CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Natural Rubber

It has been estimated that some 2000 different plant spices yield polymer akin to natural rubber and that rubber of sorts have been obtained from some 500 of them. To all intents and purposes, the natural rubber of commerce is obtained from the latex of *Hevea brasilliensis,* a native of Brazil but widely grown on plantations in tropical Africa and Asia. The production of natural rubber has grown steadily since World War II. The Southeast Asian region accounted for about 80% of the total production. The conversion of natural rubber into products is accomplished in many different ways [1].

2.1.1   The Chemical Formula of Natural Rubber

The empirical formula for the natural rubber (NR) molecule appears to have been first determined by Faraday who reported his finding in 1826. He concluded that carbon and hydrogen were the only elements present and his results correspond to the formula C_5H_8. This result was obtained using a product which contains associated non-rubber material. Subsequent studies with highly purified materials have confirmed Faraday's conclusion [1]. Isoprene was found to have the formula C_5H_8, for which Tilden proposed the structure.
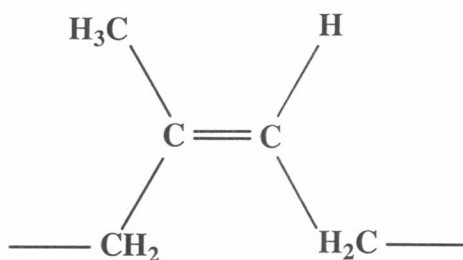
Figure 2.1 Isoprene unit.

The linear structure proposed by Pickles provided the possibility of structural isomer with both *cis*- and *trans*- repeating units. In fact, the natural rubber molecule is not a pure *cis*-1,4 polyisoprene. Besides, it contains very small amounts of functional groups in rubber chain termed as abnormal groups, such as aldehyde groups [4], ester or lactone group [5], and epoxides [6, 7]. Structural studies using ^{13}C-NMR spectroscopy disclosed that the rubber molecule contains about two to three *trans* isoprene units [8]. Recently, detailed structure characterization of natural rubber was investigated by ^{13}C-NMR and ^{1}H-NMR spectroscopies [9, 10]. From the relative intensity of the signal and the degree of polymerization of highly purified natural rubber, the number of *trans* isoprene existing at the initiating terminal of the rubber molecule is estimated to be two. Accordingly, the structure of natural rubber is assumed to be as shown in Figure 2.2.
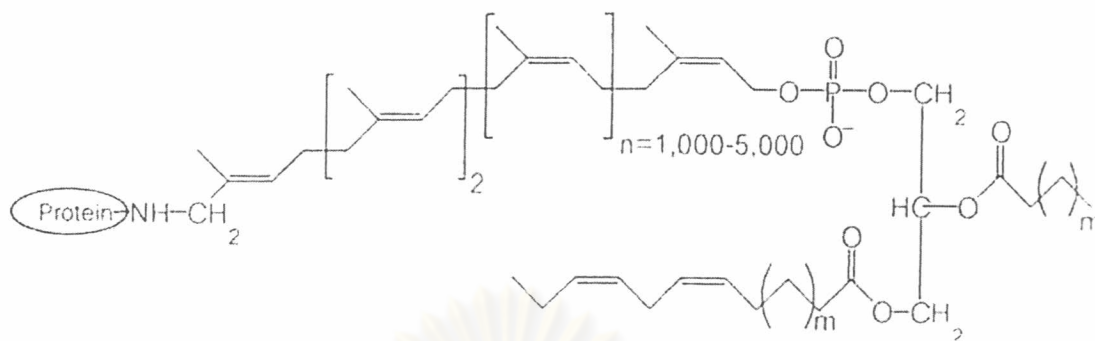
Figure 2.2 Presumed structure of natural rubber.

2.1.2 Composition of Natural Rubber

The chemical composition of fresh *Hevea* latex is complex when compared to synthetic latex. This is because fresh *Hevea* latex is a cycloplasm. It has been known for a long time that fresh *Hevea* latex contains, in addition to rubber hydrocarbon, a large number of non-rubber constituents (many proteinous and resinous substances, carbohydrates, inorganic matter, water, *etc.*) present in relatively small amounts. Many of these are dissolved in the aqueous serum of the latex, others are adsorbed at the surface of the rubber particles and the non-rubber particles suspended in latex [4]. The typical composition of natural rubber and fresh latex is shown in Table 2.1.

Table 2.1 Typical composition of fresh *Hevea* latex [10].

Ingredient	Average value (% w/w)
Total solid content	36.0
Dry rubber	33.0
Proteinous substance	1.0-1.5
Resinous substance	1.0-2.5
Carbohydrates	1.0
Inorganic matter	Up to 1.0

2.1.3 Physical Properties [11]

Physical properties of natural rubber may slightly be due to the non-rubber constituents present and to degree of crystallinity. When the natural rubber is held below 10°C, crystallization occurs, resulting in the change of density from 0.92 to about 0.95. The average molecular weight can range from 200,000-500,000. Some average physical properties of natural rubber are shown in Table 2.2.

Table 2.2 Some physical properties of natural rubber [11].

Properties	Value
Density	0.92
Refractive index (20°C)	1.52
Coefficient of cubical expansion	0.00062/°C
Cohesive energy density	63.7 cal./c.c.
Heat of combustion	10,700 cal/g.
Thermal conductivity	0.00032 cal./sec./cm^2/°C
Dielectric constant	2.37
Power factor (1,000 cycles)	0.15-0.2
Volume resistivity	10^{15} ohms/c.c.
Dielectric strength	1,000 volts/mm^2

2.1.4 Natural Rubber in Manufacturing

There are many standard specifications in defining a range of grades of rubber in the world. The Rubber Manufactures Association has a further set of standards for quality and packing of latex natural rubber grades as shown in Table 2.3.

Table 2.3 International natural rubber type and grade specification [12].

Type	Natural rubber	Description
1	Ribbed smoked sheet	Coagulated sheet, dried and smoked latex. Five grades available.(RSS1-5)
2	White and pale crepe	Coagulated natural liquid latex milled to produce a crepe.
3	Estate brown crepe	Fresh lump and other high-quality scrap generated on the plantation.
4	Combo crepe	Lump, tree scrapes and smoked sheet cutting are milled into a crepe.
5	Thin brown crepe	Unsmoked sheet, wet slab, lump and other scrap from estates and small holding.
6	Thick blanket crepe	Wet slab, lump and unsmoked sheet milled to give a crepe.
7	Flat bark crepe	All types of scrap natural rubber including earth scrap.
8	Pure smoked blanket crepe	Milled smoked rubber derived exclusively from ribbed smoked sheet.

a)   **Smoke Sheet [10]**

The largest single type of dry rubber is the ribbed smoked sheet (RSS), and recently air dried sheet. Field latex is strained into large bulking and blending tanks, diluted with an equal volume of water to a dry rubber content of

15 %, then coagulated. To 1,000 parts of the diluted latex, 50 parts of a 1% formic acid solution are added. Acetic acid can also be used. The process is to treat the latex in aluminum tanks and slotted for partitions. The coagulum is then passed as separate sheets or a continuous slab through a series of squeeze and wash rolls at even speed, with continuous water spraying. After going through the five or six rolls set progressively tighter. The rubber has been squeezed down to the control thickness. The characteristic rib pattern is embossed primarily for increased surface area for drying. The wet sheets are passed into a smoke –house. The temperature ranges from about 50-60°C. The entire period covering about 3-4 days. Finally, the rubber is baled for shipping to manufacturers.

b)   Standard Thai Rubber (STR) [13]

STR is the name of type of natural rubber that are produced in Thailand. The processing materials of the various STR grades are shown in Table 2.4.

c)   Lump and Scrap

Lump and scrap are field grade materials derived from latex naturally coagulated in different manner such as in the tapping cup or other suitable vessels, and in the trace of tapping. Field grade materials are USS, green crepe, cup lumps, field coagulum, scrap or mixture with contain certain proportion of each of them according to the STR grade intended to process.

Table 2.4 Processing materials of STR Grades.

Grade	Processing Materials
STR XL, STR5L	Whole field latex bulked and formic acid coagulated under strictly controlled conditions.
STR5	Either whole fresh coagulum or unsmoked sheet (USS) or blend of them subjected to further crumb processing.
STR10, STR20	Field grade materials based on USS, lump, scrap, green crepe or mixture.

2.2 Reinforcement of Natural Rubber

a) Reinforcement [1]

Reinforcement basically relates to composites built from two or more structural elements or components of different mechanical characteristics and whereby the strength of one of these elements is imparted to the combined with the set of favorable properties of the other component. This set must include easy shaping into the required form of final article and stabilization of this shape within a reasonable time. One typical example of reinforcement is that of concrete with embeded steel rods or cable where the high tensile strength of the steel is imparted to the concrete to give it increased flexural and impact strength. The best definition may be: A reinforcing filler improves the modulus properties (tensile strength, tear resistance, and abrasion resistance) of the final vulcanizate.

b) Basic Factors Influencing Elastomer Reinforcement

There is an improvement of modulus and tensile strength. This is very much dependent on the particle size of the filler; small particles have a much greater effect than coarse ones. Particle size is directly related to the reciprocal of surface area per gram of filler; thus the effect of smaller particles actually reflects their greater extent of interface between polymer and solid material.

The reduction in properties at higher loading is a dilution effect, general to all fillers, merely due to a diminishing volume fraction of polymer in the composite. If the volume percentage of filler becomes so high that there is not enough rubber matrix to hold the filler particles together, strength approaches zero. Before this stage of loading is reached, the compound attains a level of stiffness where it becomes brittle and, at the normal rate of testing (e.g. 50 cm per minute) such a brittle compound would show poor strength. At much lower rate of stretching, the decline in strength with higher loading would be less; the height and place of the maximum in the strength vs. loading curve are rate dependent. The maximum occurs at higher loading when testing at slower rate. The place of the maximum is also dependent on the particle size of the filler.

c) The Reinforcement Mechanism

A very schematic picture of a slippage process when stress is applied to a polymer reinforced with carbon black is drawn in Figure 2.3. Three chains of different lengths between two carbon black particles in the direction of stress are displayed. As the stretching process proceeds from stage 1, the first chain slips at the

points of connection A and A' until chain 2 is also stretched between B and B' (stage 2). Elongation continues until finally a stage 3 is reached in which all three chains are stretched to their maximum and share the imposed load. The homogenous stress distribution causes a high improvement in strength. In stage 4 the tension is relieved and the test piece has retracted.
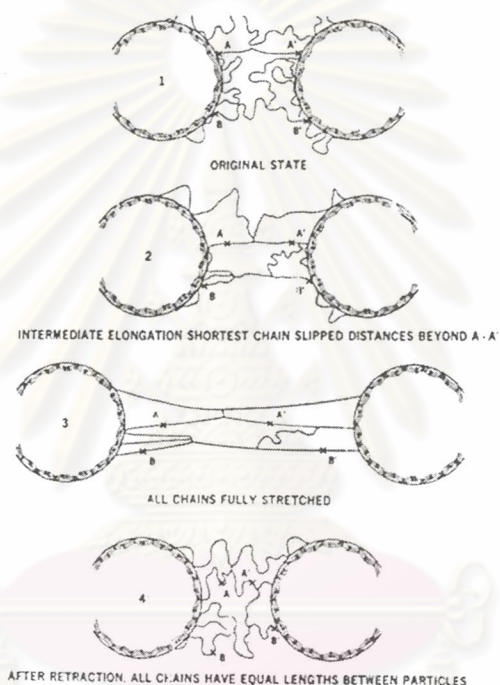

Figure 2.3 Molecule slippage model of reinforcement mechanism.

Carbon black has been widely used as a reinforce filler for natural rubber in many applications especially tire industries due to its effective reinforcement and low cost. However, silica is a more appropriate filler where colorless material is desirable. Adverse mechanical properties of silica-filled natural rubber are often problematic due to poor adhesion between natural rubber matrix and polar silanol groups on silica surface. Several approaches have been used to promote adhesion by lowering interfacial energy at the interfaces including chemical modification of

natural rubber by oxidation or grafting of polar monomers to increase rubber polarity. Abdel- Bary and coworkers studied graft copolymerization of waste rubber powder with different polar monomers such as acrylic acid, acrylonitrile and acrylamide using different gamma radiation induced grafting conditions. The effects of different parameters such as monomer concentration, radiation dose, inhibitor concentration and type of reaction solvent on the graft yield were studied. It was found that the maximum graft yield obtain is 90%, 24% and 42% for acrylic acid, acrylamide and acrylonitrile, respectively. The grafted rubber powder obtained was also tested an ion exchanger for copper and lead. Thus, it is interesting to evaluate the grafted was rubber powder as an expensive ion exchanger [14]. Pastor-Blas and coworkers studied the effectiveness of the improvement of adhesion of synthetic vulcanized styrene-butadiene rubber (SBR) using oxygen plasma, which was ascribed to an increase in wettability, the creation of surface roughness and some oxidation of the surface [15]. Fuhrmann and coworkers studied graft copolymerization of ground tyre rubber (GTR) with methacrylic acid by photoinitiated polymerization. The grafted GTR worked as impact modified in epoxy compounds and improved mechanical properties or polyurethane formations effectively. Such the presence of reactive carboxy groups on surface of GTR, provides the possibility of covalent linkage with polar groups during blending process [16].

Surface treatment of silica filler can also be used to improve silica-polymer matrix compatibility by introducing hydrophobic moieties. O'Haver and coworkers studied polymerization of various monomers such as 1,3-butadiene with vinyl

acetate, acrylonitrile, 4-methoxystyrene, 4-chlorostyrene and methyl methacrylate solubilized in adsorbed surfactant bilayer on the silica surface. It was found that 4-methoxystyrene/butadiene modification afforded the most promising candidate based on an evaluation of a silica-filled natural/styrene-butadiene rubber. Moreover, physical testing showed that cure time was decreased and mechanical properties were increased [17].

Another promising way to improve adhesion between rubber matrix and silica is to generate interfacial chemical bonding by adding silane coupling reagents during the curing process. Parker and coworkers studied crosslinking between natural rubber and silica by using bis-(3-(triethoxysilyl-propyl) tetrasulfide and 3-mercapto-propyltrimethoxysilane as silane coupling agents. Solid-state ^{13}C NMR was utilized in analysis of crosslinked structure in silica-filled natural rubber. Hewitt and coworkers discovered that pre-coating of the silane coupling reagent on silica was found necessary for uniform surface coating that yielded improved crosslinking density. It was also found that amines, glycols and soluble zinc compounds interfere with the silane-silica reaction [18]. When the coupling agent was pre-added to the silica the problem of silica-zinc interaction was resolved [19]. Besides, Manna and coworkers studied the role of Z-6032 (N-3(N-vinylbenzylamino)ethyl-γ-aminopropyl trimethoxy silane monohydrogen chloride) in bonding between precipitated silica and epoxidized natural rubber(ENR). Fourier transform infrared spectroscopic data showed that silica is bond to ENR through formation of Si-O-C bond, where as in the presence of silane coupling agent, silica is bonded to the coupling agent through Si-O-Si bond and ENR is bond to the coupling agent through C-N-C bond formation.

Results from the studies of physical properties and rheology reveal that precipitated silica interacts chemically with ENR during high temperature (180°C) molding. It has also been reported that an addition of silane coupling agent increases the crosslink density [20].

For the research reported here, an alternative approach to increase reinforcement between natural rubber and silica by forming chemical bonding of vinyl-containing silica with polyisoprene, the main polymeric composition of natural rubber. The use of silane chemistry to modify surface properties of inorganic materials in both research and technology has been well established [21]. Reaction of porous silica and single surfaces of silicon dioxide with monofunctional silanes having wide range of alkyl group ($R(CH_3)_2Si-X$, where X = halogen, OR, OH, NH_2 or OSO_2CF_3) were reported [22]. Comparisons of modified silica with one reacted with di- and tri-functional silanes were also extensively explored and documented. To introduce vinyl groups on material surfaces makes several modifications possible. Vinyl-terminated alkylsilane monolayers were prepared by adsorption of $CH_2=CH(CH_2)_nSiCl_3$ onto silicon dioxide surfaces [23].

Fadeev and coworkers studied reactions of monofunctional silanes with single silicon oxide surfaces (Si wafer) to prepare modified surfaces whose structures and wettabilities were controlled by the alkyl groups. It was found that wettabilities and roughness were dependent on types of alkyl groups on modified surfaces. The highest carbon content on the surface as well as the highest contact angle were obtained using vapor phase reaction [24].
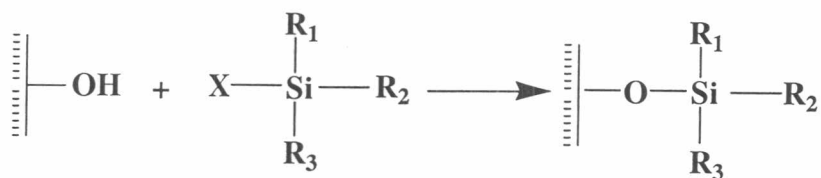
$$R_1, R_2 \text{ or } R_3 = CH_3 \text{ or } —\!\!/\!\!/$$

$$X = \text{Halogen}$$

Scheme 2.1 Reaction between a silicon oxide surface with alkylsilane reagents.

Despite considerable work reported on reinforcement of natural rubber, very few has concentrated on a direct surface analysis of network formed at silica/natural rubber interfaces because of the limitation of surface-sensitive techniques and the inaccessability of cured network. To overcome this difficulty, silicon dioxide flat surface was chosen as a model for silica while squalene was selected as oligomeric model for polyisoprene, the main polymeric composition of natural rubber by comparing with squalane, a saturated analogue of squalene.
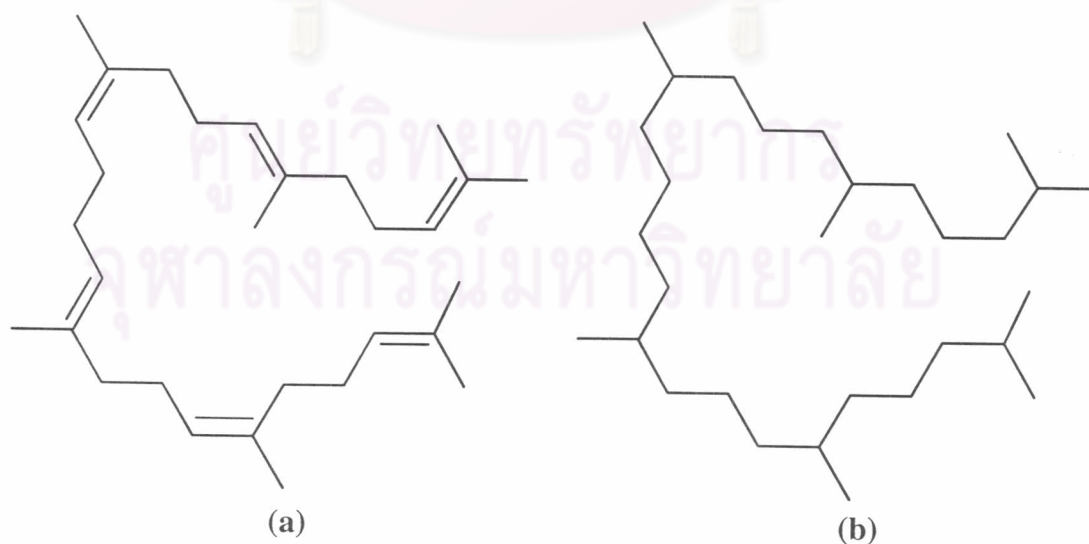

(a)   (b)

Figure 2.4 Structure: (a) squalene (b) squalane.

Tasi and coworkers studied chemical reactions between squalene which is a model system of natural rubber and plasma polymerized acetylene films on steel substrates. The crosslinking between vinyl groups of acetylene film on steel with squalene in the presence of carbon black, zinc oxide, sulfur, stearic acid, cobalt naphthenate and diary-*p*-diphenyleneamine was followed by using secondary ion mass spectrometry (SIMS), x-ray photoelectron spectroscopy (XPS). The results showed that surface crosslinking can be formed more effectively at squalene/modifiled steel intereface than at squalene/modifiled steel interface [25].

2.3 Description of Curing Parameters [26]

Scorch is premature vulcanization in which the stock becomes partly vulcanized before the product is in its final form and ready for vulcanization. It reduces the plastic properties of the compound so that it can no longer be processed. Scorching is result of both the temperature reached during processing and amount of time the compound is exposed to elevated temperatures. This period of time before vulcanization is generally referred to as "scorch time". Since scorching ruins the stock, it is important that vulcanization dose not start until processing is complete.

Rate of Cure is the rate at which crosslinking and the development of the stiffness (modulus) of the compound occur after the scorch point. As the compound is heated past the scorch point, the properties of the compound change from a soft to a tough elastic material required for use. During the curing step crosslinks are

introduced, which connect the long polymer chains of the rubber together. As more crosslinks are introduced, the polymer chains become more firmly connected and the stiffness or modulus of the compound increases. The rate of cure is an important vulcanization parameter since it in part determines the time the compound must be cured, i.e., "the cure time".

State of Cure In general, "state of cure" is a term used to indicate the development of property of the rubber as cure progresses. As the crosslinking or vulcanization proceeds, the modulus of the compound increases to various "states of cure". Technically, the most important state is the so-called "optimum". Since all properties imparted by vulcanization do not occur at the same level of cure, the state of optimizing may not be the best for other properties.

Cure Time Cure time is the time required during the vulcanization step for the compounded rubber to reach the desired state of cure.

Overcure A cure which is longer than optimum is an "overcure". Overcures may be of two types. In one type, the stock continues to harden, the modulus rises, and tensile and elongation fall. In other cases, including most natural rubber compounds, reversion occurs with overcure and the modulus and tensile strength decrease

2.4 Cure Meters

Instead of curing each test compound at separate ranges of temperatures and making separate tensile tests, many laboratories use a cure meter, of which several types have been developed. Using this instrument, modules change is monitored during the cure. Many properties are obtainable from the data; the most common being minimum and maximum stiffness, scorch time, cure time to 90% or 95% of maximum stiffness, and a cure rate index.

2.4.1 Rheometer The most widely used cure meter is rheometer, in which the specimen is contained in a sealed test cavity under a positive pressure and maintained at an elevated temperature. A biconical disk, embedded in the specimen, is oscillated through a small arc. The autographically recorded force is proportional to the shear modulus of the rubber. An envelope of a typical cure curve is given in Figure 2.6. The minimum torque (M_L), maximum torque (M_{HF}), scorch time (t_{s2}) and time to 90% cure ($t_c(90)$) are indicated. Also obtainable are initial viscosity at zero time, minimum viscosity, and reversion (time after M_{HF} to reach 98% of M_{HF}).

Many illustrations of rheometer use have been described as well as of the viscurometer, which works on a similar principle. The biconical rotor used in each instrument produces a shear rate which is uniform over the rotor surface. For instruments such as the Mooney viscometer, which use a flat disk, the shearing rate is near zero at the central shaft and a maximum at the disk periphery.
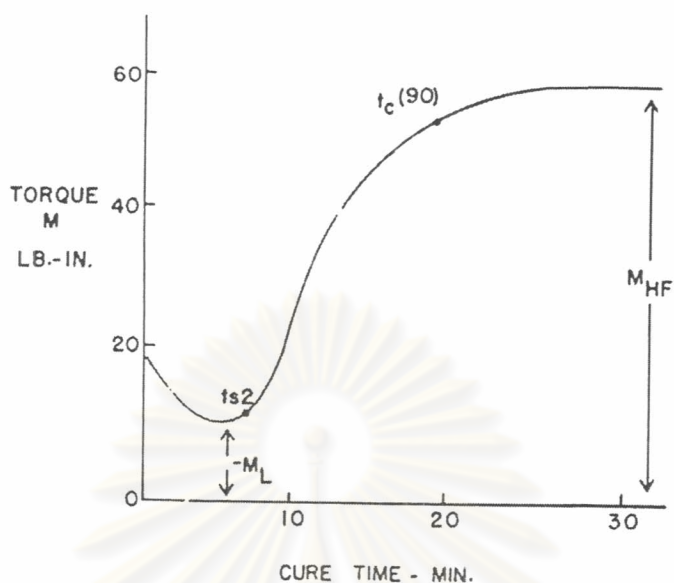
Figure 2.5 Envelope of rheometer cure curve which attains an equilibrium torque.

2.4.2 Rotating Disk Viscometer

The shearing action is performed by disk rotating in shallow cylindrical cavity filled with the rubber under test, as shown in Figure 2.6. The rubber is squeezed into the cavity under considerable pressure. The surface of the disk and the dies which form the cavity are grooved to avoid slippage. The test specimen consists of two pieces which completely fill the test chamber.
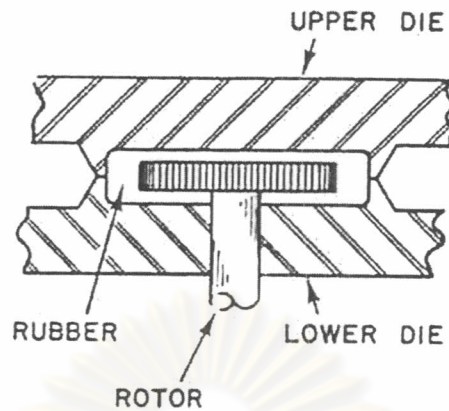
Figure 2.6 Mooney Chamber and rotor.

2.5 Tests for Mechanical Properties

2.5.1 Stress-Strain Tests

Physical testing of rubber often involves application of a force to specimen and measurement of resultant deformation or application of a deformation and measurement of the required force. Two common modes of deformation, tensile and shear are shown in Figure 2.7. Stress is the force per unit cross sectional area (F/A for either tensile or tear deformation). Strain is the deformation per unit original length ($\Delta L/L$) in tensile tests or deformation per unit distance between the contacting surfaces in shear tests. Stress is usually expressed in unit of newton per square meter (N/m^2).
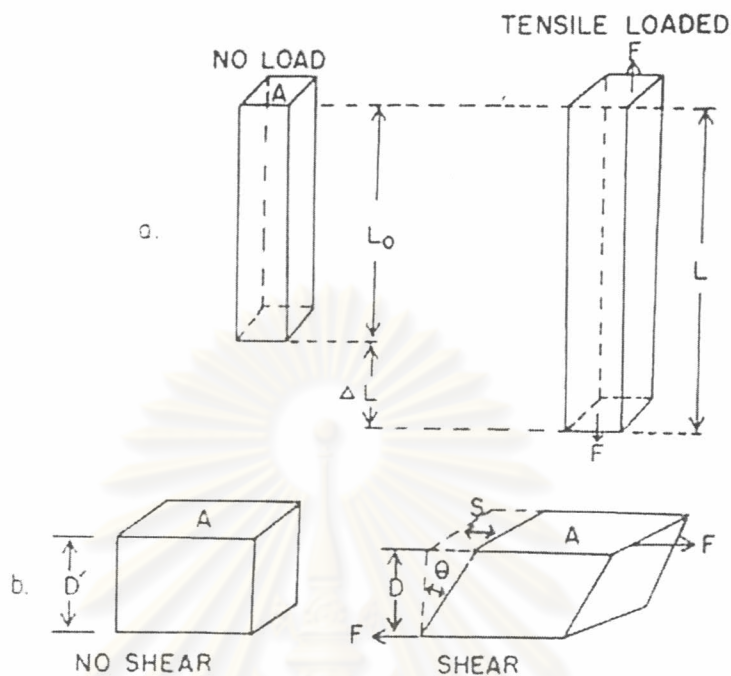
Figure 2.7 a) Tensile stretching of bar; b) Shear of a rectangular block.

2.5.2 Tear Test

Tear test results are strongly dependent on the type of specimen used, the rate of tearing, and the temperature. The method is useful only for laboratory comparisons and is not applicable for service evaluations, except when supplemented by additional tests, nor for use in purchase specifications. Nevertheless, many such tests are run, perhaps because they seem to be logical extensions of the hand tear evaluation which was so useful to the old-time compounder.

Three types of tear specimens are classified by Buist : indirect tearing as in the trousers specimen (Figure 2.8), tearing perpendicular to the direction of

stretching as in the ASTM methods, and tearing in the direction of stretching as in the Russian test piece. Except in the ASTM Die C specimen nicks of prescribed lengths are cut into the region of desired stress concentration.

Rate of stretching in the ASTM method is 20 inches per minute. An increase in rate would normally decrease the tearing energy for SBR rubbers but give a more complicated effect in natural rubber. In theory, a portion at least of tire wear is a result of high speed tear, such a test has been considered for evaluation of abrasion resistance.
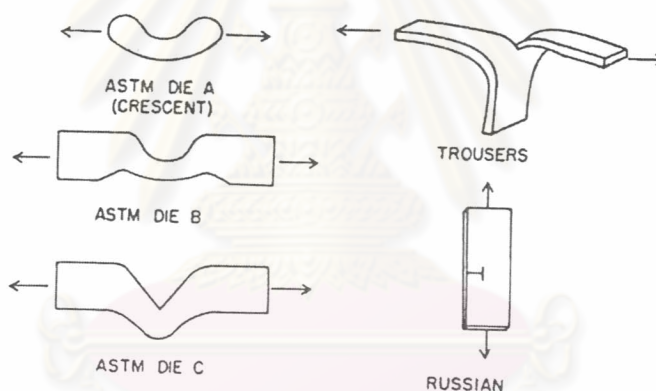

Figure 2.8 Types of tear specimens.

2.5.3 Hardness

Hardness, as applied to rubber, may be defined as the resistance to indentation under conditions which do not puncture the rubber. Different instruments designed to measure hardness do not usually agree well with each other for any of several reason: defination of scale end points, shape and size of indentor point , total

load applied, rate and time of load application. Hardness is a property of rubber which must be expressed in terms of instrument parameters rather than basic units. A high modulus rubber is, of course, also hard, but the relationship is not easy to quantify.

The spring-loaded pocket durometer is the most common instrument for measuring hardness of elastomers. The shore durometer in particular is known and used world-wide. In this instrument the scale runs from zero hardness for a liquid to 100 for a hard plane surface such as glass. The type A durometer is used for soft stocks, up to a reading of 90. Above 90 the type D durometer, having a different indentor shape and different stiffness spring, is used. One reason for the popularity of this instrument is its portability for field use and adaptability to fairly irregular surfaces. Difficulties arise, however, in reporducibility of results by different operators.

2.6 Surface Characterization

2.6.1 X-ray Photoelectron Spectroscopy (XPS)

This technique, which is often referred to as Electron Spectroscopy for Chemical Analysis (ESCA), is generally regarded as an important technique for polymer surface characterization. The quantitative technique can provide atomic composition of a surface with a sampling depth on the order of 10-20 Å depending on the sample and instrumental conditions.

The basic principle of XPS involves the photoelectric effect. The analysis is accomplished by irradiating a sample with monoenergetic soft x-rays and analyzing the energy of the electrons emitted. An elemental analysis can be obtained due to the unique set of core electrons for each element. The number of electrons emitted are counted as a function of their energy. Quantitative information can be calculated from peak areas and atomic sensitivity factors obtained from samples with known composition. The photon energy is greater than the binding energy of the electron in the atom, and the electron ejected from the atom should have a kinetic energy (E_k) approximately equal to the difference between the photon energy and the binding energy (E_b). Therefore, the basic equation for XPS is:

$$E_b = h\nu - E_k - \phi$$

................(1)

Where h is Planck's constant, is x-ray frequency and is the spectrometer work function. All energies are usually expressed in electron volts (eV). Note that the result reported in this work are not correct for sample charging.

The technique is surface selective. Although the photons can penetrate many microns deep into the sample, the electrons generated at depth have relatively low kinetic energy (0-1000 eV) and cannot travel very large distance in matter. Only those electrons emerging from a certain depth (10-200 Å) without losing their kinetic energy from inelastic collisions comprise the main photoelectron peaks. Common anode material used as x-rays sources are magnesium, aluminum, titanium whose K_αx-rays have energies of 1254, 1487, 4510 and 5417 eV, respectively. Although the titanium and chromium x-rays have higher energies that can eject electrons in deeper

core shells and can provide information in deeper sampling region, magnesium and aluminum anodes are preferable due to their narrow line widths and lower tendency to damage samples.

Practical surfaces are rarely uniform and homogeneous in composition and structure. The surface often consists of samples is thus very useful. This can be accomplished by the varible angle technique. By varying the take-off angle (θ_T) between the detector and the surface, electrons travel from similar vertical depths with different distance before reaching the detector. At small θ_T , a smaller depth is sampled than at high θ_T. The surface sensitivity is thus enhance at low θ_T.
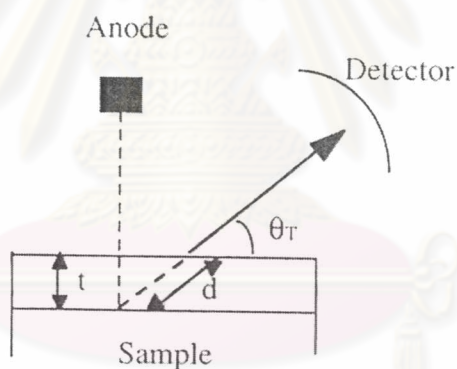
Figure 2.9 The sample/detector geometry of varible angle XPS.

2.6.2 Contact Angle

Contact angle is considered one of the most surface-sensitive techniques and can provide information on outermost few angstroms of solids. The equipment required is relatively simple and inexpensive. The basis of the contact angle

technique is the three-phase equilibrium at the contact point at the solid/liquid/vapor interface (Figure 2.10).
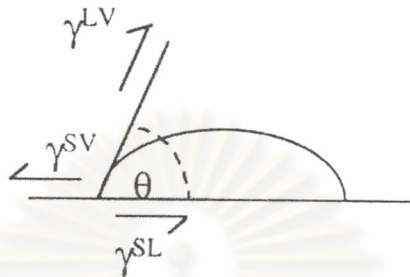

Figure 2.10 Contact angle geometry indicating the three-phase equilibrium.

The contact angle was associated to the surface energy of the solid and the liquid surface tension by Young in 1850. The calculation is based on the energy balance approach to the three-phase equilibrium. The cosine contact angle ($\cos\theta$) is directly related to the surface energy by Young's equation , where γ^{sv} , γ^{sl} and γ^{lv} are the surface of the solid-vapor, solid-liquid, liquid-vapor interfaces, respectively.

$$\gamma^{sv} - \gamma^{sl} = \gamma^{lv} \cos \theta$$

.....................(2)

Direct interpretations from this equation can be made based on several assumptions that predict only one intrinsic contact angle (θ_0) regardless of how that angle is measured. The assumption are: (1) the solid surface is rigid and nondeformable (surface modulus> 3.5×10^5 dynes/cm^2), (2) the solid surface is highly smooth, (3) the solid surface is chemically homogenous, (4) the solid surface does not interact in any way with the liquid other than the three-phase equilibrium (i.e. swelling), (5) the surface functional groups do not reorganize in response to

change in the environment during the measurement and (6) the liquid must not cause extraction or partitioning of material from the solid phase to the liquid phase.

In practice, some of these assumption are generally not valid and the observed contact angles depend on the way they are obtained. Generally, two contract angle values are measured (see Figure 2.11). The advancing contact angle (θ_A) can be measured as the solid/liquid contact area increases. The receding contact angle (θ_R) can be measured as the solid/liquid contact area decreases.
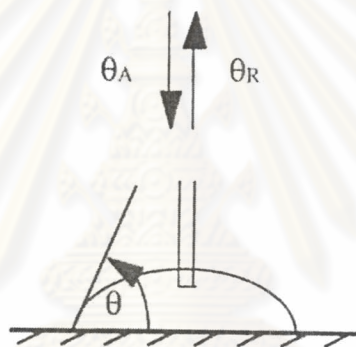

Figure 2.11 Measurement of advancing/receding contact angles (θ_A/θ_R).

2.6.3 Ellipsometry

Ellipsometry is a sensitive optical technique for determining properties of surfaces and thin films. If linearly polarized light of a known orientation is reflected at oblique incidence from a surface then the reflected light is elliptically polarized. The shape and orientation of the ellipse depend on the angle of incidence, the direction of the polarization of the incident light, and the reflection properties of the surface. Ellipsometry measures the polarization of the reflected light with a quarter-

wave plate followed by an analyzer; the orientations of the quarter-wave plate and the analyzer are varied until no light passes though the analyzer. From these orientations and the direction of polarization of incident light are expressed as the relative phase change, Δ , and the relative amplitude change, Ψ, introduced by reflection from the surface. These values are related to the ratio of Fresnel reflection coefficients, R_p and R_s for p and s- polarized light, respectively.

An ellipsomer measures the changes in the polarization state of light when it is reflected from a sample. If the sample undergoes a change, for example a thin film on the surface changes its thickness, then its reflection properties will also change. Measuring these changes in the reflection properties allow us to deduce the actual change in the film's thickness.
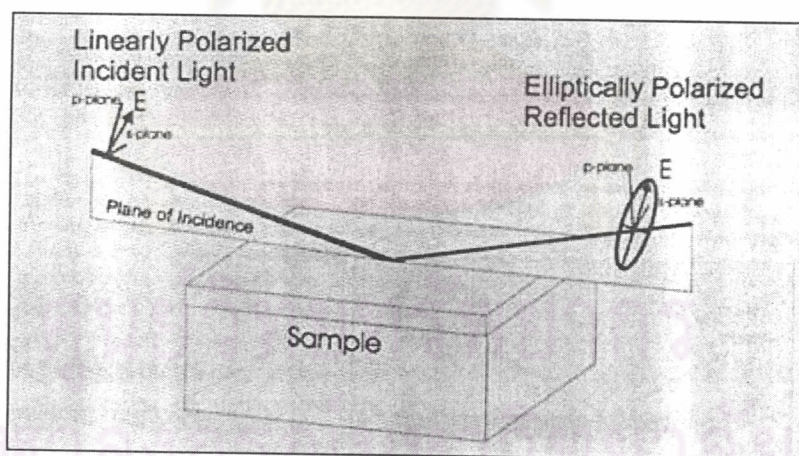

Figure 2.12 Schematic of the geometry of an ellipsometry experiment.