



5. Progress in Radiation Vulcanization of Natural Rubber Latex

K. MAKUUCHI

Takasaki Radiation Chemistry Research Establishment, JAERI

1233 Watanuki, Takasaki, Gunma, 370-12 Japan

1. INTRODUCTION

Radiation-induced crosslinking of natural rubber in latex can be accomplished by irradiating NR latex. The dose at which the maximum tensile strength (T_b) is found is called vulcanization dose (D_v). The D_v of NR latex is more than 250 kGy that is too high to be used in industry. The first RV accelerators proposed was carbon tetrachloride. Addition of 5 phr of carbon tetrachloride can reduce. The RVNRL was selected as one of the regional projects of the International Atomic Energy Agency (IAEA) known as the Regional Cooperative Agreement in the Asia and Pacific Region (RCA) in 1981. A pilot plant for the RVNRL was built in Jakarta in 1983. The products from the pilot plant were tested and evaluated by several institutes in the region during 1983-1985. The results were as follows:

- Low tensile strength (less than 20MPa)
- Poor aging properties
- Inconsistent properties
- Not economic due to high dose requirement
- No advantages

The results caused argument among the RCA member states and the IAEA whether the project should be continued or stopped. The preliminary R&D in the TRCRE on RVNRL indicated that the properties of RVNRL could be improved by proper selection of an accelerator. Finally, the IAEA decided to support the R&D on RVNRL at Takasaki. The following R&D were carried out in 1985 – 1989.

- Selection of NR latex to improve tensile strength
- Selection of accelerator to reduce required dose
- Selection of process factors to avoid inconsistency
- Selection of antioxidants to improve aging properties
- Biological safety test to find advantages of RVNRL

As an accelerator n-butyl acrylate (n-BA) was selected by reason of its high accelerating efficiency, no residue in the final dipped products and tolerable price. The inferior aging properties of RV NR latex film was improved by the addition antioxidants such as TNPP and

DAHQ. Standard procedures were provided to produce high quality dipped products from RVNRL to meet international standards. Stringent quality control factors such as storage period of NR latex and leaching/drying conditions of RV NR latex film were standardized. Cost reduction and quality improvement of RVNRL were achieved. Figure 1 shows the process of RVNRL thus developed. It consists of two steps, (1) mixing NR latex with n-BA, RV accelerator, and (2) irradiating the mixture.

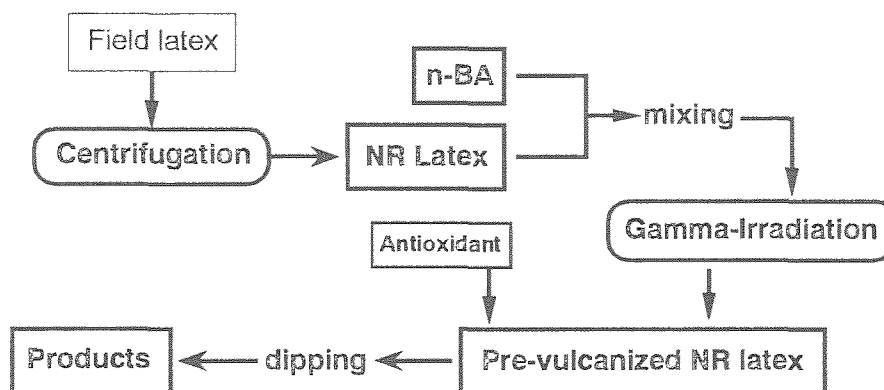


Figure 1 RCA Process of RVNRL

The RV NR latex has the following advantages over conventional SV NR latex;

- Absence of N-nitrosamines
- Very low cytotoxicity
- Easy degradation in the environment
- Transparency and softness
- Less formation of SO₂ when burned

These advantages indicate that RVNRL can be used for the manufacture of latex. The RVNRL technology has been transferred toward commercial application of RVNRL China, India, Indonesia, Malaysia, Philippines, Sri Lanka, Thailand and Vietnam. Pilot plants have been set up in Indonesia, India, Malaysia and Thailand. Commercial production of rubber gloves from RVNRL began in Thailand.

Then, the protein allergy of latex products became serious issue in the world latex industry. A new R&D was organized in TRCRE to reduce the remained protein in RV NR latex products. In addition, RVNRL with low energy electron accelerator was developed to reduce the initial investment and irradiation cost of RVNRL. In this paper, such progress in RVNRL will be reviewed.

2. REDUCTION OF EXTRACTABLE PROTEINS

Recently life-threatening latex allergy is emerged as a serious problem for health care workers and others who use latex products. Water extractable protein (EP) from NR latex is considered to be primary source of the allergic reactions. The symptoms of the allergy are Urticaria (development of wheals, flares, hives) and Anaphylaxis (increased heart rate, lowered blood pressure, unconsciousness, life threatening). It is desirable to remove as much of the EP as possible from the latex products to minimize the reactions. It was expected that irradiation of NR latex may denature the NR proteins and not cause allergic reactions. However, the irradiated NR latex still exhibited moderate allergenic response when the allergic reactions were evaluated by a passive cutaneous anaphylaxis test in mouse-rat system ⁽¹⁾.

The extractable protein in irradiated NR latex film increased with increasing dose probably due to disintegration of NR proteins by radiation and increase in water solubility. The EP was easily discharged by centrifugation ⁽²⁾. Also it was found that EP in the dried RVNRL film was completely discharged by short leaching when water soluble polymers (WSP) such as poly(vinyl alcohol) (PVA), poly(ethylene oxide) (PEO) were added into RV NR latex. Figure 2 shows effect of PVA addition and centrifugation on amount of EP. The control in the figure refers RV NR latex (DRC 50%) film of without WSP and centrifugation. It is clear that the centrifugation is effective to reduce EP. However, it is hard to reduce to non-detectable level. Combination effect of WSP addition and centrifugation was found to reduce EP more ⁽³⁾. Figure 3 indicates that centrifugation followed by the addition of WSP is more practical than the centrifugation in the presence of WSP.

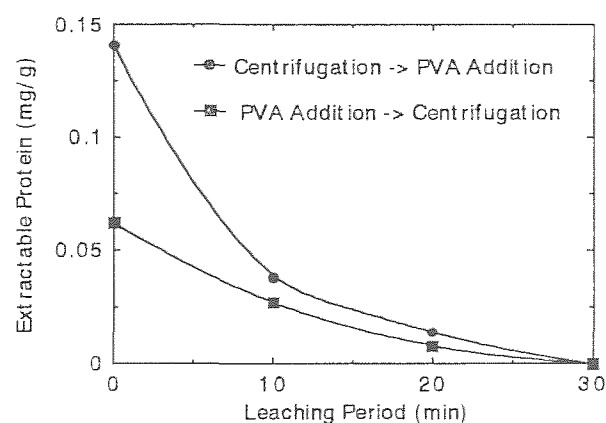
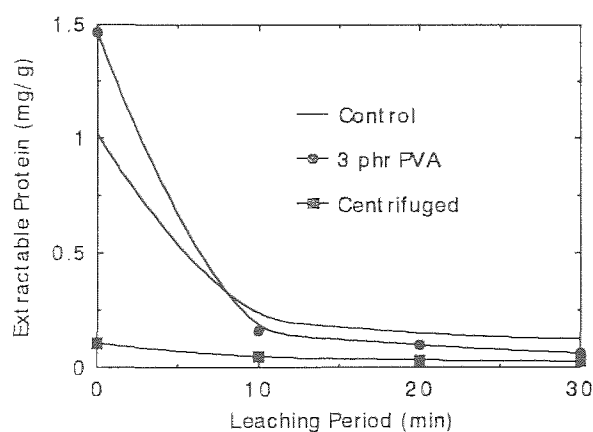


Fig. 2 Effect of PVA addition and centrifugation Fig. 3 Comparison of PRE-centrifugation and POST-centrifugation

Figure 4 shows the effect of PVA concentration and leaching period on the reduction of EP. Probably 3phr of low molecular weight PVA is sufficient to reduce the amount of EP. PVA is a common ingredient to increase the viscosity of latex and emulsion. This means the addition of PVA to RV NR latex causes increase in the viscosity of the latex, resulting in difficulty of dipping process. However, viscosity of the viscosity does not change when low molecular weight PVA is added to the RV NR latex. These results indicate that low molecular weight WSP may not affect the stability of the RV NR latex.

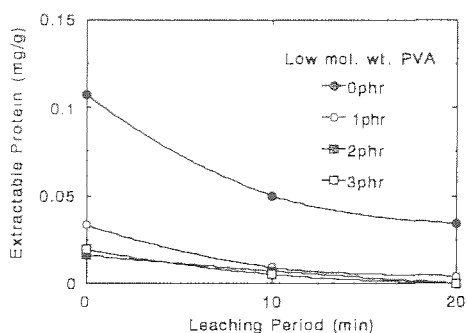


Fig. 4 Effect of PVA concentration

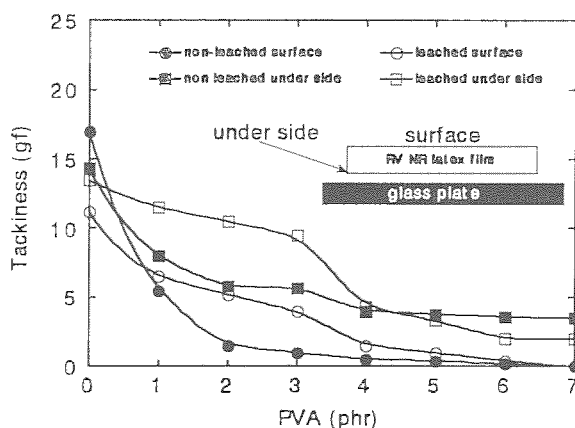


Fig. 5 Tackiness of RV NR latex film

Drastic decrease of tackiness by incorporation of WSP was achieved. The tackiness decreased with increasing PVA concentration as shown in Figure 5. The film surface has less tackiness compare to under side. This could be explained by migration of PVA and accumulated more on the surface than the under side when latex films are dried. After PVA added latex films were leached, tackiness showed slight increase in both surfaces. This is due to removal of PVA from the surface during leaching process. Surface analysis with IR spectrometer could not confirm the localization of PVA on the surface due to low concentration of PVA.

3. RVNRL WITH LOW ENERGY ELECTRON ACCELERATOR ⁽⁴⁾⁻⁽⁶⁾

Radioactive isotope Co-60 is used as a radiation source for R&D and pilot plants of RVNRL. However, the installation of Co-60 irradiation facility in NR latex dipping factory may not be feasible due to high initial investment, high irradiation cost and decay of activity of 12% per year. Development of a low-cost irradiator for the NR latex dipping factory is an urgent subject for further promotion of RVNRL technology. The low energy electron accelerator has fewer difficulties compared with Co-60. Advantages of a low energy electron

accelerator for RVNRL are (a) self shielding, (b) small size and (c) high output. Low investment and irradiation cost can be expected. The low energy electron accelerator has been proved to be a versatile, practical and economic radiation source for radiation processing such as crosslinking of plastic films and surface curing. However, the penetration of the low energy electron beams (EB) in NR latex is very limited. The problem of low penetration of EB was solved by means of an irradiation vessel with effective stirrer. The stirrer with four blades was installed obliquely as shown in Figure 6. The stirrer was installed at the bottom. NR latex was irradiated without n-BA with an accelerating voltage of 300kV. The preliminary results are shown in Figure 7. Remarkable effect of stirring speed on efficiency of RVNRL was observed. The stirring efficiency of this system is an essential factor to vulcanize NR latex homogeneously.

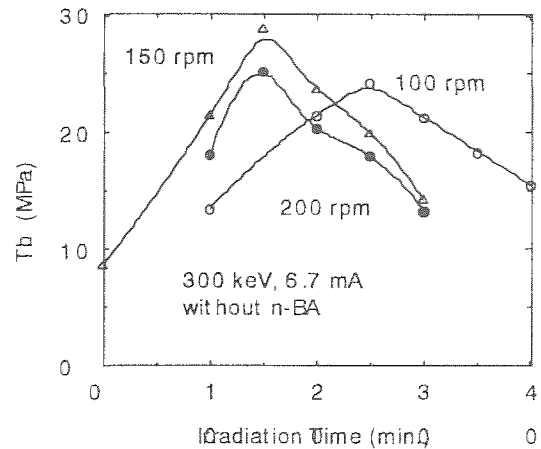
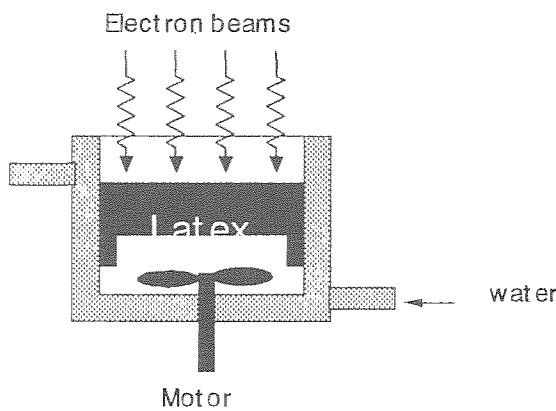


Fig. 6 Reaction vessel for RVNRL with low energy EB

Fig. 7 Effect of stirring speed on RVNRL with low energy EB

4. NEW RVNRL PROCESS

Recent progress in RVNRL was reviewed. Combination of dilution, WSP addition, and centrifugation of RVNRL is promising process to reduce the amount of EP of the rubber films to a level less than 5 μ g/g, and to shorten the leaching time to 20-30 min. It was also demonstrated that low energy electron accelerator can be used for RVNRL. Combining these results, a new RVNRL process has been designed as shown in Figure 8.

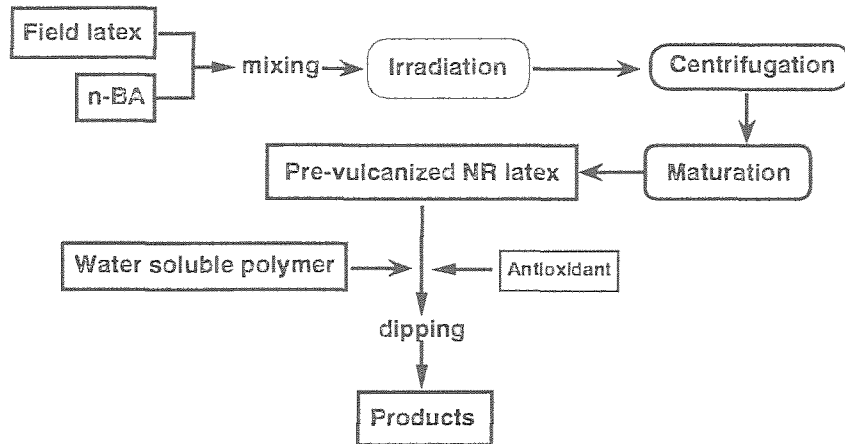


Figure 8 New RVNRL Process

REFERENCES

- (1) K.MAKUUCHI, F. YOSHII, K. HYAKUTAKE, T. KUME, AND K.SUZUKI: Allergic Response of Radiation Vulcanized Natural Rubber Latex, *J. Soc. Rubber Ind. Japan.* 68(4), 263 (1995)
- (2) S. VARGHESE, Y. KATSUMURA, K. MAKUUCHI AND F. YOSHII,: Effect of Water Soluble Polymers on Radiation Vulcanized Natural Rubber Latex, *Rubber Chem. Tech.*,72, 308 (1999)
- (3) Y. S. SOEBIANTO, R. M. UPUL, K. MAKUUCHI, F. YOSHII, AND T. KUME: Extractable Protein of Radiation Vulcanized Natural Rubber Latex, presented at the 8th Japan-China Bilateral Symposium on Radiation Chemistry, October 25 - 29,1999, Kyoto, Japan
- (4) K. MAKUUCHI, F. YOSHII AND J. A. G. S. G. GUNAWARDENA: Vulcanization of Natural Rubber Latex with Low Energy Electron Accelerator. *Radiat. Phys., Chem*, 46 (4-6), 979 (1995)
- (5) K. MAKUUCHI, F. YOSHII, T. TAKEMI, S. KINOSHITA AND FEROZA AKHTAR: Vulcanization of Natural Rubber latex with Low Energy Electron Accelerator. *J. Soc. Rubber Ind. Japan*, 69(7), 500 (1996)
- (6) FEROZA AKHTAR, F. YOSHII, AND K. MAKUUCHI: Extractable proteins from Electron Beam Irradiated Natural Rubber Latex. *Proceeding of the 2nd International Symposium on RVNRL*, p. 133, Kuala Lumpur, Malaysia. 1996.