire. Furthermore, silica can also replace carbon black to improve many properties, for example, lowering rolling resistance, improving traction, reducing heat build up, increasing tear and abrasion resistance (Barlow, 1993), etc.

Unfortunately, silica is hydrophilic which limits the compatibility comparing to hydrophobic rubber. Silica-to-silica attraction is high owing to its hydrogen bonding. As a result, silica forms large aggregate and resists the flow of rubber matrix. These disadvantage points make rubber composite show high viscosity and the mixture be stiff (Barlow, 1993). In addition, since the mixture is incompatible, the properties of rubber composite will decrease instead of the expected excellent properties. Therefore, the way to improve compatibility between silica and rubber is the addition of compatibilizer, which is compatible with both hydrophilic and hydrophobic groups, as shown in Figure 2.3.

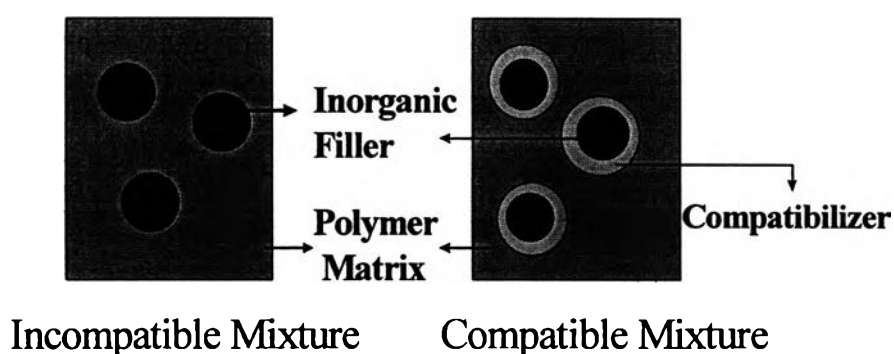


Figure 2.3 Compatibility of inorganic filler and rubber matrix.

For the silica filler, the effective compatibilizer is silane coupling agent. The silane coupling agent will bind the rubber and silica together. Thus, after

treatment with silane, viscosity of the composite decreases which results in enhancing processability, good mechanical strength and excellent properties.

2.2 Silane Coupling Agent

The simple structure of silane coupling agent is RSiX_3 where R is organofunctional group that is compatible and reacts with polymer matrix. X is hydrolyzable group and is usually alkoxy group or Cl. The hydrolyzable group will be hydrolyzed by water and then coupled onto substrate surface. The water for hydrolysis can be added from external source or may come from the water at the substrate surface (Anderson, 1987). The reaction of silane can be described by Figure 2.4. Firstly, the alkoxy group of silane will be hydrolyzed at random to be the hydroxyl group and lose alcohol as a by-product. Then, the silane hydrolyzate is probable to condense with each other to form oligomers. After that, the silane will be coupled onto substrate surface with a loss of water. There is also a case that unhydrolyzed silane is coupling directly onto the substrate surface with an elimination of alcohol (Akovali, 1993).

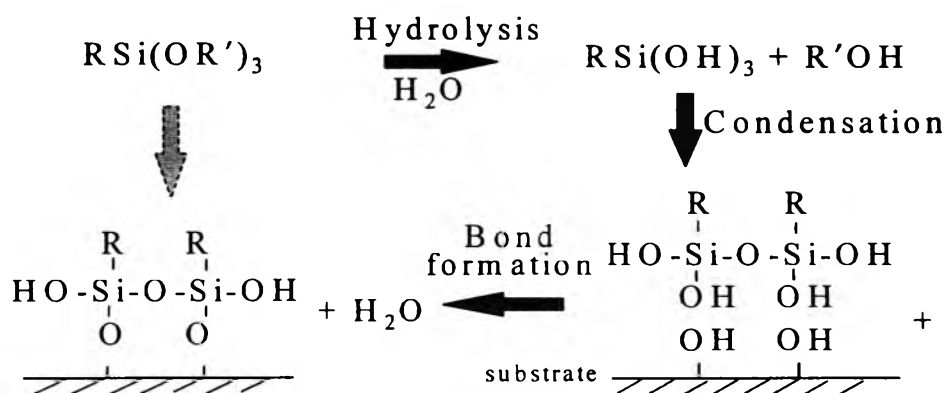


Figure 2.4 Reaction of silane coupling agent.

The requirement of silane coupling agent for rubber is that the silane compound have the sulfur group for vulcanization across the isoprene chain. Major silane often used in rubber industry can be raised as bis[3-(triethoxysilyl)propyl]tetrasulfide (Si-69) and mercaptopropyltrimethoxysilane (A189) (Figure 1.5).

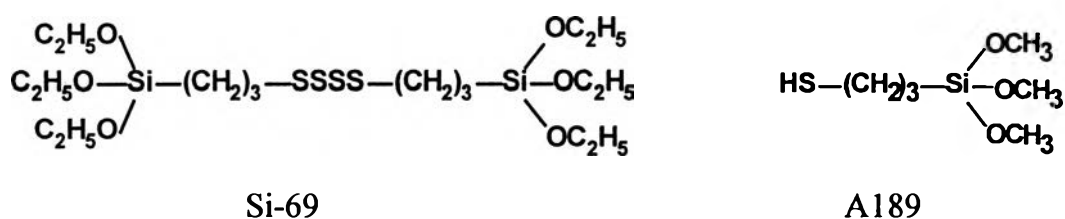


Figure 2.5 Structure of Si-69 and A189.

In this work, we focus on the silane Si-69 coupling agent onto the silica surface. The ethoxy group will be hydrolyzed and coupled onto silica surface. The sulfur molecule in Si-69 will act as a vulcanizing agent when the silane treated silica is mixed with rubber.

2.3 Adsorption Behavior of Silane

The adsorption behavior of the silane onto substrate surface has 2 types; chemisorbed and physisorbed silanes. Chemisorbed silane is the silane that has at least one covalent bond with the substrate surface. The covalent bond is a strong bond, thus the chemisorbed silane is maintained under physical force. On the other hand, physisorbed silane is the silane that does not form any covalent bond with the substrate surface. Steric hindrance between silica and silane is an important factor to generate physisorbed silane by the secondary

force which is not available for silane to condense with silica surface (Akovali, 1993). Secondary forces concerned in the system are hydrogen bond and van der Waals force which makes the physisorption. Thus, the physisorbed silane can be formed as small oligomers stabilized by physical bond on the substrate surface or next to the chemisorbed silane (Akovali, 1993). Physisorbed silane can be destroyed easily by a physical force such as washing by organic solvent which has the same solubility parameter, especially THF.

As mentioned above, the adsorption behavior of silane onto silica plays an important role on the properties of silica and rubber composite (Ishida, 1990, Ishida, 1985, Ishida *et al.*, 1984, Ishida *et al.*, 1984, and Miller *et al.*, 1985). For the past decades, there are many researches focused on the preparation of rubber-silica composite material. However, few studies are concerned with the molecular level to investigate the media polarity and silane concentration effect of the chemisorbed and physisorbed silanes onto silica surface. The scope of the present work is to understand those effects on the adsorption behavior by quantitative FTIR and SEC techniques.