CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Progress Made In Development [5]

Rubber has been used for centuries by the South American Indians. They most probably were the people who discovered that if latex (a milky fluid that circulates in the inner portions of the bark of many tropical and subtropical trees and shrubs) is dried, it can be pressed into useful objects such as bottles, shoes and balls. Initially in the western world, the new material was merely a scientific curiosity. Some years later a British scientist Joseph Priestley remarked on its usefulness for rubbing pencil marks from paper, and so the popular term rubber was coined. Other applications gradually developed, notably for waterproofing shoes and clothing.

However, it was not until the 1830s when John Haskins and Edward Chaffee organised the first rubber-goods factory in the United States that the commercial rubber industry really began to flourish. At the time rubber had many weaknesses. It softened with heat and hardened with cold; it was tacky, odorous, and perishable. In 1834 the German chemist Friedrich Ludersdorf and the American chemist Nathaniel Hayward discovered that the addition of sulphur to gum rubber lessened or eliminated the stickiness of finished rubber goods. In 1839, the American inventor, Charles Goodyear, using the findings of the two chemists, discovered that cooking rubber with sulfur removed the gum's unfavourable properties, in a process called vulcanization.

Vulcanized rubber has increased strength and elasticity and greater resistance to changes in temperature than unvulcanized rubber; it is impermeable to gases, and resistant to abrasion, chemical action, heat, and electricity. Vulcanized rubber also exhibits high frictional resistance on dry surfaces and low frictional resistance on water-wet surfaces. The vulcanization process remains fundamentally the same as it was in 1839.

With the invention of the bicycle, the motor car and the pneumatic rubber tyre, demand for rubber grew rapidly. By 1900 more than 40,000 tons were used each year. Today the world's natural rubber use is over 4,500,000 tons per annum. The economic competition from synthetic rubber has stimulated research and development in natural rubber by increasing productivity in the field, improving consistency and quality of the product and packaging, and developing natural rubbers with specific properties. Increased productivity has been achieved by increasing the production of trees by cross-pollination of high-rubber-producing clones of the rubber tree (*Hevea brasiliensis*), use of chemical stimulants, and better tapping and collection methods. These methods have proven particularly successful on Asian estates where over 90% of the world's supplies are produced, Thailand is the largest producer.

With improved productivity and better processing methods and controls, much better quality and consistency have been obtained. This has made possible the development of standard rubbers to meet specifications on a number of properties including dirt & ash content, viscosity, and copper & manganese content. A number of modified forms of natural rubber have been developed to suit particular conditions including the following; superior processing, oil extended, special tyre rubber, deproteinized and chemically modified. Despite synthetic rubber having the larger

share (over 75%) of the worldwide rubber market, natural rubber continues to have high demand, due to its better elasticity, resilience and heat transfer properties.

2.2 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].

Natural rubber fresh latex is a dispersion of rubber particles and non-rubber particles in an aqueous serum phase. Apart from the rubber hydrocarbon, a large number of non-rubber constituents (mainly are carbohydrates, lipids and proteins) are also present in relatively small amounts in the latex. Some are associated with the rubber particles themselves. The rubber particles of the fresh latex are packaged with many of polyisoprene molecules and are surrounded with surface active molecules (mainly proteins and phospholipids) which are believed to be at the particle- serum interface in the form of interfacial film or membrane [6].

2.2.1 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].

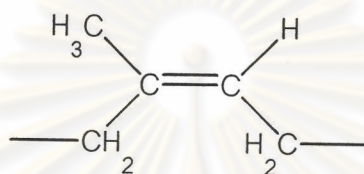Isoprene was found to have the formula C_5H_8, for which Tilden proposed the structure.

Figure 2.1 Isoprene unit

The linear structure proposed by Pickles provided for the possibility of structural isomer with both cis- and trans- repeating units.

Chemical and spectroscopic analysis observe the presence of non-rubber component in natural rubber, such as protein, lipid, sugar, etc. It has been postulated that these non-rubber constituents are the causes for outstanding properties of natural rubber.

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 [7], ester or lactone group[8], and epoxides [9, 10]. Structural studies using ^{13}C-NMR spectroscopy disclosed that the rubber molecule contains about two to three *trans* isoprene units [11]. Recently, detailed structure characterization of natural rubber was investigated by means of ^{13}C-NMR and ^{1}H-NMR spectroscopies [11, 12]. 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.
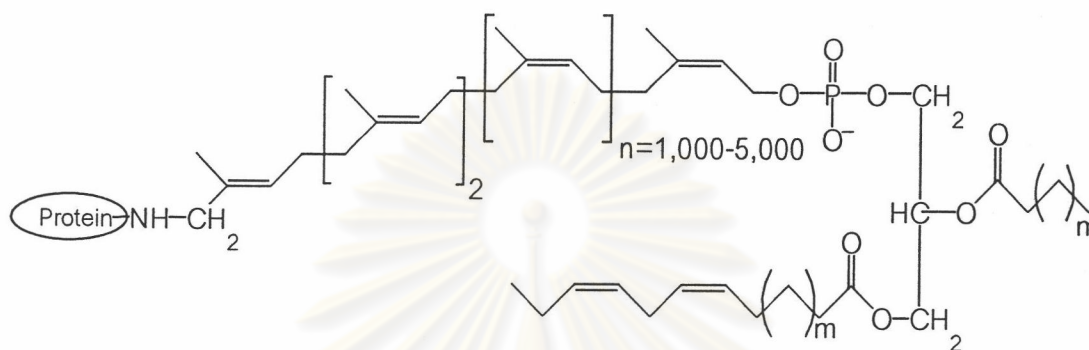

Figure 2.2 Presumed structure of natural rubber

2.2.2 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 [7].

The typical composition of natural rubber and fresh latex is shown in Table 2.1.

Table 2.1 Typical composition of fresh *Hevea* latex [13]

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
Water	Add.to 100

2.2.3 Particulate Composition [14]

A typical particulate composition of fresh *Hevea* latex is as follows:

a) Rubber Particles

In fresh latex, rubber particles constitute 25-45% by volume of the latex. The rubber particles in fresh latex are protected by complex film containing proteins and lipids. The rubber hydrocarbon predominantly cis-1,4-polyisoprene, at least 99 %, contained in the particles, is non water-soluble and occurs as molecular aggregates. The rubber particles are usually spherical with diameters ranging from about 0.02 μm to 1 μm, but in a latex from certain mature clones the larger particles may be pear shaped.

b) Lutoids

The most abundant non-rubber particles are the lutoids. They comprises 10-20% (volume) of the whole latex and contain about 12% solids. The lutoids are spherical membrane-bounded bodies typically 2-5 μm in diameter and enclosed by a membrane which is very rich in phosphatidic acid and may explain their negative surface charge. Inside the lutoid is an aqueous solution (often call "B-serum") which contains dissolved substances such as acids, mineral salts, proteins, sugars and polyphenol oxidase. The intact lutoids are osmotically sensitive and the addition of water causes them to swell and burst and this causes a marked increase in the viscosity of the latex [15].

c) Frey-Wyssling Particles

The Frey-wyssling particles are spherical, often bright yellow and of high refractive index. They are larger in size and have a slightly higher density than the rubber particles. They often appear in clusters. The yellow colour is due to the presence of carotenoid pigments.

2.2.4 Chemical Composition

The non-rubber components (excluding water) in fresh latex are mainly proteins, lipids, quebrachitol and inorganic salts, but as would be expected from the cytoplasmic nature of latex, a large number of other substances are present in small amounts.

a) Proteins

The total protein content of fresh latex is approximately 1-1.5% of which about 20% adsorbed on the rubber particles and a similar proportion is associated with the bottom fraction. The remainder is dissolved in the serum phase. The adsorbed proteins. together with adsorbed lipids, impart colloidal stability to the latex and remain associated with the rubber phase when the latex is coagulated by acid during the manufacture of dry rubber (sheet, crepe of crumb). About half of the serum and bottom fraction proteins are also coagulated and remain associated with the rubber in the process. Starch gel electrophoresis revealed the presence of twenty-two protein components in the latex. The two major proteins are α-globulin and hevein [13].

b) Lipids [13]

Lipids are water-insoluble and are concentrated mainly in the rubber phase with small quantities in the bottom fraction and in the Frey-Wyssling particles. Lipids may be divided into neutral and polar lipids. In *Hevea* Latex the polar lipids are the phospholipids. Neutral lipids are acetone soluble but undegraded phospholipids are not. The total lipids on rubber particles have been reported to vary from 1.4-3.2 % (on dry rubber content) or 0.6-1.7% (on latex). The amount of phospholipid is, however, constant at about 1.0% (on dry rubber content). Thus the clonal variation of the total lipids can be ascribed to differences in the content of the neutral lipids.

c) Inositols and Carbohydrates

Quebrachitol (methyl inositol) is the most concentrated single component in the serum phase, amounting to about 1% of the whole latex. Small amounts of inositol isomers, sucrose, glucose, galactose, fructose and two pentoses have also been

detected. In the absence of adequate preservation, the carbohydrates, but possible not the inositols, are metabolized by bacteria and converted to volatile fatty acid (mainly formic, acetic, and propionic acids). These acid are not present in fresh latex and their concentration in commercial latex is a measure of the degree of bacterial decomposition which the latex has undergone.

Table 2.2 Lipid composition of *Hevea brasiliensis* latex of RRIM 501 [13]

Lipid	% of total lipids	Composition % of latex
Neutral Lipids	53.6	0.87
-Esters		0.14
-Triglycerides		0.56
-Tocotrienols		0.03
-Sterols		0.04
-Fatty acid, alcohols, diglycerides and monoglycerides		0.10
Glycolipids	32.9	0.44
-Esterified steryl glycoside		0.05
-Monogalactosyl diglyceride		0.04
-Digalactosyl diglyceride		0.34
Phospholipids	14.0	0.23
-Phosphatidyl ethanolamine		0.05
-Phosphatidyl chloine		0.13
-Phosphaidyl inoitol		0.05
Total lipids		**1.64**

d) Inorganic Constituents

The total concentration of inorganic ions in fresh latex is approximately 0.5% of which more than half normally consists of potassium (0.12-0.25%) and phosphate ions (0.25%). Small amounts of magnesium, copper, iron, sodium and calcium are also present. The relative proportions of these ions, which show both genetically and environmental variations can have a marked influence on the colloidal stability of the latex. In particular a high ratio of magnesium to phosphate ions is often found in lattices of low stability.

Other minor constituents of latex include ribose nucleic acids (RNA), pyrophosphate nucleoside and low molecular weight thiols.

2.2.5 Physical Properties [16]

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 number average molecular weight can range from 200,000-500,000. Some average physical properties of natural rubber are shown in Table 2.3.

Table 2.3 Some physical properties of natural rubber [16]

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

2.3 The Processes Used in Industry to Produce Rubber [5]

Natural rubber, harvested as latex undergoes a number of steps (see Figure 2.3) before it is ready for use. All natural rubber originates in the *Hevea* tree, and it starts its journey when the tree is tapped. Trees are rarely tapped more often than once every two days. A tapper starts the trek around the plantation before dawn. At each tree a sharp knife is used to shave off the thinnest possible layer from the intact section of bark. The cut must be neither too deep, nor too thick. Either will reduce the productive life of the tree. This starts the latex flowing, and the tapper leaves a little cup underneath the cut.
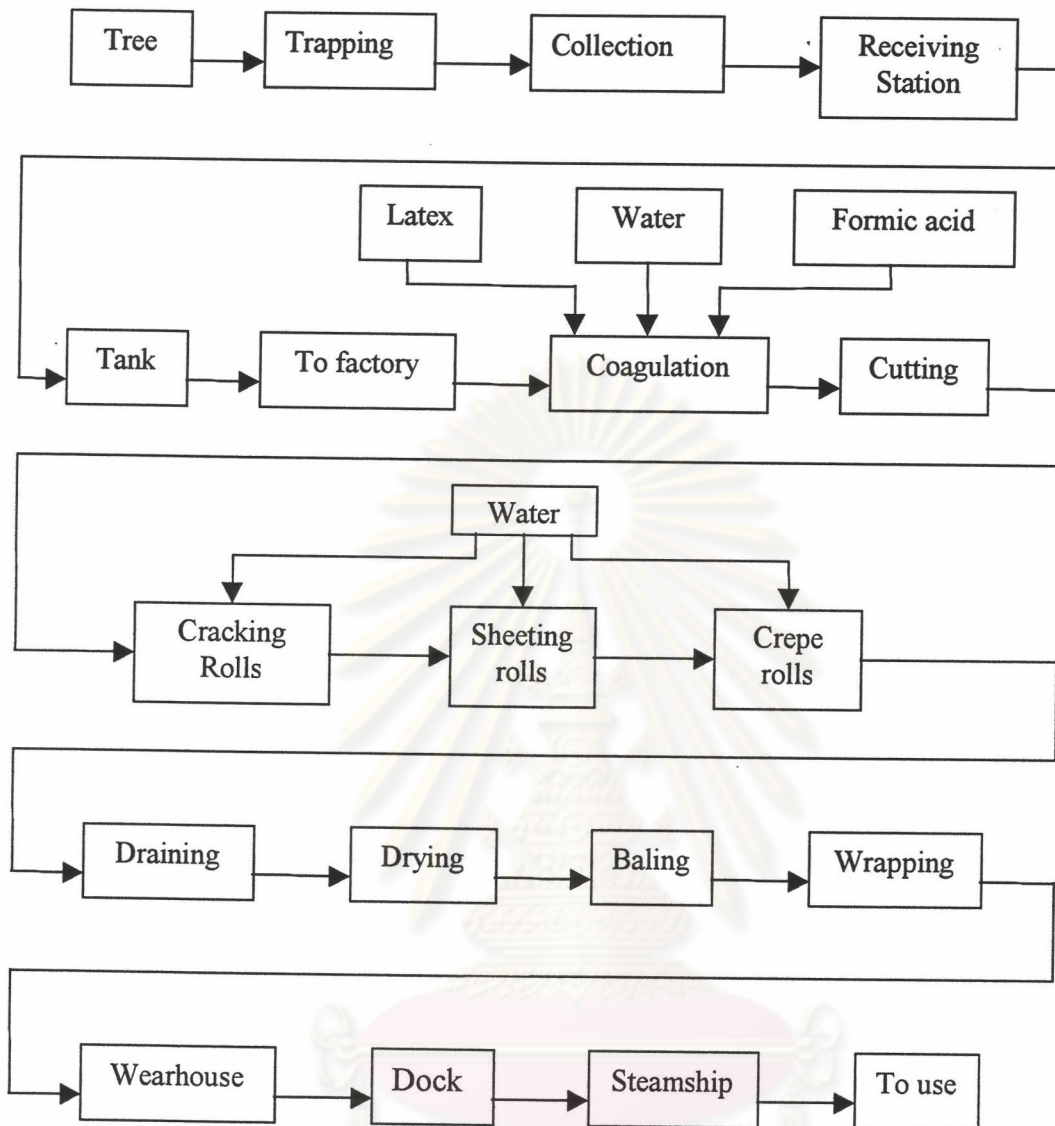
Figure 2.3 Stepwise production of natural rubber

In ordinary circumstances, this latex will normally coagulate into a lump in the bottom of the cup, called *'cup lump.'* If the plantation manager wants to make latex, then the tapper must add a stabilising agent to the cup. Usually this is ammonia, which prevents the latex from coagulating. The tapper returns a few hours later and

collects the stuff in the cup -- either cup lump or latex. The double round trip usually finishes at about 2 pm.

Figure 2.4 Tapping process

After the collection of the tapped latex, the rubber is taken to a receive station where it is strained into holding tanks prior to being trucked to a factory for processing.

In the factory, rubber is recovered from its mixture by coagulation with formic acid and water. This causes the suspended rubber particle within the latex to clump together forming crumbs that resemble curds of milk. After being pressed between rollers to consolidate the rubber into 0.6-cm (0.25-in) slabs or thin crepe sheets, the rubber is air- or smoke-dried for shipment.

2.3.1 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 2.4.

Table 2.4 International natural rubber type and grade specification [17]

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	Compo 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 [16]

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) [18]

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 2.5.

Table 2.5 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.

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.

2.4 Odor from Natural Product

People smell odors because the odor molecule (called the odorant) fits into a molecular receptor in our nose. It turns out that any similar chemical fitting into the slot of the receptor will be perceived as a similar smell, even though the chemical is different. Unpleasant odor can also result from the breakdown of foods and other organic products in storage areas as well as the decomposition of wastes and unwanted by-products in various industrial processes, disposal sites, garbage bins, and pet litter boxes. The volatility of an organic compound is usually expressed as its vapor pressure [19].

The analysis and evaluation of odor is an inseparable combination of chemistry and instrumental methods (e.g., GC, spectroscopy). There are many techniques used to prepare the sample for analyses (see Table 2.6).

Table 2.6 Analytical techniques for odor characterization

Techniques	Description
Distillation Techniques	
▪ Steam distillation	▪ Less destructive than direct distillation, primarily to separate volatile organic from non-volatile materials.
▪ Fractional distillation	▪ Classical packed column and high reflux ratios, based on boiling-point differences, appropiate for small amounts of sample.
▪ Vacuum degassing/ molecular distillation	▪ Most useful for isolating small amounts of volatiles from nonvolatile oils, used short time to heat the sample, reduces chances of artifact formation or losses of heat sensitive materials.
Extraction	
▪ Direct solvent extraction	▪ Simple and general lack of detrimental effect on the sample components, high solvent purity, ease of removal and lack of odor alteration.
▪ Selective extraction techniques	▪ Combine features of isolation and separation methods.
▪ Simultaneous steam distillation/solvent extraction	▪ Suitable for continuous analysis and to increase the efficiency of techniques.

Table 2.6 (Cont.)

Techniques	Description
Vapor-Phase Isolation Technique ■ Equlibrium Headspace Techniques ■ Direct evolution of volatiles (including Porus polymer collection)	■ Analyze directly in vapor , rapid and easy to apply, the sensitivity is limited. ■ Use the adsorbents to adsorb the volatile and removed the volatile after thermal evolution.

2.5 Mal-odor Reduction Substances

The method of reducing mal-odor from the material is changing a mal-odor to more pleasant character by masking and/or reducing the odor intensity to more acceptable level by counteraction. For odor masking, a mixture may show a stronger intensity (hyperaddition), the same intensity (complete addition), or a lower intensity (hypoaddition) than the sum of the components. The most common observation is hypoaddtion. Regardless of the effects on intensity, the odor-masking effect works primarily by modifying the perceived character of mal-odor. Odor counteraction is a phenomenon in which two or more odors are mixed and give a combined odor intensity less than that of either of the individual components [20].

The reduction substances that are commonly used as cyclodextrin, carbon black, chitosan, surfactants and zeolite are used to reduce mal-odor from the rubber samples.

2.5.1 Cyclodextrin

Cyclodextrins (CDs) is the mal-odor counteractant that has been used to control odor from detergent compositions [21]. The natural CDs are produced from starch by the action of cyclodextrin glycosyltransferase (CGTase), an enzyme produced by several organisms, Bacillus macerans being the earliest source. Structurally, CDs consist of 6, 7, or 8 (α,β and γ respectively) D-glucopyranosyl units connected by alpha-(1,4) glycosidic linkages. The most stable three dimensional molecular configuration for these non-reducing cyclic oligosaccharides takes the form of a toroid with the upper (larger) and lower (smaller) opening of the toroid presenting secondary and primary hydroxyl groups, respectively, to the solvent environment. The interior of the toroid is hydrophobic as a result of the electron rich environment provided in large part by the glycosidic oxygen atoms.
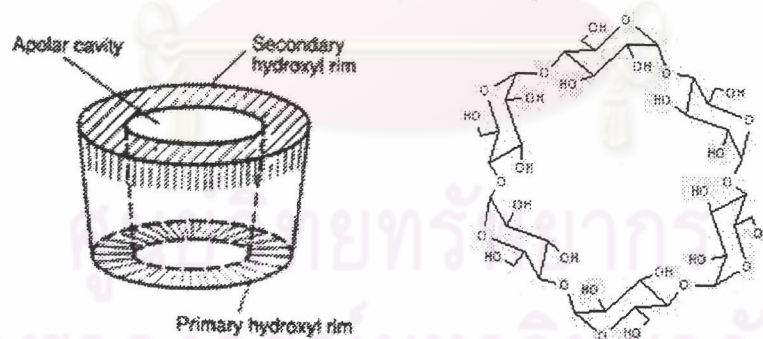

Figure 2.5 Cyclodextrin cavity [21]

2.5.2 Carbon black [22]

Carbon black is the material that is normally used as a reinforce filler in natural rubber. It's also known as one of the most effective substance for removing

organic contaminants from water. Due to its highly porus structure with large surface area, carbon black can adsorb a lot of organic chemicals that are often responsible for taste, odor and color problems.

2.5.3 Chitosan

Chitosan, β-(1→4) –2- deoxy-D-glucan, is a polysaccharide generally obtained from natural chitin after N-deacetylation by alkaline treatment. Chitin, poly-β-(1→4)-N-acetyl-D-glucosamine, a cellulose-like biopolymer, is the second most abundant natural polysaccharide in the world. Chitin is present in marine invertebrates, insects, fungi and yeasts [23]. The molecular structures of chitin and chitosan are illustrated in Figure 2.6. Chitosan is insoluble in water, but it becomes soluble and cationic when it is dissolved in acidic solvents. Free amino groups in the structure of chitosan become positively charged and form bonds with functional groups, including -OH and-COOH [24].
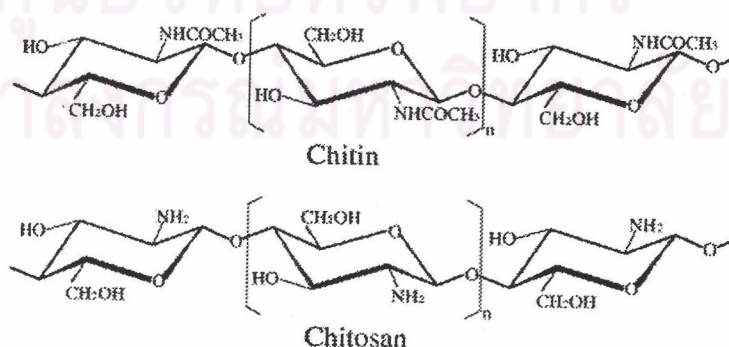

Figure 2.6 Molecular structure of chitin and chitosan

2.5.4 Zeolite 13x

Zeolites have a rigid crystalline structure with a network of interconnected tunnels and cages, similar to a honeycomb. While a sponge needs to be squeezed in order to release water, zeolites give up their contents when they are heated or under a reduced pressure. The name "*zeolite*" comes from the Greek words zeo (to boil) and lithos (stone), literally meaning "the rock that boils." Zeolites have the ability to absorb liquids and gases such as petroleum or hydrogen - but remain as hard as a rock [25]. This structure has 7 A° outer pore and 15A° inner pore.
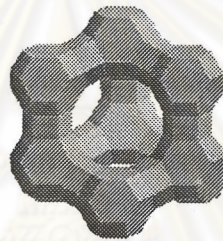
Figure 2.7 The FAU structure of zeolite

2.5.5 Surfactants [26]

Surfactants are among the most versatile products of the chemical industry. A surfactant (a contraction of the term surface-active agent) is a substance that, when present at low concentration in a system, has the property if adsorbing onto the surface or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces (or interfaces). The term interface indicates a boundary between any two immiscible phases; the term surface denotes an interface where one phase is a gas, usually air.

Surface-active agents have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as a lyophobic (hydrophobic)group, together with a group that has strong attraction for solvent, called the lyophilic (hydrophilic) group. This is known as an amphipathic structure. The hydrophobic group is usually a long-chain hydrocarbon residue, and less often a halogenated or oxygenated hydrocarbon or siloxane chain. The hydrophilic group is an ionic or highly polar group. Depending on the nature of the hydrophilic group, surfactants are classified as:

- Anionic: The surface-active portion of the molecule bears a negative charge, e.g. $RCOO^-Na^+$ (saop), $RC_6H_4SO_3^-Na^+$ (Alkyl aryl sulphonate). Sodium Dodecyl Sulphate (SDS) is the most powerful ionic denaturant known to solubilise proteins by producing conformational changes in the molecules.

- Cationic: The surface-active portion bears a positive charge, e.g. $RNH_3^+Cl^-$ (salt of the long chain amine), $RN(CH_3)_3^+Cl^-$ (quaternary ammonium Chloride). Some of them have bactericidal properties and are therefore used as disinfectants as Benzalkonium chlorides.

- Zwitterionic: Both positive and negative charges may be present in the surface-active portion, e.g. $RNH_2^+CH_2COO^-$ (long-chain amino acid).

- Nonionic: The surface-active portion bears no apparent ionic charge, e.g. $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long-chain fatty acid).

2.6 Mal-odor from Natural Rubber

Fulton has studied the problems of odor during rubber processing. It was found that coagulation and subsequent conversion of coagulum into bale rubber affect the smell of natural rubber. The field grade material tends to have a stronger smell than rubber prepared by the deliberately controlled coagulation of latex. The main constituents of the effluent gases from the rubber industry are low molecular weight volatile fatty acid, which can be effectively removed by water scrubbers with efficiencies of 92-99% [4].

Isa has studied how to control the mal-odor in Standard Malaysia Rubber (SMR) factories. The mal-odor from SMR factories is mainly attributed to the obnoxious volatile components which are present in the exhaust gases discharged into the air through a chimney during the drying stage of SMR processing. The volatile compounds are originally produced from the microbial breakdown of the non-rubber components during the storage of scraps and cup lumps prior to processing. Prior to the characterization by gas chromatography, the exhaust gases were collected by adsorption on charcoal adsorption tube to collect the exhaust gases. It was found that the volatile compound in the exhaust gases were low molecular weight volatile fatty acids such as acetic acid, propionic acid, butyric acid and valeric acid. The mal-odor can be reduced by a water-scrubber system [27].

Fabienne and Linda studied the volatile odor compounds from full-fat and reduced fat-frankfurters. Volatile odor was sampled using the headspace technique and characterized by GC/MS. The volatile odor compounds include aliphatic compounds, mainly from lipid oxidation, sulfur containing compounds, terpenes from the added spices and phenol from the smoke [28].

Reed and coworkers reported the method of removing mal-odor from fabrics by mal-odor counteractant such as cyclodextrin, zeolite, clay and essential oil. These substances help to control odor from detergent compositions, to protect perfumes in detergent, to improve the solubility of compounds like nonionic surfactant and to improve their removal [29].