CHAPTER IV

RESULTS AND DISCUSSION

In this work, the deproteinization of natural rubber latex was made by two methods: 1) saponification of latex and washing by centrifugation followed by coagulation 2) saponification of latex and coagulation followed by washing. The properties of deproteinized natural rubber latex such as nitrogen content, gel content, ester content, ash content, molecular weight and molecular weight distribution were determined.

4.1 Saponification of Latex and Washing with Centrifugation Followed by Coagulation

4.1.1 Stability of Latex during Saponification and Washing Step

Proteins on surface of rubber particles act as surfactant to stabilize rubber particles in latex emulsion. Saponification is the method that the protein is decomposed and removed from rubber particles and the stability of latex emulsion is decreased, which caused the coagulation of latex during saponification. Therefore, the addition of an appropriate surfactant is required to stabilize the latex during the saponification reaction and washing by centrifugation.

Two types of surfactant were used in this study. One is sodium dodecyl sulfate (SDS), anionic surfactant, the other is iso-octylphenoxy polyethoxyethanol (Triton X-100), non-ionic surfactant. Commercial concentrated latex diluted to 10% and 30% DRC was used as the starting material. Table 1 shows the stability of the latex during saponification and washing. The latex was saponified with %NaOH at 70 °C and 3 h.During saponification and washing, 30% DRC latex coagulated partially in the presence of Triton X-100 and coagulated completely in the presence of SDS. On the other hand, 10% DRC latex was stabilized with Triton X-100 and the partial coagulation was observed for SDS during saponification. The initial nitrogen content of the control rubber was 0.3%. It is remarkable that the nitrogen content of resulting rubber decreased to 0.023% in case of 30% DRC latex in the presence of SDS and Triton X-100.

It is reasonable to presume that the effect of surfactant depends on the hydrophile–lipophile balance value (HLB), pH of the solution and concentration of rubber particles. The result indicates that Triton X-100, nonionic surfactant gives the higher stability of latex than SDS, anionic surfactant. The stability of latex with surfactant is independent of the concentration of latex. This may be due to the dissociation of anionic surfactant in saponified latex with strong base (pH ~ 13).

Detailed study of effect of surfactant on stability of latex was proceeded by the observation of the mechanical stability time (MST). MST is a measure of the colloidal stability of latex. Table 4.2 shows MST of latex after saponified with 5%(w/v) NaOH in the presence of various kind of surfactants (0.2%, w/v) at 70^{0}C for 3 h. MST of saponified latex in the presence of nonionic surfactant is higher than saponified latex in the presence of anionic surfactant. In case of 0.2% (w/v) Triton X-100, MST of saponified latex is about 90 sec. (original value is 120 sec.). It shows that Triton X-100 is the best surfactant for stabilize rubber particle in latex during saponification.

The MST of freshly trapped latex is always low [21]. It increases very rapidly for three to four weeks correlated to the increasing of higher fatty acid soaps. The fatty acid soaps arise from the hydrolysis of some lipids (mainly phospholipids and glycolipids) on the surface of the rubber particles. The MST of concentrated latex is typically about 600 seconds. From Table 4.2, MST of fresh latex (non-ammonia preserved, age in refrigerator for one month) is about 120 sec. Various factors which are associated with the inherent properties of the latex system could be responsible for the low latex stability. These factors include clone of rubber, lower concentration of higher fatty acid soaps, lower content of proteins and saponifiable lipids on the rubber particle surface and excessive quantity of inorganic cations in the serum phase.The MST of ammonia-preserved latex increase after aging for one month due to the adsorption of the surface active soap molecules on the rubber particle surface, arising from ammonia and hydrolysed lipid. In the other hand, nonammonia-preserved latex shows decrease in MST after aging.

Table 4.1 Stability of latex during saponification and washing in the presence of surfactant

Latex	Surfactants (1%, w/v)	Stability in Saponification	Stability in washing (centrifugation)	Nitrogen Content, %
Control	-	-	-	0.3
10% DRC	SDS	Poor	Poor	NA
30% DRC	SDS	Poor	Poor	0.023
10% DRC	Triton X-100	Good	Good	NA
30% DRC	Triton X-100	Fair	Good	0.023

NA = not available

Table 4.2 MST of original and saponified latex with 5% NaOH in the presence of various surfactants (0.2%, w/v)

Surfactant	Chemical name	MST
Nonionic surfactant		
Triton X-100	Isooctylphenoxypolyethoxyethanol	90
Emergen 105	POE lauryl ether (1:5)	32
Emergen 1.8	POE lauryl ether (1:8)	34
Emergen 109P	POE lauryl ether (1:9)	28
Emergen 120	POE lauryl ether (1:20)	26
Emergen 408	POE Oleyl ether	35
Anionic surfactant		
Neopelex F-24	-	23
Levenol WX	-	38

4.1.2 Effect of Number of Centrifugation on Washing Efficiency

Centrifugation is the process of washing the decomposed protein from the saponified latex. The effect of centrifugation was studied for the saponification of 10% DRC latex with %NaOH and Triton X-100 followed by single or double centrifugation.

Table 4.3 presents the nitrogen content of purified rubber saponified with NaOH in the presence of Triton X-100 with single and double centrifugation. Nitrogen content decreased with increasing number of centrifugation and concentration of Triton X-100. Double centrifugation of saponified latex with 0.2%(w/v) Triton X-100 decreased nitrogen content from 0.3%(initial value of control natural rubber) to 0.0036%. It was found that double centrifugation was more effective than single centrifugation. Double centrifugation could remove the protein from latex at 4-5 times of single centrifugation. For the single centrifugation, the residual nitrogen content decreased from 0.3% to about 0.02 % (Figure 4.1).

After double centrifugation, the nitrogen content of saponified rubber was extremely low, compared with that of purified rubber by enzymatic deproteinization followed by double centrifugation. In this work enzymatic deproteinization was done as control. The nitrogen content of purified rubber by enzymatic deproteinization was 0.023%. This indicates that saponification of latex is very effective to decompose the proteins in latex and the decomposed proteins in serum can be washed out after centrifugation. The double centrifugation results in the production of saponified rubber with the lowest nitrogen content.

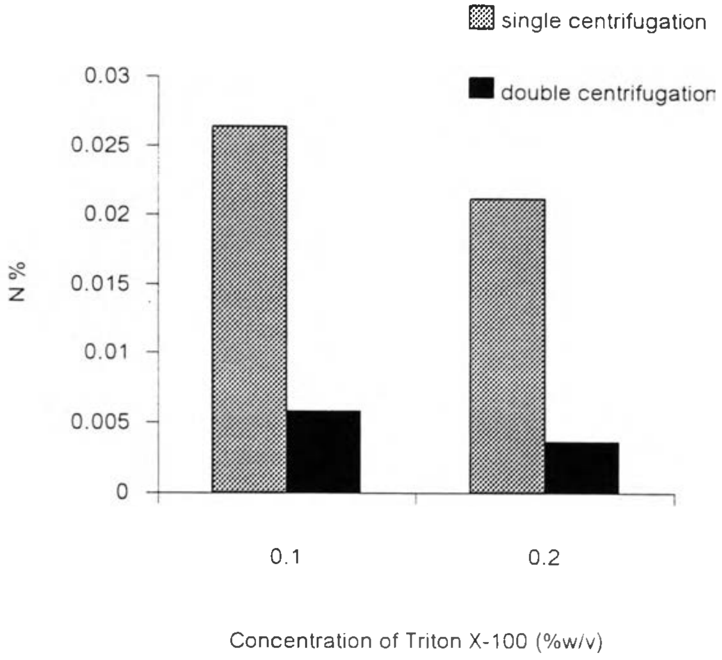


Figure 4.1 Effect of number of centrifugation on nitrogen content

Table 4.3 Nitrogen content of purified rubber affected by number of centrifugation, NaOH and surfactant

Latex	Surfactant concentration , %(w/v)	Nitrogen content, %		
		5%(w/v), NaOH Single Centrifugation	5% (w/v), NaOH Double centrifugation	Triton X-100 Double Centrifugation
10% DRC	0.1	0.0214	0.0058	0.017
10% DRC	0.2	0.0212	0.0036	0.012

Nitrogen content of control natural rubber = 0.30%

4.1.3 Effect of Surfactant on Saponification

Saponification of 10% DRC latex was carried out with NaOH (5% w/v) at 70° C for 3 h. Table 4.3 and Figure 4.2 show that the nitrogen content of purified rubber decreased from 0.3% (control) to 0.017 and 0.012% in the presence of 0.1 and 0.2% w/v Triton X-100, respectively. The addition of Triton X-100 showed a synergistic effect with the saponification, which caused the decrease in the nitrogen content in DPNR (Deproteinized Natural Rubber). Nitrogen in latex consists of the nitrogen substances dissolved in water and the protein linked with rubber particle. This type of nitrogen substance can be solvated by surfactant and separated from latex emulsion by washing out with centrifugation. In the saponification, NaOH reacted with nitrogen substance or protein linked with rubber particle, which was decomposed into short chain.The decomposed protein dissolved in water phase and was washed out by centrifugation. Therefore, nitrogen content of the saponified rubber with NaOH in the presence of 0.1 and 0.2%, (w/v) Triton X-100 decreased from 0.3% (control) to 0.0058 and 0.0036%, respectively.

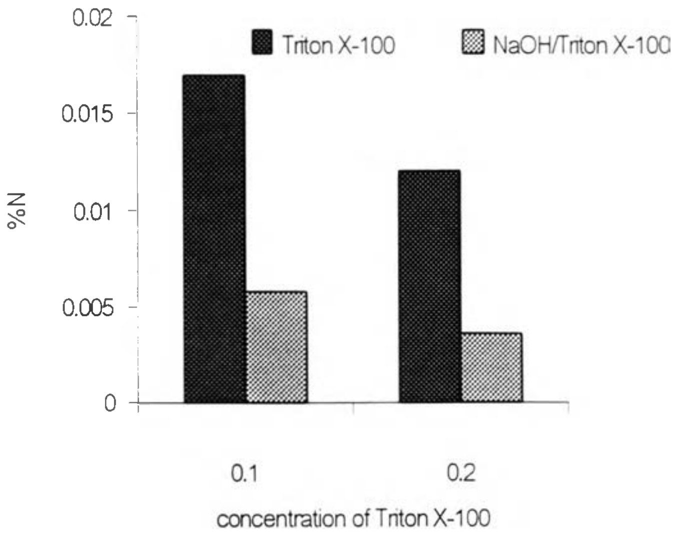


Figure 4.2 Nitrogen content of DPNR by saponification with NaOH/Triton X-100

4.1.4 Effect of Addition Method and Surfactant Concentration on Saponification and Washing Efficiency

Effect of concentration of Triton X-100 (0.1-0.4% w/v) on the stability of saponified latex was studied for the saponification of 10% DRC concentrated latex with 5% NaOH at 70^0 C for 3 h. The washing of saponified latex was carried out in the presence of Triton X-100 at first and second centrifugation as well as in the course of saponification as shown in Figure 4.3.

For experiments 1-4 of Table 4.4, the addition of 0.1% (w/v) triton X-100 to the saponification and washing of latex was not enough to stabilize latex. Saponified latex coagulated partially and perfectly in case of the addition of surfactant in saponification and washing step, respectively. Nitrogen content of saponified rubber decreased to the range of 0.006 to 0.05% in this case.

For experiments 5-8, the addition of 0.2% (w/v) Triton X-100 to the saponification of latex is enough to stabilize the latex during the first and second centrifugation steps. In this case, the nitrogen content decreased from 0.3%(control) to 0.0067%. The addition of 0.2% (w/v) Triton X-100 before the second centrifugation further decreased the nitrogen content as low as 0.0036% with a slight increase in the ash content to 0.32% after washing. In case of addition of 0.2% (w/v) Triton X-100 to the washing of saponified latex (in the absence of surfactant) can not stabilize the saponified latex. It partially coagulated in washing step and the nitrogen content decreased to 0.0124%.

For experiments 9-12, the addition of 0.4% (w/v) Triton X-100 perfectly stabilized saponified latex. Nitrogen content of saponified latex decreased to the range of 0.006 to 0.0002 in this case. However, the addition of 0.4%(w/v) Triton X-100 effected the coagulation of saponified latex. The coagulation of latex in the presence of high concentration of surfactant was difficult.

The addition of 0.2% (w/v) Triton X-100 to the saponification of latex, (experiment 6) was chosen to be the most appropriate condition to stabilize latex during the saponification and washing. The nitrogen content of purified latex was 0.0036%

which reached the low value for the purpose of the purification. Surfactant also showed synergistic effect to the saponification and washing due to its roles of catching the decomposed protein.

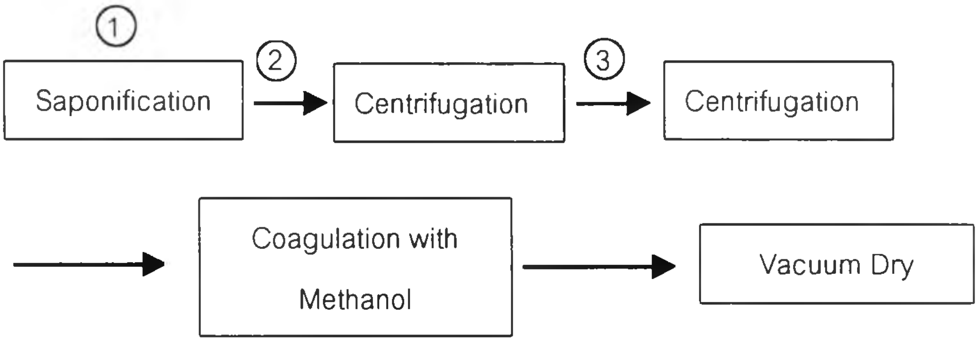


Figure 4.3 Addition of Triton X-100 in course of saponification and washing by double centrifugation

Table 4.4 Stability of saponified latex and nitrogen content of rubber saponified with 5% NaOH at 70^{0}C for 3 h. followed by double centrifugation.

Expt. No.	Concentration of Triton X-100, %(w/v)			Latex stability	Nitrogen content
	Saponification	Washing step			
	①	②	③		
1	0.1	0	-	Partially coagulate	0.0058
2	0.1	0	-	Partially coagulate	0.0098
3	0	0.1	-	Perfectly coagulate	0.0206
4	0	0.1	-	Perfectly coagulate	0.0463
5	0.2	0	0.2	Good	0.0036
6	0.2	0	0	Good	0.0067
7	0	0.2	-	Partially coagulate	0.0124
8	0	0.2	-	Partially coagulate	0.0124
9	0.4	0	0.4	Good	0.0002
10	0.4	0	0	Good	0.0038
11	0	0.4	0.4	Good	0.0075
12	0	0.4	0	Good	0.0064

4.1.5 Effect of NaOH Concentration on Saponification

From Table 4.4, the best condition for purification of natural rubber latex is the saponification with 5% (w/v) NaOH and the addition of 0.2% (w/v) Triton X-100 during the saponification (Experiment 6 in Table 4.4). The saponification condition was used to study the effect of NaOH concentration on the properties of purified rubber.

4.1.5.1 Effect of NaOH Concentration on Nitrogen Content

The effect of NaOH concentration (1-5%, w/v) was studied for the saponification of 10% DRC field latex in the presence of 0.2%, w/v Triton X-100 followed by double centrifugation and coagulation with methanol.

Table 4.5 and Figure 4.4 show that the nitrogen content of saponified latex decreased with increasing NaOH concentration. The nitrogen content lower than 0.02% was achieved at NaOH concentration higher than 4% under these conditions.

Figure 4.5 illustrates FTIR spectra of original rubber and purified rubber saponified with 1-5 %(w/v) of NaOH. These spectra showed that the bands at 3210 cm^{-1} and 1540 cm^{-1}, which are the characteristic vibration of N-H stretching and amine, respectively [20], decreased in intensity after saponification. Furthermore, the intensity of these bands decreased with increasing NaOH concentration. It was persumed that the residue nitrogenic substances in purified rubber were the decomposed polypeptide, present in a coagulum. In this case, it is necessary to remove these compounds by washing before coagulation.

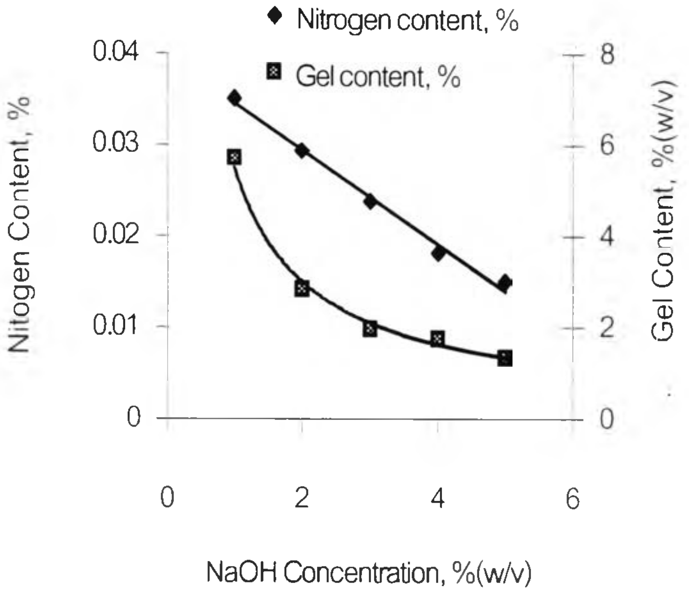


Figure 4.4 Effect of NaOH concentration on nitrogen content of rubber saponified with NaOH and 0.2% (w/v) Triton X-100 at 70^{0}C for 3 h. and washing by double centrifugation.

Table 4.5 Nitrogen content and gel content of saponified natural rubber with 1-5%, (w/v) NaOH at 70^{0}C for 3 h.

NaOH concentration, %(w/v)	Nitrogen content, %	Gel content, %
Control	0.570	7.10
1	0.035	5.70
2	0.029	2.83
3	0.024	1.98
4	0.018	1.76
5	0.015	1.34

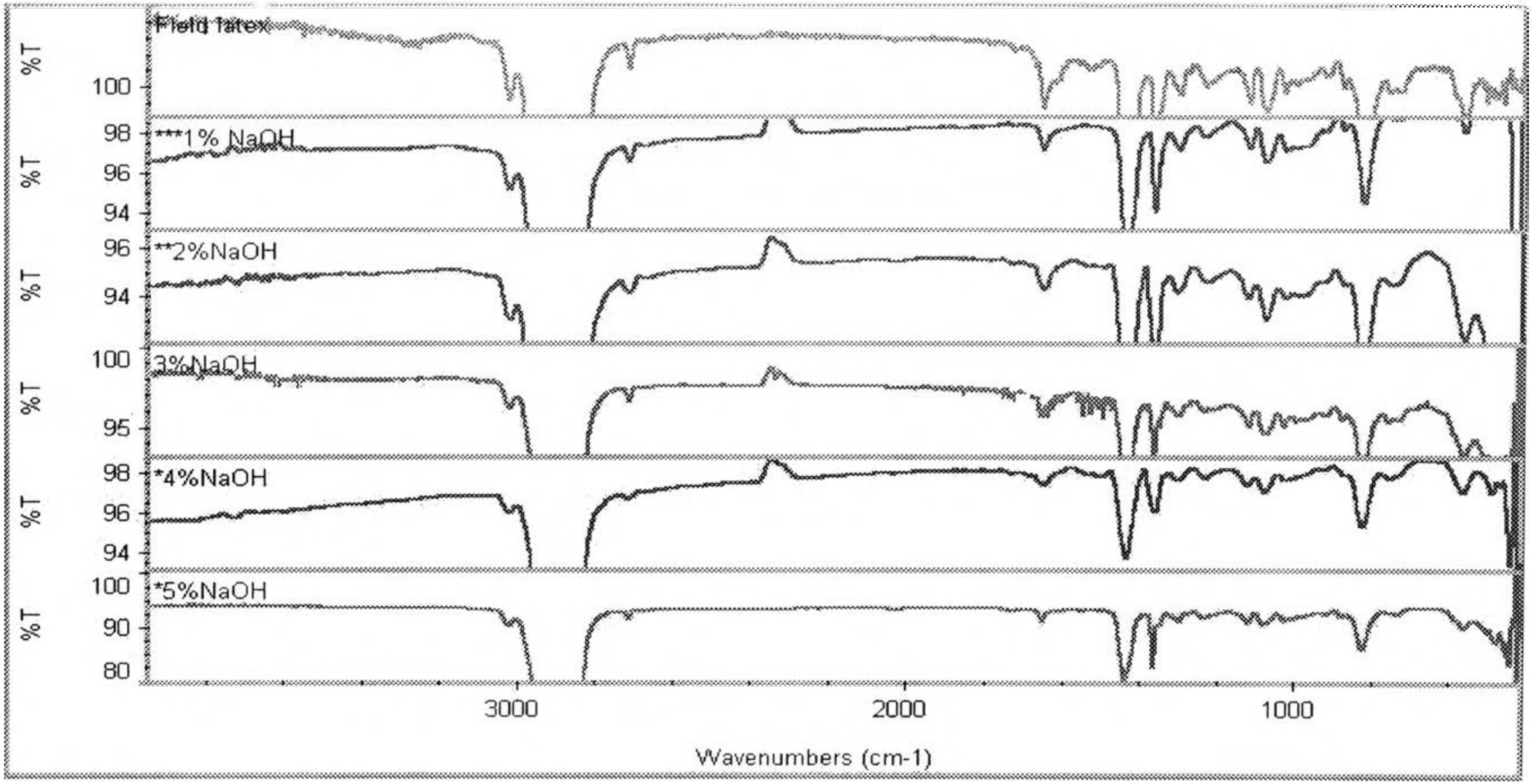


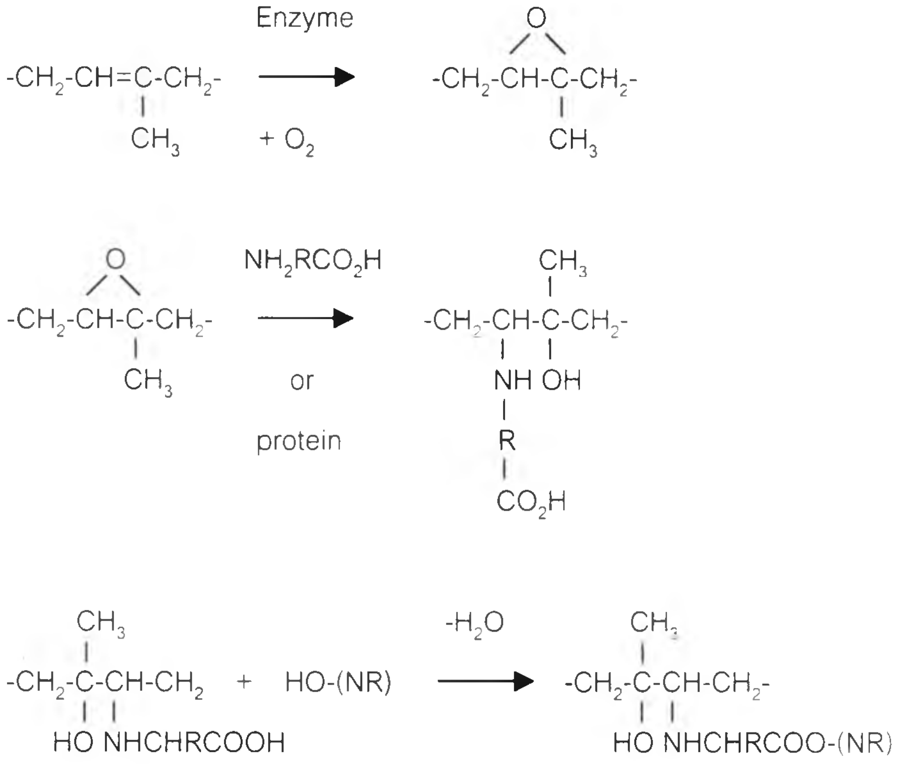
Figure 4.5 FTIR spectra of original rubber and purified rubber saponified with various concentrations of NaOH

4.1.5.2 Change in Gel Content after Saponification

Table 4.5 and Figure 4.4 shows the change in gel content of rubber from field latex after saponification with NaOH (1-5% w/v). The gel content of 7% in the rubber from field latex was reduced to 1-2% after saponification. The gel content decreased with increasing NaOH concentration.

It is generally accepted that the gel fraction of natural rubber is the branched molecules originated from cross-linking reactions due to abnormal groups present in the rubber matrix, which lead to the storage hardening of rubber [21]. Although the mechanism of these reactions has not been disclosed, the chemical reactions via aldehyde groups (R-C-R'), epoxide group and formation of lactone ring have been postulated. Recently, an ionic crosslinking mechanism has been proposed to interpret the phenomena that can not be satisfactorily explained by the reactions postulated thus far [21]. The mechanism of storage hardening is illustrated in Figure 4.5. Enzymatic epoxidation may occur within the tree at the same time as the biosynthesis (equation 4.1). Subsequent reactions of protein or free amino acids with some of epoxide groups would lead to the incorporation of amine groups (equation 4.2). Subsequent crosslinks are formed under low humidity conditions at dry rubber phase (equation 4.3).

The treatment of latex with NaOH decomposes peptide linkages as well as ester linkages such as fatty acid ester, phosphorus ester in rubber molecules. The decrease in the gel content after saponification in this experiment implies that the most of gel fraction in the rubber from fresh latex is not tri-dimensional polymer crosslinked via carbon-carbon or carbon-oxygen linkages, which is usually termed hard gel. It is well known that the gel fraction in dry natural rubber is so-called soft gel, which can be solubilized by the addition of a small amount of polar solvent to good solvent. The gel fraction in rubber from fresh latex is actually composed of crosslinked polymer by fatty acid ester, phosphorus ester, and/or peptide linkage, which is solublized by the treatment with NaOH. The reaction of ester with strong base, called saponification, is involved in the preparation of soap, and is one of the oldest organic reactions known.



$$-CH_2-CH=\underset{\substack{|\\CH_3}}{C}-CH_2- \xrightarrow[+\,O_2]{Enzyme} -CH_2-\overset{\substack{O\\\diagup\diagdown}}{CH-\underset{\substack{|\\CH_3}}{C}}-CH_2- \qquad (4.1)$$

$$-CH_2-\overset{\substack{O\\\diagup\diagdown}}{CH-\underset{\substack{|\\CH_3}}{C}}-CH_2- \xrightarrow[\substack{or\\protein}]{NH_2RCO_2H} -CH_2-\underset{\substack{|\\NH\\|\\R\\|\\CO_2H}}{CH}-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\OH}}{C}}-CH_2- \qquad (4.2)$$

$$-CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\HO}}{C}}-\underset{\substack{|\\NHCHRCOOH}}{CH}-CH_2 + HO\text{-}(NR) \xrightarrow{-H_2O} -CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\HO}}{C}}-\underset{\substack{|\\NHCHRCOO\text{-}(NR)}}{CH}-CH_2- \qquad (4.3)$$

Figure 4.6 The mechanism of storage hardening in natural rubber due to abnormal groups

4.1.5.3 Change in Ester Content after Saponification Observed by FTIR and ^{13}C-NMR

The residual fatty acids, after acetone extraction of the free fatty acids in natural rubber, are referred to long-chain fatty acids linked-up to rubber chain. These linked fatty acids can be detected by FTIR and ^{13}C-NMR measurements.

(a) FTIR method

The presence of residual ester group in saponified rubber was confirmed by IR spectroscopy.-C=C- unit shows a characteristic absorption at 1664 cm^{-1} and carbonyl group of fatty acid ester linkage shows a characteristic absorption band at 1738 cm^{-1}. From Figure 4.6, the field latex natural rubber and deproteinized natural rubber show the clear absorption band of carbon-carbon double bond and ester group in the fatty acid esters at 1664 cm^{-1} and 1738 cm^{-1}, respectively.

Ester content was calculated by quantitative analysis of FTIR technique. Ester standard calibration curve was obtained by plotting of peak height ratio of absorption band at 1664 cm^{-1} and 1738 cm^{-1} against ester content (mmol/g rubber). The standard solution was known and accurate in concentration of methyl stearate and synthetic rubber (Clariflex) in chloroform solution. The fatty acid ester content of saponified rubber then was obtained by comparison of the relative intensity of the peaks at 1738 cm^{-1} and at 1664 cm^{-1}, using the following equation.

Ester content (mmol/kg rubber) =(A_{1739}/A_{1664}) /Gradient of calibration curve (4.4)

where the gradient of calibration curve was determined in Appendix F.

From Table 4.6, the ester content of saponified rubber was in the range of 12 to 25 mmol/kg rubber for NaOH concentration of 1-5%, (w/v). While the ester content of control field latex rubber contained the fatty acid ester group of 11.24 mmol/kg rubber, the ester content of purified rubber by saponification was about the same as in the control field natural rubber. It showed that the saponification under the conditions of 1-5% (w/v) NaOH at 70°C for 3 h was not strong enough to cleave the ester linkage in natural rubber. On the other hand, the saponification was effective to cleave only protein linkage in natural rubber.

Table 4.6 Ester content from FTIR technique of saponified natural rubber with 1-5%, (w/v) NaOH at 70°C for 3 h.

Rubber	NaOH concentration, %(w/v)	Ester content, (mmol/kg rubber)
FL-NR	0	11.24
S-DPNR	1	12.07
S-DPNR	2	18.62
S-DPNR	3	20.03
S-DPNR	4	21.69
S-DPNR	5	25.78

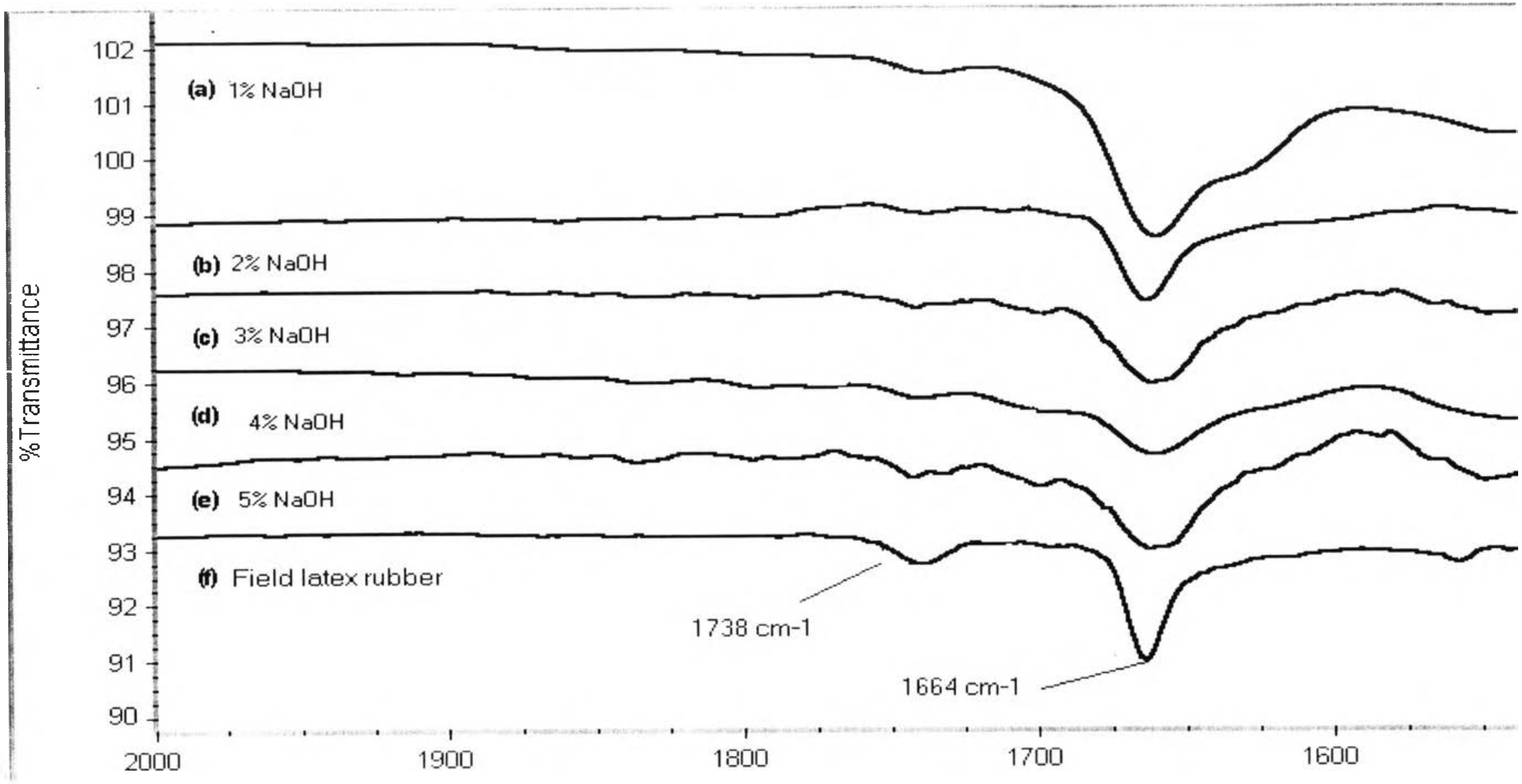


Figure 4.7 FTIR spectra of field latex rubber and purified rubber saponified with various concentrations of NaOH for determination of ester content.

(b) ^{13}C-NMR method

The determination of ester content by ^{13}C-NMR method was made by using 30-40 mg rubber in d-chloroform solution. Figure 4.7 shows the ^{13}C-NMR spectra of field latex and saponified latex. The signals at 14.01, 29.71 and 34.42 ppm in the ^{13}C-NMR spectrum are due to terminal methyl ($-CH_3$), methylene, ($-CH_2-$) and methylene ($-O_2C\underline{C}H_2$) carbons of fatty acid, respectively. The number of ester group per rubber chain was calculated by the relative intensity of methylene ($-CH_2-$) in ester molecule at 29.71 ppm and methyl group ($-CH_3$) in the isoprene unit at 23.5 ppm [22]. Table 4.6 shows the ester/IP unit, degree of polymerization (DP) and number of ester unit/rubber chain.

From Table 4.7, the ester content of saponified rubber was in the range of 10 to 12 mmol/kg rubber for NaOH concentration of 1-5%, (w/v). While the ester content of control field latex rubber contained the fatty acid ester group of 9.3 mmol/kg rubber, the number of ester group per rubber chain of saponified rubber was about the same as of field latex rubber. Therefore, at the saponification condition used in this work, the ester linkage was not cleaved. The clevage of ester linkages in natural rubber was reported only by the tranesterification with freshly prepared sodium methoxide in toluene solution or the saponification with KOH/2-propanol in toluene solution [15].

Table 4.7 Ester content of field natural rubber and deproteinized natural rubber.

Sample	W_{real24}	W_{real29}	Ester/IP unit	$\overline{DP}_n$	No. of ester /rubber chain
Field latex	2.270	0.0899	0.0033	2835	9.3
DPNR (1% NaOH)	1.625	0.0827	0.0042	2250	9.5
DPNR (2% NaOH)	2.330	0.0699	0.0025	2805	7.0
DPNR (3% NaOH)	1.656	0.0870	0.0044	2863	12.5
DPNR (5% NaOH)	2.750	0.1321	0.0040	2569	10.2

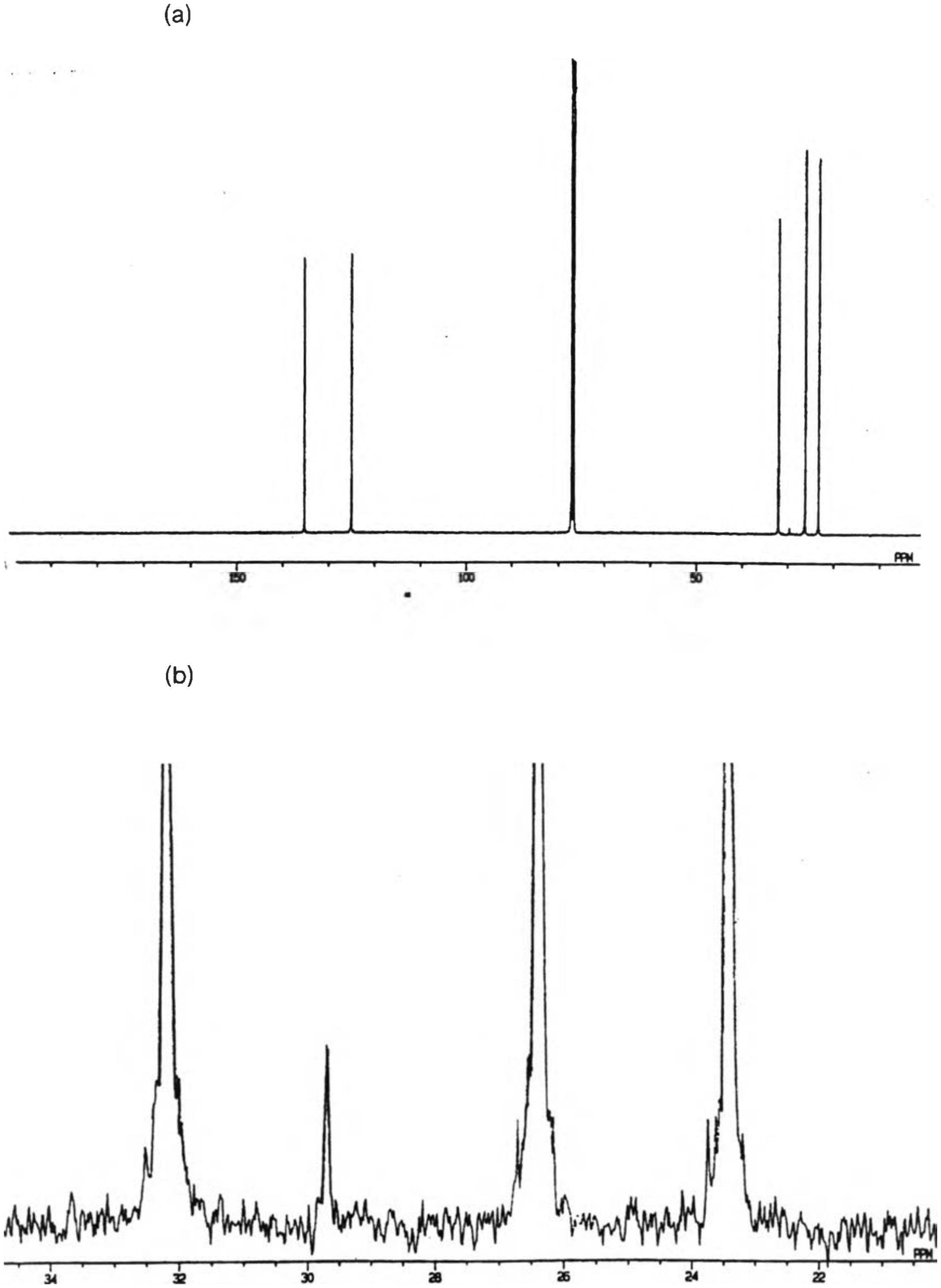
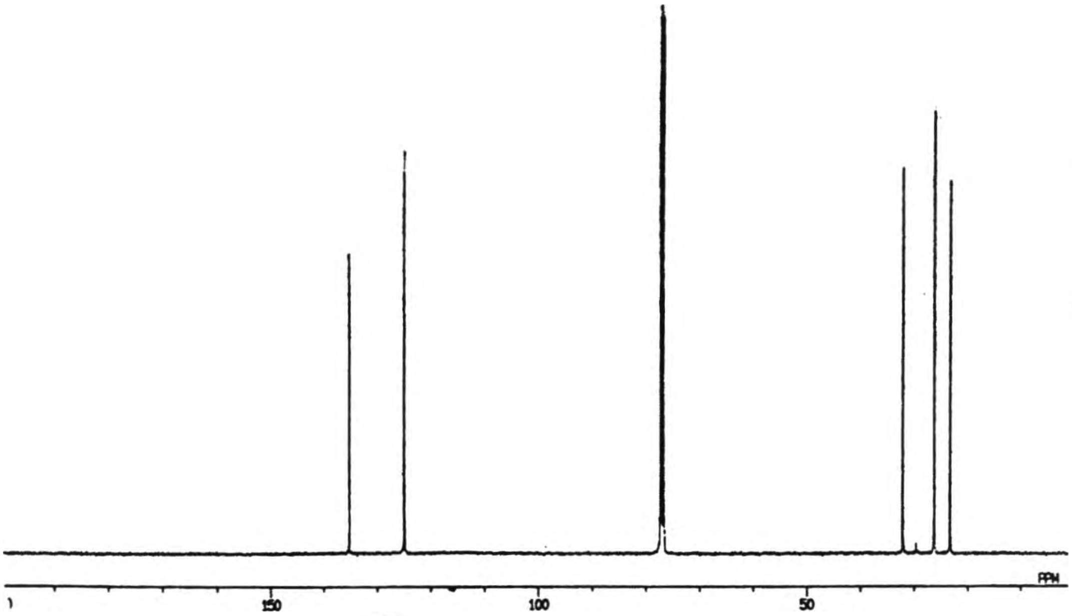


Figure 4.8 ^{13}C-NMR spectra of (a) field latex natural rubber, (b) field latex natural rubber (expanded), (c) saponified natural rubber and (d) saponified natural rubber (expanded)

(c)



(d)

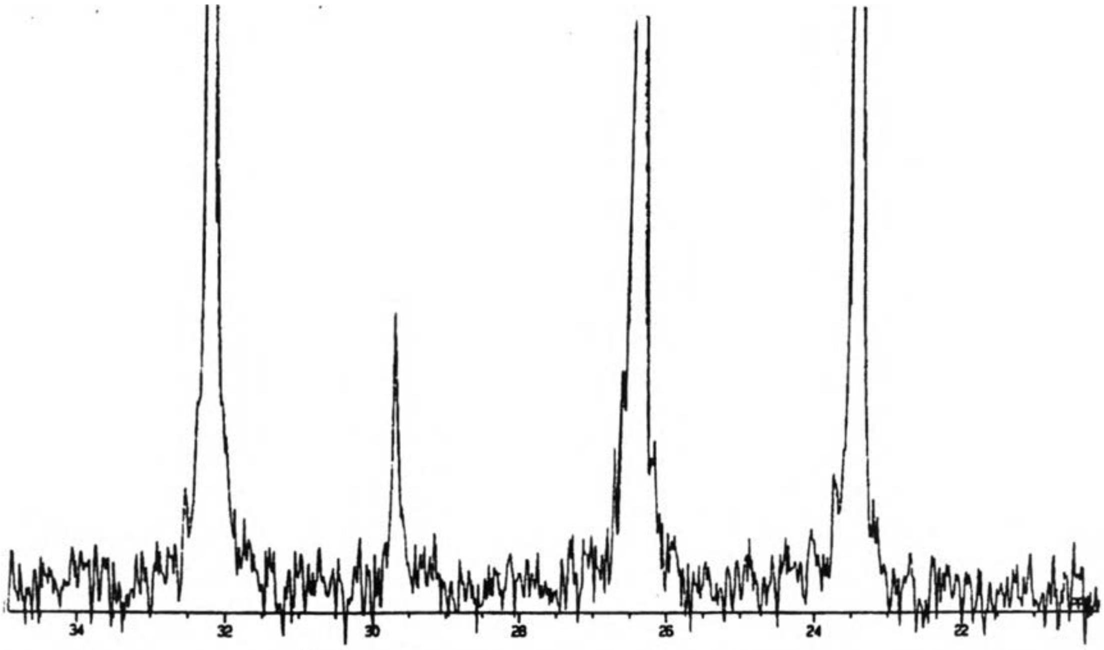


Figure 4.8 (continued) ^{13}C-NMR spectra of (a) field latex natural rubber, (b) field latex natural rubber (expanded), (c) saponified natural rubber and (d) saponified natural rubber (expanded)

4.1.5.4 Molecular Weight Change of Natural Rubber after Saponification

The molecular weight of original/ field latex rubber by GPC method shows that NR has bimodal molecular weight distribution.The number-average molecular weight, weight-average molecular weight and molecular weight distribution of field latex are in the order of 10^5, 10^6 and 2 respectively (Figure 4.8a). Table 4.8 shows the change in molecular weight of field natural rubber and purified natural rubber saponified with various concentrations of NaOH. The $\overline{M}_w$ and $\overline{M}_n$ of purified natural rubber decreased to 2/3 of the control sample. This result suggests that protein does not relate to the branch-points of rubber chain, although it was reported that protein was involved in the gel formation.

Table 4.8 Molecular weight and molecular weight distribution change of field natural rubber and saponified rubber.

Sample	Concentration of NaOH	$\overline{M}_n$ (PS)	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$ (PI)
Field latex	0	233,600	3,572,000	2.81	192,800
Saponified	1	183,300	735,900	4.01	153,100
rubber	2	145,300	478,200	3.29	122,800
“	3	236,100	1,775,000	7.52	194,700
“	4	205,800	705,100	3.43	170,900
“	5	210,600	1,600,000	3.14	174,700

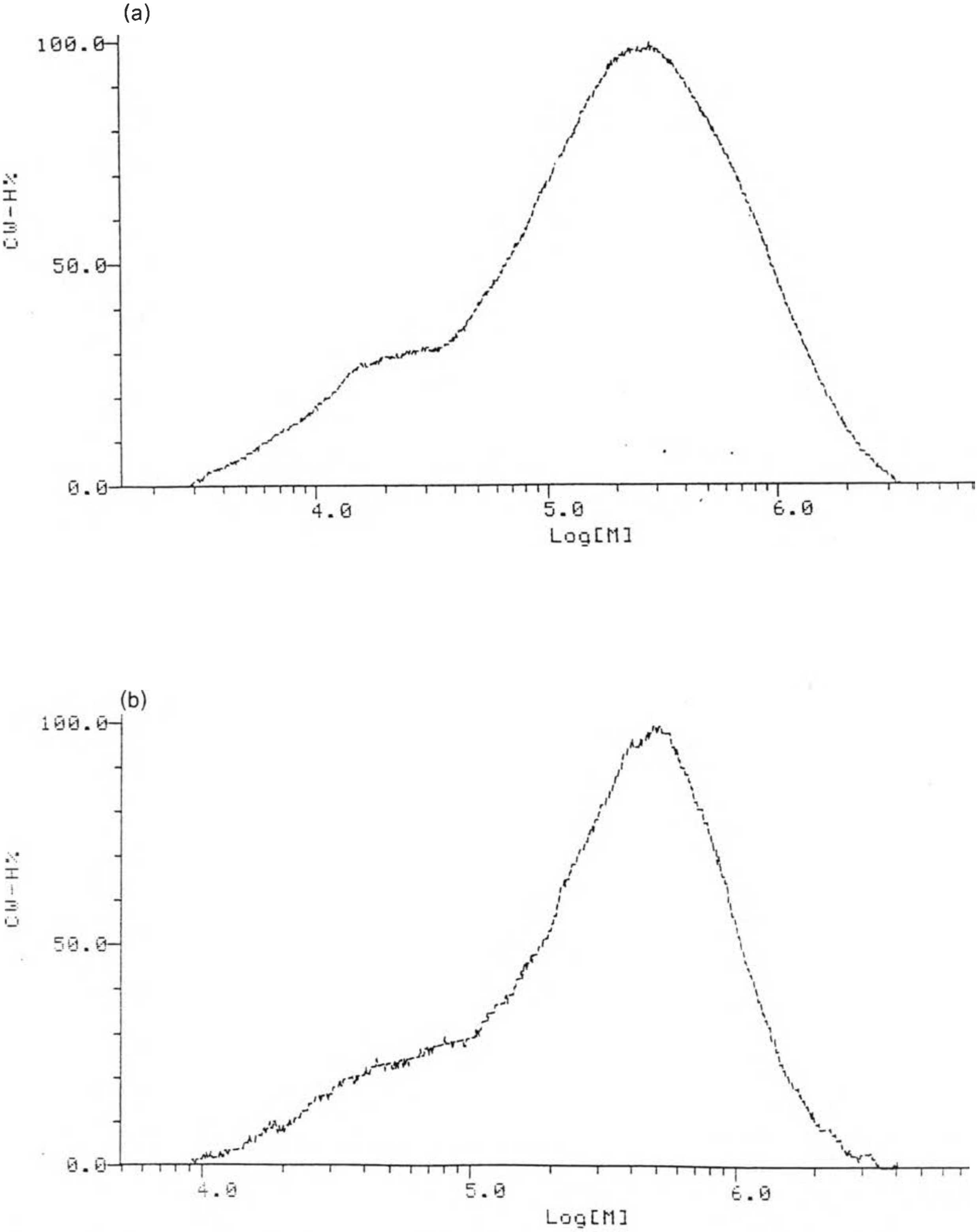


Figure 4.9 Molecular weight distribution of natural rubber by GPC method (a) Molecular weight of field natural rubber (b)-(d) Molecular weight of purified natural rubber by saponified with 1%, 3% and 5% (w/v) NaOH, respectively.

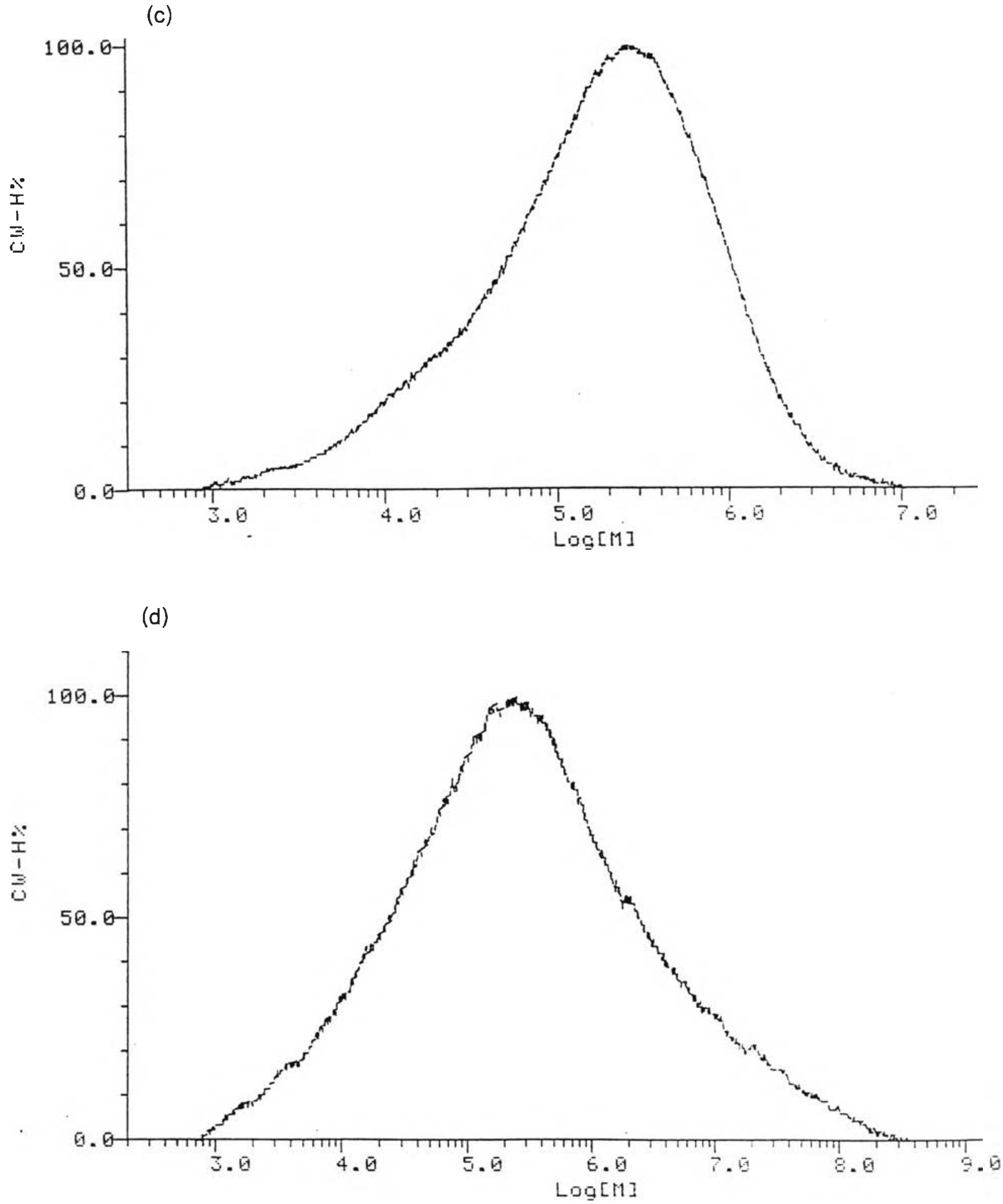


Figure 4.9 (continued) Molecular weight distribution of natural rubber by GPC method (a) Molecular weight of field natural rubber (b)-(d) Molecular weight of purified natural rubber by saponified with 1%, 3% and 5% (w/v) NaOH, respectively.

4.2 Saponification of Latex and Coagulation Followed by Washing

Saponification of 30% DRC field latex with 5% NaOH in the presence of 0.1% Triton X-100 was carried out at 70^0C for 3 h. In this case, 0.1% Triton X-100 was sufficient to stabilize latex during saponification. Coagulants or creaming agent were added to coagulate saponified latex with high speed stirring at 50^0C. In this section, the effects of three coagulants or creaming agent on crumb appearance, nitrogen and ash content were studied.

4.2.1 Creaming and Coagulation by NaCl

Sodium chloride is well known as the creaming agent in synthetic rubber production. Saponification of field latex with 5% NaOH was carried out with and without surfactant (Triton x-100). Then the saponified latex is processed to the heavy cream by adding brine (NaCl) solution even in the absence or presence of surfactant. However sodium chloride is not effective to coagulate the saponified latex. The resulting cream latex with about 60% DRC was obtained. It was found that the saponified natural rubber latex remained stable in emulsion system at high-speed mechanical stirring, the saponified latex was not coagulated.

4.2.2 Effect of $Ca(NO_3)_2$ on Coagulation Process and Washing Efficiency

The coagulation process of saponified rubber was studied by various concentrations of $Ca(NO_3)_2$ (1.0, 0.5 and 0.25 %(w/v). Big crumb was obtained during the coagulation process at the stirring speed of 200-800 rpm. and 50°C. Saponified latex coagulated to big crumb with small surface area, which was difficult to wash out the residue NaOH, surfactant and the decomposed protein. From Table 4.9, high ash (2-4%) and nitrogen content (0.02-0.04 %) rubber was obtained for the coagulation with very dilute solution of $Ca(NO_3)_2$.

$Ca(NO_3)_2$ is a salt which can dissociate in aqueous solution resulting in the ionic equilibrium change in solution, which can salting out the hydrophobic substance in aqueous system. $Ca(NO_3)_2$ shows as expected the effect on the stability of natural latex emulsion system. Equilibrium change in the latex emulsion system causes the coagulation of rubber from emulsion system. From the result, it suggests that $Ca(NO_3)_2$ is too strong salt to be used as coagulant in saponified latex coagulation process even in very dilute solution. The other reason which should be noted here is that the saponified latex is destabilized by the decomposition of protein from the surface of rubber particle, therefore it tends to be easy to coagulate and results in big crumb by using strong salt.

Table 4.9 Nitrogen and ash content of saponified rubber coagulated by $Ca(NO_3)_2$ with high speed mechanical stirring at 50°C

$Ca(NO_3)_2$, %(w/v)	$[Ca(NO_3)_2]$ solution, % (w/v)	Nitrogen content, %	Ash content, %
1.00	1.00	0.042	2.0
0.50	0.50	0.035	2.0
0.25	0.10	0.037	1.9
0.25	0.25	0.037	2.2
0.25	0.50	0.027	4.6

4.2.3 Effect of H_2SO_4 and sodium stearate on coagulation process and washing efficiency

Sulfuric acid is a common acid used in the coagulation process of natural rubber production. In this method, the high speed-blender was used as very high speed-mechanical stirring. Sodium stearate was used as the suspending or crumbing agent. Sulfuric acid was added to the saponified latex in the presence of sodium stearate at $50^{0}C$ with very high speed stirring. From Table 4.10, the coagulation of 5% DRC saponified latex with H_2SO_4 in the presence of 1%, (w/v) of sodium stearate gives very fine crumb compared with crumb from $Ca(NO_3)_2$ as shown in Figure 4.9. Nitrogen and ash content obtained by this method was less than 0.2% and about 0.5%, respectively.

The pH of 8 was appropriate condition for the coagulation process. At this point, the initiation of coagulation was occurred and completed after leaving the latex for a while without further stirring. Fine crumb was obtained because (a) very high speed and turbulent stirring affected the size of crumb by suspending the small crumb and preventing them from coalescence (b) sodium stearate acted as suspending agent to prevent the sticking of fine crumb.

Table 4.10 Nitrogen and content of saponified rubber coagulated by H_2SO_4 in the presence of sodium stearate at $50^{0}C$ with very high-speed blender.

DRC of latex (before coagulation)	Concentration of sodium stearate, %(w/v)	pH	Nitrogen content, %	Ash content, %
10	0.1	8	0.019	0.22
10	0.1	4	0.029	0.39
10	1.0	8	0.019	0.48
5	1.0	8	0.014	0.56

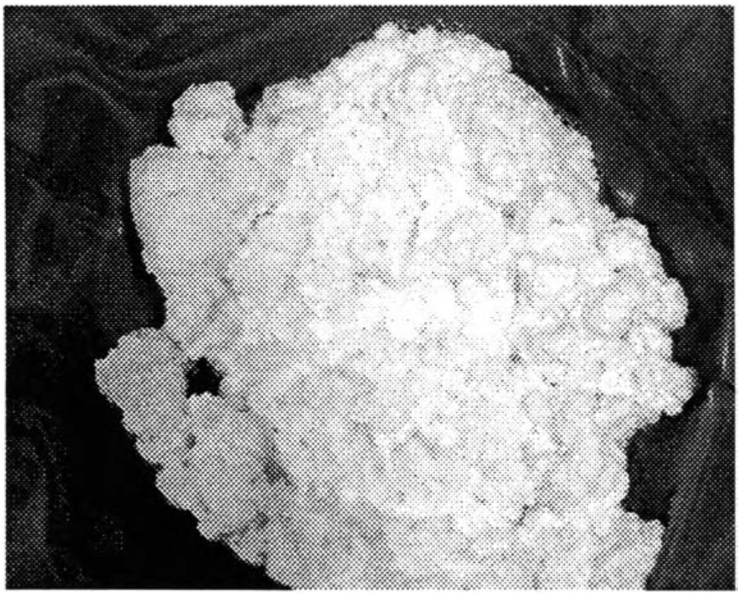


Figure 4.10 Coagulum obtained by the addition of H_2SO_4 in the presence of sodium stearate

4.3 The Effect of Antioxidant on Thermal Oxidative Aging of DPNR.

Saponification of latex was carried out at 70°C for 3 h. After washing by centrifugation, 0.15 phr. antioxidant was added to cream phase of rubber. Efficiency of antioxidant was investigated by determination of molecular weight, original plasticity (P_0) and plasticity retention index (PRI).

Table 4.11 shows molecular weight of saponified natural rubber after addition of antioxidant and aging at 120°C for 36 h. It show that molecular weight of DPNR is slightly decrease after aging even with an antioxidant.

Table 4.12 shows the original plasticity (P_0) and plasticity retention index (PRI) of DPNR. P_0 is the original plasticity and P_{30} is the aged plasticity after heated at 140°C for 30 min. PRI is the percentage change of the original plasticity when the rubber is heated at 140°C for 30 min. From Table P_0 of DPNR is less than original rubber about the half. It means that DPNR is softer than original rubber. However PRI of both rubber are about the same. It shows that ordinary antioxidant is capable to prevent thermal oxidative aging of rubber. Substances like the tocotrienols [23], protein and amino acid had been shown to have a positive relationship with the resistance of NR towards oxidation. They could act as natural antioxidants for NR. Saponification and washing process in production of DPNR remove this natural-occuring antioxidant is necessary to prevent the oxidation.

From Table 4.11 and Table 4.12, it can conclude that addition of only 0.15 phr. of antioxidant after saponification and washing is effective to prevent rubber from thermal oxidative aging.

Table 4.11 Molecular weight and molecular weight distribution of original and saponified rubber which added 0.15 phr. antioxidant and aging at 120^{0}C for 36 h.

Anitioxidant, 0.15 phr.	$\overline{M_n}$	$\overline{M_w}$	$\overline{M_w}/\overline{M_n}$
Original	47040	164400	3.495
2,5-di-tert-butylhydroquinone	47180	158600	3.363
Koclac 200	48370	169300	1.984
Koclac PBK	45500	147100	3.231

Table 4.12 P_0 and PRI of saponified rubber which added 0.15 phr.

Antioxidant, 0.15 phr.	P_0	P_{30}	PRI
Original	59.0	41.0	69.49
2,5-di-tert-butylhydroquinone	27.5	15.0	54.54
Koclac 200	31.0	15.5	50.0
Koclac PBK	28.0	16.0	57.14

4.4 Green Properties of Deproteinized Natural Rubber

Table 4.13 and Figure 4.10 show green strength, P_0 and PRI of ordinary and saponified rubber. P_0 values of both saponified natural rubbers decreased sidnificantly. Modulus and elongation at break decreased after saponification. It is resonable that low green strength, P_0 and PRI derived from decrease in molecular weight of branch-points. The weight-average molecular weight of DPNR decreases significantly due to structural change of rubber after saponification. The saponification is effective to cleave the branch-points from protein of rubber molecule. Saponification produced lower molecular weight or linear chain of natural rubber. Linear rubber molecule shows lower green strength than higher crosslinked rubber molecule [24].

Table 4.13 Green Properties, P_0 and PRI of Deproteinize Natural Rubber.

Properties	Original rubber	DPNR (Method 1)	DPNR (Method 2)
Modulus, N/mm^2	4.26	0.53	0.22
Elongation at break, %	992.4	746.1	635.6
P_0, min	59.0	35.5	48.0
PRI	69.49	35.41	7.39

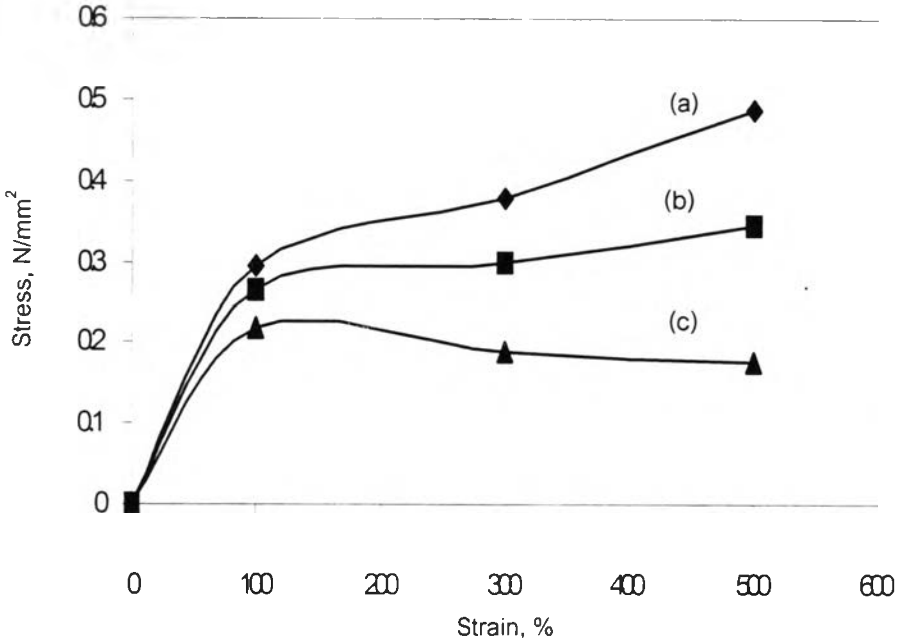


Figure 4.11 Stress-strain curve of (a) original rubber (b) DPNR (method 1) and (c) DPNR (method 2)