Electron beam vulcanization as a sustainable processing technology for value-added natural rubber in the agroindustry

Mili Purbaya[1*]

[1]Indonesian Rubber Research Institute, Jalan Raya Palembang – Pangkalan Balai Km. 29, Sembawa, Banyuasin, Sumatera Selatan 30953, Indonesia

Abstract. Natural rubber (NR), a key agricultural commodity in tropical agroindustry, is widely used in value-added products such as gloves, medical devices, and packaging materials. However, conventional sulfur-based vulcanization remains energy-intensive and generate chemical residues, posing environmental and occupational challenges. This study introduces electron beam (EB) irradiation as a cleaner and energy-efficient alternative for vulcanizing NR compounds used in glove production. NR compounds films were irradiated with various EB, characterized and compared with thermally vulcanized samples. The results demonstrated that EB irradiation effectively promotes C-C crosslink formation at optimal conditions, producing high-quality rubber films without high thermal input. Compared with conventional methods, EB vulcanization offers significant advantages in reducing energy use and chemical waste while maintaining excellent material performance. These findings highlight the potential of EB irradiation as an innovative green processing technology, advancing sustainability and eco-friedly rubber manufacturing within the agro-industrial value chain.

1 Introduction

Natural rubber (NR), derived from *Hevea brasiliensis*, is a vital agricultural commodity in many tropical countries and plays a crucial role in agro-industrial development. Its unique mechanical properties, such as high elasticity, resilience, and tensile strength, make it a key raw material for various value-added products, including medical gloves, industrial components, and consumer goods. The development of efficient and sustainable processing technology for NR is essential to improve the competitiveness of rubber-based agro-industries and support rural economies dependent on rubber cultivation.

Vulcanization is one of the most critical stages in NR processing, as it improves durability, elasticity, and performance by forming cross-links between polyisoprene chains. Conventionally, sulfur-based thermal vulcanization has been widely adopted, however,

[*]Corresponding author: milipurbaya3107@gmail.com

it requires high temperatures and chemical additives, leading to significant drabacks such as high energy consumption, emission of sulfur-containing by-products, and potential health risks from N-nitrosamine formation when using certain accelerators. These concerns highlight the need for greener, safer and more energy-efficient vulcanization technologies aligned with sustainable agro-industril principles.

Electron beam (RB) irradiation has emerged as a promising alternative. Unlike conventional and other thermal methods such as hot air, infrared, and microwave vulcanization [1-4], EB vulcanization operates at room temperature and induces cross-linking through high-energy electrons [5], offering precise control, shorter processing time, lower energy demand, and reduced chemical residues. These characteristics make it particularly suitable for high-purity applications, such as in food-contact materials and medical gloves [6-8]. Moreover, EB irradiation can reduce the extractable protein in NR, known allergens, and has been reported to exhibit antimicrobial [9-12], adding futher value to sustainable product development in health-sensitive industries.

Despite these advantages, the large-scale adoption of EB vulcanization in the agroindustry remains limited due to the high initial investment, the need for specialized equipment, and limited technical expertise in process optimization. Addressing these challenges is crucial to transform EB technology from laboratory research to industrial implementation.

This study investigates the effectiveness of EB irradiation as a sustainable vulcanization method for NR compounds used in glove manufacturing. The research focuses on optimizing irradiation parameters and analysing the resulting crosslink density, swelling ratio, gel fraction, and chemical structure using FTIR. The findings are expected to contribute to the development of cleaner, more efficient, and agroindustry-aligned processing technologies that can strengthen the sustainability and value chain of natural rubber as a strategic agricultural product.

2 Materials and methods

2.1 Materials

The NR latex compound used in this study was formulated for rubber glove applications and obtained from the Rubber Authority of Thailand. The formulation was designed based on 100 parts by weight of dry rubber (phr) to represent typical agro-industrial glove formulations. The compound contained 167 g of concentrated natural rubber latex (60% dry rubber content) as the primary raw material, 2 g of zinc oxide (50% dispersion) as an activator, 2 g of potassium hydroxide (10% solution) and 0.2 g of teric 16A16 (10% solution) as stabilizers, and 2 g of Wingstay-L (50% dispersion) as an antioxidant. To accelerate vulcanization, 0.8 g of ZMBT and 0.8 of ZDEC (both in 50% dispersion) were incorporated, while 1.6 g of sulfur (50% dispersion) was added as a curing agent or sensitizer. Finally, 170.5 g of deionized water was included to achieve uniform dispersion of all components. In the electron beam vulcanization system, sulfur acted primarily as a sensitizer to promote radiation-induced crosslinking, whereas in the thermal vulcanization system, it served as the main curing agent.

Toluene (RCI Labscan CO., Ltd., Bangkok, Thailand) was used as the solvent in swelling and crosslinking tests. The main instruments used were an electron beam generator (MB10-50, Mevex Corporation, Canada), a mechanical stirrer (IKA RW20, IKA Labortechnik, Germany), a Memmert oven (ITS Co., Ltd., Thailand), a universal testing machine (Tinius Olsen 5ST, USA), and a Fourier-transform infrared (FTIR) spectrometer (Nicolet^{TM} iS50, ThermoFisher Scientific, USA).

2.2 Methods

2.2.1 Sample preparation

The latex compound was prepared following standard glove production procedure. All ingredients were mixed using a mechanical stirrer until a homogeneneous dispersion was achieved. The compounded latex was then cast onto clean glass plates and air-dried at room temperature to form uniform rubber films with a thickeness of 1-2 mm. The formulation was used consistently both EB and thermal vulcanization processes to enable a direct comparison of their effects on material properties.

2.2.2 Electron beam irradiation

Electron beam vulcanization was performed at the Thailand Irradiation Center using an MB10-50 EB accelerator operating at 10 MeV, 5000 μA beam current, and 50 kW power. The conveyor speed was set at 1.299 m/min to deliver a target dose of 50 kGy. The samples were irradiated at doses of 1, 3, 5, 10, 20, and 30 kGy. These irradiation doses were selected based on previous studies that demonstrated effective NR crosslinking within this dose range [13]. Rubber films, not exceeding 2 mm in thickness, were placed in aluminium trays (80 x 80 cm) and irradiated under controlled conveyor speed to ensure accurate dose delivery. After irradiation, samples were stabilized at ambient temperature for 24 hours before further analysis.

2.2.3 Thermal vulcanization (reference)

For comparison, a control set of NR films was vulcanized using conventional thermal curing. The compounded latex films were cured in an oven at 100 ºC for 30 minutes and then conditioned at room temperature for 24 hours before testing.

2.3 Characterization of vulcanized samples

2.3.1 Swelling test, gel fraction, and crosslink density

Swelling tests were performed according to ASTM D297-15 using toluene as the solvent. Samples were weighed before and after immersion, and the swelling ratio was calculated as the ratio of the swollen weight to the oven-dried weight (dried at 70 ºC for 24 hours). The gel fraction was determined by comparing the dried sample weight after swelling to the original weight before immersion. Crosslink density was calculated using the Flory-Rehner equation, which relates the degree of swelling to the molecular weight between crosslinks.

2.3.2 Fourier transform infrared spectroscopy (FTIR)

The chemical structure of vulcanised rubber was analysed using a Nicolet™ iS50 FTIR spectrometer with Attenuated Total Reflectance (ATR) mode. Spectra were recorded in the range of 4000-400 cm^{-1} at a resolution of 8 cm^{-1} with 32 scans per sample. Background spectra were taken before each test. For reliability, five different spots on each rubber film were measured.

3 Results and discussion

3.1 Effect of electron beam irradiation on crosslinking behaviour

In conventional glove manufacturing, natural rubber gloves are typically produced by dipping formers into a latex compound, followed by thermal vulcanization at temperatures of 100-120 ºC [14]. In this study, natural rubber compounds were cast into films to simulate glove materials, allowing uniform irradiation and controllled evaluation of crosslinking behavior. Vulcanization was performed using electron beam irradiation at doses ranging from 1 to 30 kGy, with thermally vulcanized films (100 ºC, 30 min) serving as reference samples.

The effect of electron beam irradiation on the network structure of natural rubber films was assessed through swelling ratio, crosslink density, and gel fraction, which collectively indicate the effciency of crosslink formation and stability of the polymer network. As shown in Figures 1, the swelling ratio decreased sharply with increasing irradiation dose up to 10 kGy, indicating enhanced crosslinking that limited solvent diffusion. Beyond this dose, a slight increase in swelling was observed, implying that excessive irradiation induced chain scission and partial degradation of rubber matrix.

The calculated crosslink density followed a similar trend, peaking at 10 kGy, which represents the optimal balance between crosslinking and degradation reactions (Figure 2). Electron beam irradiation promotes intermolecular crosslinking via free radicals generation, but at higher doses, these radicals can also trigger main chain cleavage, leading to network deterioration. Compared with thermally vulcanized films, the 10 kGy EB-irradiated samples exhibited a higher crosslink density, demonstrating that EB vulcanization can achieve efficient curing under ambient conditions without the need for elevated temperature or accelerators.

Gel fraction analysis supported these findings, showing a consistent increase up to 10 kGy, followed by a decline at higher doses (Figure 3). This behavior confirms that crosslink formation dominates at moderate doses, while chain degradation becomes significant at excessive irradiation. The overall trends of swelling, crosslink density, and gel fraction are consistent with previous finding by Purbaya *et al.* (2023) for electron beam-vulcanized natural rubber latex [15]. However, the present study extends these insights by using pre-cast NR films rather than direct irradiation of latex, providing more uniform dose distribution and enabling precise evaluation of materials performance relevant to glove applications.

From an industrial perspective, these results highlight the importance of dose optimization in electron beam vulcanization. A moderate dose of around 10 kGy offers efficient crisslinking while minimizing degradation, which is critical for maintaining elasticity, mechanical strength and product safety. Such process optimization supports the transition toward cleaner and more energy-efficient rubber processing technologies that align with sustainability goals in agroindustry.

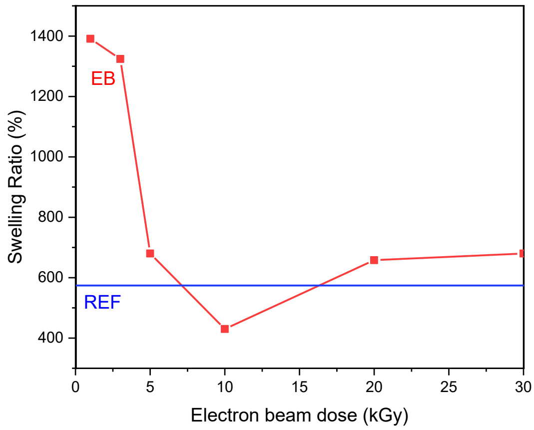

Fig. 1. Swelling ratio of natural rubber films vulcanized by various electron beam doses (EB) and thermal energy (REF).

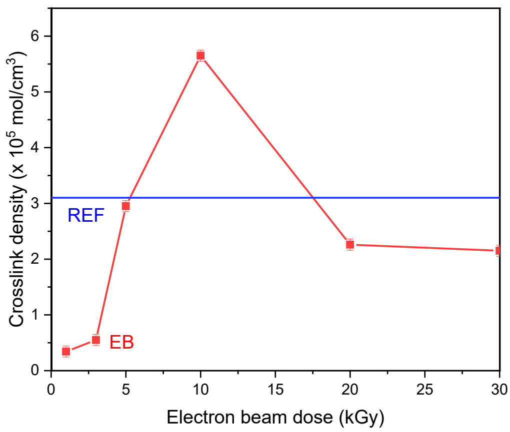

Fig. 2. Crosslink density of natural rubber films vulcanized by various electron beam doses (EB) and thermal energy (REF).

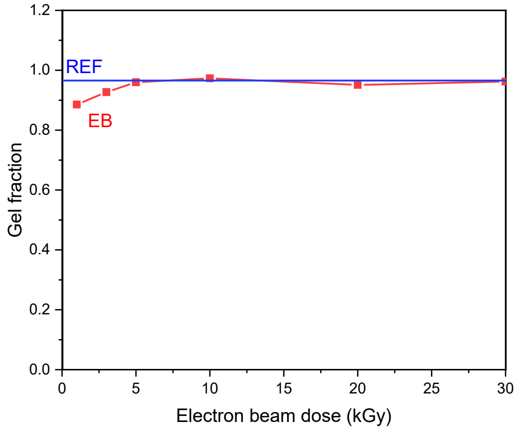

Fig. 3. Gel fraction of natural rubber films vulcanized by various electron beam doses (EB) and thermal energy (REF).

3.2 FTIR analysis of chemical structure

To elucidate the chemical mechanisms underlying electron beam-induced vulcanization, ATR-FTIR spectroscopy was conducted. Electron beam irradiation generates high-energy electrons that initiate radical formation along natural rubber chains, enabling crosslinking through carbon-carbon (C–C) and, to a lesser extend, carbon–sulfur (C–S) bridges depending on the availability of sulfur in the compound. The proposed mechanism is illustrated in Figure 4.

The ATR-FTIR spectra of unvulcanised, thermally vulcanized, and electron beam-irradiated natural rubber films are presented in Figures 5 dan 6. The spectra of all samples showed characteristic absorption bands of natural rubber, including C–H stretching at 2956 and 2921 cm^{-1}, symmetric C–H stretching at 2852 cm^{-1}, and a strong C=C stretching band near 1660 cm^{-1}, confirming the unsaturated nature of polyisoprene [19-21]. Protein-related peaks were observed at 1624 cm^{-1} (Amide I) and 1592 cm^{-1} (Amide II), indicating the presence of minor non-rubber components [22]. Deformation vibration of the –CH_2– and –CH_3 groups appeared around 1445 cm^{-1}, 1375 cm^{-1}, and 1310 cm^{-1} [23], while absorptions between 1241–1035 cm^{-1} corresponded to C–O–C and C–C stretching, typical of natural rubber's backbone structure. The cis-1,4-polyisoprene configuration was confirmed by the out-of-plane C=C–H bending near 840 cm^{-1} [20].

In thermally vulcanized samples, a distinct band near 750 cm^{-1} was attributed to C–S stretching, indicating the formation of sulfur crosslinking [24]. In contrast, electron beam-irradiated samples exhibited stronger absorptions at 1126 cm^{-1} (C–C stretching) and 1660 cm^{-1} (C=C stretching), along with a noticeable reduction of the unsaturation band near 836 cm^{-1}). This suggests that electron beam irradiation primarily promotes C–C bond formation while consuming C=C double bonds, consistent with radical-mediated crosslinking mechanisms.

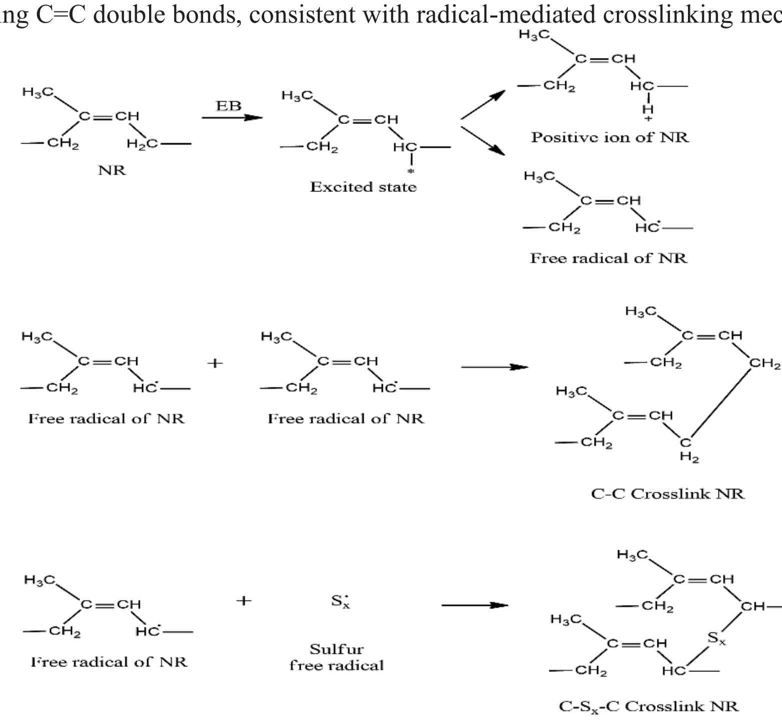

Fig. 4. Proposed mechanism of the natural rubber crosslinking induced by EB radiation.

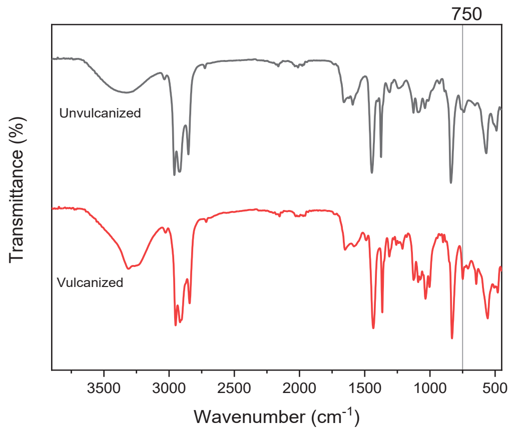

Fig. 5. ATR-FTIR spectra of unvulcanized and thermally vulcanized natural rubber films.

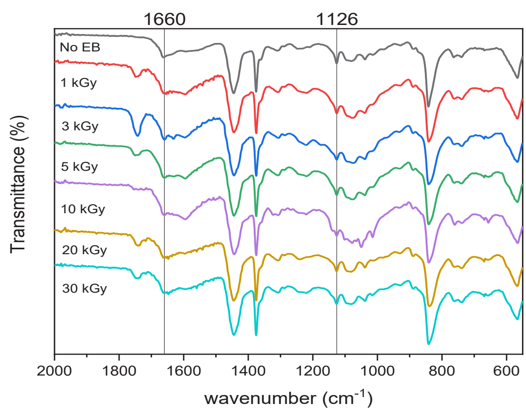

Fig. 6. ATR-FTIR spectra of natural rubber films subjected to varius electron beam doses.

Interestingly, no significant C–S absorption peaks were detected in EB-irradiated films, confirming that process favor cleaner, sulfur-free crosslinking. Althout sulfur was present in the formulation, it likely acted as a radical stabilizer or sensitizer rather than forming covalent C–S–C bridges. This obcervation aligns with previous reports that under EB exposure, sulfur crosslinks are either limited or unstable, especially at higher doses where chain scission dominates.

Figure 7 presents the intensity of C–C to C=C as a function of irradiated dose. The ratio increased with dose up to 10 kGy, signifying enhanced C–C bond formation, and subsequently declined at higher doses, reflecting partial degradation of polymer chains. This behavior corroborates the swelling and gel fraction analysis, empasiizing the need for dose optimization to balance crosslinking and degradation reaction.

For an industrial viewpoint, these finding demonstate that EB vulcanization offers a cleaner and more sustainable alternative to conventional sulfur-based curing. The absence of sulfur crosslinks minimizes chemical residues and aligns with the production of high-putiry rubber products such as medical and food-grade gloves. By emilinating the need for high temperature curing, electron beam vulcanization supports environmentally responsible and energy, efficient processing within the agroindustrial rubber value chain.

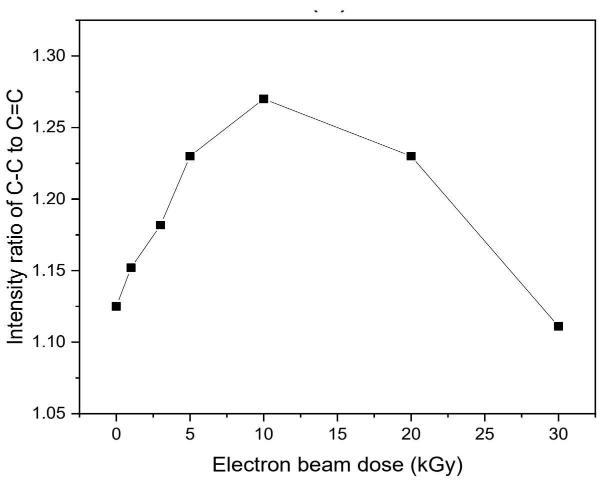

Fig. 7. Intensity ratio of C–C to C=C in electron beam-irradiated natural rubber films.

3.3 Implications for sustainable agroindustrial rubber processing

The findings from this study have direct implications for advancing sustainable agro-industrial rubber processing. Electron beam vulcanization eliminates the need for high-temperature curing and reduces or removes sulfur-based chemicals, resulting in a cleaner process with minimal emissions and hazardous waste. By enabling vulcanization under ambient conditions, this method significantly lowers energy consumption and carbon emissions compared with conventional thermal systems, directly supporting environmental stewardship within the agricultural value chain.

Beyond environmental benefits, electron beam vulcanization offers economic and operational advantages for agroindustry. Althouth the initial investment in irradiation facilities is relatively high, the long-term operational costs are lower due to reduced anergy use, and shorter processing times. As the technology matures, the cost per unit of processed material continue to decrease, particularly when integrated into centralized irradiation centers or multi-purpose facilities that serve multiple agro-industrial sectors. Such shared infrastructure models have been succesfully implemented in several developing countries, demonstrating that electron beam processing can be both technically and economically feasible at scale.

From a sustainability perspective, the technology supports the production of high-purity, high-value rubber products, such as medical gloves, food-grade materials, and biodegradable items, while aligning with global green manufacturing frameworks. Moreover, its compatibility with existing latex compounding and film-forming systems allows for gradual adoption in existing rubber processing industries, minimizing transition barriers. Thus, electron beam vulcanization not only enhances product performance and safety but also contributes to circular and low-carbon agro-industrial systems that strengthen the competitiveness of plantation-based ecomonies.

4 Conclusions

This study demonstrated that electron beam irradiation is an effective and sustainable vulcanization method for natural rubber latex compounds used in glove manufacturing. Compared with conventional thermal vulcanization, electron beam-treated samples exhibited higher crosslink density and gel fraction, with optimal performance achieved at a dose of approximately 10 kGy. FTIR analysis confirmed that electron beam irradiation primarily promotes the formation of C–C crosslinks instead of sulfur-based linkages, resulting in a cleaner and safer vulcanization mechanism with minimal chemical residues.

Beyond its environmental advantages, electron beam vulcanization also present promising economic and scalability potential for implementation in developing countries. Althouth the initial investment cost for irradiation facilities is relatively high, it can be offset by lower operational energy demands, shorter processing times, and waste management requirements. Futhermore, the technology can be intergrated through centralized irradiation center or shared industrial facilities, improving accessibility and cost efficiency across multiple agro-industrial sectors.

Overall, electron beam vulcanization supports eco-friedly, energy-efficient, high-purity rubber production aligned with sustainable development goals. Its application has the potential to transform plantation-based resouces into high-value rubber products, thereby strenghtening the sustainability, efficiency, and global competitiveness of rubber-based agro-industries, particularly in emerging economies seeking cleaner and more resilient production systems.

References

1. R. Roslim, K.S. Tan, J. Jefri, *Study on morphological structures and mechanical properties of natural rubber latex films prepared at different prevulcanisation and drying temperatures*. J. Rubber Res. **21**(1), 1-16 (2018). https://doi.org/10.1007/BF03449158.
2. V. Schöppner, S. Brockhaus, C. Penner, J. Möckel, *The effects of operational parameters in hot-air vulcanisation.* Int. Polym. Sci. Technol. **43**(10), 1-6 (2016). https://doi.org/10.1177/0307174X1604301001.
3. T. Khamdaeng, N. Panyoyai, T. Wongsiriamnuay, *Material parameter of rubber glove vulcanized using combined infrared and hot-air heating.* Am. J. Appl. Sci. **11**(4), 648-655 (2014). https://doi.org/10.3844/ajassp.2014.648.655
4. H.-L. Chen, T. Li, Y. Liang, B. Sun, Q-L Li, *Experimental study of temperature distribution in rubber material during microwave heating and vulcanization process*. Heat Mass Transf. **53**(3), 1051-1060 (2017). https://doi.org/10.1007/s00231-016-1877-3
5. E. Manaila, G. Craciun, M-D. Stelescu, D. Ighigeanu, M. Ficai, *Radiation vulcanization of natural rubber with polyfunctional monomers.* Polym. Bull. **71**(1), 57-82 (2014). https://doi.org/10.1007/s00289-013-1045-6
6. K. Makuuchi, *Environmentally friendly vulcanization technology of natural rubber latex by radiation*, in Ecomaterials, Proceedings of the Symposium K: Environment Conscious Materials of the 3rd IUMRS International Conference on Advanced Materials, Sunshine City, Ikebukuro, Tokyo, Japan, August 31-September 4, (1993), 721-724. https://doi.org/10.1016/B978-1-4832-8381-4.50172-4
7. G. Craciun, E. Manaila, M-D. Stelescu, *New elastomeric materials based on natural rubber obtained by electron beam irradiation for food and pharmaceutical use*. Mater. **9**(12), 999 (2016). https://doi.org/10.3390/ma9120999
8. S. Rimjaem, E. Kongmon, M.W. Rhodes, J. Saisut, C. Thongbai, *Electron linear accelerator system for natural rubber vulcanization.* Nucl. Instrum. Methods Phys. Res. B: Beam Interact. Mater. At. **406**, 233-238 (2017). https://doi.org/10.1016/j.nimb.2016.11.016
9. K. Makuuchi, *An introduction to radiation vulcanization of natural rubber latex.* TRI Global Co., Bangkok, (2003).

10. Y.S. Soebianto, U.M. Ratnayake, K. Makuuchi, F. Yoshii, T. Kume, *Extractable protein of radiation vulcanized natural rubber latex*, in Takasaki workshop on bilateral cooperations. Radiation processing of natural polymers, Takasaki, Gunma, Japan, 1-2 November (1999), 49-55. https://inis.iaea.org/records/w1p30-ry926
11. S.O. Rogero, A.B. Lugao, F. Yoshii, K. Makuuchi, *Extractable proteins from irradiated field natural rubber latex.* Radiat. Phys. Chem. **67**(3), 501-503 (2003). https://doi.org/10.1016/S0969-806X(03)00093-8
12. D.F. Parra, C.F.P. Martins, C.H.D. Collantes, A. B. Lugao, *Extractable proteins from field radiation vulcanized natural rubber latex*. Nucl. Instrum. Methods Phys. Res. B: Beam Interact. Mater. At. **236**(1), 508-512 (2005). https://doi.org/10.1016/j.nimb.2005.04.028
13. C. Wang, F. Yoshii, K. Hyakutake, K. Makuuchi, *Reduction of residual n-butyl acrylate sensitizer in radiation vulcanized natural rubber latex.* Nippon gomu kyokaishi, 1995. **68**(11): p. 788-793. https://doi.org/10.2324/gomu.68.788
14. E. Yip, P. Cacioli, *The manufacture of gloves from natural rubber latex.* J. Allergy Clin. Immunol. **110**(2, Supplement), S3-S14 (2002). https://doi.org/10.1067/mai.2002.124499.
15. M. Purbaya, T. Kobayashi, N. Thamrongsiripak, C. Yayichelaeh, K. Boonkerd. *Electron beam irradiation for enhancing the properties of natural rubber latex.* Radiat. Phys. Chem. **212**, 111193 (2023). https://doi.org/10.1016/j.radphyschem.2023.111193.