

CHAPTER I

INTRODUCTION

Nowadays, rubber compound is widely used in many industries owing to its advantages on the vulcanisate properties and the variation approaches to improve the end products. The non-filled rubber compound or gum rubber has many inferior properties. The filled rubber compound primarily signifies an increase in ultimate properties which are obtained by adding a filler material. The physical properties of filled rubber are usually described in terms of tensile strength, stiffness, abrasion, and tearing properties. Fillers are often added to rubber for the reinforcement purpose to increase its usefulness in commercial applications. Applications of rubbers for uses in tires, belts, and engine mounts involve rapidly repeated deformations, these are well known as the dynamical properties of the rubbers. The properties are dependent on both chemical and physical interactions of the fillers with rubber. In addition, the product properties rely on the technique used to assess them.

There are many types of fillers used in the rubber industry. Fillers are divided into two types which are reinforcing and non-reinforcing fillers. The properties of the rubber products are usually found to be dependent not only on the types of the reinforcing fillers, but also on their structure and their other characteristics of the fillers, including particle size, surface area, surface activity, and degree of dispersion in the rubber phase. Carbon black and silica are known as reinforcing fillers. Carbon black is most widely used for rubber compounds to provide excellent reinforcement at a relatively low content. Unfortunately, black color of the product limits the

applications. Moreover, addition of carbon black also contributes to increased hysteresis such that compromise is a necessity. Silica, one of the non-black fillers, is used for rubber products in replacement of carbon black when colored, white translucent products are desirable. Carbon black gives the strength to the vulcanised rubber while silica gives low rolling resistance but it is expensive because coupling agent is also required. Addition of other fillers aids to reduce the cost of the rubber products and optimizes the desired properties. The non-reinforcing filler such as silicates, clay, calcium carbonate, calcium sulfate--so-called "gypsum" and other mineral fillers are important in many rubber products where they are used as economical fillers to modify processing and performance of natural rubber (NR).

In the present work, the curing, mechanical and dynamical properties of carbon black, silica, and gypsum-filled NR vulcanisates are investigated. This study is divided into two mixings based on filler type in rubber compounds. The first mixing is rubber compound with only one filler type for the study of the effect of filler particle size, structure, and surface activity on rubber compound properties which accompanying with cost reduction as an indirect benefit. The second mixing is rubber compound with mixed fillers types to investigate the effect of each filler loading (for a constant total filler volume fraction) on final properties. It is expected that compounds of partial replacement of carbon black with gypsum and silica reduces $\tan \delta$ (loss tangent), heat build up and rolling resistance.

1.1 Natural Rubber

The milky aqueous dispersion of rubber--called latex is produced by the tree *Hevea brasiliensis* (Blow and Hepburn, 1982). Solid natural rubber (NR) is obtained by the latex coagulation using some acids. The raw NR contains 93-95% cis-1,4-polyisoprene, 2-3% proteins, 2% acetone-soluble resins

(including fatty acids), water, small amounts of sugars and a little mineral matter. NR consists of the hydrocarbon component over 99.9% of linear cis-1,4-polyisoprene is shown in Figure 1.1.

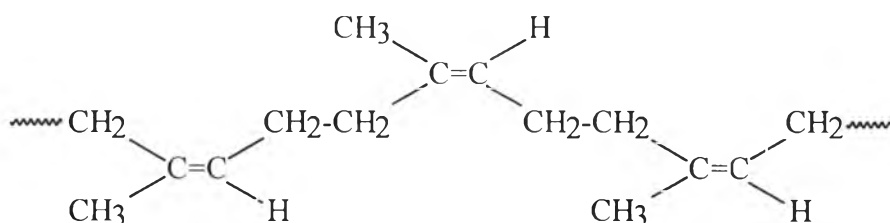


Figure 1.1 Chemical structure of NR (cis-1,4-polyisoprene).

The average of molecular weight of the polyisoprene in NR ranges from 200,000 to 400,000 with a relatively broad molecular weight distribution that is why NR has an excellent processing behavior. There is one double bond for each isoprene unit. These double bonds and the α -methylene groups contained in a NR molecular chain are reactive groups for vulcanization with sulfur. The value of the glass transition temperature (T_g) of uncured NR is proposed to be -72.6 ± 0.5 °C which is far below room temperature. As a result, rubber is soft and can be melted by heating. On the other hand, it will be rigid and brittle at low temperatures. Therefore, NR can be utilized in a narrow temperature range. NR can be improve the thermal properties by vulcanization with sulfur. Although the vulcanized rubber has advantages such as high impact strength, low T_g and flexibility, it also has many inferior properties, for example, low hardness, stiffness, abrasion and tear resistance. Consequently, these inferior properties have to be improved by adding fillers.

1.2 Carbon Black

1.2.1 Chemical Structure of Carbon Black

Carbon black is widely used as a reinforcing and coloring agent in compounding rubber, inks, paints, plastics, paper, and electrical conducting applications. Carbon blacks may contain 83 to 99% of carbon (Katz and Milewski, 1987). Other chemicals including oxygen, hydrogen and heavy metals may be chemically combined in the crystallite structure or be present on the surface of carbon black. Relatively large amounts of oxygen volatile yield carbon blacks that have a low pH, or acidic in nature. Oxygen may be present in aldehyde, hydroxyl, carbonyl, quinone, hydroquinone, lactone, and possibly chromene groupings as shown in Figure 1.2.

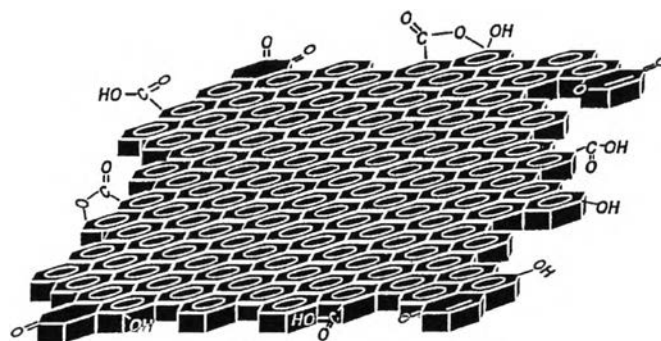


Figure 1.2 Surface chemistry of carbon black.

Although based solely on the element carbon like graphite and diamond, carbon black differs both chemically and physically from these purer and more crystalline forms of carbon. Electron microscopy shows carbon black particles of planar hexagonal nets of carbon atoms. These networks are similar to those in graphite, but in carbon black they are not so large or extensive as in graphite. The layers are also farther apart, at about 3.5 \AA , compared to 3.35 \AA for graphite as demonstrated in Figure 1.3.

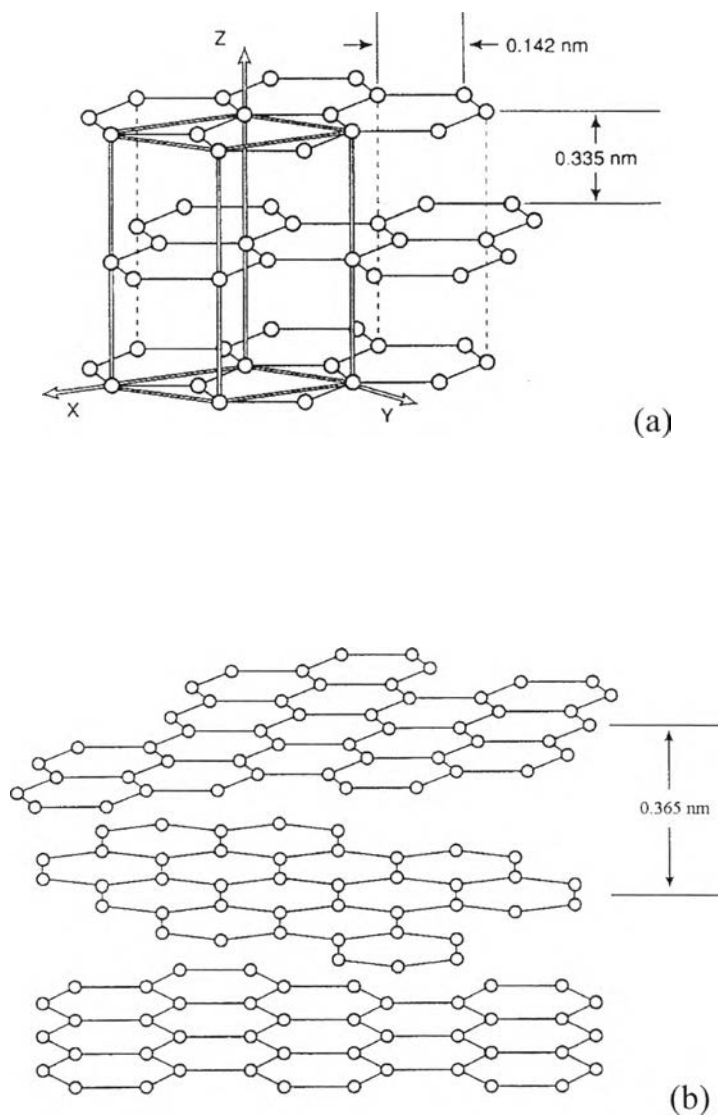


Figure 1.3 Atomic structure models: (a) graphite, and (b) carbon black

1.2.2 Particle Size

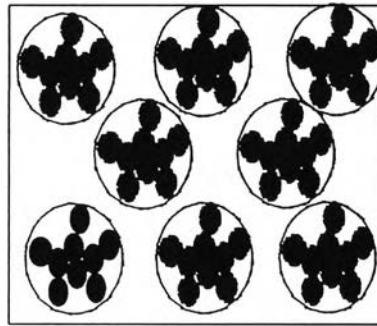
Under the electron microscope, carbon black particles appear to be spherical if a single particle can be isolated. Single individual particles are rarely seen, but particles are usually seen in clusters or aggregates.

1.2.3 Surface Area

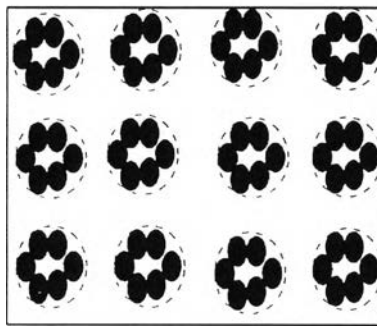
Gas adsorption techniques using the Brunauer, Emmett, and Teller (BET) procedure are used to determine the total surface area of a carbon black, with results reported as square meters per gram (m^2/g). Generally for carbon black the gas used is nitrogen. Iodine, in the liquid phase, is also often used to measure surface area by absorptive capacity. Iodine adsorption data may be reported as surface area (m^2/g) or as an “iodine number”-the number of milligrams of iodine adsorbed per gram of carbon black. Sometimes cethyltrimethyl-ammonium bromide (CTAB) is used instead of nitrogen in adsorption procedure.

1.2.4 Structure

The term “structure” refers to the joining together of carbon particles into long chain as grape-like clusters. The higher structure of a carbon black, the more irregular the shape of the aggregates, hence the less these aggregates are capable of packing together. Structure is normally measured by determining the total volume of the air spaces between aggregates per unit weight of black. The test is done by measuring the volume of a liquid dibutyl phthalate (DBP), required to fill the voids. The number of cubic centimeters of DBP per 100 grams of carbon required to produce this condition is the DBP value. Figure 1.4 represents high structure and low structure of carbon black.



(a)



(b)

Figure 1.4 Structure of carbon black: (a) high structure, (b) low structure

1.3 Silica

Silicas are considered polymers of silicic acid in which the bulk structure is produced by interlinking the SiO_4 tetrahedral. At the surface, the structure terminates in siloxane groups ($-\text{Si}-\text{O}-\text{Si}-$) and one of the several forms of silanol groups ($-\text{Si}-\text{OH}$) as shown in Figure 1.6.

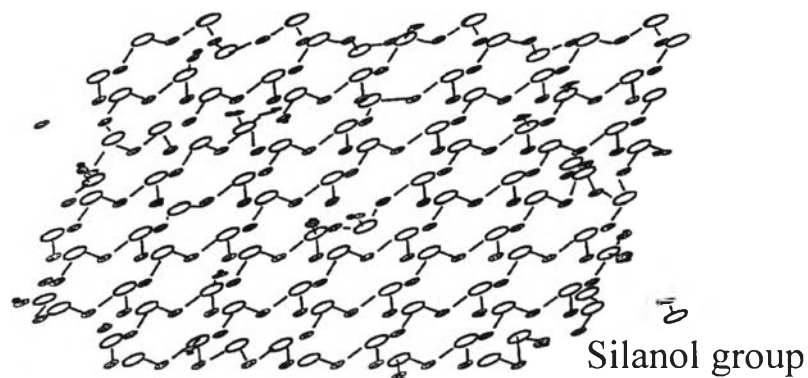


Figure 1.5 Surface chemistry of silica.

They are reinforcing fillers giving compounds of high tensile strength, hardness, tear and abrasion resistance. They are used in translucent and colored products, mechanical goods, and shoe soling. In combination with reinforcing blacks they improve tear resistance and adhesion to fabrics. Hydrated silica retards cure and requires increased dosage of accelerator or the addition of materials such as glycols or amines to promote curing.

1.4 Calcium Sulfate (Hydrated)

Calcium sulfate occurs in the anhydrous form (CaSO_4) and in the hydrated form ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) commonly known as gypsum. Calcium sulfate is an inert filler of lower specific gravity and whiter color than those of barytes. The natural property of fire resistance of calcium sulfate, led to the growth of a significant industry that produces boards and plasters as the primary wall cladding materials in modern building construction. Natural gypsum is rarely found in a pure form. The dihydrated and anhydrous forms are commonly found together. Gypsum is also obtained as a by-product of various chemical processes. The main sources are from processes involving

scrubbing gases evolved in burning fuels that contain sulfur and the chemical synthesis that is why gypsum is a low cost filler.

1.5 Dynamic Mechanical Property

Rubber are viscoelastic materials exhibiting both elastic and viscous behaviors. When they are deformed by a sinusoidal stress within the linear viscoelastic region, the resulting strain will also be sinusoidal but will be out of phase with the applied stress. The elastic and viscous stresses are related to material properties through the ratio of stress to strain, modulus. Dynamic losses are usually associated with hysteresis and specific mechanisms of molecular or structural motions in polymer materials.

The damping characteristics are extensively measured as “the tangent of the phase angle ($\tan \delta$)” and defined by

$$\tan \delta = \frac{G''}{G'} \quad (1.1)$$

Where G' is the storage modulus representing the stored elastic energy in the materials and

G'' is the loss modulus due to viscous dissipation