CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Natural rubber

Natural rubber is obtained from the tree Hevea *brasiliensis*. Rubber occurs in the trees in the form of particles suspended in a protein-containing serum, the whole constituting latex, which in turn is contained in specific latex vessels in the tree or other plant. Globally, natural rubber consumption is split with tires consuming at around 75%, automotive mechanical goods at 5%, nonautomotive mechanical goods at 10%, and miscellaneous applications such as medical and health-related products consuming the remaining 10% [10]. Today Asia is the main source of natural rubber, accounting for around 94% of output in 2005.The three largest producing countries (Indonesia, Malaysia and Thailand) together account for around 72% of all natural rubber production.

Natural rubber is a polymer of isoprene as shown in Figure 2.1. The repeating unit in natural rubber has the cis configuration. The primary source of cis-1,4-polyisoprene is used in the manufacture of natural rubber product. Natural rubber (NR) contains 98% cis-1,4-polyisoprene.
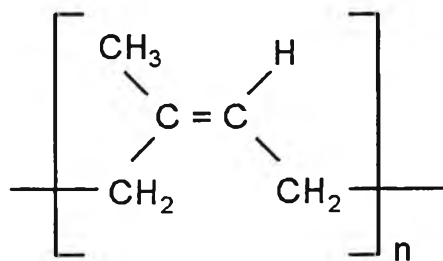

Figure 2.1 cis-1,4-polyisoprene.

2.1.1 Natural rubber latex

Natural rubber latex (NRL) is a cloudy white liquid, similar in appearance to milk. It is collected by cutting a thin strip of bark from the tree and allowing the latex

to exude into a collecting vessel over a period of hours. Fresh Hevea latex has a pH of 6.5–7.0 and a density of 0.98 g cm^{-3}. The traditional preservative is ammonia, which concentrated solution, ammonia is added in small quantities to the latex collected from the cup. The composition of typical field latex is presented in Table 2.1 [11].

Table 2.1 Composition of fresh Hevea latex.

Composition	Content (% by weight)
Total solid content	36
Dry rubber	33
Proteinous substance	1.0-1.5
Resinous substance	1.0-2.5
Carbohydrates	1.0
Inorganic matter	Up to 1.0
Water	60

Natural rubber latex has dry rubber content (DRC) of about 30 to 40%, the average being about 33%. It is necessary to increase the DRC in the natural rubber latex to 60% or more to reduce the transportation costs and enhance suitability for various latex processes. Concentrated latexes are economically useful as they contain less water to be shipped from the plantations; they are also more efficient in the manufacture of finished products directly from latex. Additionally, concentrated latex tends to be more uniform in quality than do field latices. This is due in part to the partial removal of non-rubber constituents in several concentration processes [11].

2.2 Fillers for rubber

The fillers are generally classified into carbon black and white fillers. Non-black fillers such as clays, carbonates, silicates, and precipitated silica are also needed that differ not only in their chemical structure but also in their particle size and shape. Compared to carbon black, these fillers show advantages in cut and flex resistance and heat buildup, they are non-conducting, and they are required for colored products,

but the reinforcement they provide with regard to modulus and abrasion resistance, is limited.

The principal characteristics of rubber fillers – particle size, shape, surface area and surface activity–are interdependent in improving rubber properties. In considering fillers of adequately small particle size to provide some level of reinforcement, the general influence of each of the other three filler characteristics on rubber properties can be generalized as follows: Increasing surface area (decreasing particle size) gives: higher Mooney viscosity, tensile strength, abrasion resistance, tear resistance, and hysteresis; lower resilience. Increasing surface activity (including surface treatment) gives: higher abrasion resistance, chemical adsorption or reaction, modulus, and hysteresis (except for silane-treated fillers) [12].

2.2.1 Filler properties [12]

The characteristics that filler will impart to a rubber compound are particle size, surface area structure and surface activity.

Particle Size – If the size of the filler particle greatly exceeds the polymer interchain distance, it introduces an area of localized stress. This can contribute to elastomer chain rupture on flexing or stretching. Fillers with particle size greater than 10,000nm (10 µm) are therefore generally avoided because they can reduce performance rather than extend or reinforce. Fillers with Particle Size between 1000 to 10000nm (1 - 10 µm) are primarily used as Diluents and usually have no significant effect, positive or negative on Rubber Properties. Semi- reinforcing fillers ranging from 100 to 1000nm (0.1 – 1 µm). The truly reinforcing fillers which range from 10 nm to 100 nm (0.01 - 1 µm) can significantly improve rubber properties.

Carbon black and precipitated silica are available in various particle sizes that range from semi-reinforcing to highly reinforcing. They generally exist as structural agglomerates or aggregates rather than individual spherical particles.

Surface Area – Filler must make intimate contact with the elastomer chains if it is going to contribute to reinforcement. Fillers that have a high surface area have

more contact area available, and therefore have a higher potential to reinforce the rubber chains. The shape of the particle is also important. Particles with a planar shape have more surfaces available for contacting the rubber than spherical particles with an equivalent average particle diameter. Particles of carbon black or precipitated silica are generally spherical, but their aggregates are anisometric and are considerably smaller than the particles of clay, which have planar-shaped particle. Surface area for a rubber grade carbon blacks vary from 6 to 250 m^2/g. Most reinforcing precipitated silicas range from 125 to 200 m^2/g; typical hard clay ranges from 20 to 25 m^2/g.

Structure – The shape of an individual particle of reinforcing filler (e.g. carbon black or precipitated silica) is of less importance than the filler's effective shape once dispersed in elastomer. The blacks and precipitated inorganics used for reinforcement have generally round primary particles but function as anisometric acicular aggregates.

For reinforcing fillers which exist as aggregates rather than discrete particles, carbon black and silica in particular, a certain amount of structure that existed at manufacture is lost after compounding. The high shear forces encountered in rubber milling will break down the weaker aggregates and agglomerates of aggregates. The structure that exists in the rubber compound, the persistent structure, is what affects processability and properties.

Surface Activity - A filler can offer high surface area and high structure, but still provide relatively poor reinforcement if it has low specific surface activity. The specific activity of the filler surface per cm^2 of filler-elastomer interface is determined by the physical and chemical nature of the filler surface in relation to that of the elastomer. Nonpolar fillers are best suited to nonplar elastomers; polar fillers work best in polar elastomers. Beyond this general chemical compatibility is the potential for reaction between the elastomer and active sites on the filler surfaces.

2.2.2 Reinforcing fillers

Two types of fillers that are most effective for reinforcing rubber are carbon black and silica. Particulate fillers can increase the strength of an amorphous rubber more than 10-fold. For a filler to cause significant reinforcement, it must possess high specific surface area, i.e., the particles must be small, less than 1 μm in size. Small particles have large surface area to interact with the rubber and close particle-to-particle spacing in the compound. Structure relates to irregularity in shape of filler aggregates (Figure 2.2), determined by the extent and manner of clustering of primary particles. A filler aggregate with high structure has a large void volume within the space it pervades, in which rubber molecules may become "occluded". The combination of occluded rubber and filler then becomes the reinforcing entity; so that the effective volume fraction of filler is increased (Aggregates are not broken down into primary particles upon mixing with rubber). Generally, reinforcement is enhanced by high structure and strong bonding between filler and rubber. Silica fillers are often treated with silane coupling agents to bond them chemically to rubber, or the coupling agents may be added directly to the rubber compound [13].
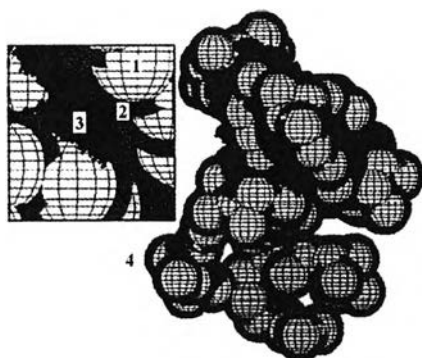

Figure 2.2 Structure of the material: (1) filler, (2) polymer layer around particles, (3) occluded polymer and (4) matrix [14].

2.3 Silica

Amorphous silica consists of ultimate particles of the inorganic silicon dioxide $(SiO_2)_n$, where a silicon atom is covalently bonded in a tetrahedral arrangement to

four oxygen atoms. Each of the four oxygen atoms is covalently bonded to either one silicon atom forming siloxane (-Si-O-Si-) or to hydrogen forming a silanol (-Si-O-H) functionality [15].

The chemistry of silica can be characterized as follows [16]:

1. Silica, which is amorphous, consists of silicon and oxygen arranged in a tetrahedral structure of a three-dimensional lattice. Particle size ranges from 1 to 30 nm and surface area from 20 to 300 m^2/g. There is no long-range crystal order, only short-range ordered domains in a random arrangement with neighboring domains.

2. Surface silanol concentration (silanol groups -Si-O-H) influences the degree of surface hydration.

3. Silanol types fall into three categories—isolated, geminal (two -OH hydroxyl groups on the same silicon atom), and vicinal (on adjacent silicon atoms)—as illustrated in Figure 2.3.
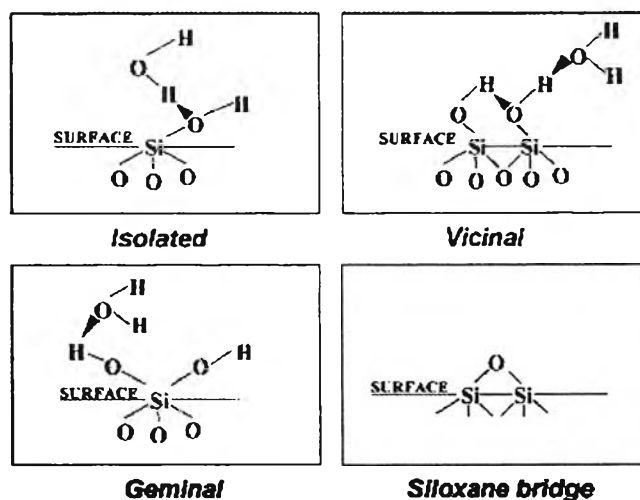

Figure 2.3 Surroundings of Si in silica: geminal, isolated, vicinal, siloxane bridges [10].

During the reaction time, primary particles are first formed in the reactor; later these particles react with each other, accompanied by dehydration, to form aggregates. Within the aggregates, the primary particles are linked together via siloxane bonds. During this process, the aggregates are deposited to form larger units, or agglomerates. In these agglomerates the aggregates are held together by hydrogen

bonding or van der Waals interactions that are considerably weaker than siloxane bonds, which are shown in Figure 2.4.
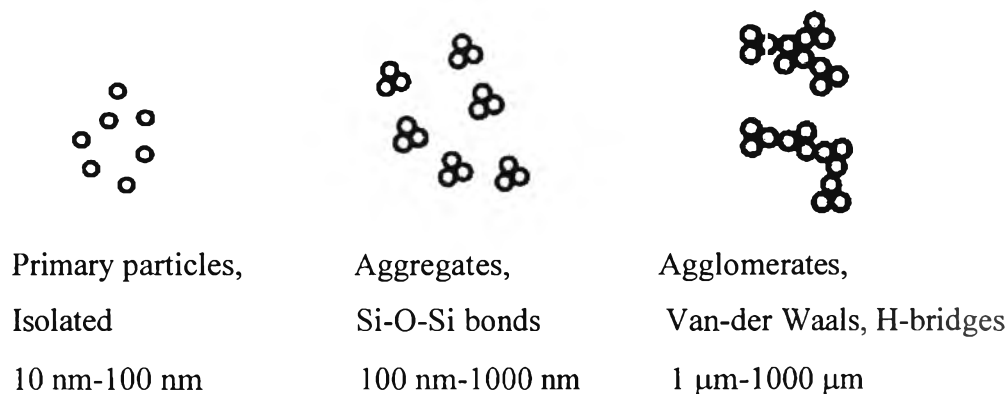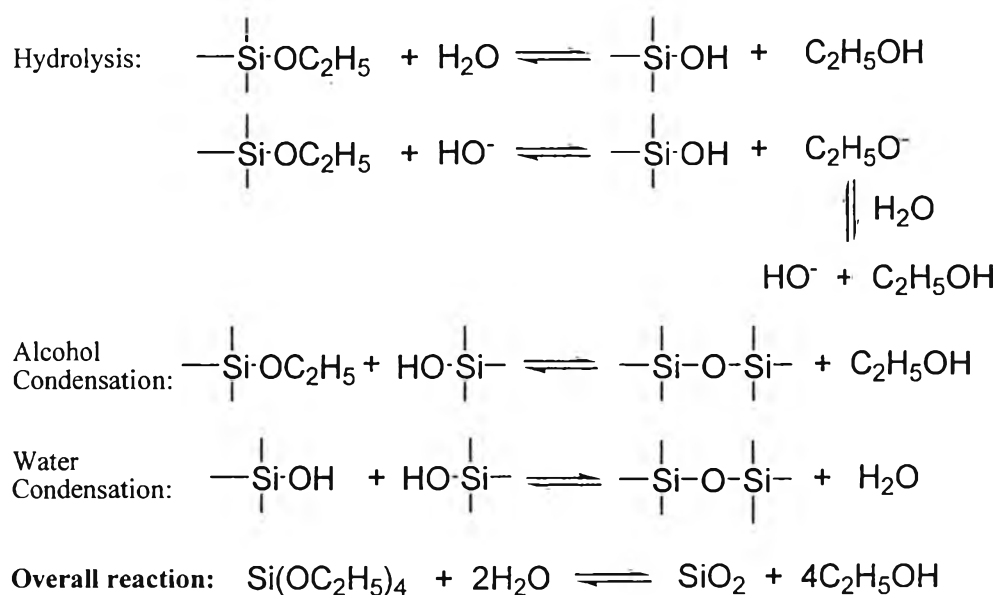

Primary particles,	Aggregates,	Agglomerates,
Isolated	Si-O-Si bonds	Van-der Waals, H-bridges
10 nm-100 nm	100 nm-1000 nm	1 μm-1000 μm

Figure 2.4 Sketches of primary particle, aggregates and agglomerates occurring in silica [10].
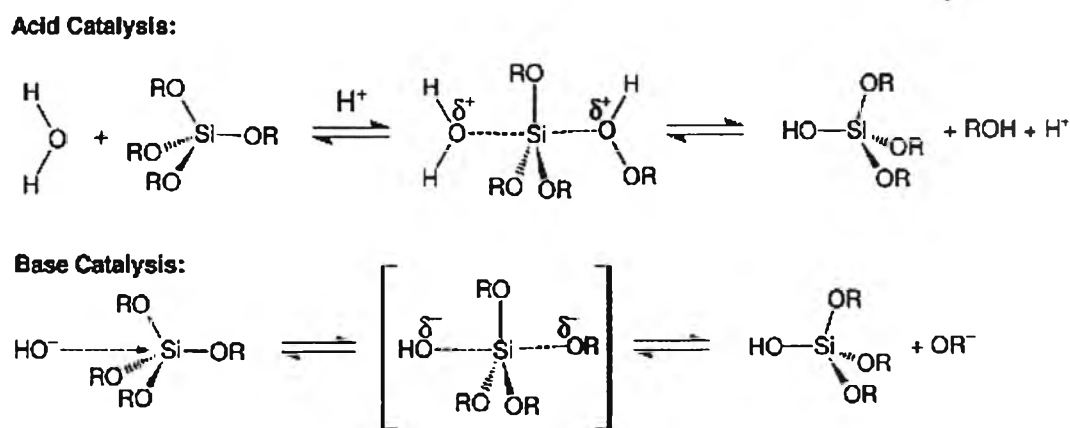
2.3.1 Silica formation by sol-gel process of TEOS

The sol-gel process occurs in liquid solution of metal alkoxide precursors such as tetraethoxysilane or tetraethylorthosilicate, TEOS, which, by means of hydrolysis and condensation reactions, leading to the formation of a new phase-called 'sol'. The sol is made of solid particles of a diameter of few hundreds of nanometer suspended in a liquid phase. Then the particle condenses in to a new phase, called 'gel' in which a solid macromolecule is immersed in a liquid phase (solvent). Hydrolysis and condensation reaction of TEOS or other metal alkoxides to form silica is shown in Scheme 2.1. Initially, metal alkoxides react readily with water. The reaction is called hydrolysis, because a hydroxyl ion becomes attached to the metal atom (so that all of the OR groups are replaced by OH). Two partially hydrolyzed molecules can link together in a condensation reaction. By definition, condensation liberates a small molecule, such as water or alcohol. This type of reaction can continue to build larger and larger silicon containing molecules by the process of polymerization [17].

Hydrolysis: $-\overset{|}{\underset{|}{Si}}\text{-}OC_2H_5 + H_2O \rightleftharpoons -\overset{|}{\underset{|}{Si}}\text{-}OH + C_2H_5OH$

$-\overset{|}{\underset{|}{Si}}\text{-}OC_2H_5 + HO^- \rightleftharpoons -\overset{|}{\underset{|}{Si}}\text{-}OH + C_2H_5O^-$

$\| H_2O$

$HO^- + C_2H_5OH$

Alcohol
Condensation: $-\overset{|}{\underset{|}{Si}}\text{-}OC_2H_5 + HO\text{-}\overset{|}{\underset{|}{Si}}- \rightleftharpoons -\overset{|}{\underset{|}{Si}}\text{-}O\text{-}\overset{|}{\underset{|}{Si}}- + C_2H_5OH$

Water
Condensation: $-\overset{|}{\underset{|}{Si}}\text{-}OH + HO\text{-}\overset{|}{\underset{|}{Si}}- \rightleftharpoons -\overset{|}{\underset{|}{Si}}\text{-}O\text{-}\overset{|}{\underset{|}{Si}}- + H_2O$

Overall reaction: $Si(OC_2H_5)_4 + 2H_2O \rightleftharpoons SiO_2 + 4C_2H_5OH$

Scheme 2.1 Hydrolysis and condensation reaction of TEOS to form silica.

The mechanisms of acid and base-catalyzed hydrolysis are shown in Scheme 2.2.

Scheme 2.2 Differences in mechanism depending on the type of catalyst used in the silicon-based sol–gel process [18].

A sol-gel process of TEOS was applied to prepare silica for reinforcement of rubbers.

In 2000, Kohjiya and Ikeda [19] studied *in situ* silica in natural rubber (NR) matrix. Preparation of the silica filled rubber compound was performed by the sol-gel method. The NR sheet was immersed in TEOS for 48 h at room temperature before

crosslink by sulfur. The silica-silica interaction of *in situ* silica seemed to be weaker than that of silica-rubber to result in better dispersion compared with the conventional silica. The *in situ* silica particles showed good reinforcement effect on the NR vulcanizate without the silane coupling agent. The *in situ* silica was homogeneously dispersed in the natural rubber matrix.

In 2002, Yoshikai *et al.* [4] reported a study on silica reinforcement of synthetic diene rubbers by a sol-gel process of TEOS in the latex. The TEOS was mixed directly into the latex of styrene butadiene rubber (SBR) and nitrile rubber (NBR). The sol-gel process of TEOS then proceeded in a mixture of latex. The silica content in the compounds, particle size and reinforcing behavior of silica were found to depend on the amount of TEOS added and the molar ratio of water to TEOS. The average particle size of silica was reported to be smaller than 100 nm. The tensile strength of SBR and NBR were over 25 MPa.

In 2003, Kojiya and Ikeda [20] prepared the *in situ* silica reinforcement of NR by the sol-gel reaction of TEOS using n-butylamine as a catalyst. γ-mercaptopropyl trimethoxysilane was used for modifying the silica surface. The reaction of TEOS in raw NR was conducted before the processing for NR vulcanizates. The *in situ* silica with coupling agent afforded the lowest viscosity compared not only with conventional silica but also with a carbon black. Lower hydrophilicity of the *in situ* silica surface may result in less filler-to-filler interaction in the reason of better performances.

A "green" (eco-friendly) composite was prepared by Ikeda and Kameda. In 2004, Ikeda and Kameda [21] prepared *in situ* silica nano-particles by a sol-gel reaction of tetraethoxysilane (TEOS) in natural rubber (NR), which was prepared by the NR sheets immersing in TEOS. The swelling degree of NR in TEOS was important for controlling the *in situ* silica content in NR. The *in situ* silica was nano-particle, and its particle size became larger with the increase of silica content from ca. 10 nm to ca. 40 nm for 10–40 phr loadings in the NR matrix, respectively. The excellent reinforcement effect of *in situ* silica for the NR vulcanizates was observed with increasing the *in situ* silica content. The *in situ* silica filling in NR is a good method to prepare the rubbery nano-composites with unique characteristics.

In the same year, Nah *et al.* [22] studied *in situ* silica-filled natural rubber nanocomposites using sol-gel process in terms of friction and abrasion properties. The sol-gel nanocomposite showed a well-dispersed morphology of much finer silica particles of around 40 nm in size. The prepared nanocomposites showed much higher London dispersive component of free energy compared with conventional melt-mixed composites. Also, much lower frictional coefficients were found for the sol-gel nanocomposites. The abrasion resistance of the nanocomposites was proven to be superior to that of melt mixed composites.

In 2008, Poompradub *et al.* [23] investigated the parameters of *in situ* silica formation in natural rubber by sol-gel reaction. The NR sheets were immersed in TEOS at room temperature for 3 hr. THF was the suitable solvent for the sol-gel reaction. N-hexylamine was the most efficient base catalyst to produce the high amount of *in situ* silica in rubbery matrix compared with n-butylamine. It was because the longer chain of n-hexylamine easily penetrated into NR matrix. The higher the mole ratio of TEOS to H_2O, the higher the silica content was obtained. To prevent the phase separation, the mole ratio of TEOS to H_2O should be less than 1:3. This sol-gel method could be applied for the preparation of the new soft nano-composite.

2.3.2 Silica formation by sol-gel process of Organotrialkoxysilanes

Organotrialkoxysilanes are typically co-polymerized with another sol-gel monomer-generally tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS). The sol-gel polymerization of organotrialkoxysilanes involving hydrolysis and condensation usually results in the formation of *low* molecular weight silica are shown in Scheme 2.3.

$$n \ R\text{-}Si\text{-}(OR')_3 + 1.5n \ H_2O \xrightarrow{\ H+ \ or \ OH\text{-}\ } \left[R\text{-}SiO_{1.5}\right]_n + 3n \ R'OH$$
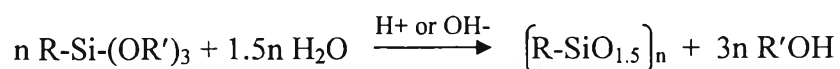
Scheme 2.3 Hydrolysis and condensation of trialkoxysilane to give polysilsesqui-oxane.

The first commercially available coupling agent was the highly reactive 3-mercaptopropyl trimethoxysilane for sulfur-cured compound and vinyltri-methoxysilane and 3-methacryloxypropyl trimethoxysilane (the structure of γ-MPS is shown in Figure 2.7) for peroxide-cross-linked rubber compounds. With the addition of these silanes are markable increase in the reinforcement of white-filled compounds was achieved [10].

In 2000, Loy, *et al.* [24] examined the sol-gel chemistry of organotrialkoxysilanes having different organic groups with methoxide or ethoxide substituents on silicon, at varying monomer concentrations, and under acidic, neutral, and the basic conditions. Polysilsesquioxane gels were prepared by the sol-gel polymerization of organotrialkoxysilane. They found that the large substituent group of organotrialkoxysilane led to the formation of oligomers and polymers in the form of oils and resins. Formation of gels from organotrialkoxysilane is significantly hindered by phase separation of oligomeric or polymeric silsesquioxanes and, to lesser extent, by sterically bulky organic substituents.

In 2009, Siramanont, *et al.* [7] studied the sol-gel process of alkyltriethoxysilanes that was dispersed in natural rubber latex to generate alkylated silica particles inside the rubber matrix. Three types of alkyltriethoxysilanes were chosen, i.e., vinyltriethoxysilane (VTOS), ethyltriethoxysilane (ETOS), and i-butyltri-ethoxysilane (BTOS). The alkylated silica particles were formed in the rubber matrix by a certain combination of TEOS and alkyltriethoxysilanes. The silane conversion to silica in the NR matrix was almost complete for TEOS, but decreased when the alkyl group of the alkyltriethoxysilanes increased in size. The study on hardness, tensile, and tear properties revealed that the uses of *in situ*-generated silica and alkylated silicas resulted in a better reinforcement capability to the rubber vulcanizates than did the conventionally added silica powder.

2.4 Characterization of mechanical properties

2.4.1 Tensile properties [25]

If rubber is stretched, squashed or otherwise mechanically deformed, the scientist says that a deformation (change in shape) called strain has been applied to the materials, as a result of an applied pressure called stress. There are certain clearly defined modes of strain, such as tensile (stretch), compression (squash), shear (a combination of tensile and compression), and torsion (twist).

The most used strain mode in the quality control rubber laboratory is tensile. In this test, a piece rubber is stretched until it snaps (tensile at break). The test piece often goes through a considerable amount of elongation before break occurs (up to around of 900%, depending on the compound). It is interesting that this test is so popular, since there are very few product applications where the rubber is stretched so much.

Tensile testing is accomplished by first molding a flat sheet of rubber about 2 mm thick, from which dumbbell shaped pieces are die cut (see Figure 2.5)

Figure 2.5 Dumbbell shaped test piece for tensile testing.

The test pieces are then stretched in a tensile testing machine and the force required to stretch the samples is measured. Values of stress (force divided by the unstretched cross sectional area of the straight portion of the dumbbell) are recorded at various levels of extension, up to the break point.

The extension is measured as percent elongation and is defined as:

$$\frac{L - L_0}{L_0} \times 100 \qquad (2.1)$$

where: L is the stretched length and L_0 is the original length.

Tensile values before the sample breaks, give the modulus of the sample. For the rubber chemist, modulus means the tensile value (stress) at a given elongation. Modulus numbers at 300% and 500% elongation are commonly measured. Note that the modulus, as defined here, is not equivalent to the modulus as understood by an engineer, which is equal to stress over strain.

2.4.2 Tear resistance [26]

High stress concentration on a rubber product applied at a cut or defect area during service can lead to the propagation of a tear rupture. Tear characteristics for a compound can be related to the compound's crosslink density and state of cure, as well as filler type and loadings. Various tear tests place a deliberate flaw in a rubber specimen to try to relate to the tear propagating force.
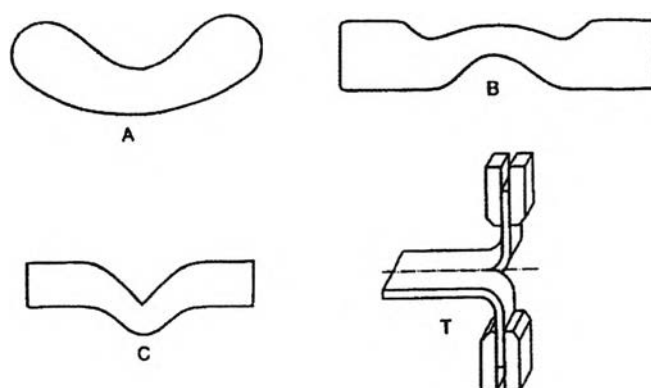

Figure 2.6 Shaping of standard tear specimens, A, B, C, and T

Figure 2.6 shows the shapes of some commonly used tear test pieces which are described in ASTM D624. Die B is a crescent-shaped test piece with large ends for better gripping in a tensile tester. This specimen is nicked with a razor blade to a

specified depth to help initiate a tear. The die C test piece has an angle to help initiate a tear and does not necessarily require a cut nick. The die T trouser tear specimen is separated by a shear force from the tension applied in opposite directions to each leg at right angles to the plane of the test piece. The tear strength (T_s) is reported as kilonewton·meter^{-1} of thickness from the formula:

$$T_s = F/d \tag{2.2}$$

where F = maximum force (in N), for die B and C, and the median or mean for die T (trouser), and d = test piece thickness in mm.

In accordance with fracture mechanics, tearing energy theoretically is a basic material property that is truly independent of the cut geometry and geometry of the rubber specimen. Most standard tear tests do not measure tearing energy. The most common shape in ASTM is that cut by die C. If the apex in the die is not kept sharp and well defined, it can result in higher apparent values of tear.

2.4.3 Tension set

The term "tension set" refers to the strain remaining after complete release of the load producing a deformation. ASTM D412 describes methods for evaluating tension set. The usual measurement of the set is intended to evaluate delayed elastic recovery. If chemical changes have occurred, however, the residual deformation may be permanent. It is expressed as a percentage of the original length or distance between gauge marks.

2.5 Swelling behavior

A reinforced vulcanized rubber possesses a substantial increase in stiffness (modulus) and a reduction in the extent to which the vulcanizate will swell in a rubber solvent. The amount of rubber which remains associated with the filler when the mixture is subsequently immersed in a rubber solvent (bound rubber) is often used as a measure of this interaction (The quantity of bound rubber normally increases on

storage or heating of the rubber-filler mix). Thus, the rubber is adsorbed on the filler surface and this alters the stress-strain properties and reduces the extent of swelling in a solvent. Since equilibrium volume swelling measurements are the principal means of assessing crosslink density, it becomes very difficult to measure crosslink density when reinforcing filler is present in the rubber because the effects of crosslink cannot be readily distinguished from the effects of rubber-filler interaction.

2.6 Thermal analysis

Thermal analysis generally covers three different experimental techniques: Thermo Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA), and Differential Scanning Calorimetry (DSC). For all experiments a selection of crucible are available (platinum, gold, aluminum, quartz) and the measurements can be done in a flow of different gases.

The basic principle in TGA is to measure the mass of a sample as a function of temperature. It is a measurement of weight loss when the cured adhesive is gradually heated ($10\text{-}20^\circ\text{C min}^{-1}$). In principle, this simple measurement is an important and powerful tool in solid state chemistry and materials science. The method for example can be used to determine water of crystallization, follow degradation of materials, and determine reaction kinetics, or study oxidation and reduction.