JAERI-Conf 2002-013

5.3 Radiation Processing of Liquid with Low Energy Electron Accelerator

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ABSTRACT

Radiation induced emulsion polymerization, radiation vulcanization of NR latex (RVNRL) and radiation degradation of natural polymers was selected and reviewed as the radiation processing of liquid. The characteristic of high dose rate emulsion polymerization is the occurrence of cationic polymerization. Thus, it can be used for the production of new materials that cannot be obtained by radical polymerization. A potential application will be production of polymer emulsion that can be used as water-borne UV/EB curing resins. The technology of RVNRL by γ-ray has been commercialized. RVNRL with low energy electron accelerator is under development for further vulcanization cost reduction. Vessel type irradiator will be favorable for industrial application. Radiation degradation of polysaccharides is an emerging and promising area of radiation processing. However, strict cost comparison between liquid irradiation with low energy EB and state irradiation with γ-ray should be carried out.

1. INTRODUCTION

In this paper, liquid includes solution, emulsion and latex. The radiation processing of liquid developed so far are as follows;

① Organic synthesis

② Waste water treatment

③ Emulsion polymerization

④ Vulcanization of NR latex

⑤ Graft polymerization in NR latex

⑥ Degradation of Natural Polymers

Several processes of organic synthesis by radiation were developed in USSR and USA in '60[1, 2]. However, they have no industrial value at present because the same substances are produced by other nonradiation processes. The waste water treatment by radiation is recognized as an important area of radiation processing[3]. It will be discussed in other part of this Workshop. The graft polymerization in NR Latex is also not dealt with in this paper because nonradiation method is commonly utilized. Thus the emulsion polymerization, vulcanization of NR latex and degradation of natural polymers will be reviewed in this paper.

2. EMULSION POLYMERIZATION

Radiation induced emulsion polymerization was studied for long time[4]. The advantages of radiation emulsion polymerization are as follows;

① Higher molecular weight

② Complete conversion

③ No purification of monomer

④ Reproducibility

⑤ No heat source

⑥ Easy control

⑦ Clean products without impurity

Only acrylic emulsions for textile printing and dyeing are produced commercially in China by radiation[5]. This process was developed by University of Science and Technology of China. Industrial production was started in 1986. This process is now widely used in China. Annual production shipment value was $ 1 Million in 1998. Figure 1 illustrates the outline of the plant of radiation emulsion polymerization.

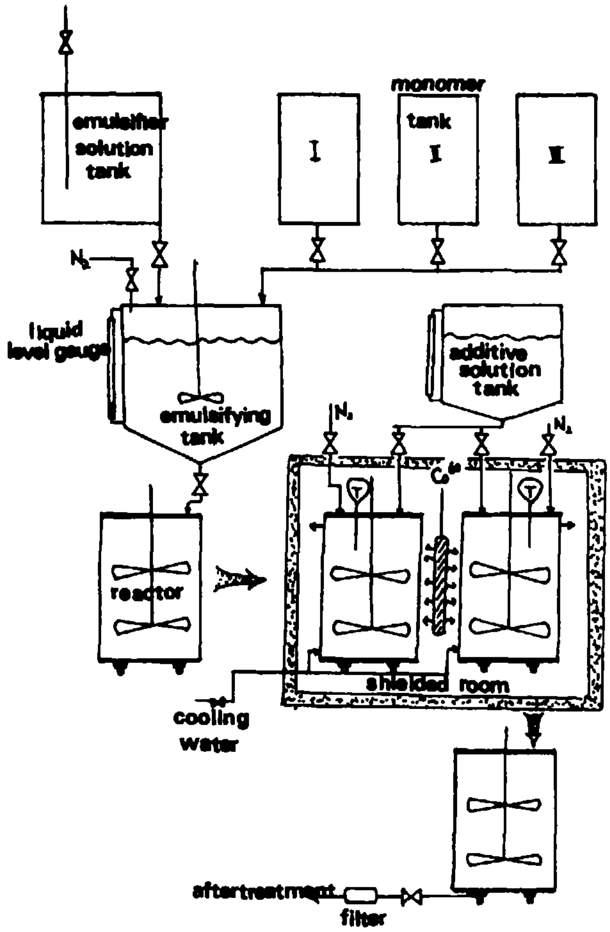


Fig. 1 Outline of the plant of radiation emulsion polymerization

A batch process was adopted in the industrial-scale production. The primary intensity of radiation source was 80 kCi and the producing capability of latex was 6 ton/day (2000 ton/y). The prepared emulsion is fed into four 600 litters movable reactors that are arranged on the two sides of the plate-form Co-60 source to receive the γ rays and carry out the emulsion polymerization independently. Each reactor is equipped with stirring and cooling systems, temperature detectors and automatic feeding entrance. The whole emulsion system is stirred at low speed during the irradiation. The preferable dose rate is 10-30 Gy/min. The temperature detector and the cooling system is set to take the reaction heat away and to keep the reaction temperature. A lower temperature is favorable to raise the molecular weight of resulted polymer, so that to raise the latex quality. Two types of latexes are produced: (1) water based latexes produced from oil-in-water emulsion and (2) oil based latexes from water-in-oil emulsion. The former are used as the binders for textile pigment print and dying and the later as thickeners for print paste

Emulsion polymerization with electron accelerator was attempted. One of the most important characteristics of irradiation with electron accelerator is the high dose rate irradiation. The advantages of the high dose rate polymerization are as follows:

① High rate of polymerization
② Predominance of cationic mechanism
③ Liability to form Oligomer

Study on the emulsion polymerization of styrene (St) in a flow system by using electron beam of 1.5 MeV was carried out by JAERI-Osaka[6, 7]. The reaction system is schematically illustrated in Figure 2. Sodium lauryl sulfate (SLS) was used as an emulsifier.

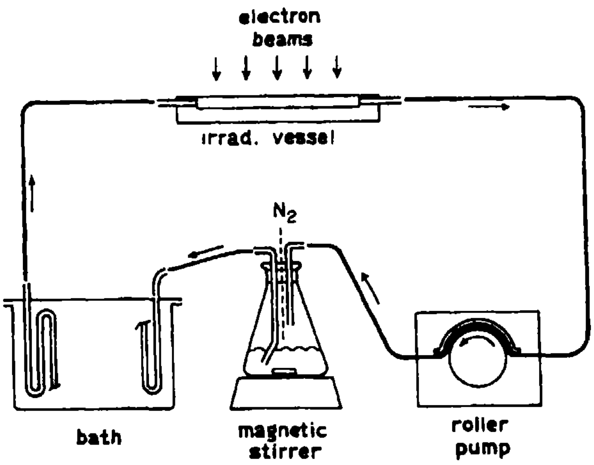


Fig. 2 System of emulsion polymerization with electron accelerator

Deaerated emulsion was circulated through an irradiation vessel after passing a heat exchanger to keep the sample temperature at 40℃. The flow rate of the emulsion was 4.7 ~ 5.0 ml/sec. The inner size of the irradiation vessel was 440×10×5 mm. The electron beam of 1.5 MeV penetrates 3 mm in the direction of the depth. The average dose rate in the vessel was 3 kGy/sec for a space of 300×10×3 mm.

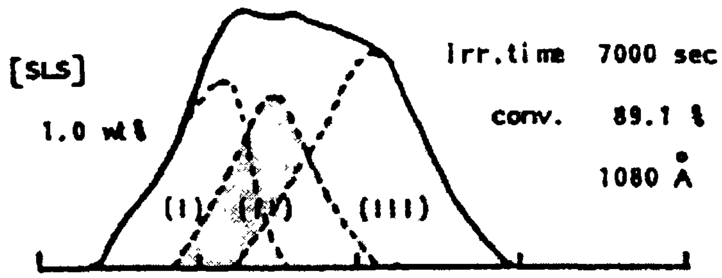


Fig. 3 GPC curves of polystyrene prepared by emulsion polymerization with EB

Figure 3 shows the typical GPC curves of polymer latex prepared by the high dose rate emulsion polymerization. The GPC curve is composed of three components. Peak I indicates the curve of oligomers with molecular weight of about 1000, Peak II polymers obtained by radical polymerization, and Peak III polymers obtained by cationic polymerization. The higher the [SLS]/[St], the more the amount of polymer produced by cationic process. The amounts of oligomer and radical polymer decrease at higher [SLS]/[St].

Figure 4 shows the GPC curves of polymers prepared under various dose rates. It is clear that radical polymer predominate at a low dose rate, while at a higher dose rate cationic polymers predominate.

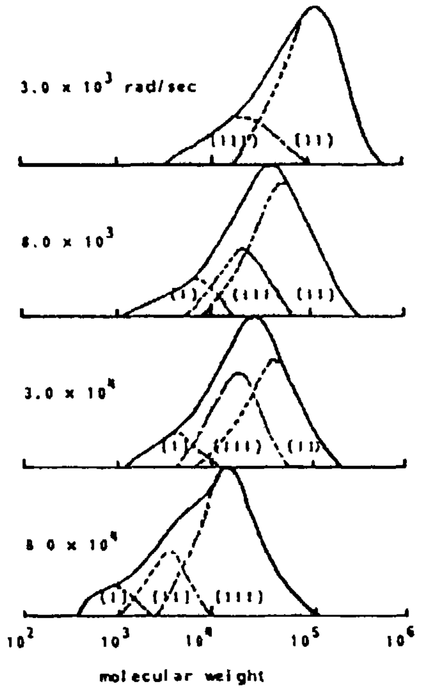


Fig. 4 GPC curves of polystyrene prepared under various dose rates

The molecular weight distributions of cationic polymers are rather narrow. Figure 5 shows the number average molecular weight (Mn) of cationic and radical polymers as a function of the dose rate, respectively. Mn of radical polymers decreases with increasing dose rate, while Mn of cationic polymer keeps. Emulsion polymerization with electron accelerator is a high dose rate polymerization.

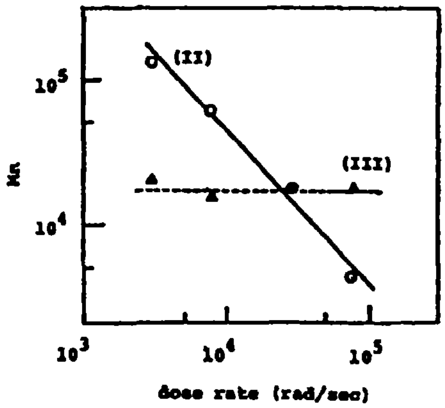


Figure 5 Number average molecular weight of cationic and radical polymers

The significant characteristic of electron beam induced high dose rate emulsion polymerization is the emergence of cationic polymer mechanism. This suggests that electron beam induced emulsion polymerization is suitable for the production of polymer emulsion that can be used as water-borne UV/EB curing resins.

3. RADIATION VULCANIZATION OF NR LATEX

Radiation vulcanization of natural rubber latex (RVNRL) means the radiation-induced crosslinking of natural rubber (cis-1,4-polyisoprene) dispersed as microscopic particles in an aqueous medium. Following excellent qualities of RVNRL have been specified[8).

① Absence of N-nitrosamines
② Very low cytotoxicity
③ Less protein content
④ Easy degradation in the environment
⑤ Transparency and softness
⑥ Less formation of SO_2 when during incineration

These arise from the facts that RV NR latex does not contain dithiocarbamates, sulfur and zinc oxide that are essential for the conventional vulcanization. Pilot plants of RVNRL have been set up in Indonesia, India, Malaysia and Thailand. Radioactive isotope Co-60 is used as a radiation source of pilot plant of RVNRL. Irradiation facility with Co-60 sources needs heavy bioshielding, resulting in high initial investment and high irradiation cost. Replenishment of decayed Co-60 sources is another factor to be considered. Thus, RVNRL by Co-60 has not come into wide. The RVNRL with electron accelerator also studied in a few countries. Generally, medium or high energy electron accelerator was used. A pilot plant with electron accelerator was installed in France[9). Figure 6 illustrates the plant. A linear electron accelerator having a mean power of 10 kW and energy of 6 MeV was used as the radiation source. The irradiation vessel is equipped with a latex circulating pump to permit continuous vulcanization. The critical problems of RV NR latex preparation with EB are as follows;

① Avoiding local overdosing
② Limiting heating of the latex.

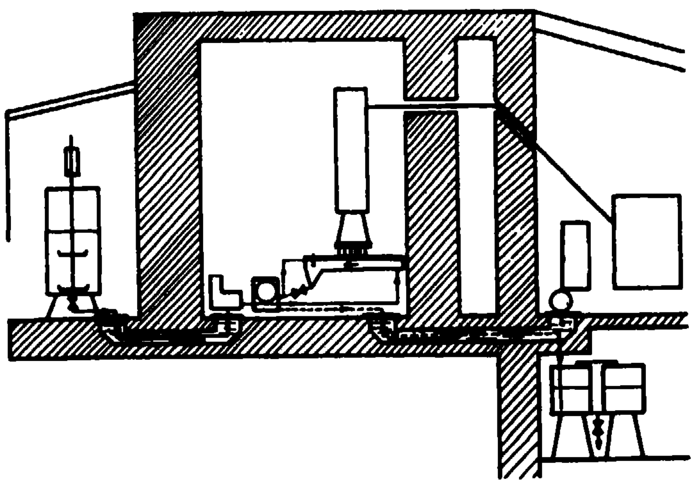


Fig. 6 Pilot plant of RVNRL with linear electron accelerator

Special care was taken in the designing of the irradiation vessel to prevent the coagulation of the latex that can occur because of over dosing and heating. It has been reported that EB irradiated NR latex and the resulting latex films exhibit good properties that make them suitable for any conventional use of rubber latex.

In China, a van de Graaff electron accelerator (2 MeV, 0.15 mA) was a radiation source[10]. The NR latex (TSC 50 %) was irradiated to 300 kGy with a dose rate of 1.2 kGy/sec. The latex was stirred during the process at 300 rpm to ensure homogeneous irradiation. The physical properties of RV NR latex films thus prepared were compared with those of a sulfur vulcanized NR latex film. The vulcanization dose was 300 kGy. The maximum tensile strength and elongation at break were 19.2 MPa and 918 %, respectively. While the tensile strength of sulfur vulcanizate was 29.0 MPa. After aging at 100 C for 24 hr the tensile strength of radiation vulcanizate increased to 22.5 MPa, while that of sulfur vulcanizate decreased to 5.9 MPa. High transparency of radiation vulcanizate was observed. The RV NR latex irradiated with EB is absolutely free from contaminants and suitable for medical use.

In Germany a 1.5 MeV, 25 mA (Dynamitron) was used for RVNRL source[11, 12]. Initially, NR latex was placed on metal plates (with thickness of about 4 mm) having elevated edges. The plates were mounted on a table that can move automatically under the electron beam scanner during radiation. Finally, flow type irradiator with metal slope was installed to irradiate NR latex continuously (300 kg for each trial). Polyfunctional monomers were used as accelerator.

German latex using industry was interested in RVNRL. The electron beam crosslinked natural rubber latex was tested for a number of different applications. Best results were obtained in the dipping industry. Trial manufactures of teats, toys, balloons, condoms, household-gloves, surgical gloves, examination gloves, catheters and medical tubes were carried out. Advantages were also seen in the productions of cork soles because of a better appearance. However, the development of radiation process by electron beam was stopped due too high investment cost.

RVNRL with a self-shielding low energy electron accelerator is supposed to be more feasible and economic than those with Co-60 source, medium and high energy electron accelerator because special building with thick bioshielding is not required for low energy electron beams (EB). However, the low energy EB has the following disadvantages:

① High absorption by air
② Low penetration in latex
③ Wide scattering in air

Figure 7 shows the percentages of absorbed electron beams in latex that was put in a vessel covered with 6 μm aluminum foil as shown in Figure 8.

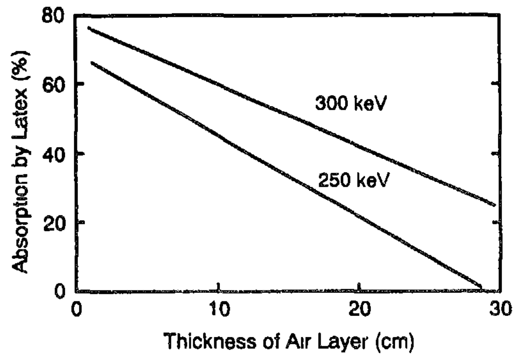


Fig. 7 Absorbed EB in latex

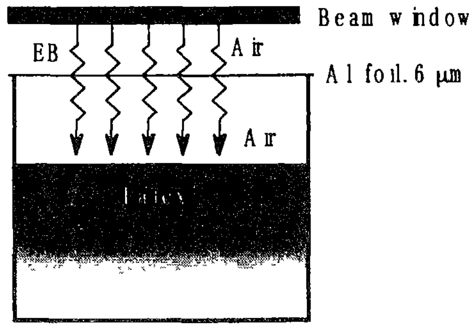


Fig. 8 Absorption of EB in vessel

With increasing the thickness of air layer between the surface of latex and the beam window absorption percentages of electron beams in latex decreases. Low penetration of low energy EB in latex causes serious technical problems.

Figure 9 illustrates a typical relationship between dose and tensile strength of NR film prepared from RV NR latex. The tensile strength increases with increasing dose, after achieving maximum value it decreases. For practical usage 70% of maximum tensile value should be kept. This means the lowest dose should be about 50% of the dose at that maximum tensile strength is achieved.

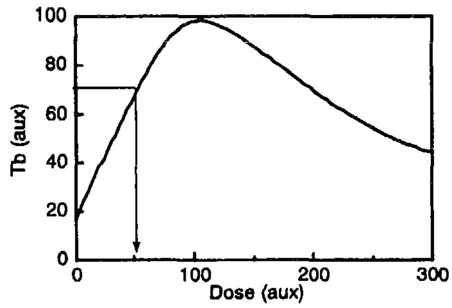


Fig.9 Dose and tensile strength Relationship of RVNRL

Figure 10 shows the depth dose curve of 250 keV EB in NR latex in the irradiation vessel covered with 20 μm titanium foil. The thickness of air layer is 10 cm. The thickness of NR latex that absorbs enough energy to vulcanize is less than 40 μm. It is hard to control the thickness of NR latex layer less than 40 μm in industry.

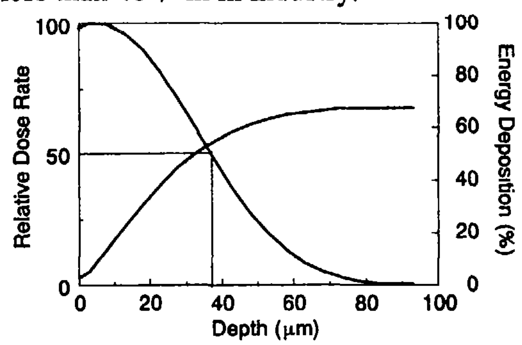
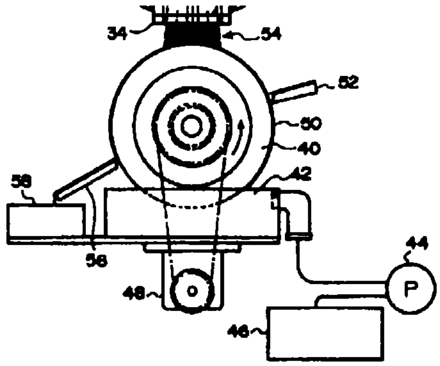


Fig. 10 Depth dose curve of 250keV EB in NR latex

Several irradiation systems were tried to vulcanize NR latex[13]. Figure 11 illustrates a rotating drum type irradiator. Surface of the rotating drum adsorbs NR latex at the bottom of drum and the latex is irradiated at the top of the drum.



34: Beam window
40: rotating drum
42: NR latex
44: latex pump
46: latex tank
48: motor
50: thin latex layer
52: thickness adjustor
56: latex collector
58: latex reservoir

Fig. 11 Rotating drum type irradiator

Figure 12 shows tensile strength and weight swelling ratio of NR film prepared from NR latex irradiated with the rotating drum type irradiator at various beam current at the fixed accelerating voltage (250 kV) and the rotating speed. With increasing beam current the tensile strength increases and the swelling ratio decreases.

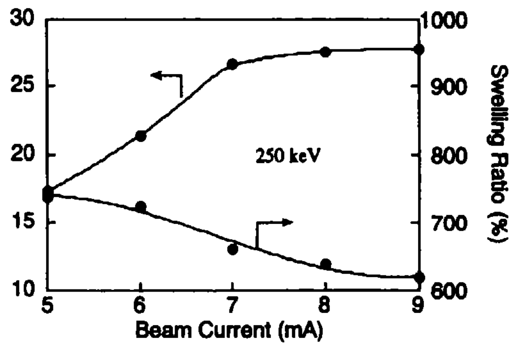
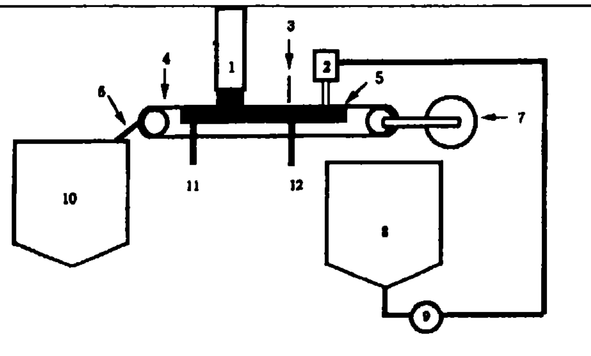


Fig. 12 Results obtained by using rotating drum type irradiator

Belt conveyer type irradiator shown in Figure 13 is a modification of rotating drum type irradiator.



1: electron accelerator
2: latex coater
3: thickness controller
4: conveyer belt
5: cooling head
6: latex collector
7: motor
8: latex tank
9: pump
10: latex reservoir

Fig. 13 Belt conveyer type irradiator

Figure 14 demonstrates a natural flow type irradiator. The NR latex flows under EB naturally due to gravitational force and circulates by using diaphragm pump.

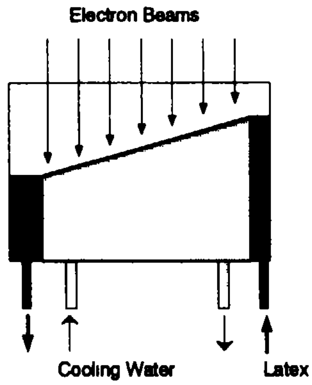


Fig. 14 Natural flow type irradiator

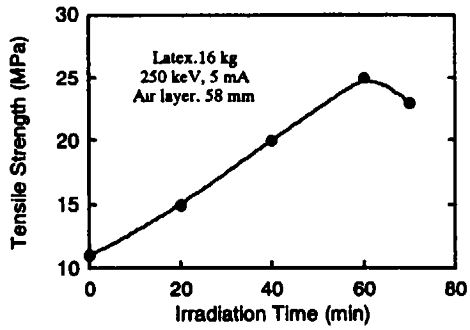


Fig. 15 Results obtained by using natural flow type irradiator

Figure 15 shows some data obtained by this irradiator.

Vessel type irradiator will be favorable for industrial application. Figure 16 shows two vessel type irradiators, prototype and its modified one. Mixing efficiency was improved in the modified irradiator by installing the stirrer at the bottom of the irradiator.

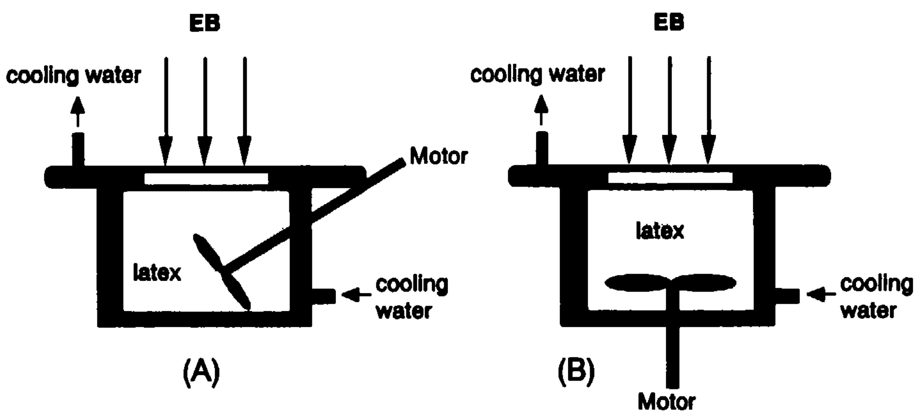


Fig. 16 Vessel type irradiators, (A) prototype, (B) modified

Problem of vessel type irradiator was the formation of small rubber blocks on the surface of latex during irradiation. Number and size of the block increase with increasing irradiation time. The rubber blocks originated from drying of latex at the wall of irradiator where the scattered electron beams hit. It is essential to design the irradiator to be larger than beam window. The irradiator should apart 15 cm from the edge of beam window.

Figure 17 shows the effect of mixing speed on RVNRL with vessel type irradiator. The capacity of the vessel is 1,450 ml latex. NR latex was irradiated in the absence of sensitizer with an accelerating voltage of 300 kV. Clearly the optimum radiation time is 25 minutes at 100 rpm (Reynolds number Re: ca 800), 15 minutes at 150 rpm (Re: ca 1,200) and around 20 minutes at 200 rpm (Re: ca 1,600). The maximum tensile strength is also achieved at 150 rpm. This indicates that suitable flow of latex is attained at the Reynolds number around 1,600. High speed stirring produces foams that cause coagulated surface layers with partially carbonized NR because almost all of energy of the electron beams is adsorbed by the foam. Formation of foams was prevented by addition of defoamer. Figure 18 shows effect of beam current (equivalent to dose rate) on the tensile strength with a 300 kV of EB energy at 150 rpm of stirring speed. It can be seen that for higher beam current reduces vulcanizing time. However, there is slight dose rate dependency of rate on vulcanization. Probably this is due to the insufficient mixing during irradiation.

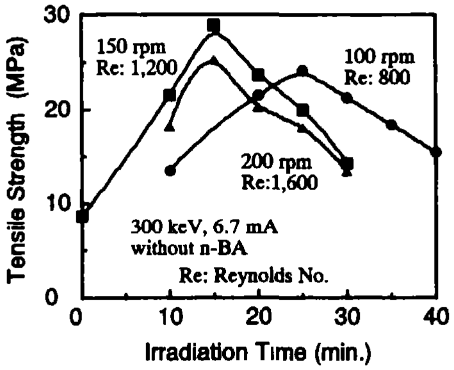


Fig. 17 Effect of mixing speed on RVNRL

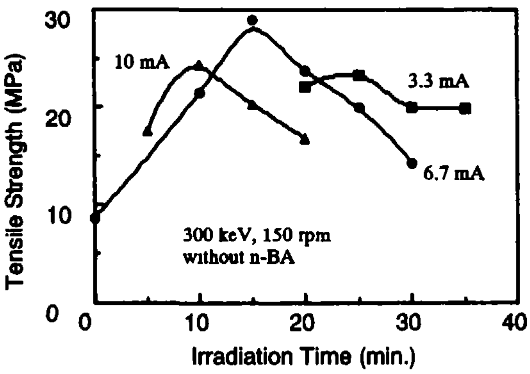


Fig. 18 Effect of beam current on RVNRL

A pilot plant of RVNRL with low energy electron accelerator was installed at TRCRE[14]. The appearance of the plant is shown in Figure 19. It consists of 250 keV-10 mA electron accelerator and vessel type irradiator having capacity of 18 litters.

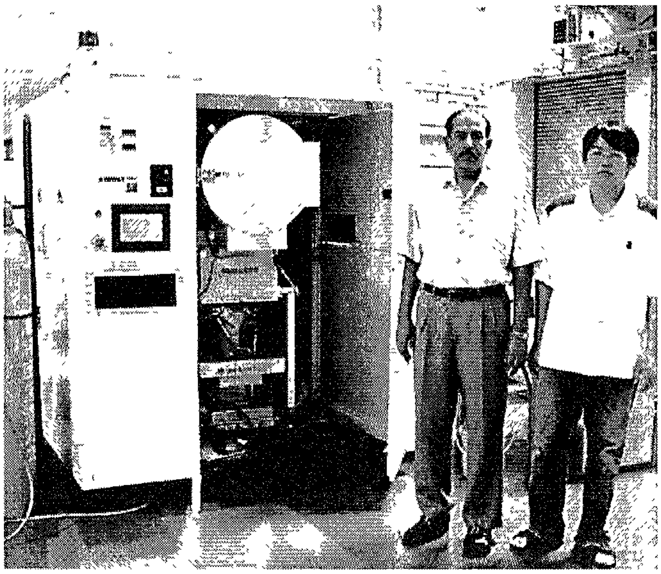


Fig. 19 Pilot plant of RVNRL with low energy electron accelerator

Figure 20 shows some results obtained by this plant. Remarkable reduction of the initial investment and vulcanization cost of RVNRL can be expected by utilization of low energy electron accelerator.

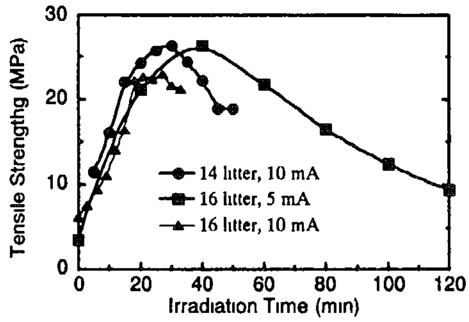


Fig. 20 Results obtained by using the pilot plant

4. RADIATION DEGRADATION OF NATURAL POLYMERS

It is well known that the polysaccharides (carbohydrates) such as sodium alginate, chitosan and carageenan are easily degraded by irradiation. Recently it was found that the degraded polysaccharide has various kinds of biological activities such as promotion of plant growth[15)], anti-bacterial activity[16)], suppression of heavy metal stress[17)]. Radiation degradation of polysaccharides is an emerging and promising area of radiation processing.

Low energy electron accelerator is useful tool to degrade polysaccharides. Figure 21 and Figure 22 show molecular weight change of sodium alginate in 1 wt % aqueous solution with γ-rays and EB, respectively. The EB irradiation was carried out by the RVNRL pilot plant described above. It is clear that there is no remarkable difference between EB and γ-rays in the degradation of sodium alginate. However, solid state degradation with γ-rays will be more easily, even though the high dose is needed. Strict cost comparison between liquid irradiation with low energy EB and state irradiation with γ-rays should be carried out.

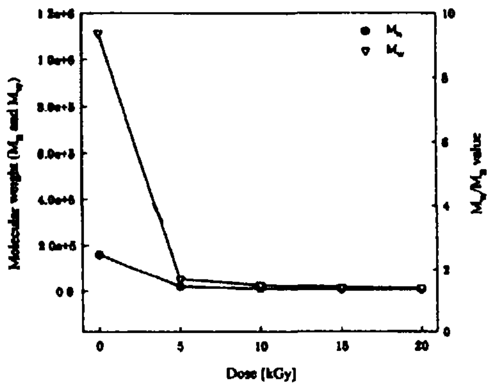


Fig. 21 Molecular weight change of sodium alginate by γ -ray irradiation

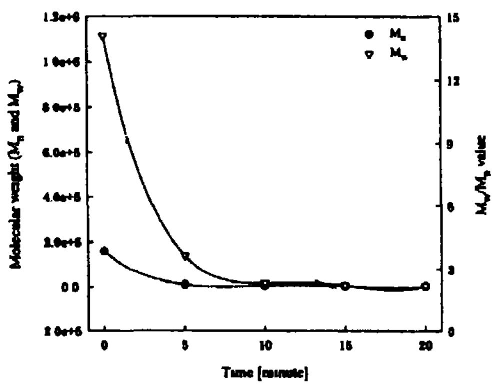


Fig. 22 Molecular weight change of sodium alginate by 250 keV EB irradiation

5. CONCLUSION

Low energy electron accelerator is a practical radiation source for processing of liquid. Emulsion polymerization, RVNRL and degradation of natural polymers are the potential application field of low energy electron accelerator. However, the reduction of price and maintenance cost of the EB machine is needed for the promotion of radiation processing of liquid with low energy electron accelerator.

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