ภาคผนวก

ผลงานตีพิมพ์เผยแพร่

1. **Ariyawiriyanan, W.**, Wijitthanasan, W. and Kawahara S. "Properties of Deproteinized Natural Rubber Using Urea Treatment and Their Application in Rubber Glove". 1st Polymer Conference of Thailand, Convention Center (1st PCT), Chulabhon Research Institute, Bangkok, Thailand. 7-8 October, 2010. P.98.

Properties of Deproteinized Natural Rubber Using Urea Treatment and Their Application in Rubber Glove

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Abstract

Properties of deproteinized natural rubber were investigated in order to apply the DPNR latex as non-allergy rubber thin film products. Removal of proteins from natural rubber was made by incubation of high ammonium natural rubber latex (HA-NR) with urea 0.1 wt%, 1 hour in the presence of surfactant at room temperature (DPNR-urea) compared incubation of HA-NR with proteolytic enzyme 0.04 wt%, 24 hours in the presence of SDS at 38°C (DPNR-enzyme). The nitrogen content of the DPNR-urea and DPNR-enzyme was reduced to 0.06 wt% and 0.05 wt%, respectively, which was lower than 0.45 wt% of HA-NR under the test condition. The reduction of protein content can be confirmed by observation a chemical structure through FT-IR technique. It is suggesting that the urea treatment is an effective method to remove protein from rubber latex. Then, physical properties of the DPNR-urea latex were investigated. Amount of water soluble protein was observed through modified lowry method and it was found that water soluble protein content after incubation HA-NR with urea was reduced to 15 μg/g (DPNR-urea) from 42,455 μg/g (HA-NR). It was found that %TSC and %DRC of DPNR-urea were similar to that of HA-NR latex. While VFA number and Mechanical stability of DPNR-urea was lower than that of HA-NR due to lower amount of protein presence in rubber latex. The mechanical properties were then observed when we applied the DPNR-urea latex to vulcanized rubber glove.

Keyword: Deproteinized Natural Rubber, Urea Treatment, Stability, Vulcanized rubber

1. Introduction

Removal of proteins from natural rubber (NR) with urea is conducted to prepare a vulcanized DPNR preparation, rapidly and efficiently. The proteins present on the surface of NR particle in the latex stage may sometimes cause an allergy [1-3] to sensitive individual and side reaction during chemical modification of NR latex [4]. In our previous work [5-7], the removal of proteins can be successfully prepared in latex stage using proteolytic enzyme to decompose the proteins and urea treatment to denaturation of the proteins.

In this study, physical properties of DPNR latex treated with urea as a denaturant in the presence of surfactant was investigated. DPNR latex was also applied for vulcanization in latex stage in order to prepare a thin film product.

2. Experimental Methods

Natural rubber (NR) latexes used in this study was commercial high ammonia NR (HANR) latex. The incubation of the latex was made with 0.1 wt% urea in the presence of 1 wt% sodium dodecyl sulfate (SDS) at

30°C. The cream fraction was redispersed in 1 wt% SDS solution to make 30 wt% dry rubber content (DRC) latex and washed twice by centrifugation (DPNR-urea) to prepare concentrated DPNR-urea latex. The NR latex was also deproteinized by incubation of the latex with 0.04 wt% proteolytic enzyme (KP-3939) in the presence of 1 wt% SDS for 24 h at 38°C followed by centrifugation. The cream fraction was redispersed in 1 wt% SDS solution to make 30 wt% DRC latex and was washed twice by centrifugation to prepare deproteinized NR (DPNR-enzyme) to prepare concentrated DPNR-enzyme latex. The rubber was recovered by centrifugation followed by coagulation with methanol and dried under reduced pressure at ambient temperature until a definite weight was achieved.

HANR latex and DPNR-urea latex was compounded by coagulant dipping technique according to the formulation as shown in table 1. The rubber glove was fabricated by dipping mold into HANR latex or DPNR-latex compounding and vulcanized at 100°C for 30 mins in hot air oven to see the possibility of latex application.

Measurement of Nitrogen content of the rubbers was made by Nitrogen Analyzer, model FP 528.

The peptide linkages were characterized by FT-IR spectroscopy JASCO FT-IR 410. Approximately 2 wt% of rubber solution dissolved in chloroform and cast on KBr disk under nitrogen gas.

The amount of water soluble protein of rubber dry film prepared from concentrated NR was measured using a Standard Test Method for Analysis of Aqueous Extractable Protein in Natural Rubber and Its Products Using the Modified Lowry Method.

Mechanical properties of tensile strength and elongation at break for NR vulcanized films were investigated according to ASTM D412. The crosshead was operated at speed of 500mm/min.

Table 1 NR glove compounding formulation.

Ingredients	Weight (gram)
NR latex (60%DRC)	167
Potassium caprilate solution, 20% dispersion	0.8
Potassium hydroxide, 10% dispersion	2
Dispersion sulfur, 50% dispersion	1.6
Zinc diethyl dithiocarbamate (ZDEC), 50% dispersion	0.8
Zinc 2-mercaptobensothiazole (ZMBT), 50% dispersion	0.8
Dispersion zinc oxide, 50% dispersion	2
Titanium, 50% dispersion	2
Wingstay-L, 50% dispersion	2
Water	The rest amount to 180 gram in total

3. Results and Discussion

Total nitrogen content of HANR and DPNR, which is proportional to the amount of proteins present in the rubber latex, is shown in Table 2. The total nitrogen content of HANR decreased from 0.45 wt% to 0.05 wt% after incubation with enzyme for 12 hours at 38°C. On the other hand, it was reduced to 0.06 wt% after incubation with urea at room temperature for 1 hour (DPNR-urea), similar to that of DPNR-enzyme. It may demonstrate that most proteins present in NR latex are attached to the rubber with weak attractive forces, can be detached with urea. The slight higher total nitrogen content of DPNR-urea prepared from HANR may indicate the strong attachment of the proteins to gel fraction of NR increasing during preservation of the HANR as reported in the previous work [8].

Table 2 Nitrogen content and amount of soluble proteins of HANR, DPNR-enzyme and DPNR-urea latex.

Sample	Nitrogen content (wt%)	Water soluble proteins (μg/g)
HANR	0.45	42,455
DPNR-enzyme	0.05	15
DPNR-urea	0.06	15

Figure 1 shows the NH stretching region of FT-IR spectra of HANR, DPNR-enzyme and DPNR-urea. HANR showed a clear band at 3280 cm^{-1}, characteristic of proteins or long-chain peptides. After the deproteinization of HANR latex with the proteolytic enzyme, the band disappeared and a band appeared at 3318cm^{-1}, which was identified to mono- or di-peptides, as reported in the previous study [5-6]. On the other hand, DPNR-urea showed the peak at 3318 cm^{-1} and no band at 3280 cm^{-1}. The relative intensity of the 3318 cm^{-1} peak in DPNR-enzyme was quite similar to that of DPNR-urea. This is supporting evidence that the DPNR-enzyme and DPNR-urea are the low protein natural rubber.

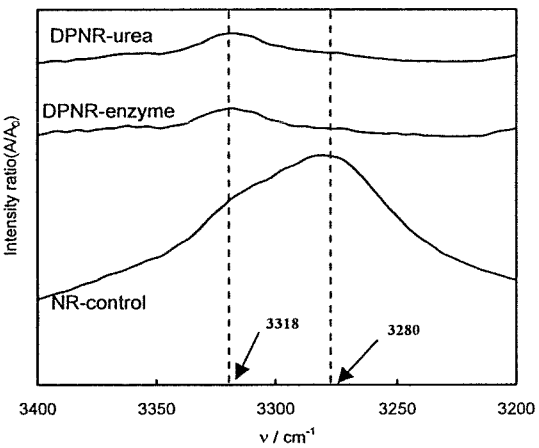

Figure 1 FTIR spectrum of HANR, DPNR-enzyme and DPNR-urea.

The amount of water soluble proteins of natural rubber; i.e. HANR, DPNR-enzyme and DPNR-urea, are also shown in Table 2. The water soluble protein content of HANR was 42,455 μg/g, which was very much higher than those of DPNR-enzyme (15 μg/g) and DPNR-urea (15 μg/g), respectively. The result confirms that urea treatment is quite effective to prepare low protein natural rubber.

Physical properties i.e. total solid content (TSC), dry rubber content (DRC), volatile fatty acid (VFA) and mechanical stability (MST) of NR were tabulated in Table 3 in order to investigate the properties of the latex before and after removal of proteins. %TSC and % DRC of DPNR latex with enzyme treatment and urea treatment were lower than a neat HANR after centrifugation twice. Then we kept the both DPNR latex (preservation with NH_4 content about 0.2 wt%) for 2 weeks before testing of VFA and MST. Volatile fatty acid number indicates a quality of preservation latex in which occurred from degradation of protein by bacteria present in the latex. VFA number of DPNR-enzyme and DPNR-urea were lower than HANR two times. This may be due to the lower amount of protein in the latex. Mechanical stability of DPNR-enzyme and DPNR-urea was found to be 840 second and 695 second which were lower than HANR (1451 second). The higher mechanical stability of HANR may be due to the ammonium preservation in HANR (NH_4 content about 0.70 wt%).

Table 3 %TSC, %DRC, VFA number and MST of HANR, DPNR-enzyme and DPNR-urea.

Sample	Total solid content (%TSC)	Dry rubber content (%DRC)	Volatile fatty acid number (VFA number)	Mechanical stability (MST, second)
HANR	61.79	60.56	0.028	1451
DPRN-enzyme	52.23	52.09	0.015	840
DPNR-urea	49.96	49.81	0.014	695

Note: %TSC and %DRC content of DPNR-enzyme and DPNR-urea will adjust to about 60 wt% before compounding.

The NR latex was then compounding using sulfur vulcanization. Tensile stress and elongation at break of HANR, DPNR-enzyme and DPNR-urea after vulcanization are shown in table 4. As can be seen in the table, tensile strength of HANR was higher than those of DPNR-enzyme and DPNR-urea about 4 times. On the other hand, elongation at break of HANR was 843 %, which is similar to DPNR-enzyme (773%) and DPNR-urea (743%), respectively. The lower strength in vulcanized DPNR may demonstrate the effect of proteins and concentration of dry rubber content but not for elongation of rubber film. It may suggest the possibility

to develop a preparation of low protein natural rubber product when elongation higher than 600%.

Table 4 Tensile strength and elongation at break of HANR, DPNR-enzyme and DPNR-urea after vulcanization.

Sample	Tensile strength (MPa)	Elongation at break (%)
HANR	20.9	843
DPNR-enzyme	5.1	773
DPNR-urea	5.7	743

4. Conclusion

Removal of protein from natural rubber latex using urea treatment was proved to be effective method to prepare vulcanized DPNR rapidly and efficiently. It was confirmed by FT-IR and amount of water soluble protein. Mechanical stability and Volatile fatty acid of DPNR-urea latex exhibited a similar value of DPRN-enzyme but incubation time of DPNR treated with urea is shorter under room temperature.

Acknowledgement

The authors are grateful to the Council of Thailand Research Fund (NRCT) for financial support this research project through, Associate Professor Dr. Jitladda Sakdapipanich, Mahidol University for supporting a centrifugation and instruments and evaluation discussion.

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