CHAPTER V

DISCUSSION

5.1 The condition for deproteinization

5.1.1 Temperature has a profound effect on enzyme activity. The higher temperature results in greater nitrogen reduction until it reached 50 ^{o}C. From Figure 5.1, the nitrogen reduction at 50 ^{o}C for 5 minutes is 62 %. The nitrogen reduction is directly related to temperature until a certain temperature is reached. At high temperature, the nitrogen reduction is decreased due to the denature of the papain and the coagulation of latex.

5.12 Effect of turbulence intensity factor Agitation produces flow and subsequently turbulence in latex. The increase in agitation speed (higher Reynolds number, Re) develops high turbulence region and a damping of turbulence causes dispersion of rubber particle and papain. The effect of agitation speed on deproteinization can be described by a turbulence intensity factor (Tasakorn, 1977):

$$\Theta = 1.1\, Re^{0.55}$$

At Θ, ranging from 50-55, the nitrogen reduction is maximum being about 84 % within 50 minutes (Figure 5.2). At this Θ range, most of energy containing eddies sizes collide with the rubber particles and the energy is transmitted to the particles. The bound protein on the polymer chain is exposed or removed out of the polymer chain. As a result the protein is easily digested by papain. At high θ, energy from eddies is transfered to the rubber particles making it unstable and coagulation is favoured to reduce this energy. The nitrogen reduction decreased by 81 %.

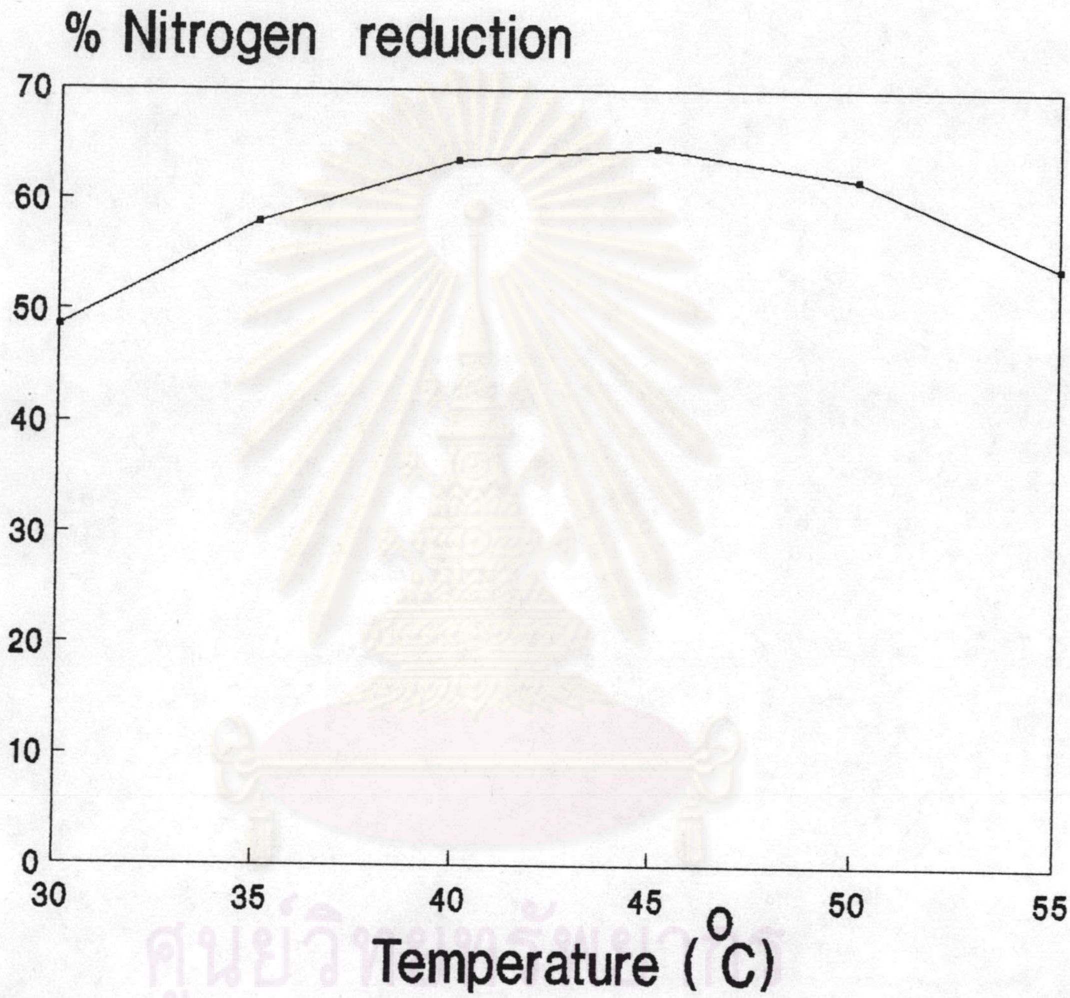

Figure 5.1 Effect of temperature on nitrogen reduction at 5 minutes

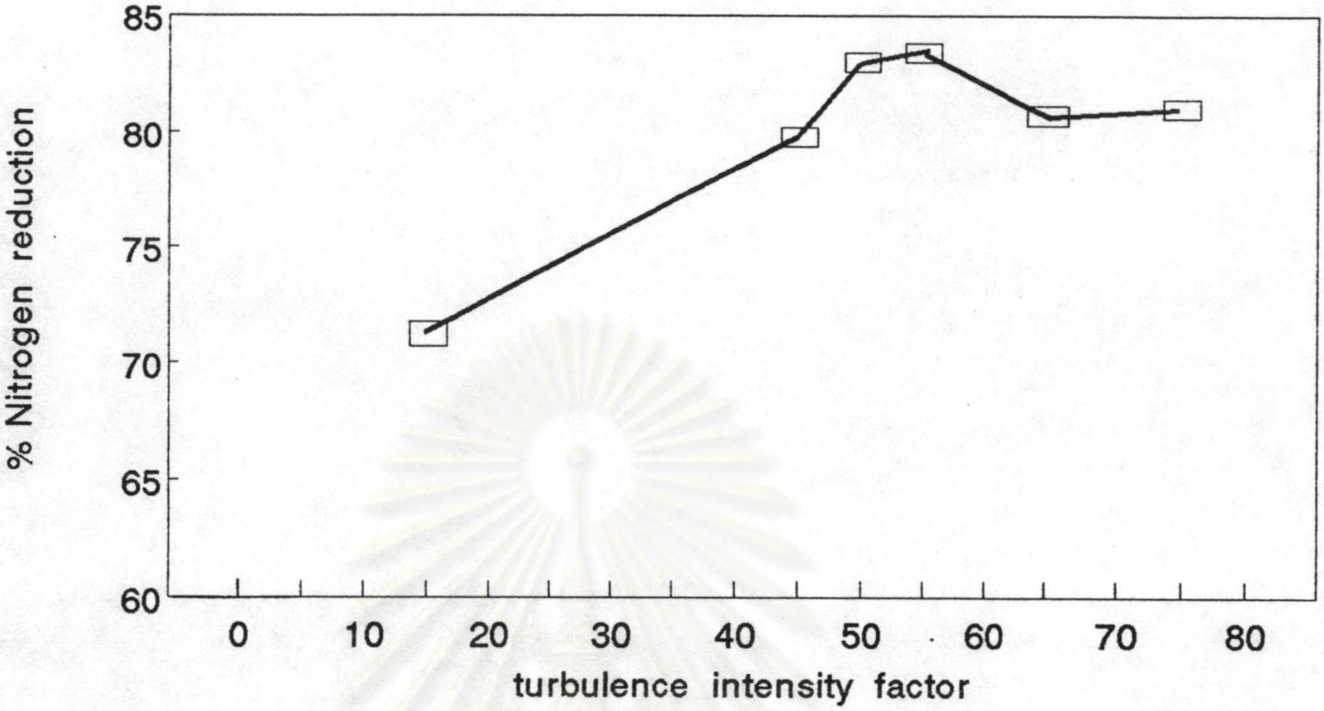

Figure 5.2 Effect of intensity factor on deproteinization

The suitable condition for fresh latex deproteinization is:

Chemical:	hydroxylamine hydrochloride	0.15	p.h.r.
	sodium metabisulfite	0.05	p.h.r.
	Triton X-100	1.1	p.h.r.
	papain	0.3	p.h.r.

Operating condition: temperature 50 ^{o}C, θ 50-55, 50 minutes and steam coagulation

The nitrogen content reduction is maximum being 82-90 %. Comparison with previous works (Visessanguan, 1992 ; Chang and et al., 1977 and John et al., 1977) indicates that the CV-DPNR production in this study required less reaction time and the removal of protein is higher.

Proteins in fresh latex are (i) bound to the rubber particles, or associated with the lutoid fraction, and (ii) freely dissolved in the serum phase which is about 60 %. Since the nitrogen reduction by papain is fast during the first 5 minutes (50-73 % reduction) and then slow down (Figure 4.1- Figure 4.4), the results indicated that free serum proteins were removed first and followed by proteins associated with rubber particles and other bound forms. The results suggest that removal of protein in serum phase by centrifugation before enzyme deproteinization may reduce production cost and increases the nitrogen reduction.

Naturally, rubber particles are stabilized by associated surface proteins absorbed and this protein are hydrophilic substances. The removal of proteins results in coagulation. To stabilize the latex, Triton X-100 is added at suitable concentration of 1.1 p.h.r.. Triton X-100, a nonionic detergent is widely used as a stabilizer (John, 1977). It has capability to increase stability of latex and so enhances the removal of proteins. Below this concentration, the stability is not prolonged, and at too high concentration the latex is very stable that coagulation can not be achieved even under steam.

5.2 Effect of deproteinization on the MWD

The molecular weight and molecular weight distribution (MWD) of rubber are different depending on the original clone of the rubber. An agitation and papain treatment do not have any effect on MWD, as it can be observed that the MWD and type of MWD curve of rubber before and after papain treatment are similar. The protein either tenaciously held or chemically bonded to the rubber is digested resulting in the MWD profile slightly shifted from high molecular weight to low molecular weight, and the molecular weight range of CV-DPNR is narrower. The broad MWD of rubber is associated with branching and cross-linking between rubber molecules and gel phase within the rubber particles. Hevea rubber contain 5 - 50 % gel phase depending on rubber clones, process condition and temperature of stage. The gel phase contains large proportion of nitrogeneous impurities. Deprotenized Hevea rubber has practically no gel phase (Tanaka 1989).

5.3 The properties of CV-DPNR

Papain treatment decreases the proteins in rubber by breaking them down to amino acids which are dissolved in the water. The various rubber clones contain different amount of protein therefore the reduction of nitrogen content is different. RRIM 600 contains the initial nitrogen content higher than GT 1 but the final nitrogen content is lower. GT 1 has the lowest nitrogen reduction suggesting that the proteins absorbed on the rubber particles in GT 1 form bond tighter than the other clones. PB 5/51 contains the lowest initial nitrogen content and it yields lowest final nitrogen content after deproteinization.

The ash and dirt content are decreased after papain treatment under steam coagulation. But the ash of 4 clones is slightly higher than the specification (ash < 0.15 %) and also rubber from acid coagulation i.e. TTR 5L, white crepe and RSS 1. Acid used in the coagulation can dissolve the ash in rubber. Steam coagulation normally yields higher level of nitrogen and ash than acid coagulation (John and Sin, 1977). The dilution of latex before coagulation (Nadarajah et al., 1973) or centrifugation of latex will remove some ash and nitrogen content in the latex.

CV-DPNR has low volatile matter which includes moisture because proteins are polar and have hydrophilic characteristics, they enhance the absorption of water in natural rubber. Associated with the high nitrogen level is a higher moisture content and the increase in volatile matter.

Rubber with light color is used in the production of light-colored rubber product, which requires a color limit of six unit or less on the Lovibond color scale. The color of CV-DPNR of 4 clones is lighter than its control and color index is lower than 6. PB 5/51 and RRIM 600 have lighter color than PB 28/59 and GT 1. The improvement of color is due to the removal of proteins and other non-rubbers such as carotenoid. The discoloration of raw rubber is usually due to the polyphenol oxidases in latex react with the naturally occurring phenolic substances and can combine with amino acid at room temperature (Rinderknecht and Jurd, 1958) and due to the non-rubber particles, particularly the brightly colored carotenoid (Nadarajah and Kurunaratne, 1971). Beside polyphenol oxidases and carotenoid, the color of rubber can also vary due to rubber clone, climatic condition, seasonal variations and manufacture processing.

Plasticity retention index (PRI) is the resistance of raw rubber to oxidative degradation by ageing. High values correspond to good ageing resistance. The removal of proteins will decrease initial plasticity (P_O) and PRI. In CV-DPNR processing, the removal of protein and washing will leach out naturally occurring antioxidants, phosphoaminolipids, amines and amino acids. The non-rubber substances naturally occurring in Hevea latex protect rubber against ageing (Silvabalasunderam and Nadarajah, 1965). Other factors which affect PRI are rubber clones, chemicals used in raw rubber manufacture, the metallic impurities (Cu, Mg, Ca and Fe) and the processing of raw rubber e.g. dilution, milling and drying.

Mooney viscosity is a rubber characteristic, which depends on the molecular weight of the polyisoprene polymers, MWD and branching of the polymer chain including linkages to some cross-linking non-rubber molecules. Rubbers with high molecular weight show high Mooney viscosity (Table 4.2 and Figure 4.8). Removal of proteins in latex will reduce the cross-linking non-rubber moleculs within the rubber resulting in the reduction of Mooney viscosity.

Yip, 1990 also reported that the Mooney viscosity of rubber sometimes changes during storage resulting in hardening. Hardening is a crosslinking reaction between the rubber molecules involving the aldehyde or carbonyl groups and certain aldehyde condensing groups in the non-rubber. Addition of a monofunctional carbonyl reagent such as hydroxylamine to latex before coagulation inhibits this reaction. The accelerated storage hardening (ΔP) is the difference between the Wallace plasticity number before and after storage at 60 ^oC over P_2O_5 for 24 hours. Because of this, hardening of CV-rubber from papain treatment increased less than the untreated CV-rubber. Mooney viscosity and ΔP are known to be related. RRIM, 1984 reported that an increase in ΔP of 8 units or less equals an increase in Mooney viscosity of 9 to 12 units or less. In this research, Mooney viscosity and ΔP are not correlative only in commercial grades (Figure 4.8d and Figure 4.9b). This is due to a few of sample tests.

Cure characteristics, scorch time, cure time, cure rate and torque rise are affected by nitrogen content of rubber compound. CV-DPNR cure more slowly than control CV non-deproteinized rubber due to the extraction of proteins capable of accelerating vulcanization. The reduction of nitrogen content increases scorch time and decreases cure rate and torque rise. A similar observation was made by John et al. (1977) for papain deproteinization rubber. The various clones show difference in cure characteristics and rubbers with lower torque rise show slower cure rate and longer scorch time (Figure 4.10). This may be due to the presence of various naturally occuring non-rubber, particularly proteins in the rubber. Not all the naturally occurring nitrogenous materials exert an influence on the cure characteristics. Amines such as ethanolamine, choline and arginine (a basic amino acid) accelerate cure rate, other amino acids such as cystine, tyrosine, glutamic acid and alanine give rise to slower cure rate (Loo and Yong, 1977).

The removal of proteins increases tensile strength, % elongation at break and tear strength, but 300 % modulus and hardness are decreased. Proteins may influence vulcanizate properties due to its enhancement of water absorption, and involvement in activating vulcanization. Water absorption reduces the mastication efficiency and the dispersion of chemicals (Perera and Siriwandena, 1985) and the increase in curative concentrations in the rubber particles, thus speeding up crosslinking reactions (Ducbacek, 1981) or giving a high yield of crosslinks resulting in the lower strength properties and higher modulus value (Wong ang Loo, 1985). Other proteins acts as a filler (Knight and Tan, 1975). The elimination of proteins, which has a stiffening action will reduce modulus and hardness. The results observed in this study are similar to that reported by John (1977) who studied the reduction of nitrogen on skim rubber.

Comparison of tensile strength between CV-DPNR and commercial grades, TTR 5L, white crepe and RSS 1 shows that tensile strength of commercial grades is slightly higher than CV-DPNR due to the difference of rubber clones, chemical using in raw rubber manufacture (hydroxylamine hydrochloride) and processing.

5.4 Estimated cost of production of CV-DPNR

The cost of CV-DPNR production based on laboratory scale production is shown in Table 5.1. The cost of CV-DPNR is about 77 Baht/kg. The major cost for CV-DPNR production is imported papain (12,500 Baht/kg). The cost can be reduced by replacing imported papain with locally produced papain (600-800 Baht/kg) and also by replacing Triton X-100 with e.g. Teepol or soap such as potassium naphthenate. Hence, the cost of CV-DPNR can be reduced from 77.36 to 34-43 Baht/kg.

Table 5.1 Production cost of CV-DPNR

	Unit cost (Baht / unit)	Consumption (unit)	CV-DPNR (Baht / kg)
Rubber	15-18 / kg	1 kg	17.50
Chemicals (laboratory grade)			
-Ammonia solution	280 / 2.5 l	12 ml	1.34
-Hydroxylamine hydrochloride	2400 / 500g	1.5 g	7.20
-Sodium metabisulfite	550 / 500 g	0.5 g	0.55
-Triton X-100	1150 / l	11 g	5.75
-Papain	1250 / 100g	3 g	37.50
Utilities			
-Power		(KW/h)	
Reactor and pump (1.08 KW)	2 / KW-h	0.108	0.22
Autoclave (2 KW)		1	2.00
Two roll-mill (1.5 KW)		0.75	1.50
Hot air oven (5 KW)		1.2	2.40
-Water		(litre)	
Latex dilution	1 / l	0.9	0.90
Coagulum washing	0.1 / l	5	0.50
Total operating cost			77.36