Application of Large Area Plasma Cathode Electron Beam for Natural Rubber Vulcanization

P. Raharjo, K. Uemura, N.N. Koval*, V. Shugurov*, V. Denisov*, V. Jakovlev*, W. Setiawan**, and M. Utama***

ITAC Ltd., 8-2 Kamisuwa Tsubame City Niigata 959-0181 Niigata, Japan
Phone: +81-(0)-256-91-3315, Fax: +81-(0)256-98-5778, E-mail:purwadi_raharjo@itac-j.co.jp
**Institute of High Current Electronics, 4, Akademichesky ave., Tomsk, 634055, Russia*
***Indonesia National Nuclear Energy Agency (PTAPB BATAN), Babarsari, Yogyakarta 55281, Indonesia*
****Indonesia National Nuclear Energy Agency (PATIR BATAN), Ps. Jumat, Jakarta 12070, Indonesia*

Abstract – In this study, irradiation of natural rubber latex using pulsed plasma cathode electron beam system has been attempted. Fundamentally different from the conventional hot filament electron sources, the present pulsed plasma cathode electron beam can be used for vulcanization process with large area of irradiation (150 × 650 mm), low electrical power consumption (< 9 kW), and high efficiency. The evaluation results show that after electron beam irradiation at 150 kV 18 A on old natural rubber latex with stirring method, an increase of the tensile strength up to 12.3 MPa can be achieved without any chemical additive or sensitizer. Higher tensile strength until 18.0 MPa can be provided on fresh natural rubber latex. It suggests that the present system can be applied as a new type of electron accelerator for cross-linking of natural rubber latex.

1. Introduction

Considering environmental issues in the future, natural rubber latex has been predicted to be more competitive against synthetic rubber. Not only due to current rising price of petroleum as raw material of the synthetic rubber, but also productions of goods such surgical gloves, catheters, condoms, tires etc. from natural rubber latex (Hevea brasiliensis) could be more environmental-friendly compared to the synthetic rubber. Moreover, waste of the natural rubber disposals can be easily decomposed by soil microorganisms, and plantation of the Hevea trees can contribute important roles for reducing the earth global warming.

Unfortunately, there are still remaining problems for obtaining optimal application of the natural rubber, i.e., the vulcanization problem and the content of nitrosamine or allergenic protein in the Hevea rubber latex. Sulfur and other chemical additives used in conventional vulcanization of the rubber are known as the main obstacle in the recycling process of the rubber tire wastes. Nitrosamine, which may be formed from the rubber precursor additives, has been reported to be responsible for cancer diseases (carcinogen) in the human body [1]. In addition, natural rubber latex itself inherently contains allergenic protein, which may lead to mortality for some allergic peoples.

To solve the problems, irradiation process on the natural latex has been already attempted in Indonesia National Nuclear Energy Agency since 1979 by using gamma-ray ^{60}Co [2]. However, irradiation process using the gamma-ray requires huge and thick shielding concrete building for irradiation protection of the operators, which may not be economically reliable for in-situ fresh latex processing near the Hevea plantation area. For the latex treatment, consecutive process of fresh latex just after harvesting is strongly required; otherwise, the expected mechanical properties of the vulcanized rubber will be deteriorated due to bacterial and/or oxidation during the storage [3].

Instead of gamma ray, irradiation with low energy electron beam (EB) becomes a new alternative method for providing the in-situ fresh latex processing. Owing to low electric energy consumption of compacted electron beam machines, mobile irradiation facilities in rural area may be possible to be realized in the future.

Makuuchi et al. have developed electron beam system with accelerating voltage about 200–500 kV for natural rubber vulcanization irradiation [4]. The system applies stirring process with impeller to obtain homogenous beam irradiation. However, as commonly used in conventional electron beam systems, the latex EB irradiation system uses a filament for the electron source, which will not be reliable for providing large area irradiation. Another disadvantage of the conventional EB system is in the maintenance of the electron beam source as short lifetime of the filament.

In this study, irradiation of natural latex by using pulsed plasma cathode electron beam with low accelerating voltage less than 200 kV is introduced. The electron source is fundamentally different from conventional electron beams using hot filament electron sources. With the pulsed plasma cathode electron beam, it is possible to obtain large area of latex irradiation without beam scanning, to provide highly efficient vulcanization process of natural rubber latex.

2. Experimental procedure

Natural rubber latex used for the present electron beam irradiation test is high ammonia (HA) concentrated latex from Jalupang Rubber Plantation PTPN VIII Subang Bandung, Indonesia harvested on May 14, 2006. This latex is indicated as old latex in this study, due to its 2-year storage period before the irradiation. Fresh latex, with storage period less than 6 months, is also irradiated for comparison. The natural rubber latex samples are irradiated without any chemical additive or sensitizer, using "DUET" electron beam system available at Institute of High Current Electronics, Tomsk Russia.

Figure 1 shows the picture and schematic illustration of the electron beam system.

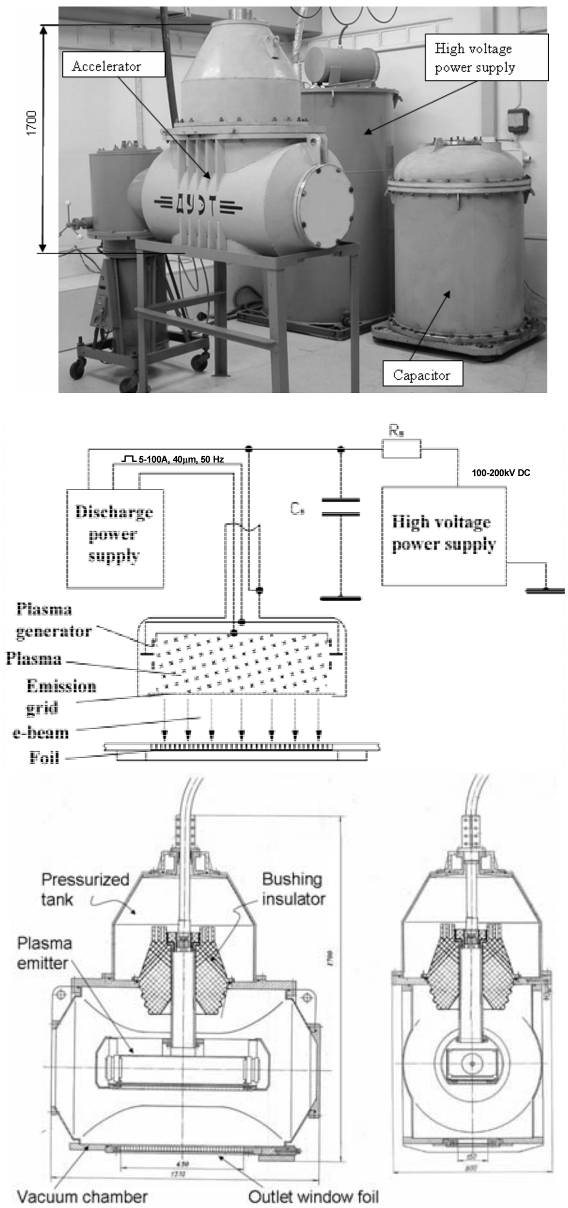

Fig. 1. Photo and schematic illustration of the electron beam system. The intense gas plasma is generated by pulsed low-pressure arc discharges and a hollow electrode. From the plasma, electrons are extracted and accelerated to perform pulsed large area electron beam irradiation in the atmosphere

The system can be operated at relatively low accelerating voltage of 100–165 kV with beam current up to 100 A. The beam is pulse type with beam duration and frequency are 40 mks and 0.1–50 Hz, respectively. The above parameters are independently adjustable which allow various applications. The beam outlet window is made of Al–Be foil with thickness of 40 mkm and size of 150 × 650 mm. Unlike conventional electron beam systems, in the present system there is no use of hot filament, and larger irradiation area is possible to be attained.

As shown in Fig. 1, the accelerator of the EB system consists of a cylindrical vacuum chamber with diameter of 700 mm and length of 1300 mm. In the accelerator, there is a plasma emitter box in the form of a hollow rectangular parallelepiped with sizes of 800 × 200 × 150 mm. Two coaxial arc plasma-generators are installed on lateral side of the emitter box. The plasma-generator consists of Mg cathode, triggering electrode, and dielectric insulator between the cathode and the electrode. At the bottom side of the emitter box, there is a horizontal extraction window from where electrons are extracted out. The 150 × 650 mm window is covered with a stainless steel emission grid having cell sizes of 0.4 × 0.4 mm. The plasma emitter box is mounted to a bushing insulator made from polythene by using tubular rod through which the input cables from the plasma-generator power supply are connected. To afford electrical strength for the voltage up to 200 kV, the upper part of the bushing insulator is surrounded by insulating gas in a pressurized tank (nitrogen at pressure 0.6 MPa).

The electron source in "DUET' accelerator is low-temperature volumetric plasma generated by vacuum arc discharge, which can perform high beam current density (up to 1 A/cm^2) with high beam homogeneity (± 15%) and large irradiation area (about 10^3 cm^2) at comparatively low energy consumption (less than 2 kW). Once an arc discharge is initiated due to the breakdown of dielectric in the plasma-generators, a discharge between the plasma-generator cathodes and hollow anode will be ignited [5]. The hollow anode function is fulfilled by internal walls of the plasma emitter box. Modulation of beam current in this system can be carried out by parameter adjustments of the pulse arc discharge.

High DC voltage 100–200 kV is applied between the plasma emitter and the vacuum chamber to extract and accelerate electrons passing through the emission grid. The DC accelerating voltage has benefit to avoid electron energy loss during penetration into atmosphere or higher pressure gas through the thin foil of the outlet window. It also allows for obtaining almost mono-energetic beam, due to the absence of electron acceleration in front of the window and no decay of high voltage impulse, which usually takes places in traditional pulse accelerators.

Another advantage of DUET accelerator is its possibility of independent parameter adjustment (for beam current, accelerated electrons energy, pulse duration, pulse repetition frequency), which can allow us to vary the irradiation conditions on gases, liquids or other products over wide-range regimes of parameters. Also, the plasma cathode can provide an electron accelerator with high efficiency and longer lifetime, compared to conventional hot-filament cathodes.

In this experiment, the EB irradiation is subjected on 360g natural rubber latex placed inside a special stirring vessel with irradiation parameter conditions shown in Table 1. Total irradiation dose of 183 kGy has been achieved by using 150 kV accelerating voltage and 18 A beam current in 20000 pulses. Since the plasma is generated by pulse arc discharge, the beam duration can be defined indirectly from the duration of arc discharge parameter, which is 40 mks in the present experiment. With pulse repetition at 10 Hz, the treatment can be conducted in several minutes.

Table 1. EB irradiation

EB irradiation parameter	Values
Accelerating voltage (kV)	150
Electron beam current (A)	18
Pulse duration (μs)	40
Energy density per pulse (J/cm^2)	0.06
Total dose (kGy)	183
Pulse number	20000
Sample mass (g)	360

The stirring system shown in Fig. 2 has been specially fabricated to perform homogenous irradiation on the natural rubber latex. A rotating stirrer is installed in the axes of double cylindrical vessels having 86 mm opening diameter for beam irradiation. Due to low energy electron beam (less than 200 keV) in the current process, penetration depth of electron in the sample will be very small (not more than 1 mm). Only the upper layer will be modified by the EB irradiation.

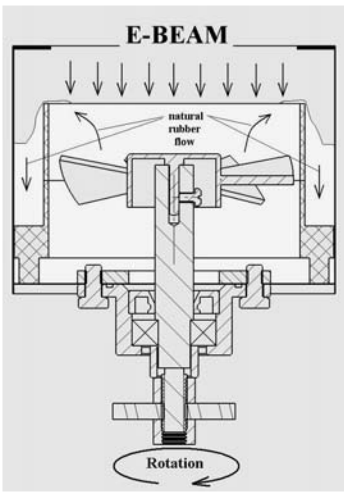

Fig. 2. Electron beam irradiation condition with special stirrer for latex mixing during the irradiation process

The stirring system is designed to flow down the irradiated upper layer of latex surface into the outer cylinder to make continuous irradiation for the next layer beneath the upper layer.

After the irradiation, the rubber latex liquid is solidified and formed into flat rubber films using coagulant dipping method for test pieces of the mechanical evaluation. The latex former is first coated with a layer of $CaNO_3$ as coagulant agent before dipped into the irradiated natural rubber latex [6]. In this method, the coagulant converts the liquid latex film into a wet-gel on the former. The rubber thin film is then cleaned in warm water, dried in air, and dried at 90 °C for 15 min in an oven. For the comparison, with the same method, the similar samples are also prepared from initial and gamma ray irradiated natural rubber latex. The gamma ray irradiation on fresh natural rubber latex was conducted in February, 2008 at PT. REL-ION (Bekasi, Indonesia) with irradiation dose of 25 kGy and normal butyl acrylate (n-BA) additives.

To verify the vulcanization process as the effect of the irradiations, mechanical properties such as tensile strength, swelling ratio in toluene for 24 hours, and permanent set of the rubber thin film are evaluated according to ASTM standard [7].

3. Results and discussion

Cross-linking in natural rubber is defined as the linking of two or more molecular chains of the polymers (cis-1, 4-polyisoprene) by means of covalent bonds. This creates a three dimensional network with an infinite molecular mass. Historically, the vulcanization means cross-linking of rubber molecules with sulfur. Now, however, cross-linking without sulfur is also called as vulcanization. As the cross-linking occurs, mechanical properties of the polymer will be changed.

Table 2 shows the results of mechanical property evaluation on the films of latex irradiated with the plasma cathode electrode beam, in comparison with initial and gamma ray irradiation. As shown in the table, the permanent set of natural rubber prepared by EB has significantly decreased compared to the initial sample. The permanent set is defined as the deformation remaining after a specimen has been stressed in tension for a definite period, and released for a definite period. Decrease of permanent set in the EB-irradiated sample means that the vulcanization (cross-linking) of natural rubber latex has occurred due to the EB irradiation.

Existence of cross-linking after EB irradiation can be verified also by the increase of modulus and the decrease of elongation at break of the samples. Modulus is an indicator to the stiffness of rubber films which is directly dependent to cross-linking density [8]. According to Alliger, the elongation at break is also reduced by excessive cross-linking. Hence, the increase of modulus and decrease of elongation at break after the irradiation in Table 2 indicate that the plasma cathode EB irradiation, as well as gamma-ray irradiation, can be used to vulcanize the natural rubber latex.

Table 2. Mechanical properties of the natural rubber latex after the plasma cathode EB irradiation in comparison with initial and gamma-ray irradiation

Mechanical properties	Initial	EB irradiation (old)	EB irradiation (fresh)	Gamma ray irradiation
Permanent set, %	75	15	15	23
Elongation at break, %	1060	1040	1120	1000
Modulus 600%, MPa	0.4	1.9	n.a	2.1
Tensile strength, MPa	2.2	12.3	18	18.6
Swelling ratio in toluene (immersed for 24 hours), %	completely diluted	270	300	160

As shown in Fig. 3, the tensile strength of the EB irradiated natural rubber remarkably increases from 2.2 MPa in initial latex. The increase of the strength is also presented by the gamma-ray irradiation. As indicated by Makuuchi, the higher tensile strength of the radiation vulcanization natural rubber latex film can be attributed by both interparticle cross-linking and entanglement of the polymer chains [9]. Lower tensile strength (12.3 MPa) in the old latex might be due to degradation of the latex after the storage for about 2 years. The EB irradiation on fresh latex without any chemical additives, however, can provide higher tensile strength up to 18.0 MPa, which is almost similar to the gamma-ray irradiation with n-BA additives.

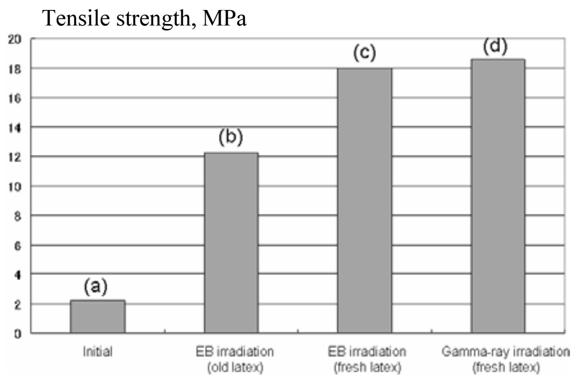

Fig. 3. Tensile strength of natural rubber latex before (a), and after irradiation with electron beam and gamma ray (b, c, d). The tensile strength can be remarkably increased after the EB irradiation. Compared to the old latex (b), EB irradiation on fresh latex (c) exhibits higher tensile strength up to 18.0 MPa, which is almost similar to the gamma-ray irradiation (d)

Swelling ratio is also another indicator of the degree of cross-linking. In this study, swelling ratio corresponds to the increasing of film area (in cm^2) after and before immersed in toluene for 24 hours. If volume fraction of the rubber network in the swollen gel can be expressed as the reciprocal swelling ratio, then lower swelling ratio is indicating higher crosslink density, according to Flory-Rehner equation (1) [10]:

$$\nu = \frac{-\left[\ln\left(1-\upsilon_r\right)+\upsilon_r+\mu\upsilon_r^2\right]}{V_o\left[\upsilon_r^{1/3}-\upsilon_r/2\right]}, \qquad (1)$$

where v is the cross link density; υ_r is the volume fraction of the rubber network in the swollen gel; V_o is the molar volume of the toluene (106.4 cm^3/mol); μ is the rubber–toluene interaction parameter (0.393 for natural rubber).

Power consumption of the EB system is estimated from power supply units of the accelerator and the vacuum system. The “DUET” EB system in the present experiment contains accelerator and vacuum pumps (mechanical rotary pump and diffusion pump), with electrical power consumption are 7 kW and 1.8 kW at 10 Hz, respectively. Therefore, it is possible to make treatment of latex sample with comparatively low power consumption, i.e., less than 9 kW.

4. Conclusions

In this study, irradiation of natural rubber latex using pulsed plasma cathode electron beam system has been attempted. Fundamentally different from conventional hot filament electron sources, the pulsed plasma cathode electron beam can be used for vulcanization process with large area of irradiation (150 × 650 mm), low electrical power consumption (< 9 kW), and high efficiency.

The evaluation results reveal that after electron beam irradiation at 150 kV 18 A on old natural rubber latex with stirring method, an increase of the tensile strength up to 12.3 MPa can be achieved without any chemical additive/sensitizer. The EB irradiation on fresh natural rubber can provide higher tensile strength until 18.0 MPa. It suggests that the present system can be applied as a new type of electron accelerator for cross-linking of natural rubber latex.

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