ORIGINAL ARTICLE

Improvement of RVNRL film properties by adding fumed silica and hydroxy apatite

Adul Thiangchanya[1], Chayagrit Siri-upathum[2], Nutchanart Na-ranong[3] and Manit Sonsuk[4]

Abstract

Thiangchanya, A., Siri-upathum, C., Na-ranong, N., and Sonsuk, M.
Improvement of RVNRL film properties by adding fumed silica and hydroxy apatite
Songklanakarin J. Sci. Technol., 2003, 25(1) : 53-61

The effect of adding fumed silica and hydroxy apatite to Radiation Vulcanized Natural Rubber Latex (RVNRL) for improving tear strength, aging properties, degradability and water-soluble protein content of rubber films has been investigated. The addition of fumed silica and hydroxy apatite in RVNRL improves tear strength and aging properties of rubber films, whereas tensile strength and degradability of rubber films were unchanged during storage at room temperature. The water-soluble protein content in rubber films was reduced by immobilization of the fumed silica and hydroxy apatite and enhanced by addition of ZnO. This may reduce allergy problems of natural rubber latex products caused by water-soluble protein. The MST of the RVNRL with fumed silica and hydroxy apatite indicated that the latex must be used within two months after mixing because of its stability.

Key words : natural rubber latex, radiation vulcanization, fumed silica, hydroxy apatite, water-soluble proteins

---

[1]M.Sc. (Organic Chemistry), Asst. Prof., Department of General Science, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112 [2]M.Eng. (Nuclear Technology), Asst. Prof., Department Nuclear Technology, Faculty of Engineering, Chulalongkorn University, Bangkok 10330 [3]Ph.D. (Polymer Chemistry), Rubber Research Institute of Thailand, Chatuchak, Bangkok 10900 [4]M.Sc. (Polymer Science), Chemistry Division, Office of Atomic Energy for Peace, Chatuchak, Bangkok, 10900 Thailand.
Corresponding e-mail : tadul@ratree.psu.ac.th

Received, 13 August 2002 Accepted, 7 November 2002

บทคัดย่อ

อดุลย์ เที่ยงจรรยา[1] ชยากริต ศิริอุปถัมภ์ [2] นุชนาฏ ณ ระนอง[3] มานิตย์ ซ้อนสุข[4]

การปรับปรุงสมบัติของแผ่นฟิล์มยางจากน้ำยางธรรมชาติที่วัลคาไนซ์ด้วยการฉายรังสีด้วยฟูมซิลิกา และไฮดรอกซีแอพพาไตต์

ว. สงขลานครินทร์ วทท. 2546 25(1) : 53-61

งานวิจัยนี้ เป็นการศึกษาถึงผลของการเติมฟูมซิลิกาและไฮดรอกซีแอพพาไตต์ ลงในน้ำยางธรรมชาติที่วัลคาไนซ์ด้วยการฉายรังสี เพื่อปรับปรุงสมบัติบางอย่างของแผ่นฟิล์มยางที่ได้ เช่น ความทนต่อการฉีกขาด สมบัติการเสื่อมสภาพ และปริมาณโปรตีนที่ละลายน้ำได้ที่มีอยู่ในแผ่นฟิล์มยาง ผลการศึกษาพบว่า การเติมฟูมซิลิกาและไฮดรอกซีแอพพาไตต์สามารถเพิ่มความทนต่อการฉีกขาดและสมบัติการเสื่อมสภาพของแผ่นฟิล์มยางได้ในขณะที่ความต้านแรงดึงและความสามารถในการสลายตัวของแผ่นฟิล์มยางไม่เปลี่ยนแปลงระหว่างการเก็บยางไว้ที่อุณหภูมิห้อง ส่วนปริมาณโปรตีนที่ละลายน้ำได้ที่มีอยู่ในแผ่นฟิล์มยางสามารถลดลงได้ โดยเฉพาะเมื่อใช้ ZnO ร่วมด้วยจะสามารถลดได้อย่างมาก จึงเป็นแนวทางหนึ่งในการแก้ปัญหาการแพ้โปรตีนในผลิตภัณฑ์ยางธรรมชาติได้ จากค่า MST ของน้ำยางที่เติมฟูมซิลิกาและไฮดรอกซีแอพพาไตต์ บ่งชี้ว่า หลังจากการผสมสารเคมีแล้ว จะต้องใช้น้ำยางภายในเวลา 2 เดือน เนื่องจากหลังจากนั้น น้ำยางสูญเสียความคงตัว

---

[1]ภาควิชาวิทยาศาสตร์ทั่วไป คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์ อำเภอหาดใหญ่ จังหวัดสงขลา 90112 [2]คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย กรุงเทพฯ 10330 [3]กลุ่มอุตสาหกรรมยาง สถาบันวิจัยยาง จตุจักร กรุงเทพฯ 10900 [4]กองเคมี สำนักงานพลังงานปรมาณูเพื่อสันติ จตุจักร กรุงเทพฯ 10900

Physical properties as tear and tensile strength of Radiation Vulcanized Natural Rubber Latex (RVNRL) film are known to be inferior to that of Sulfur Vulcanized Natural Rubber Latex (SVNRL) film from vulcanizable latex. Many attempts have been made to improve the physical properties of RVNRL film. Blending of Poly (methyl methacrylate) (PMMA) in emulsion form prepared by the redox reaction (Egusa and Makuuchi, 1981) can increase tensile strength of RVNRL film with about 12%. RVNRL-grafted PMMA also increases tensile strength of the films from its product to some extent (Thiengchanya and Sonsuk, 1996). These papers, however, do not report on the improvement of tear strength. Co-vulcanization of redox vulcanization followed by radiation vulcanization can double tear strength, but the aging of the film is accelerated strongly (Siri-upathum and Sonsuk, 1996). Fumed silica prepared in dispersion form and added to sulfur pre-vulcanized latex produced rubber films with a slightly improved tensile strength, together with greatly improved tear strength (Jodingrer, 1996). The fumed silica may serve as rubber particle reinforcement. Enhancement of the physical properties of the rubber films was ascribed to the binding of the binder (hydrophillic) to the rubber protein (amphoteric) and to the surface of rubber particles (hydrophobic). In our experiment fumed silica and another binder, namely hydroxy apatite, which is a biomaterial, was used for this purpose. Investigation of the effects leads to the observation that rubber protein immobilization can also reduce the problem related to protein allergy from natural rubber latex dipped products

Materials and Methods

Sulfur vulcanized natural rubber latex (SVNRL) was obtained from Songkla Rubber Research Center. Concentrated high ammonia (HA) latex came from Chanatex Co. Ltd. (Thailand). Technical grade zinc oxide (ZnO) was obtained from Kitphaiboon Chemicals Co. Ltd.. Fumed silica aggregate with average diameter of 120 nm was ordered from Cabot Corporation, USA.

Hydroxy apatite with particle size 15-25 µm was obtained from Taihei Chemical Industrial Co. Ltd., Japan, and was further ball milled to about 0.2 µm before preparation of its dispersion.

Preparation of binder dispersion

Except for fumed silica dispersion, which was obtained in the form of dispersion from the supplier, other binders including ZnO were prepared in the form of dispersions by ball milling with the dispersing agent (Vultamol). The dispersions with a total solid content (TSC) of 15% and pH of 9.5-10 (adjusted by KOH solution) were prepared.

Irradiation of HA latex

Concentrated HA latex was diluted to 50% dry rubber content using 1% ammonia solution and stabilized by 0.2 phr KOH . Then 5 phr of n-BA was added drop-wise into the latex while stirring and stirring continued for 30 minutes until irradiation. About 5 liter of the mixture was irradiated in a BSV-06 Gamma Irradiator, dose rate 1.1 kGy/hr, to a total vulcanization dose of 13.5 kGy. RVNRL was used without adding antioxidant to avoid interference.

Blending of the binders dispersion to the irradiated latex

The binder dispersion was added to the irradiated latex at concentrations of 1, 2, 3 and 4 phr with and without 0.17 phr ZnO for each binder while stirring for 1 hour. Maturation of the mixture for at least 3 days before casting into film was needed to enhance the tear strength of the film (Jodingrer, 1996).

Preparation of rubber films

The films of about 0.6 mm thick were prepared by casting about 20 ml of latex onto a glass plate of 14x14 cm. The films were air-dried at room temperature until they became transparent. Leaching of the rubber films was done in water at room temperature and by hot water in a constant temperature bath as specified. The films were air-dried and finally oven-dried at 70°C for 1 hour. The films were kept in a dessicator until testing.

Measurement of physical properties of the films

The tensile strength of the films was measured according to ASTM-D-412-92 and trouser tear strength was measured according to ASTM-D-624-91, using the Lloyd Tension Meter.

Measurement of aging properties of rubber films

The rubber films (RVNRL, RVNRL + fumed silica 2 phr, RVNRL + hydroxy apatite 2 phr and SVNRL) were aged in a hot air oven at 100°C for 22 hours. The tensile strength of the original and aged rubber films were compared and reported as retention of tensile strength of the aged rubber film.

Measurement of the degradability of rubber films

1. At room temperature: Rubber films (RVNRL, RVNRL + fumed silica 2 phr, RVNRL + hydroxy apatite 2 phr and SVNRL) were hung at room temperature as a control (i.e., unexposed to degradation factors). The maximum and minimum temperatures were 30 and 25°C, respectively. Films were tested weekly and retention of tensile strength was reported.
2. Naturally degraded: Rubber films (RVNRL, RVNRL + fumed silica 2 phr, RVNRL + hydroxy apatite 2 phr and SVNRL) were placed outdoors for exposure to natural air and sunlight. The films were tested at fixed times, depending on the rubber films, and retention of tensile strength was reported.

Determination of water-soluble protein in rubber films

Determination of water-soluble protein in rubber films was done by using the modified Lowry method with minor changes according to the procedure developed by the Rubber Research Institute of Thailand (RRIT) (Na-ranong *et al.*, 1997). Soluble protein was extracted with 35°C water for 180 minutes. The leachate was centrifuged and to a known volume 0.15% solution of sodium salt of deoxycholic acid was added, plus a 35% solution of trichloroacetic acid (TCA), followed by a 40% solution of phosphotungstic acid (PTA). The mixture was stirred well and the precipitates were collected after by high speed centrifuging. The precipitate was then dissolved in a 0.2 M NaOH solution, after which a solution of Na_2CO_3, $CuSO_4$, sodium citrate and 72% solution of Folin-Ciocalto reagent were added. After stirring by a Vortex mixer and transferring it to a cuvette, a UV spectrophotometer measured the absorbance at 750 nm. The measurement was done in parallel with an ovalbumin protein standard which went through the same procedure.

Results and Discussion

Experiments on adding fumed silica into RVNRL

1. Mechanical properties of RVNRL films with fumed silica

Tensile strength, elongation at break, and modulus of RVNRL with different amounts of fumed silica are shown in Table 1. It was found to be hardly affected by addition of fumed silica. Enhancement of the trouser tear strength of the films from about 5 kN/m to about 10 kN/m was the only effect with the optimal content of 2 phr fumed silica. Table 2 shows no significant change of physical properties of the film after adding 0.17 phr ZnO together with fumed silica.

2. Effect of leaching temperature on water-soluble protein content of rubber films

Figure 1 Shows water-soluble protein content of rubber films after water leaching at various temperatures and leaching times. The optimum leaching temperature and leaching time were 75ºC and 7 minutes, respectively. At room temperature, the lowest water-soluble protein was observed at leaching time of 15 minutes. Leaching time may be much longer than this (24 hours) to maximize tensile strength of RVNRL films (Gazeley *et al.*, 1988). If the protein content is considered, a short leaching time of 7 minutes at

Table 1. Mechanical properties of RVNRL with fumed silica films.

Fumed silica (phr)	Tensile strength (MPa)	Trouser tear strength (kN/m)	Elongation at break (%)	Modulus (MPa)		
				100%	300%	600%
0	20.59	5.8	960	0.11	0.32	0.63
1	21.25	9.8	945	0.16	0.37	0.64
2	21.51	10.4	980	0.14	0.36	0.69
3	21.23	10.4	930	0.18	0.48	0.84
4	17.78	9.6	956	0.18	0.42	0.78

Table 2. Mechanical properties of RVNRL with fumed silica and 0.17 phr active ZnO films.

Fumed silica (phr)	Tensile strength (MPa)	Trouser tear strength (kN/m)
0	20.40	5.4
1	19.68	9.6
2	21.62	10.2
3	20.24	10.8
4	19.12	10.4

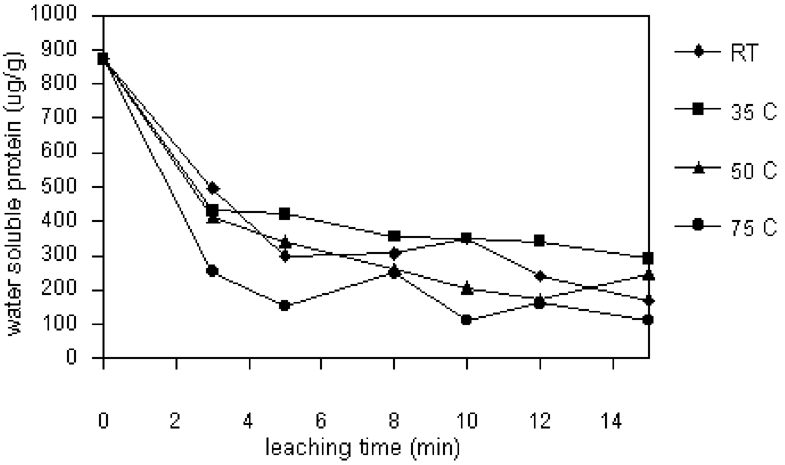

Figure 1. Water-soluble protein content in rubber films after leaching in water at different temperature and leaching time.

75°C may be more practical in the manufacturing process of the rubber dipping products.

3. Effect of fumed silica on water-soluble protein content in rubber films

Effect of fumed silica with 0.17 phr active ZnO and without ZnO on water-soluble protein content in RVNRL films is shown in Figure 2. It indicates that 3 phr of fumed silica with 0.17 phr ZnO reduces water-soluble protein content to less than 30 µg/g. This is in good agreement with previous reports when using sulfur pre-vulcanized rubber films, and indicates that there is a complex chemical binding between protein, ZnO and silica (Jodingrer, 1996). Water-soluble protein content of the films at 2 and 3 phr of fumed silica with 0.17 phr of ZnO and leaching at 75°C was found to be almost the same when compared with the film which was leached at the room temperature. This may be due to the strongly combined effect of protein immobilization by silica/ZnO.

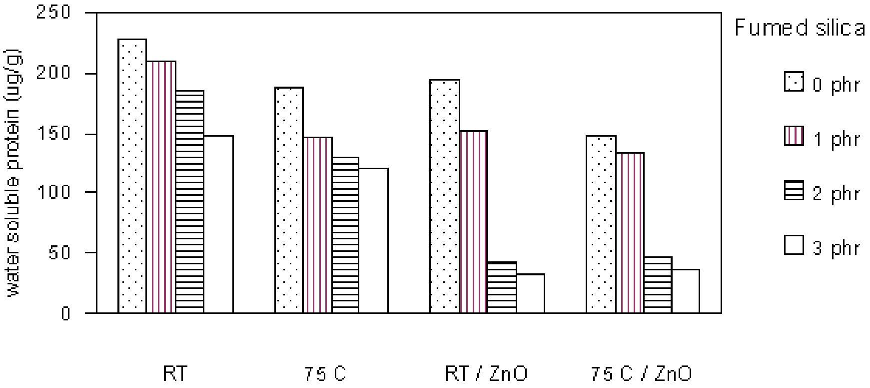

Figure 2. Effect of ZnO co-added with fumed silica into RVNRL on water-soluble protein content in rubber film after leaching at room temperature (RT) for 15 min and at 75ºC for 7 min.

Table 3. Mechanical properties of RVNRL films with hydroxy apatite.

Hydroxy apatite (phr)	Tensile strength (MPa)	Trouser tear strength (kN/m)	Elongation at break (%)	Modulus (MPa)		
				100%	300%	600%
0	23.42	5.2	942	0.15	0.38	0.68
1	22.18	7.4	968	0.17	0.45	0.71
2	24.15	9.2	934	0.12	0.42	0.82
3	23.64	9.1	922	0.14	0.48	0.78
4	23.24	9.3	938	0.16	0.52	0.84

Experiment on adding of hydroxy apatite into RVNRL

1. Mechanical properties of RVNRL films with hydroxy apatite

Tensile strength, elongation at break and modulus of RVNRL films with different amounts of hydroxy apatite are shown in Table 3. There were no significant changes in the tensile strength, elongation at break and modulus of the films after adding hydroxy apatite 1-4 phr. Trouser tear strength of the films at 2 phr and higher levels of hydroxy apatite was almost double when compared with the film without the hydroxy apatite.

2. The Effict of hydroxy apatite on water-soluble protein content in rubber films

Effect of hydroxy apatite with and without 0.17 phr active ZnO on water-soluble protein content in the RVNRL films is shown in Figure 3. As in the case of adding fumed silica, the decrease of water-soluble protein content in rubber films is observed only after ZnO is co-added with hydroxy apatite. Two phr of hydroxy apatite with 0.17 phr ZnO reduces water-soluble protein in rubber films to about 120 µg/g. This is not as low as in the case of adding fumed silica. For the RVNRL film without ZnO, the water-soluble protein content decreases only slightly.

The immobilization mechanism of water-soluble proteins in the case of adding hydroxy apatite appears to be different from that when adding fumed silica. That is, silica forms zinc-protein complex via a positive charge. Binding of proteins to relatively large and immobile silica particles prevents their migration from inside the

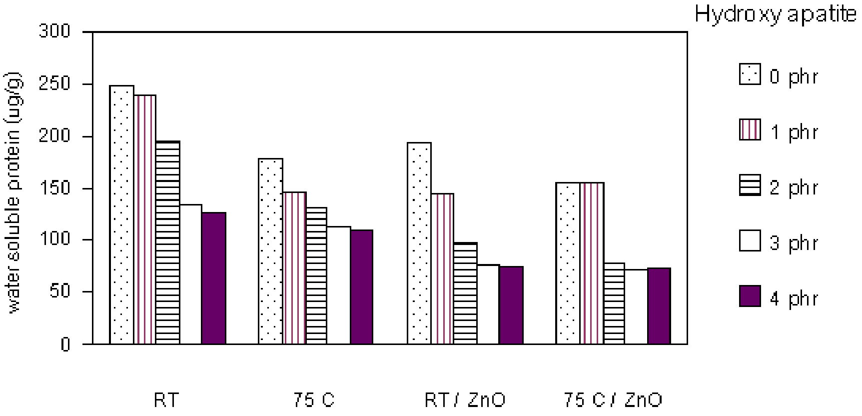

Figure 3. Effect of ZnO co-added with hydroxy apatite into RVNRL on water-soluble protein content in rubber film after leaching at room temperature (RT) for 15 min. and at 75ºC for 7 min.

films to the surface (Richard *et al.*, 1997). Hydroxy apatite consists of calcium phosphate, and thus has both positive and negative charges. In the 9-10 pH range of rubber latex, the proteins are in switter-ionic state, ionic interaction as well as adsorption effects appear to contribute to protein binding. Acidic proteins may bind to calcium ions whereas basic proteins may bind to phosphate groups. Hydroxy apatite, however, may not have as much surface area as fumed silica which is usually in the range of 50-400 m^2/g (Jodingrer, 1996). This is the reason protein immobilization is not as high as with fumed silica. Enhancement of protein immobilization after co-added of ZnO with hydroxy apatite to the latex indicates that there is also a complex binding between protein, ZnO and calcium phosphate, as in the case of fumed silica.

Determination of aging properties and degradability of rubber films

1. Aging properties: The retention of tensile strength of rubber films is shown in Table 4. Both fumed silica and hydroxy apatite provide good aging properties for the rubber films. However, the fumed silica shows 74% retention of tensile strength and is therefore a more effective ingredient than hydroxy apatite (i.e., 58% retention of tensile strength).

2. The degradability of rubber films

2.1 At room temperature: The retention of tensile strength of rubber films is shown in Figure 4. The tensile strengths are insignificantly changed after exposure at room temperature for 8 weeks. It appears that the RVNRL film with fumed silica and hydroxy apatite as well as SVNRL film are stable, which has important implications for

Table 4. Percentage retention of tensile strength of rubber film after aging at 100ºC for 22 hrs.

Sample	Retention of tensile strength (%)
RVNRL	34.68
RVNRL+Fumed silica (2 phr)	74.02
RVNRL+Hydroxy apatite (2 phr)	57.88
SVNRL	36.44

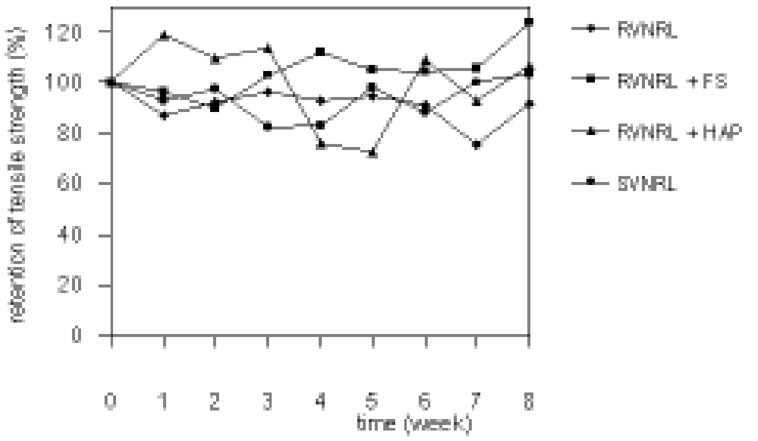

Figure 4. Retention of tensile strength and storage time of rubber films at room temperature.

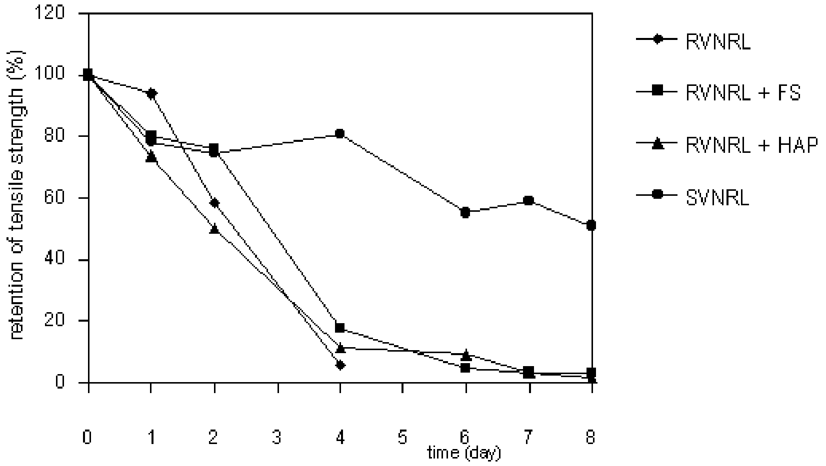

Figure 5. Retention of tensile strength and exposed time of rubber films at outdoor condition.

storage of products made from these materials.

2.2 Natural degradation: The retention of tensile strength of rubber films is shown in Figure 5. The tensile strength of all RVNRL films rapidly decreased within 4 days exposure. They were heavily degraded after that. On the other hand, the retention of tensile strength of the SVNRL film decreased at a slower rate, to approximately 50% retention of tensile strength after 8 days exposure.

Determination of latex stability after addition of fumed silica and hydroxy apatite

The mechanical stability time (MST) of RVNRL with fumed silica and hydroxy apatite is shown in Table 5. The MST rapidly decreased to less than the standard value, 650 seconds, after two months. This indicates that the latex was not stable after prolonged shelf life of more than two months.

Conclusions

At concentration of 2 phr for both fumed silica and hydroxy apatite in RVNRL, tear and aging properties of latex films were improved. That is, trouser tear strength of the films increases from about 5 kN/m to approximately 10 kN/m. The latex with the additives, however, must be used within two months after mixing because of its stability. Consequent effect of soluble protein immobilization in the films by the additives may reduce the Type I allergy, caused by soluble proteins in natural rubber products.

Table 5. MST of RVNRL with and without fumed silica or hydroxy apatite at different storage times.

Sample	Storage time (months)						
	0	2	4	6	8	10	12
RVNR Latex	1950	2082	1126	1018	-	884	816
RVNR Latex with 2 phr fumed silica	1872	680	276	139	-	-	-
RVNR Latex with 2 phr hydroxy apatite	1784	678	192	96	-	-	-

Acknowledgments

The authors thank the International Atomic Energy Agency Authority for funding our project. They also thank Dr.Olgun Guven, IAEA and Dr. K. Makuuchi, Takasake JAERI for giving assistance. They also thank RRIT staff for their valuable support.

References

Egusa, S. and Makuuchi, K. 1981. Characterization of carboxylated lattices prepared by radiation-initiated emulsing polymerization, comparison with chemically prepared lattices, J. Colloid and Interface Sci., 79(2): 350-364.

Gazeley, K.F., Gorton, A.D.T and Pendle, T.D. 1988. Natural Rubber Science and Technology. Oxford Science Publ.

Jodingrer, A. 1996. Cab-O-Sperse for proteins reduction and reinforcement of latex articles (Seminar on the latest changes and development of the malaysian latex-based industry, Kuala Lumpur).

Na-ranong, N., Ratanawekinrak, K. and Kajornchaiyakul, W. 1997. Determination of soluble protein in NR latex medical gloves (Annual Report, Rubber Research Institute of Thailand).

Richard, F., Geiger Jr., Morris, M.D. and Jorginder, A. 1997. Production of low protein gloves containing Cab-O-Guard^{TM} dispersion of fumed silica (Int. Rubber Conference, Kuala Lumpur).

Siri-upathum, C. and Sonsuk, M. 1996. Development of an efficient process for radiation valcanization of natural rubber latex using hydroperoxide with sensitizers, (Proc. Of The 2nd Int. Sym. On Radiation Vulcanization of Natural Rubber Latex, Kuala Lumpur).

Thiengchanya, A. and Sonsuk, M. 1996. The Effect of PMMA on radiation vulcanized natural rubber latex: Tensile strength and degradability properties of rubber films, (in Thai) Songklanakarin J. Sci. Technol., 18(2): 193-199.