

Reduction of Water Extractable Proteins in Natural Rubber Latex Films by Ultrasonic Leaching System

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Reduction of water extractable proteins (EP) in dry natural rubber latex films could be accelerated by incorporating ultrasonic waves into the leaching system. The rate of EP reduction for prevulcanised latex films was found to be higher than that of post-vulcanised latex films, due to the larger surface area of prevulcanised latex films. It was also observed that leaching of latex films in the presence of ultrasonic waves did not affect the tensile strength of both aged and unaged films.

Natural rubber latex has been known to contain small amounts of naturally occurring proteins. It has been claimed that when in contact with human body, some of these proteins, which are of water soluble in nature, in latex products such as gloves, could cause allergy to certain sensitive individuals¹⁻⁵. Although the number of such sensitive individuals is very small, much effort has been put to reduce the water-soluble proteins or extractable proteins (EP) in latex products⁶⁻¹¹.

Proper leaching^{6,9} and chlormation^{10,11} has been reported to be effective processing methods in reducing the EP of natural rubber latex films. In the production of medical gloves, both wet-gel and dry-film leaching are necessary to obtain low EP latex film. The wet-gel leaching is a process of washing the wet rubber gel deposited on former before drying, whereas dry-film leaching is the same process after the rubber

film has been dried and vulcanised. The need to incorporate dry-film leaching in the production processes was realised when the residual proteins were found to continue migrating from the inner surface to the outer surface of the latex film on the former during the drying process^{6,7,9}. Prolonged leaching of the film, both in wet gel and dry film states, is expected to be effective in removing the EP from the rubber film. However, this would require longer processing time which incurs extra production cost.

This paper examines the possibility of accelerating the reduction of the EP level of latex film by incorporating ultrasonic waves into the leaching system.

MATERIALS AND METHODS

Commercial prevulcanised latex was supplied by RIVERTEX (Malaysia) Sdn Bhd while post-

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vulcanised latex was obtained by compounding commercial high-ammonia latex using the formulation shown in *Table 1*. Calcium nitrate was used as coagulant for latex film preparation. All latex films were leached in wet-gel state at 70°C for one min and dried at 100°C for 30 min. Dry-film leaching in the presence of ultrasonic waves was performed at 47 KHz using a laboratory ultrasonic bath. Ageing test was carried out at 70°C for 7 days. The tensile strength of the latex film was measured by an Instron Tensiometer. Extractable protein content of the latex film was determined by RRIM Modified Lowry method¹².

RESULTS AND DISCUSSION

Effects of Leaching Dry NR Films under Ultrasonic Waves on EP Level of Latex Films

Previous work¹³ showed that leaching dry NR films in the presence of ultrasonic waves could accelerate the reduction of nitrosamine in prevulcanised latex films when compared to those leached without ultrasonic vibration. However, the corresponding reduction in the nitrosatable level was found to be less significant. In the present study, the effect of leaching in the presence of ultrasonic waves on the EP content of latex films was investigated. The EP levels of the dry-film leached samples for prevulcanised latex films are shown in *Figure 1*. As expected, the EP of the samples decreased with prolonged leaching time. It was also found that in the presence of ultrasonic waves, the EP level of the samples could be reduced at a rate faster than that without ultrasonic. In the case of the samples which had been leached for a short period of time, e.g. 30 s, the EP level decreased with increasing leaching temperature, indicating that leaching temperature is an important factor in reducing the EP level of the samples under these

conditions. This is not unexpected since the solubility of water soluble proteins is expected to increase with increasing leaching temperature. It is interesting to note that the EP level appeared to reach a plateau even after prolonged leaching at high temperature in the presence of ultrasonic waves. This is probably because the rate of migration of EP from the inner surface to the outer surface of the film was too slow. This requires much longer time than the period of leaching adopted. The ultrasonic waves are expected to accelerate the migration of the water soluble proteins to the surface and therefore a low EP latex film could be obtained within a shorter period of time when compared to those leached without ultrasonic waves.

In the case of post-vulcanised films, a similar trend of result was obtained as shown in *Figure 2*. In this case, however, the decrease in EP with leaching time in the presence of ultrasonic waves was slower than those of prevulcanised films. This is probably due to the bigger surface area of prevulcanised film, arising from the original particulate structure of latex particles as demonstrated by electron microscopic studies¹⁴. Therefore, more proteins could be leached out from the film at a high rate through a bigger contact area with the water.

Effects of Leaching Dry NR Films under Ultrasonic Waves on Tensile Properties

Recently, it has been reported that SBR could be devulcanised using ultrasound, producing the low molecular weight of the sol fraction^{15,16}. In view of this, it is important to find out the effects of ultrasonic treatment in the present study on the tensile strength of the unaged and aged films. The effect of ultrasonic treatment on the latex films, if any, is expected to be more prominent in the samples which had been treated at higher temperatures. Therefore, the ratio of tensile

TABLE 1 FORMULATION FOR LATEX POST-VULCANISATION

Ingredients	Dry weight
Latex	100
Potassium laurate	0.26
Potassium hydroxide	0.25
Sulphur	1
Zinc di- <i>n</i> -butyldithiocarbamide	0.5
Zinc oxide	0.2
Antioxidant, <i>Wingstay L</i>	2

TABLE 2 TENSILE RETENTION OF LATEX FILMS AFTER ULTRASONIC TREATMENT

Leaching time (min)	Tensile retention after ultrasonic treatment (ultrasonic/control)			
	Prevulcanised latex		Post-vulcanised latex	
	Unaged	Aged	Unaged	Aged
0.5	1.08	1.10	0.99	0.97
1	1.03	1.04	1.00	1.02
2	1.01	0.98	1.05	0.95
3	1.03	1.11	0.99	1.01

Wet-gel leaching 70°C, 1 min

Ageing conditions 70°C, 7 days

Ultrasonic dry-film leaching with ultrasonic waves at 70°C

Control dry-film leaching at 70°C

strength of the films leached with ultrasonic waves to that leached without ultrasonic waves, both at 70°C, was investigated. The results in Table 2 showed that the tensile strength of the films remained almost unchanged after the treatment with ultrasonic waves. Although ultrasonic waves can cause devulcanisation of cured rubber, under the condition employed in the present study, no detectable level of devulcanisation was observed.

CONCLUSION

The incorporation of ultrasonic waves into the leaching system accelerates the reduction of water extractable protein content of prevulcanised and post-vulcanised latex films without affecting the tensile strength of both aged and unaged samples. This method may be useful for producing low protein latex products within a short leaching time.

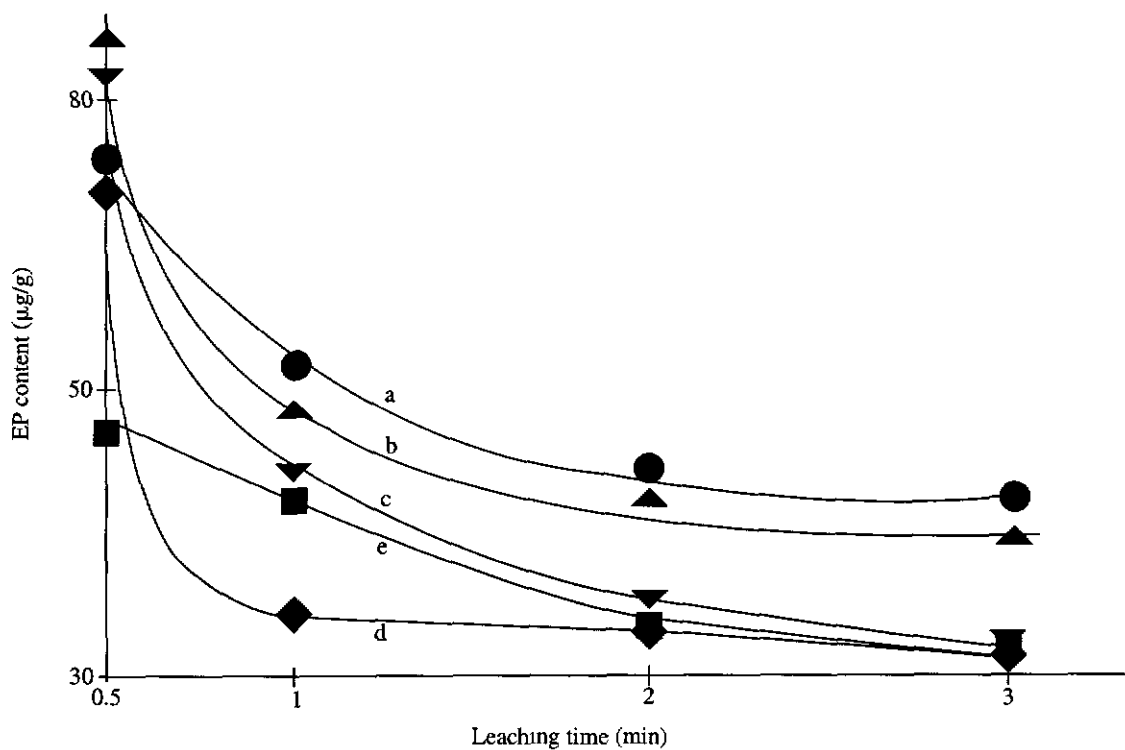


Figure 1. Extractable protein content of prevulcanised latex films: (a) Control, 70°C (b) Ultrasonic, 25°C (c) Ultrasonic, 35°C (d) Ultrasonic, 55°C and (e) Ultrasonic, 70°C.

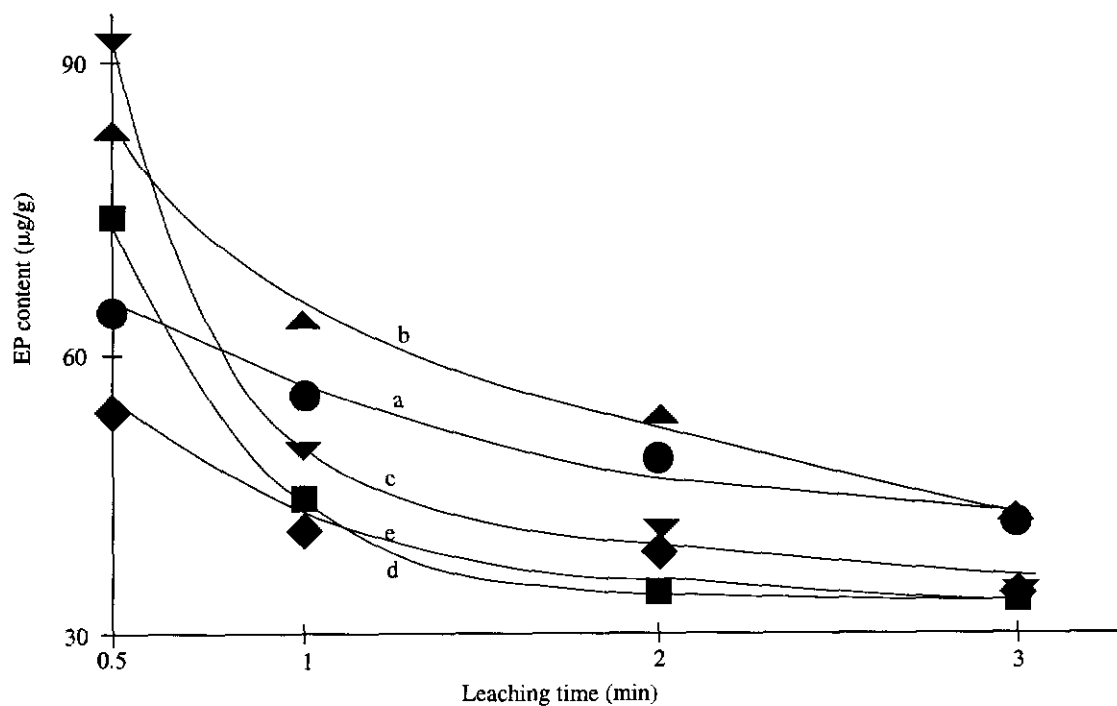


Figure 2. Extractable protein content of post-vulcanised latex films: (a) Control, 70°C (b) Ultrasonic, 25°C (c) Ultrasonic, 35°C (d) Ultrasonic, 55°C and (e) Ultrasonic, 70°C.

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REFERENCES

1. TURJANMAA, K., LAURILA, K., MAKINEN-KILJUNEN, S. AND REUNALA, T. (1988) Rubber Contact Urticaria: Allergenic Properties of 19 Brands of Gloves. *Contact Dermatitis*, **19**, 362-367.
2. AXELSSON, I.G.K., ERIKSSON, M. AND WRANGSJO, K. (1988) Anaphylaxis and Angioedema due to Rubber Allergy in Children *Acta Paediatr. Scand.*, **77**, 314-316.
3. TURJANMAA, K. AND REUNALA, T. (1989) Condoms as a Source of Latex Allergen and Cause of Contact Urticaria. *Contact Dermatitis*, **20**, 360-364.
4. YIP, E., TURJANMAA, K., NG, K.P. AND MOK, K.L. (1994) Allergic Responses and Levels of Extractable Proteins in NR Latex Gloves and Dry Rubber Products. *J. nat. Rubb. Res.*, **9**, 70-78.
5. CENTRE FOR DEVICES AND RADIOLOGICAL HEALTH, FOOD AND DRUG ADMINISTRATION (1991) Medical Alert Issued on Allergic Reactions to Latex-containing Medical Devices *Med. Dev. Bull.*, **9**, 1.
6. NG, K.P., YIP, E. AND MOK, K.L. (1994) Production of Natural Rubber Latex Gloves with Low Extractable Protein Content: Some Practical Recommendations. *J. nat. Rubb. Res.*, **9**, 87-95.
7. YIP, E., TURJANMAA, K., NG, K.P. AND MOK, K.L. (1994) Allergic Responses and Levels of Extractable Proteins in NR Latex Gloves and Dry Rubber Products *J. nat. Rubb. Res.*, **9**, 79-86.
8. HAFSAH, M.G. (1994) Factory Production of Examination Gloves from Low Protein Latex. *J. nat. Rubb. Res.*, **9**, 96-108.
9. AMIR, H.Y. (1994) Effect of Leaching on Extractable Protein Content. *Latex Proteins and Glove Industry* (Abdul Aziz, S.A.K. ed.), 51-58. Kuala Lumpur: Rubber Research Institute of Malaysia
10. NOR AISAH, A. (1994) Chlorination of Gloves. *Latex Proteins and Glove Industry* (Abdul Aziz, S.A.K. ed.), 59-67. Kuala Lumpur: Rubber Research Institute of Malaysia
11. SUBRAMANIAM, A., YIP, E., NG, K.P. AND MOK, K.L. (1994) Extractable Protein Content of Gloves From Prevulcanised NR Latex. *Latex Proteins and Glove Industry* (Abdul Aziz, S.A.K. ed.), 76-80. Kuala Lumpur: Rubber Research Institute of Malaysia.
12. YEANG, H.Y., YUSOF, F. AND ABDULLAH, L. (1995) Precipitation of *Hevea brasiliensis* Latex Proteins with Trichloroacetic Acid and Phosphotungstic Acid in Preparation for the Lowry Protein Assay. *Anal. Biochem.*, **226**, 35-43.

- 13 ENG, A H (1997) Reduction of Trace Nitrosamines and Nitrosatables in Prevulcanised Latex Films *Proc. Int Rubb Conf Kuala Lumpur, Malaysia, 1997*, 49-53
- 14 GORTON, A.D T (1988) Prevulcanised Natural Rubber Latex for Dipping *Proc. Int Rubb. Conf. Penang, Malaysia 1988*, 85-103
- 15 LEVIN, V Y, KIM, S H., ISAYEV, A I, MASSEY, J AND MEERWALLE, E (1996) Ultrasound Devulcanisation of Sulphur Vulcanised SBR Crosslink Density and Molecular Mobility *Rubb Chem. Technol* , **69**, 104-114
16. JOHNSTON, S., MASSEY, J, MEERWALL, E, KIM, S H, LEVIN, V Y AND ISAYEV, A I (1997) Ultrasound Devulcanisation of SBR Molecular Mobility of Gel and Sol *Rubb Chem Technol* , **70**, 183-201