CHAPTER V

DISCUSSION

Effect of mixing

Mixing in vessel of batch reactor has a circulation that moves fluid into all parts of vessel. Flow was produced by a rotating agitator. Liquid viscosity which is the property of a liquid to resist flow affects the flow. In turbulent flow, the fluid and flow variables vary with time. Turbulent flow pattern produce the size of the small eddy. Turbulence can help speed up the process by breaking the fluid into many small clumps, and thus allowing more area for molecular diffusion. The chemical reaction occurs on the surface of the fluid clumps. The particle of fluid undergoes a series of random movements, superimposed on the main flow. The eddy movements bring about mixing throughout the turbulent core which is referred to as "eddy diffusion". For turbulent flow, the value of the eddy mass diffusivity will be very much larger than the molecular diffusivity in the turbulent core (Welty et al., 1983).

The mixing at high agitation speed results in the increase of Reynolds number which can be represented by terms of turbulence intensity factor (Tasakorn, 1977)

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

where θ is turbulence intensity factor

Re is impeller Reynolds number

At θ, ranging from 55-58 and Reynolds number of 1200-1400, the nitrogen reduction is maximu at about 86-88% (Figure 5.1 and 5.2). At increasing values of the Reynolds number, the eddies grow to the point at which they separate from the body and swept down to the stream. The energy transfers into latex which produce the eddies. The chemical reaction can simultaneously occur with the molecular diffusivity
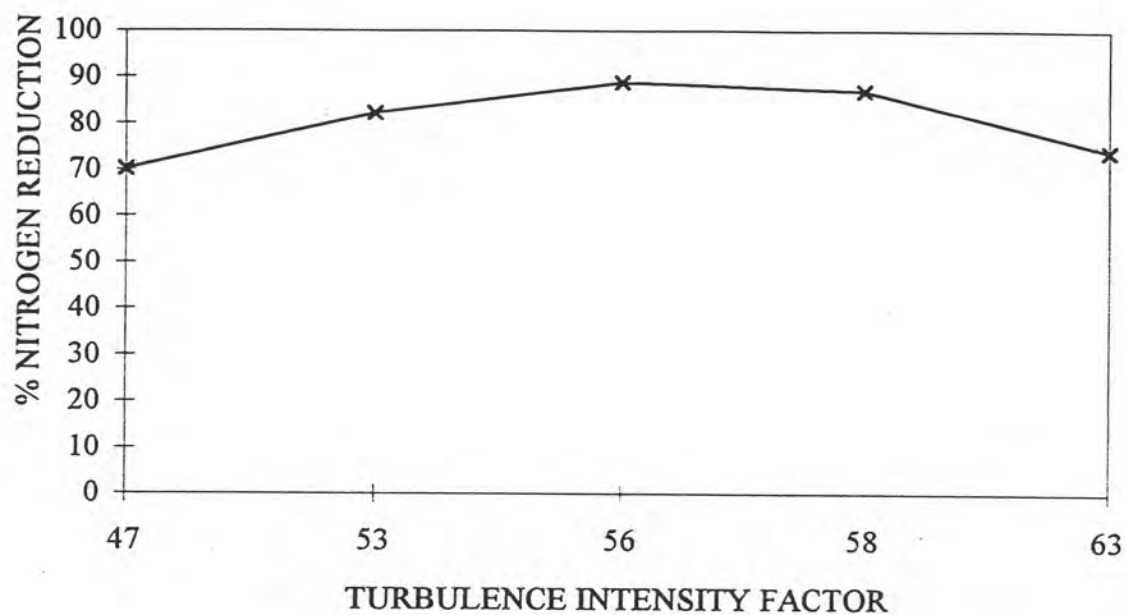
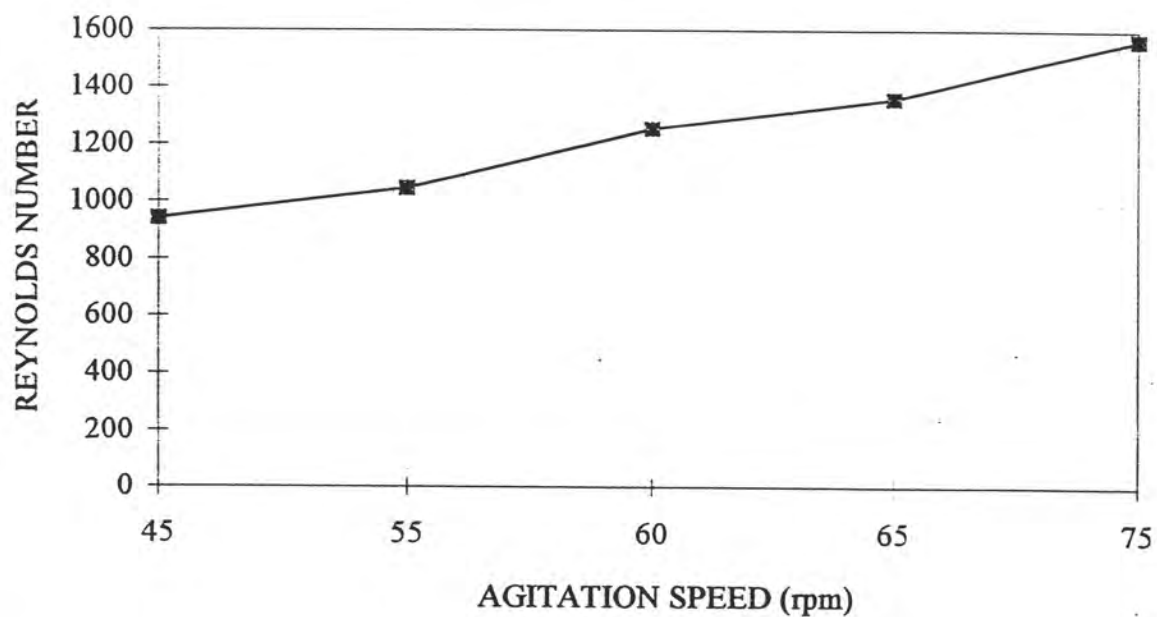Figure 5.1 Effect of the turbulence intensity factor (θ) on deproteinization

Figure 5.2 Effect of agitation speed on Reynolds number

(Figure 5.3). At high turbulence intensity factor over 62 , the high energy derived from agitation is transferred to the latex to make it unstable. The excess energy must be removed by collision and vibration of rubber particles. The energy gained on collision of rubber particles induces conglomerate preventing enzyme diffusion into rubber particles (Figure 5.4). Turbulence intensity factor less than 50 causes ineffective attempts of enzymes transport into the latex since energy transferred into latex is not enough to enhance the chemical reaction and molecular diffusivity.

Effect of storage on Mooney viscosity of CV-NR and CV-DPNR

There are two problems associated with the high viscosity of natural rubber; the first problem is that natural rubber becomes hardening during processing, shipment and storage and has its viscosity increased by 10 to 40 Mooney units. The latter problem is that different rubber clones give a variable viscosity rubber (Nadarajah, 1985).

RRIM 600 has the lowest Mooney viscosity. PB 5/51 contains the lowest amount of nitrogen content and has the highest initial Mooney viscosity. The Mooney viscosity of CV-DPNR is lower than its CV-NR. The reduction of Mooney viscosity of RRIM 600 has the highest value compared with its control. Mooney viscosity of CV-DPNR prepared from all rubber clones shows the increase of between 1-12 units from the starting value. The increase of Mooney viscosity of RRIM 600 has the lowest slope followed by PB 5/51 and GT 1 (Figure 4.4 (a)-(c)). Addition of Hydroxylamine hydrochloride (HH) into latex cannot completely prevent storage-hardening or increase of Mooney viscosity but can delay an increase of Mooney viscosity in both CV-NR and CV-DPNR.

Comparative study on the rate of increasing Mooney viscosity between CV-DPNR at 60 rpm and CV-NR for 12 months at room temperature show that RRIM 600 has the lowest rate of increasing Mooney viscosity followed by PB 5/51 and GT 1 respectively as shown in Table 5.1 indicate that removal of protein can inhibit storage hardening more effectively than adding HH, but the molecular structure of rubber is
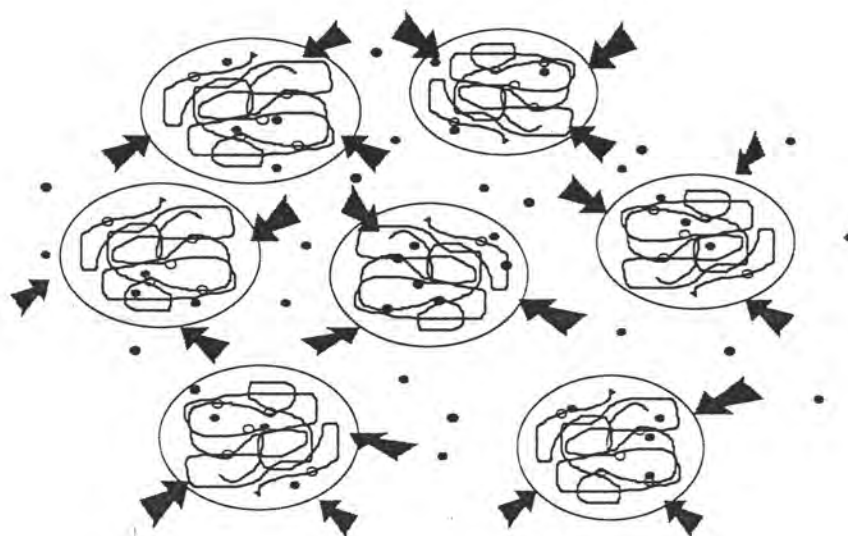
127

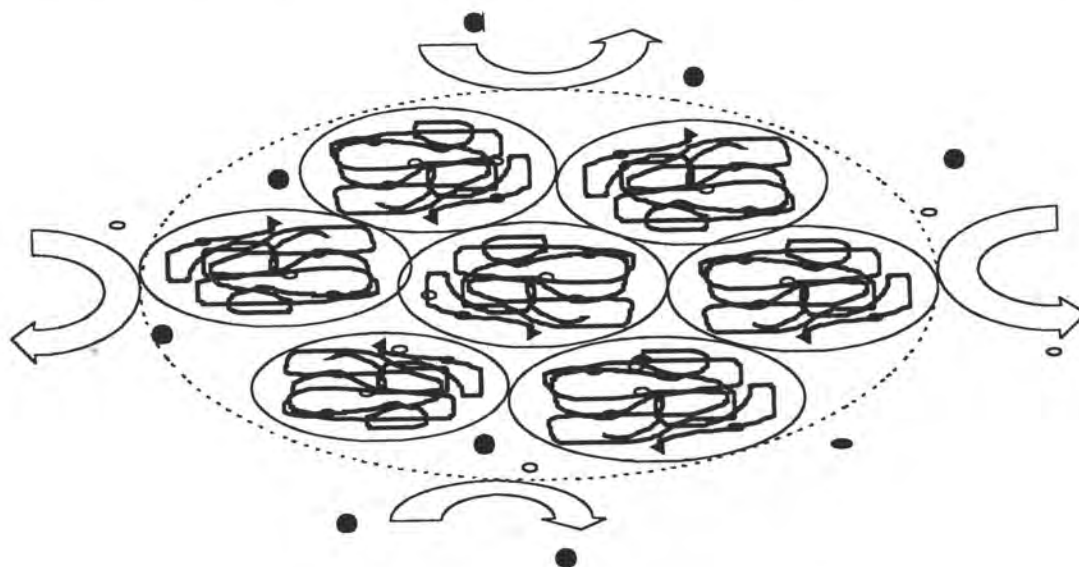Figure 5.3 Effect of the optimal turbulence intensity factor (θ) on deproteinization

Figure 5.4 Effect of the high turbulence intensity factor (θ) on deproteinization

the most important factor to be considered. CV-DPNR at various agitation speed has the different remaining nitrogen content. The nitrogen content reduction of CV-DPNR at various agitation speed is in the range of about 70-89%. At optimal agitation speed of 60-65 rpm, the nitrogen content of CV-NR and CV-DPNR is between 0.45-0.46 % and 0.05-0.08% and has the lowest increase of Mooney viscosity (Figure 4.2). When the CV-DPNR and CV-NR prepared from RRIM 600 clone are stored at the room temperature for 6 months, CV-NR at 75 rpm and CV-DPNR at 60 rpm have the lowest rate of increasing Mooney viscosity or a change of slope 0.48 and 0.17 respectively. (Figure 5.5 and Table 5.2). CV-DPNR at optimal agitation speed has the lowest increase of Mooney viscosity and initial Mooney viscosity. CV-NR at optimal agitation speed has the lowest increase of Mooney viscosity but the highest initial Mooney viscosity. The increase of Mooney viscosity of CV-DPNR at high agitation speed is similar to its control but that of CV-NR at high agitation speed is higher than its control (Figure 4.3 (a)-(d)).

Effect of agitation speed and deproteinization on MWD

The molecular weight and MWD of NR show that there are variations among rubber clones. The higher viscosity clonal rubbers have a unimodal type of distribution and the lower viscosity rubbers have a bimodal distribution. Clonal rubbers show a wide distribution with the values of Mw/Mn ranging from about 4 to 10 (Subramaniam, 1993). The low molecular weight peak appears between 1×10^5 and 2×10^5 and the high molecular weight peak appears between 1×10^6 and 2.5×10^6 despite of the different shape of distribution curves (Nair, 1970). Deproteinization have rather small effect on MWD of NR. The MWD curve of CV-DPNR skew slightly from high molecular weight to low molecular weight (Figure 4.5). The range of molecular weight of CV-DPNR is narrower than CV-NR by reason of some non-rubber components especially protein was removed and washed out the rubber.

Table 5.1 Linear relationship between initial Mooney viscosity and rate of viscosity change for various rubber clones

Rubber clones	% N content			Initial Mooney viscosity		Linear equation	
	initial	final	%N reduction	CV-NR	CV-DPNR	CV-NR	CV-DPNR
RRIM 600	0.578	0.065	88.7	58.9	57.2	$y = 0.96x + 58.9$	$y = 0.12x + 57.2$
GT 1	0.599	0.110	81.6	70.7	69.2	$y = 1.92x + 70.7$	$y = 1.82x + 69.2$
PB 5/51	0.401	0.040	90.0	91.2	88.3	$y = 2.10x + 91.2$	$y = 1.87x + 88.3$

Table 5.2 Linear Relationship between agitation speeds, initial Mooney viscosity and rate of viscosity change for RRIM 600 clone at various agitation speeds.

Agitation speed (rpm)	No Papain	% N	With Papain	% N
0	$y = 0.74x + 60.8$	0.453	-	-
45	$y = 0.74x + 60.5$	0.454	$y = 1.11x + 59.1$	0.135
55	$y = 0.95x + 60.7$	0.449	$y = 0.29x + 58.2$	0.081
60	$y = 0.93x + 60.8$	0.451	$y = 0.17x + 57.0$	0.051
65	$y = 1.07x + 60.8$	0.451	$y = 0.25x + 58.1$	0.059
75	$y = 0.48x + 68.7$	0.454	$y = 0.82x + 59.1$	0.118

CV-NR at various agitation speed

a)

CV-DPNR at various agitation speed
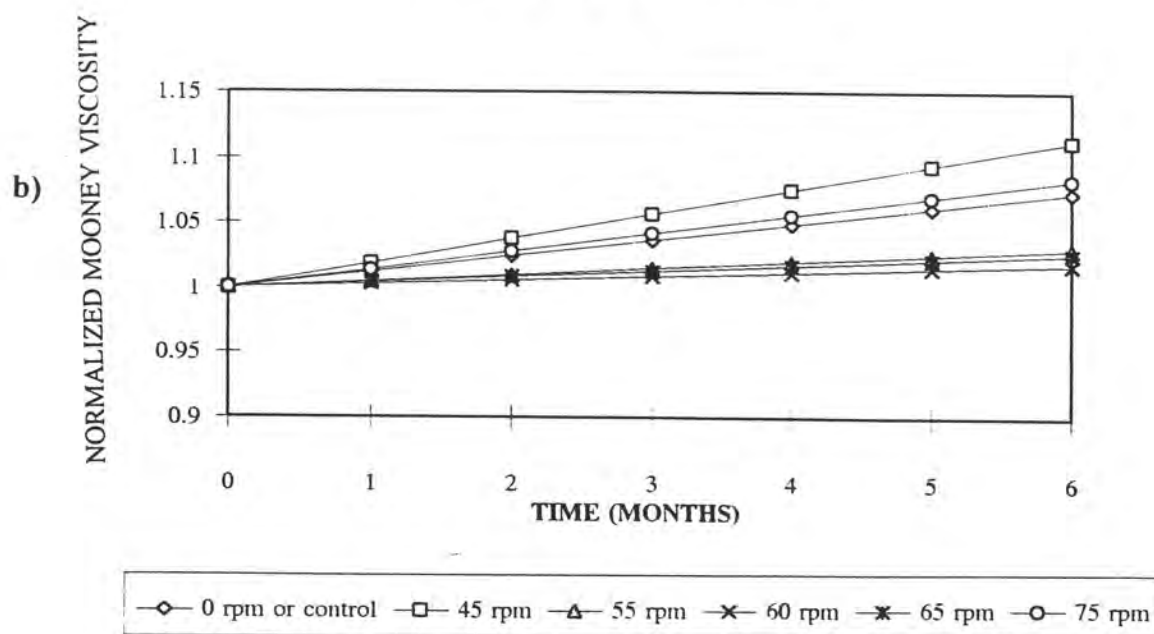

b)
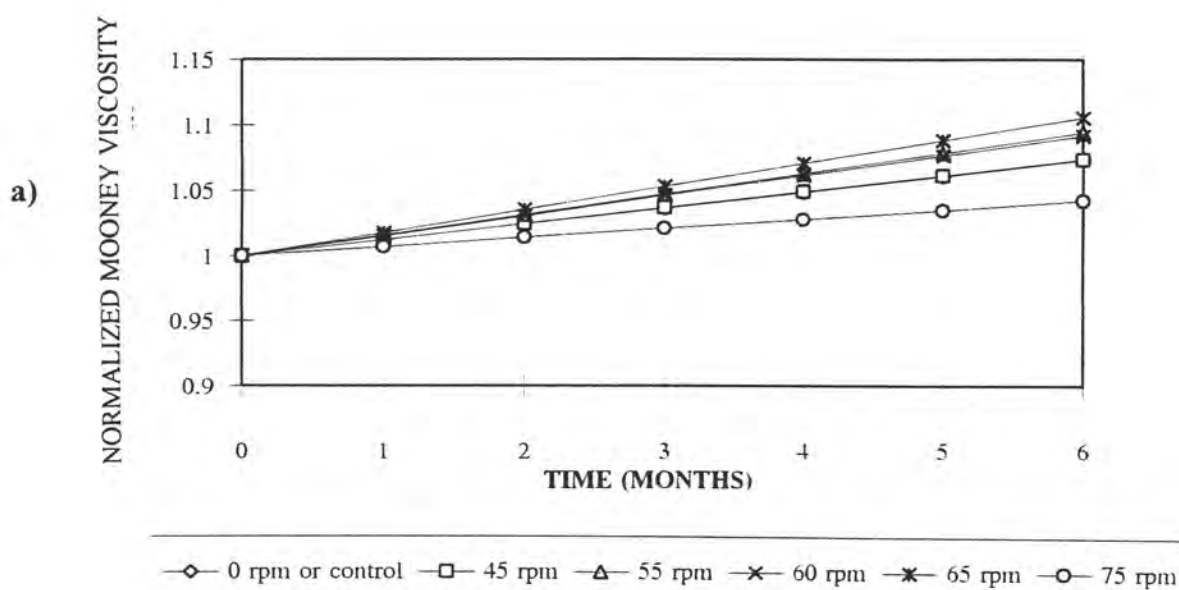
Figure 5.5 Normalized Mooney viscosity of CV-NR and CV-DPNR at various agitation speed produced by RRIM 600 clone.

a) For CV-NR   b) For CV-DPNR

Agitation have slight effect on MWD except at high agitation speed (Figure 4.6 (a)-(e) and 4.7 (a)-(e)). At high agitation speed, rubber particles in latex form agglomeration resulting in the lower reduction of proteins. This shows differences of Mw, Mn and MWD.

Optimum condition of latex deproteinization by Alcalase

The optimized condition for deproteinization by Alcalase is at pH range 8-9, 60 °C with the concentration of 0.4 p.h.r. and required 8-10 h to reach the maximum nitrogen reduction (Visessanguan, 1992). Latex deproteinization by Alcalase in the stirred-tank was carried out at agitation speed 60 rpm. It takes 4 hr.,and the resulted rubber has the lowest nitrogen content of 0.14% (Figure 4.8). The maximum nitrogen reduction is about 72%.

Proteins present in fresh latex of *Hevea brasiliensis* latex are approximately 2-4% by weight of which about 20% is adsorbed on the rubber particles and a similar amount is associated with the lutoid fraction. The residual amount is dissolved in the serum phase. The proteins adsorbed on the rubber particles have not been studied in much detail due to the complication in eliminating them (Fong, 1992). Deproteinization of latex is the digestion of protein by enzyme. Enzyme converts the proteinaceous non-rubbers into water soluble forms which can be washed away during dewatering. The removal of proteins in latex makes the latex unstable. Stabilization of the latex during the enzymatic treatment with an anionic soap does not interfere with the subsequent vulcanization of the rubber (Smith. 1971). Rubber particles can be stabilized by stabilizing agents namely Triton X-100, Teepol, sodium stearate. The stabilizer used in this research is Triton X-100 or Nonidet P-40 which replaces protein in the rubber particles. In addition to latex stabilization, Triton X-100 can enhance latex deproteinization (John et al., 1977).

To prevent the autocoagulation and delay coagulation during enzymolysis, Triton X-100 was added to stabilize latex with the optimal concentration of 1.15 p.h.r. Below this concentration, the digested latex exhibits autocoagulation before reaching optimal time resulting in high remaining nitrogen content. At the excess amount of

Triton X-100, latex can be stabilized well but can not be coagulated with steam (Table 4.3).

There are several methods for latex coagulation such as acid coagulation, steam coagulation, autocoagulation. From previous studies, steam coagulation of latex have many advantage over acid coagulation because it requires shorter time and yield higher product. Rubber from steam coagulation has lower nitrogen and volatile matter and lighter color as compared with acid coagulation (RRIM Planter's Bulletin, 1987).

Selection of enzyme for deproteinization (Alcalase and Papain)

Several proteolytic enzymes have been used in latex deproteinization including pepsin, trypsin and Papain. Baker (1940) has reported that trypsin is the most effective of the three enzymes; but trypsin is the animal enzyme and not readily available. Papain is the most conveniently available because it can be derived from vegetable sources. Papain is more effective than Alcalase. Papain is a bio-enzyme which hydrolyses the naturally occurring proteins in the latex into water soluble forms which are then washed away during subsequent processing (Chang et.al, 1978). Wentworth suggested that serum protein was preferentially attacked by the enzyme, thus reducing decomposition of the protein in the rubber phase. Papain-treated rubber can be stored under normal storage condition for up to 2 years without fungus infection and can resist to mould growth which has been reported by Anandan and Loganathan (1984).

In the case of Alcalase, it is appropriate for latex concentrate and fresh latex with high ammonia due to its preference of alkaline pH range 8-9 at the optimal condition. Papain shows the highest deproteinizing activity in neutral pH range 7-8, therefore, it is suitable for use with field latex.

Selection of starting material

The preparation of DPNR from latex concentrate is not convenient because it has numerous disadvantages. However, use of fresh latex instead of latex concentrate

provides a significant saving in processing cost for both chemicals or labour. Furthermore, the overall yield of DPNR from latex concentrate is lower than that from field latex. (Chang et al., 1978) Field latex was selected to prepare CV-DPNR because latex concentrate would have to be heated to remove ammonia for pH adjustment to the optimum value. Field latex is easy to adjust to optimum pH for Alcalase (8-9) and Papain (7-8).

The properties of CV-DPNR

Raw rubber properties

RRIM 600 has the highest initial nitrogen content but the maximum percent nitrogen content reduction after deproteinization (84%) when compared with other rubber clones. PB 5/51 has the minimum nitrogen reduction but it has the lowest initial nitrogen content. After deproteinization, the remaining nitrogen content in GT 1 is higher than RRIM 600 and GT 1 (Figure 4.9 (a)).

Papain-treated rubber has lower nitrogen content than Alcalase-treated rubber and control (Figure 4.11 (a)). The per cent nitrogen reduction of Papain and Alcalase-treated rubber was about 84% and 72% respectively.

Steam coagulation increased the ash content of the resulting rubber. The use of steam coagulation results in higher nitrogen and ash content than acid coagulation (John and Sin, 1977). Both nitrogen and ash contents decreased on dilution of latex prior to enzyme treatment. The low ash level is important in order to reduce the moisture absorption of NR (Yapa and Sriyani, 1975). The ash content of CV-DPNR was decreased in this research but still slightly higher than the RRIM specification (ash < 0.15%) because latex was treated at high % DRC and coagulated by steam.

The dirt content in raw rubber depends on process and caution. CV-DPNR has lower dirt than CV-NR (Figure 4.9 (b)). The dirt of Alcalase-treated rubber is lower than Papain-treated rubber which may be due to composition and clarification of enzymes.

Proteins are polar and have hydrophilic behavior which they emphasize the absorption of water in natural rubber. The volatile matter is the moisture and the amount of any other material which is volatile at 100°C. The volatile matter of CV-DPNR decreased because proteins in rubber is removed.

Alcalase-treated rubber has higher volatile and ash than Papain-treated rubber because the amount of remaining nitrogen content in Alcalase-treated rubber is higher than Papain-treated rubber (Figure 4.11 (c)-(d)).

Initial plasticity index and plasticity retention index (PRI) is the resistance of raw rubber to oxidative degradation before and after ageing. PRI is expressed as a percentage of aged to initial plasticity. The high PRI shows that raw rubber has good ageing resistance. Naturally,the non-rubber substances present in latex will protect rubber against ageing. The factors which affect PRI are rubber clones, chemical used, metallic impurities and the processing of the raw rubber. (Silvabalasunderam and Nadarajah, 1965). The increase of high drying temperature result in low Po and PRI. The drying temperature has some effect on Po and PRI (Chang et al. , 1978). The removal of protein in the rubber will reduce non-rubber constitutes resulting in the reduction of P_0 and PRI.

Mooney viscosity is an important parameter which depends on its clonal characteristic e.g. the molecular weight of polyisoprene polymers, molecular weight distribution and the polymer chain including linkages to some cross linking non-rubber molecules (Yip, 1990.). Nair (1970) has reported that rubber with high molecular weight has high viscosity and vice versa. Besides the variation of clones, the processing can affect Mooney viscosity of the raw rubber. Mooney viscosity of rubber increase during storage and transportation. Mooney viscosity of CV-DPNR was decreased after deproteinization. Non-rubber molecules may be involved in cross-linking between rubber molecules. Deproteinization is the removal of proteins which also reduce the cross-linking via non-rubber molecules..

There are noticeable differences in raw rubber properties of DPNR prepared from Papain and Alcalase in which Alcalase-treated rubber has lower PRI and Mooney viscosity than Papain-treated rubber (Figure (f)-(g)).

The discoloration of latex occurs although the polyphenol oxidase or PPO had been destroyed. The main cause of non-enzymatic browning appears to start with the reaction between carbonyl and amino groups to give an unsaturated carbonyl amino derivative. Most natural substances contain phenolic compounds and some polyphenols enter into reaction leading to discoloration, as it is claimed to start melanin formation (Nadarajah and Karunaratne, 1971). The different rubber clones contain the different amount of non-rubber constitutes involving in the darkening of rubber. Carotenoid pigments are markedly claimed as discoloring factor (Nadarajah and Karunaratne, 1971). The discoloration can be inhibited by sodium metabisulfite. Sulfite can limit the reaction between carbonyl and amino group which give discolored product and retard non-enzymatic browning (Burton et al., 1963). The reduction of proteins and other non-rubber substances in rubber result in the light color rubber.

The improvement of the color of rubber should be good for light-color product. The color of CV-DPNR is paler than CV-NR (Figure 4.10 (a)-(c)). RRIM 600 has the lightest color in three different clones; RRIM 600, GT 1 and PB5/51. The color of PB 5/51 is lighter than GT 1.

The color of Alcalase-treated rubber is slightly lighter than Papain-treated rubber (Figure 4.12).

The raw rubber properties of CV-NR at various agitation speeds is not significantly different except for Mooney viscosity (Figure 4.13). At high agitation speed over 75 rpm, latex was stirred vigorously making it unstable which conglomeration and sometimes coagulation of latex may take place resulting in the increase of Mooney viscosity.

Cure characteristics

Cure characteristic is defined as the time available for converting uncured rubber compound into a product. The different rubber clones have the variation in cure characteristics. Natural rubber has long cure rate, scorch time and low torque rise. The cure parameters affected were the scorch time, cure rate and torque modulus

(ΔT). There is a variation of cure characteristic in clone rubbers Scorch time is the time to onset of vulcanization at a particular temperature and thus represents the time available for processing. Cure rate is the time to cure a given product to its optimum state. The amount of impurities or contaminants retained in rubber can affect cure characteristic. The removal of non-rubber constitutes especially proteins will improve the homogeneity of mixing and chemical dispersion (Bloomfield, 1973). John et al. (1977) has reported that CV-DPNR has scorch time increased but torque rise and cure rate decreased. The naturally occurring amines tend to support vulcanization. The removal of nitrogen content causes the reduction in the rate of vulcanization. The cure rate of DPNR increase with the amount of %N retained in rubber. In this research CV-DPNR has slower cure time than CV-NR. Treatment of field latex with Papain increased the scorch time but cure rate and torque rise were decreased.

The high Mooney viscosity and nitrogen content of rubber can influence cure behavior. The cure characteristic of CV-DPNR at various agitation speeds do not have a significant difference from CV-NR (Figure 4.17). Mooney viscosity of rubber at high agitation speed is higher than that of rubber at low agitation speed. The cure rate of CV-DPNR at high agitation speeds is increased.

Properties of vulcanizates

The presence of hydrophilic impurities such as proteins and inorganic salts can enhance the absorption of water in natural rubber. The uptake of water by NR has an effect on the processability and physical properties of NR. The tensile strength decreased with increase in moisture content while the heat build-up increases (Perera and Siriwardena, 1985). The tear strength of rubber is shown to be dependent on the Mooney viscosity (Kadir and Thomus, 1984).

All the CV-DPNR produced has shown increases in tensile strength, % elongation at break and tear strength, while 300% modulus and hardness are decreased. John (1977) has reported that the reduction of nitrogen content on skim

rubber decreases modulus and hardness and increases the tensile strength and % elongation at break. The removal of proteins from rubber decreases modulus and hardness while tensile strength, tear strength and % elongation at break increases.

Tensile properties of vulcanizates appear to be independent of the method of manufacture.

There are significant difference in vulcanizate properties observed between Alcalase-treated rubber and Papain-treated rubber. The remaining nitrogen content in Papain-treated rubber is lower than Alcalase-treated rubber resulting in the distinction of vulcanizate properties. The 300% modulus and hardness of Papain-treated rubber are lower than Alcalase-treated rubber. Tensile strength and % elongation at break of Alcalase-treated rubber decreased compared with Papain-treated rubber and control rubber (Figure 4.20).

At optimal agitation speeds of 60-65 rpm, the removal of protein is at the maximum value. Tensile strength, % elongation at break, 300% modulus and tear strength of CV-DPNR at optimal agitation speed were decreased. Hardness of CV-NR has the highest value at high agitation speed (Figure 4.22).

Ageing, or the change of physical properties with time is generally confused with the change in physical properties after the rubber has been exposed for prolonged periods at elevated temperature. Low nitrogen rubbers obtained by enzymatic treatments show poor retention of tensile properties on oxidative ageing. The physical changes are predominantly the result of two reaction: cross linking and oxidative chain scission. The change in properties of the rubber depends on the relative rates of two reactions. Cross linking produces an increase in storage hardening whereas chain scission has the reverse effect (Sivabalasunderam and Nadarajah, 1965).

For all rubber clones, tear strength, 300% modulus and hardness of CV-NR and CV-DPNR was increased after ageing, therefore an increase in cross-linking should dominate chain scission in this case. The CV-NR and CV-DPNR have the reduction of % elongation at break (Figure 4.24).

The increase of temperature cause the change of physical properties of rubber. For rubber at various agitation speeds, ageing tends to increase tear strength and 300%

modulus of CV-NR and CV-DPNR, while elongation at break and hardness were decreased (Figure 4.28-4.29). After ageing, tear strength, 300% modulus and hardness of Papain-treated rubber have lower values than Alcalase-treated rubber but tensile strength was constant and % elongation at break was decreased (Figure 4.29). For rubber at various agitation speeds, ageing trends to increase tear strength and 300% modulus of CV-NR and CV-DPNR, while elongation at break and hardness were decreased (Figure 4.28-4.29) After ageing, tear strength, 300% modulus and hardness of Papain-treated rubber have lower values than Alcalase-treated rubber but Tensile strength was constant and % elongation at break was decreased (Figure 4.26).

Ageing has slightly effect on color of the rubber. The color of rubber before ageing has not significant difference compared with before and after ageing (Figure 4.25.4.27 and 4.30).