CHAPTER I

INTRODUCTION

At the present, the utilization of natural rubber (Para rubber) has been increased due to some properties such as good elasticity, insulation, superior in the raw rubber strength than synthetic rubber and its excellent mechanical properties as vulcanized rubber (European patent no. 0 584 597 A1, 1993). Although synthetic rubber are available, but due to its higher price and lower elasticity than natural rubber (as quoted by Koosakul, 1994), the consumption of natural rubber has gradually increased. In 1992, the consumption of natural rubber has risen by 3.1 % (Seifert, 1993). Natural rubber, therefore, remains a useful raw material for manufacturing rubber products.

1. Natural rubber (Para rubber)

1.1 Structure and composition

Fresh field latex obtained from Hevea brasiliensis is a milky white or slightly yellowish opaque liquid. Hevea latex contains, in addition to the rubber hydrocarbon, a large number of non-rubber constituents present in relatively small amounts. The chemical and physical characteristics of latex are influenced by clones of rubber, age of rubber and season of tapping. A typical composition of fresh latex is shown in Table 1.

Fresh latex can be separated into three major zones by ultra-

centrifugation :

Table 1 The composition of latex (Fong, 1992)

Composition	Per cent
Rubber hydrocarbon	36.0
Water	58.5
Proteineous substances	1.4
Neutral lipids	1.0
Phospholipids	0.6
Ash	0.5
Inositols and carbohydrates	1.6
Other nitrogen compounds	0.3

1) Rubber particles The uppermost layer of rubber particles constitute 25 % - 45 % of the volume of latex. The rubber particles are usually spherical with diameters ranging from about 0.02 μm to 3 μm and pear-shaped of mature rubber. These particles in fresh latex are protected and stabilized by negatively charged complex film containing proteins and lipids (Smith, 1953 and Fong, 1992). The composition of rubber is an unsaturated hydrocarbon which is non water-soluble contained in the particles as molecular aggregates. The rubber hydrocarbon is predominantly cis-1,4-polyisoprene (at least 99%) (Figure 1) having the formular $(C_5H_8)_n$ where n is about

10,000 and C_5H_8 is the monomer isoprene.

A small yellow layer below the rubber phase is Frey-Wyssling particles which are larger spherical and have a slightly higher density than the rubber particles. The bright yellow color is due to the presence of carotenoid pigments.

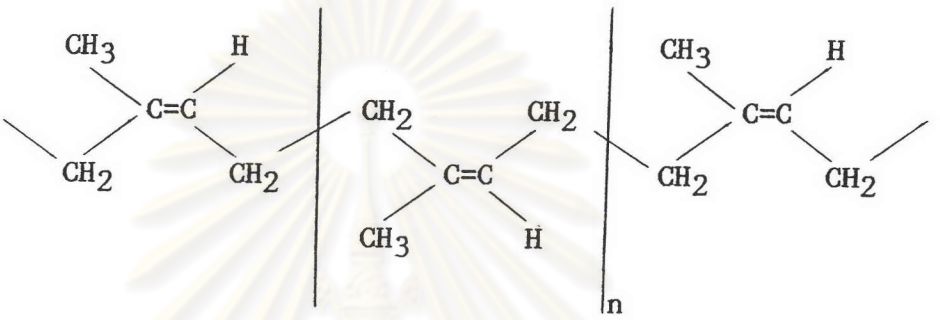


Figure 1 The chemical structure of Hevea rubber

2) The C-serum phase or the aqueous phase

3) The bottom fraction The more dense fraction consists of mostly lutoids and small amounts of other non-rubber particles (Cook and Sekhar, 1953; Moir, 1959). Lutoids which are spherical membrane-bounded bodies typically 2 μm to 5 μm in diameter and have negatively charged surface comprise 10 - 20 % (volume) of the whole latex and contain about 12 % solids. Inside the lutoid is an aqueous solution pH 5.5, called as B-serum which contains dissolved substances such as acids, mineral salts, proteins, sugars and a polyphenol oxidase while the pH of ambient serum is about 6.5-6.9 (Fong, 1992).

1.2 Molecular weight (Mw) and molecular weight distribution (MWD)

The molecular weight (Mw) and molecular weight distribution

(MWD) are inherent properties of the polymer mass and directly related to intrinsic viscosity and plasticity (Subramaniam, 1975). The MWD are either distinctly bimodal with two peaks, the one at lower molecular weight generally being less than that at higher weight, or skewed unimodal with a shoulder or plateau on the low molecular weight side of the peak (Fuller, 1990) (Figure 2). The dispersion in weights was wide, the ratio of the weight to the number average molecular weight, polydispersity ($\bar{M}w/\bar{M}n$), ranging from 2.5 to 10. Although the shapes of the distribution varied considerably, the molecular weight range was generally between 3 x 10^4 to about 10^7 and Mw had a value between 1.6 and 2.3 x 10^6 (Fuller,1990). The molecular weight and MWD of natural rubber show great variations due to different clones, processing and the time and method of the mastication (Subramaniam, 1993).

1.3 Rubber particle stabilization and coagulation

The rubber particle is stabilized because the surface of particle is surrounded by a layer of proteins absorbed which carry negative charges, and proteins are hydrophilic substances. Then there is an envelope of water molecules surrounding the rubber particle. These water molecules, acting as a sheath, prevent direct contact between particles. Chemical destabilizing agents such as acid, metallic ions and organic solvents destabilize the structure of water molecule and bring about to the coagulation of latex. The stability of latex can be maintained after tapping mostly by adding ammonia solution. Ammonia, an alkali preservative, has no effect on rubber, no deposits and can easily be deammoniated. It increases the pH of latex then inhibits bacterial growth, sequesters some metallic ions

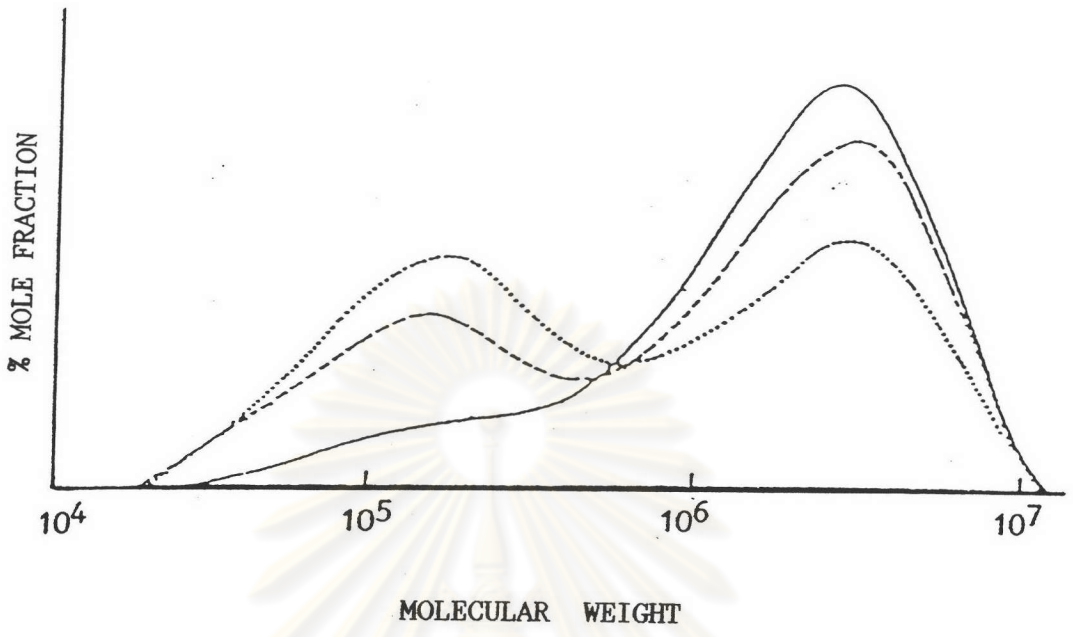


Figure 2 Types of molecular weight distribution curves of natural rubber (Subramaniam,1980)

Type 1 : Distinctly bimodal distribution where peaks are of nearly the same height.

Type 2 : Distinctly bimodal distribution where the peaks in the low molecular weight region is small.

Type 3 : A skewed unimodal distribution with a "shoulder"or "plateau" in the low molecular weight region.

resulting in an increment of the rubber particle stability. Triton X-100 (Iso-octyl-phenoxypolyethoxyethanol, Nonidet P-40) is a nonionic detergent which has the capacity to solubilize proteins and also stabilize the colloidal state of rubber particles (John et al., 1977).

Latex can be coagulated by itself (autocoagulation) or by acid with a long range of time. Complete coagulation in a shorter time was obtained by steaming with 1 kg/cm^2 pressure in 10 min and the yield of rubber from steam coagulation was about 2 % higher than that from acid coagulation (John and Sin, 1974).

2. Solid natural rubber

2.1 Gel content

The gel phase in the natural rubber consists of two types of gel : macrogel and microgel. Macrogel is insoluble in solvents and can be seen as swollen rubber floating in the solution when dry natural rubber is dissolved in a solvent. Microgel is soluble in solvents and is not visible to the naked eyes (Subramaniam, 1993). The presence of gel correlates with an increment in the bulk viscosity of the rubber. Microgel causes crosslinking between rubber molecules within the rubber particles (Freeman, 1954) while the macrogel is associated with the abnormal groups distributing along the rubber chain causing the storage hardening in dry rubber (Wood, 1952). On the contrary, Subramaniam (1993) reported that storage hardening also increases the macrogel content. With longer time of heating of accelerated storge hardening, the macrogel content

increases steadily and reaches a plateau.

2.2 Storage hardening

The problem encountered in the introduction of natural rubber to technical specifications was apparently uncontrollable hardening during manufacture, shipping and storage termed as storage hardening. The increment in the bulk viscosity or the arise of stiffening in rubber is due to the chemical reaction in which rubber molecules in main rubber chain is crosslinked involving the aldehyde or carbonyl groups incorporated on the main rubber chain and amino acids or some aldehyde groups present among the non-rubber constituents (Roberts, 1990 and Subramaniam, 1975). The variation of viscosity is due to many factors, clonal rubber, gel content and non-rubber constituents. There are advantages to control the viscosity in consumer's factory by easier milling, pre-mastication saving, consistency of compound vulcanization and stock storage. The inhibition of storage hardening of the rubber is produced by adding mono-functional amines or carbonyl condensing reagent. Chin (1969) reported that 0.15 p.h.r. of hydroxylamine hydrochloride was suitable to stabilize viscosity due to availability, low cost and compatibility with latex. Its function is blocking the crosslinking site in the rubber molecules resulting in restriction of the rise in viscosity of rubber. For production, the rubber can be divided into three arbitrary ranges of the Mooney viscosity, soft (with a ML 1+4 of less than 50), medium (with a ML 1+4 between 50-75) and hard (with a ML 1+4 of higher than 75) (as quoted by Koosakul, 1994).

2.3 Discoloration of natural rubber

The color of latex is clonal characteristics due to non-

rubber constituents such as carotenoid pigments which is the cause of yellow color of some lattices (Nadarajah and Karunaratne, 1971). There are many factors causing discoloration of latex and rubber e.g. season, process of latex after tapping, chemicals etc. However, the most important factor is the enzymatic reaction which is catalyzed by the polyphenol oxidase type (Nadarajah and Karunaratne, 1971). The oxidation reaction of natural-occurring phenolic compounds which disperse in aqueous phase of latex or C-serum gives colored products and brings about to rubber discoloration (De Haan-Homans, 1949). The color substance does not affect the properties of the latex, but the discoloration is objectionable in the manufacture of light color rubber; therefore, the discoloration is prevented by adding the reducing agent, sodium metabisulfite at 0.05 p.h.r.

3. Protein and its effect

Among non-rubber constituents, proteins are major component. The total protein content of fresh latex is approximately 1-1.5 % of which about 20 % is adsorbed on the rubber particles and a similar proportion is associated with the bottom fraction (or B-serum). The remainder is dissolved in the serum phase (C-serum) of the latex. The proteins adsorbed on the rubber particles, together with adsorbed lipids, impart colloidal stability to the latex and have isoelectric point (pI) ranging from pH 4.0 to pH 4.6 depending on the clone (pI of rubber clone RRIM 600 is about 4.3). This variation in pI indicates that more than one protein is adsorbed on the rubber particle and the relative proportion of the adsorbed proteins is a

clonal characteristics.

α-globulin is the protein present in the highest concentration in fresh latex serum. It is coagulated by heat and precipitated from the solution at approximately the same pH at which fresh latex is coagulated, suggesting that it may be one of the proteins adsorbed on the surface of the rubber particles and thus partly responsible for the colloidal stability of the latex.

Approximately 20% of the dry matter in the bottom fraction of latex from mature tree is water-soluble protein, of which about 70 % is hevein. Hevein contains an abnormally high amount of sulfur (about 5 %) which is present as disulfide groups in cysteine. It is readily soluble in water and is not coagulated by heat. These properties indicate that sheet rubbers should contain very little hevein.

Protein distributed in different phase of Hevea latex are believed to affect the properties of rubber in many aspects from the raw rubber properties to the vulcanized rubber properties due to thier polar and hydrophilic nature (Perera and Siriwardena, 1985). Tanaka (1984) had shown that newly-formed network, containing a large proportion of nitrogen content, may be occured by the formation of protein with other particles resulting in the hardening phenomenon. Nadarajah and Karunaratne (1971) reported that polyphenol oxidase, is in charge of latex and rubber discoloration. Proteins can act as filler, having variable stiffening effect resulting in modulus variation (Metherell, 1980), poor dispersion of vulcanized curatives (Bloomfield, 1973) and also absorb water affecting the degree of cross-linking in the vulcanizing system (Elliott et al., 1970). Moreover, it has been recently reported in United States that

medical instruments with the use of natural rubber such as surgical gloves cause allergic symptoms (EP 0 584 597 A1, 1993).

4. The deproteinization of natural rubber

4.1 Deproteinized natural rubber

In order to overcome the problem affected by proteins and improve the rubber properties, the elimination of protein from rubber have been attempted. The rubber with a low protein or nitrogen content has been generally known as " Deproteinized Natural Rubber ", DPNR or "Low Nitrogen Natural Rubber", LNNR and its compositions have been specified by Rubber Research Institute of Malaysia (RRIM)(1977) as shown in Table 2.

The advantages of DPNR which are (1) low affinity for water due to the elimination of naturally-occurring hydrophilic substances, (2) enhance resilience, (3) reduce creep, (4) superior fatique life (Yapa and Yapa, 1974), (5) resistance to mold growth (Anandan and Loganathan, 1984) and (6) uniformity in cure behavior (Bernard, 1973) are well exploited when DPNR is used for engineering and medical application.

Table 2 Specification of DPNR (RRIM, 1977)

Properties	DPNR from clarified field latex	Proposed specification
Dirt (%wt)	0.005	No test value > 0.015
Nitrogen (%wt)	0.12	No sample > 0.12 on test
Ash (%wt)	0.13	No sample > 0.15 on test
volatile matter(%wt)	0.25	No value > 0.5
Initial plasticity (P_O)	32	-
Plasticity Retention Index (PRI)	85	60 (minimum)
ΔP (P_H-P_O)	7	No value > 9 on test
Mooney viscosity	51	45-55
		55-65

4.2 Deproteinization methods

There are three main methods which have been successfully investigated for removal of proteins from Hevea rubber.

1. By treatment with some kinds of surfactant or detergent by which proteins are eluted from the rubber surface. However, Archer (1975) and Yapa & Yapa (1984) reported that although the addition of surfactant improves the degree of deproteinization, it affects the PRI value adversely.

2. By chemical treatment which the rubber is soaking with

NaOH for 24 hr, the rubber proteins are hydrolyzed by chemical reaction. However, chemical or alkaline hydrolysis is known to adversely affect the oxidative resistance and PRI property of the resulting rubber (Yapa, 1984).

3. By biochemical treatment with proteolytic enzymes such as papain, trypsin, Alcalase, Superase etc. which hydrolyze proteins in to small peptides and amino acids which are more soluble for washing out. Although the deproteinization scheme can be carried out by combination of these treatment in order to remove protein out as much as possible. However, enzyme treatment is the most suitable method because it can be carried out in mild condition and quite specific with less side effect on rubber molecules.

Baker (1940) has reported that trypsin is the most effective of three enzymes, trypsin, pepsin and papain at 30 ^{o}C. However, trypsin, an animal enzyme, is unlikely to be available as cheaply and conveniently as an enzyme from vegetables source, like papain which can be produced in the plantations by growing the papaya trees as an intercrop during the immature phase when replanting(Senanayake,1968).

Yapa and Balasingham (1974) reported the advantages of papain over Superase that papain can be used in wider range of pH. The coagulation of latex by papain can be occurred at high pH values, thus giving light colored rubber even if ammonia is used at high dosages as preservative. On the contrary, papain is also active under acid conditions so it can be used as a deproteinizing agent as well as a coagulant for field latex (Nadarajah et al, 1973).

Visessaguan (1992) reported that the deproteinization by papain shows more advantages than Alcalase, because the lower

concentration of papain and shorter digestion time are required. By papain treatment, the maximum percent of nitrogen reduction are approximately 30-50 % (Yapa, 1975) and 70-75 % (Visessaguan, 1992).

The main drawback as regards commercial implementation of papain treatment is the low available and consequent high price of papain in natural rubber producing countries (Yapa,1980). Papain can be used only one time treatment and also be contaminated protein in rubber latex after enzymic treatment.

To overcome the disadvantages of free papain, immobilization of papain was considered to be used.

5. Papain immobilization

5.1 Papain

Papain is the main protein constituent of latex of the green fruits, leaves and trunk of Carica papaya, a small soft wood tree which is native to tropical countries. Crude papain is collected from full-grown but still unripe fruits by making longitudinal scratches on the fruit, and allowing the collected drippings to coagulate. The coagulated latex is dried to reduce moisture content to 5-8 %. Papain, plant proteolytic enzyme, is the sulfhydryl protease having a sulfhydryl or thiol group (-SH) at its active site. Papain can catalyze the hydrolysis of a variety of peptide,ester,and amide bonds of synthetic substrates,for example,Benzoly-L-arginine-p-nitroanilide (BAPNA), Benzoly-L-arginine ethyl ester (BAEE), Benzoyl-L-arginamide. Properties of papain are shown in Table 3. Thiol-protease, papain, is activated by mild reducing agents, low molecular weight thiol

compounds such as cysteine, sulfide, sulfite, and cyanide (Arnon, 1970). Since papain activity depends on a free SH group, it is inactivated by reagents or conditions which modify this functional group. α-Halogen acids or amides and N-ethyl-maleimide irreversibly inhibit the thiol group while heavy metal ions and organic mercurial salts inhibit in a fashion that can be reversed by low molecular weight thiols, particularly in the presence of EDTA which chelates such metals (Liener, 1974).

The overall reaction pathway for the catalytic of papain, thiol protease, is best described by the scheme shown in Figure 3. This mechanism shows the formation of an enzyme - substrate complex which results in the acylation of the enzyme (to form a thiol ester) and its subsequent deacylation, the overall reaction leading to a regeneration of the enzyme and the eliminatoin of the products of hydrolysis.

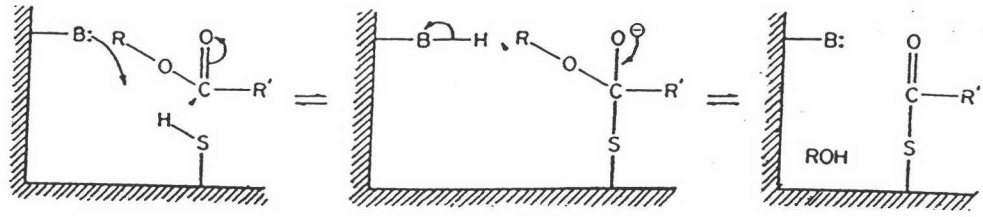
Papain is used extensively in the food industry for chilled-proofing, the tenderization of meat and has application in tanning and textile industries and is used medicinally as digestive aids.

Table 3 Properties of papain

Property	Papain
Enzyme Commision (E.C.)	3.4.4.10
source	Carica papaya
pI	8.75
molecular weight	20,700 - 24,000
working pH	5 - 8
working temperature (^{o}C)	40 - 75
Specific for hydrolysis of peptide bond	wide
activator	reducing agents , thiol-compound and cysteine
inhibitor	oxidizing agents and metal ions

source : Ward (1983) and Arnon (1970)

a. Acylation



b. Deacylation

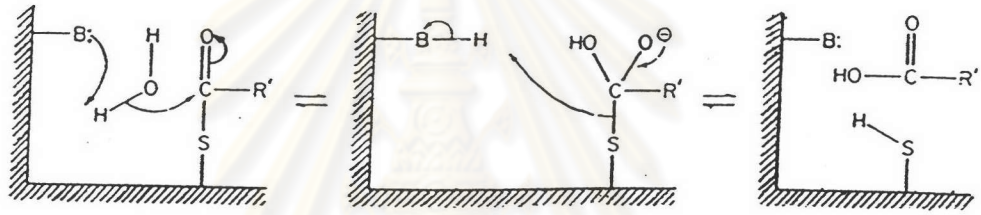


Figure 3 A mechanism of action for papain catalyzed hydrolysis (Liener, 1974)

5.2 Enzyme immobilization methods

Enzymes, such as papain, consisting of protein are biological catalyst. Enzymes characteristically have the ability to catalyze a reaction under very mild conditions in neutral aqueous solution at normal temperature and pressure, and with very specificity. Although enzymes are efficient and effective catalysts, they are not ideal for practical applications. Namely, enzymes are generally unstable and can not be used repeatedly or at elevated temperature. Moreover, the

enzyme and the other contaminating proteins can be generally removed by denaturation, by pH or heat treatment during procedure to isolate the product from the reaction mixture. This is uneconomical, as active enzyme is lost after each batch reaction.

In order to eliminate the disadvantages and obtain superior catalyst for applications, immobilized enzymes which are defined as "enzymes physically confined or localized in a certain defined region of space with retention of their catalytic activities and can be used repeatedly and continuously" have been used.

A specific conformation and active center interacting with the substrate are regarded as essential features of the catalytic activity of enzyme. The active center consists of two sites having different functions. One is the reactive or catalytic site participating in the catalyst action, and the other is the specific or binding site controlling the substrate specificity of the enzyme. These sites are usually composed of several amino acid residues held in a specific spatial relationship. The three - dimensional conformation of the entire enzyme protein also has an important effect on the catalytic activity. If the amino acid residues at the active center are altered, the catalytic activity may be decreased and enzyme properties such as substrate specificity are changed. Consequently, to retain the catalytic activity of the enzyme in the immobilized state, it is necessary to retain the native structure as far as possible. Therefore,high temperature, high salt concentration, organic solvents and strong acid or alkali treatments must be avoided to preserve the structure integrity of enzymes. Accordingly, in order to prepare active immobilized enzyme, the most suitable

immobilization method is selected and should be carried out under very mild and extremely well-controlled conditions.

There are 3 methods for enzyme immobilization. The preparations and characteristics of them are shown in Table 4.

Table 4 Preparation and characteristics of immobilized enzymes (Chibata, 1978)

	Carrier binding method			Crosslinking method	Entrapping method
	Physical adsorption	Ionic binding	Covalent binding		
* Preparation	easy	easy	difficult	difficult	difficult
* Enzyme activity	low	high	high	moderate	high
* Substrate specificity	unchange-able	unchange-able	changeable	changeable	unchange-able
* Binding force	weak	moderate	strong	strong	strong
* Regeneration	possible	possible	impossible	impossible	impossible
* General applicability	low	moderate	moderate	low	high
* Cost of immobilization	low	low	high	moderate	low

5.2.1 Carrier-binding method (Chibata, 1978)

The binding of enzymes to water-insoluble carrier is the oldest immobilization method. This method requires with regard to the selection of carrier as well as binding techniques. The amount of enzyme bound to the carrier and the activity after immobilization depend markedly on the nature of the carrier. Although, the selection of the carrier also depends on the nature of enzyme itself, the following aspects must be considered ; (1) particle size, (2) surface area and (3) chemical composition.

The carrier-binding method can be further divided into three categories according to the binding mode of the enzyme,that is, physical adsorption, ionic binding and covalent-binding.

1) Physical adsorption method

The physical adsorption method for the immobilization of enzyme is based on the physical adsorption of enzyme on the surface of the carrier. This method is simple and effective and often cause little or no conformation change of the enzyme proteins, or destruction of its active center. However, this method has the disadvantage that the adsorbed enzyme may release from the carrier during utilization, because the binding force between the enzyme and carrier is weak. Both inorganic materials such as activated carbon, porous glass, acid clay, alumina etc. and natural polymers such as starch, chitin and gluten etc. have been employed as carriers for this method.

2) Ionic binding method

The ionic-binding method is based on the ionic binding of enzyme to carrier containing ion-exchange residues. In some cases,

not only ionic binding but also physical adsorption may take part in the binding.

3) Covalent binding method

The covalent-binding method is based on the bridge of enzyme and carrier by covalent bonds. The functional groups that take part in the covalent binding of enzyme to the carrier are as follows: (1) amino group, (2) carboxyl group, (3) sulfhydryl group, (4) hydroxyl group, (5) imidazole group and (6) phenolic group. This method can be further classified into 6 types according to the mode of linkage. The selection of conditions for immobilization by covalent binding is more difficult than in case of physical adsorption and ionic binding. The reaction conditions required for covalent binding are relatively complicated and not particularly mild. Therefore, in some cases, covalent binding alters the conformational structure and active center of the enzyme, resulting in major loss of activity and / or changes of substrate specificity. However, the binding force between enzyme and carrier is strong and the leakage of the enzyme hardly occur even in the presence of substrate or salt solution of high ionic strength.

The carrier - binding with bifunctional reagents or the carrier cross-linking method is one of the covalent-binding types. This method is based on the formation of cross-links between the amino groups of carriers and the amino groups of enzyme protein by means of bi- or multi functional reagents. Glutaraldehyde which is the most commonly employed as the functional reagent is used to immobilize enzyme by causing the formation of Schiff bases between the amino groups of carriers and of enzymes.

5.2.2 Carrier for enzyme immobilization

The carriers utilized for the immobilization of enzymes may broadly classified into two groups 1) organic 2) inorganic (Messing, 1975). The characteristics of a carrier considered to be desirable for the purpose of immobilization have been given as follow (1) large surface area, (2) permeability, (3) hydrophilic character, (4) chemical, mechanical and thermal stability, (5) insolubility, (6) regenerability.

The earliest work on immobilization was done using inorganic carriers due to their suitable properties which are high mechanical strength, thermal stability, resistance to organic solvents and microbial attack. However, later on, organic carrier were used more widely (Messing, 1975) because a wide variety of functional reactive groups can be put on them. Therefore, most of the commercially available immobilized enzyme are obtained from organic carriers.

The natural organic polymers used for immobilization are proteins, polysaccharides and carbon materials. Polysaccharides constitute the widely used class of carriers ; they have been used both for the entrapment (eg. alginate, carageenan) and coupling (eg. agarose, dextran, cellulose derivative) of biocatalysts. Chitin, for instance, as organic and polysaccharide carrier, is reported to have favourable characteristics for immobilization of enzymes (Stanley, 1978 and Leuba, 1979). For example, chitin has been used to immobilize acid phosphatase (Stanley, 1975), α-chymotrypsin (Stanley, 1975), glucose isomerase (Stanley, 1976), β-galactosidase (Kennedy & Doyle, 1973) and D-glucose oxidase (Masri, Randall & Stanley, 1975).

Chitin is unbranched polysaccharide having chemical structure as shown in Figure 4.

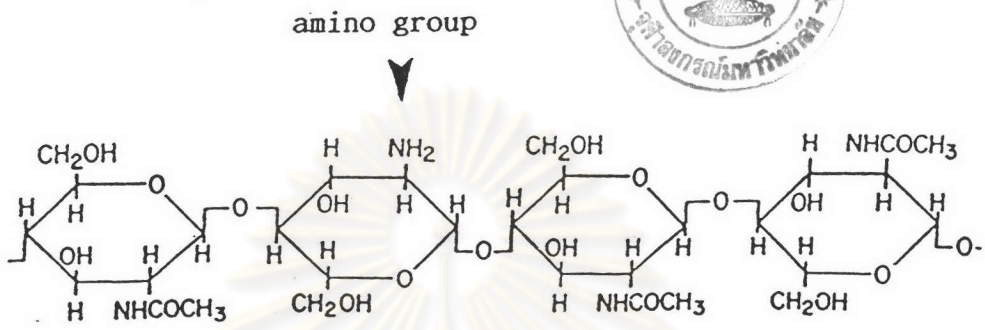


Figure 4 Chemical structure of chitin

The advantages of using chitin as enzyme carrier are that : (1) chitin, the exo-skeleton of many marine crustaceans, is a cellulose-like polymer which is made up of N-acetyl-2-amino-2-deoxy-β-D-gluco-pyra-nose held together by β-1,4 linkages (Muzzarelli, 1977). It has been reported that proteins and pigments can be adsorbed on or covalently bound to nonacetylated amino groups in chitin, although five out of every six amino groups in the polymer are acetylated (Stanley, 1975). (2) chitin is very widely distributed in animals, fungy, algae etc. especially in crustacea, about 58-85 %, such as in crab, shrimp (Muzzarelli,1977). Therefore, it is available in large quantities from processing waste of seafood canneries, at very low cost (Stanley, 1975). (3) According to Jin (1988), the

preparation of immobilized enzyme using synthetic polymers are not ideal for food and medical uses. From this reason, natural materials have been suitably used for immobilization of enzyme.

According to the advantages and extensively used of papain and chitin as previously described, immobilization of papain on chitin was investigated and, afterthat, also used to deproteinize the natural rubber latex which is affected from non-rubber components, especially proteins.

6. Objectives of the research

1) To determine the optimal conditions for papain immobilization on chitin comparing between physical adsorption and covalent-binding method.

2) To study the properties of immobilized papain on chitin such as effect of pH and temperature on the activity and stability, continuous operation and also kinetics expression.

3) To determine the optimal conditions for the deproteinization of rubber latex (clone RRIM 600) by using immobilized papain on chitin in laboratory scale.

4) The DPNR produced from immobilized papain and free papain will be tested for their raw properties and physical properties and their results will be compared to that of control sample (untreated rubber).

5) To estimate the production cost; the cost consists of field latex, chemicals and utilities.