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31 Radiation Processing in Japan

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1. Introduction

Economic scale of nuclear industry in Japan in 1997 was investigated by a study group organized by TRCRE JAERI in 1999. Table 1 shows summary of the investigation. It was ¥15.85 trillion ($13,108 million), including nuclear energy industry and radiation applications in industry, agriculture and medicine. This value is higher than GDP (Gross Domestic Product) of Malaysia ($9,788 million) and lower than that of Thailand ($15.391 million). Total production value of radiation application accounted for 54% of nuclear industry. Clearly, radiation application has larger economic impact than that of nuclear energy industry.

Table 1 - Economic Scale of Nuclear Industry in 1997 (Unit: ¥billion)

	Field	Production Value		Share
Radiation Application		8,573.8		54.1%
	Industry		7,266.6	
	Agriculture		116.7	
	Medicine		1,190.5	
Nuclear Energy		7,274.2		45.9%
	Nuclear Power Generation		5,661.3	
	Nuclear Industries		1,612.9	
	Total	15,848.0		

Industrial application of radiation is divided into five groups, namely non destructive test (NDT), RI instruments, radiation facilities, radiation processing and ion beam processing. Table 2 shows actual production value by these groups. More than 70% of the total production value was brought about by ion beam processing. Ion beams are used for the production of IC and semiconductors. There were about 310 NDT inspection companies. Inspection service charges were evaluated as production value, instead of production value of radiography apparatus. NDT using radiation was estimated to be 24.6% of service charges of ¥126.7 billion. RI instruments used were thickness gauges, level gauges, density gauges, moisture gauges and gas chromatograph. Total production value was estimated to be ¥65.4 billion. Total installation costs of radiation facilities were estimated to be ¥369.3 billion in medical field and ¥29.9 billion in industrial field. Economic scale of radiation processing is evaluated by production value of radiation processed products. It was estimated to be ¥1.39 trillion.

Table 2 - Production Value of Industrial Application of Radiation (Unit: ¥100 million)

Field	Production Value
Non Destructive Test	312
RI instruments	654
Radiation Facilities	4,274
Radiation Processing	13,867
Ion Beam Processing	53,559
Total	72,666

In this paper present and future economic prospect of radiation processing of polymers will be reviewed.

2. Radiation Processing

Radiation processing is defined as an industrial application of chemical reactions induced by radiation. Radiation reactions are utilized in polymer processing, radiation sterilization and food irradiation. Main radiation reactions are chain scission, recombination of radicals, addition of radicals to unsaturated double bond and oxidation. Practically important radiation reactions are crosslinking of polymers by recombination of polymer radicals, initiation of radical polymerization and degradation of polymers. Table 3 shows production value of radiation processed products. Polymer processing accounts for 80% of the total value of radiation products.

Table 3 - Production Value of Radiation Processing (Unit: ¥100 million)

Field	Production Value
Polymer Processing	11,026
Sterilization	2,903
Food Irradiation	19

2.1 Polymer processing

Crosslinking, graft polymerization, EB curing, degradation and polymerization are the main fields in polymer processing by radiation. No plant is operated for radiation polymerization in Japan. Table 4 shows the production value of radiation processed polymer products. Contribution of the crosslinking technique to the economy is outstanding among them due to wide applications to improve thermal and mechanical properties of polymers.

Table 4 - Production value of Radiation Processed Products (Unit: ¥100 million)

Field	Production Value
Crosslinking	10,981
EB Curing	30
Graft Polymerization	10
Degradation	5

2.1.1 Radiation crosslinking

The first success in radiation processing in Japan was the production of heat resistant wires by crosslinking in 1964. Subsequently, large numbers of radiation crosslinked products are supplied to the car industry and electronic industry. Table 5 shows the production value of radiation crosslinked products. Tires are outstanding among the radiation crosslinked products, followed by wire/cable, foams and heat shrinkable tube/film. Other crosslinked products include small rubber parts, SiC fiber and latex gloves.

Table 5 – Production Value of Radiation Crosslinked Products (Unit: ¥100 million)

Field	Production Value
Tires	10185
Wire & Cable	450
Foams	179
Heat Shrinkable Tube & Film	165
Other crosslinked products	2

A. Tires

Six companies (Bridgestone, Yokohama Tires, Sumitomo, Toyo Tires, Ohtsu Tires, and Michelin-Okamoto) produce about 170 million tires in Japan. Among them five companies installed electron accelerators. Fig. 1 shows increases in production of radial tires and total energy of medium energy electron accelerators (500 - 800 keV) installed in tire manufacturers. These accelerators are used for pre-vulcanization of carcass ply of radial tires to increase green strength. Pre-vulcanization of inner liner of radial tires is also applied by few companies by using low energy electron accelerators. Radial tires accounted for 91.3 % of tires in 1997. Total production value of tires by five companies was ¥1.110 trillion. The production value of radiation processed tires was estimated to be ¥1,018.5 trillion.

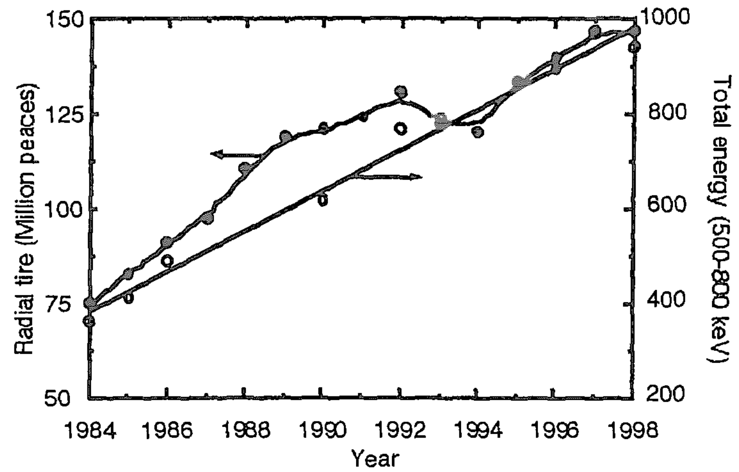

Fig. 1 - Production of radial tires and total energy of medium energy electron accelerators in tire industry in Japan

B. Wires and cables

Total production value of wires and cables was ¥1.2335 trillion in 1997. Radiation crosslinking of wires and cables was applied by 16 companies. Production value of radiation crosslinked wires and cables were estimated to be ¥45 billion. The radiation crosslinked wires and cables show excellent heat resistant and abrasion resistance. Main markets of radiation crosslinked wires and cables are car industry and electrical industries. Huge amounts of radiation crosslinked wires and cables are incorporated in a car to reduce the total weight and to increase processability of the car.

C. Polyolefin foams

Radiation crosslinked, closed-cell type polyolefin foams were developed by Sekisui Chemical and Toray. Polyolefin foams are lightweight, heat insulating, shock absorbing, highly moldable, and non-water-absorbency. Due to these properties polyolefin foams have a wide range of applications such as molded interior car components, insulation materials for construction uses, jointing materials, pipe covers, miscellaneous industrial materials, consumer goods, and healthcare and sports products. Polyethylene and polypropylene are representative polyolefins used for production of plastic foams. Production values of polyethylene foams and polypropylene foams were ¥9.85 billion and ¥8.0 billion, respectively.

D. Heat shrinkable tubes

Heat shrinkable tubes were commercialized by four companies and total production value was estimated to be ¥15 billion. Crystalline polymers such as polyolefin and fluoropolymers are used for these products. Heat shrinkable tubes are used in many areas besides cars and airplanes. Protection of connecting parts of wedded wires and cables, optical fibers and pipelines. Heat shrinkable films produced by radiation are used for food packaging. Domestic production and import of the heat shrinkable films were 500 tons and 1,000 tons, respectively. Production value of heat shrinkable films was estimated to be ¥1.5 billion.

E. Other crosslinked products

Rubber parts built in cars such as O rings and oil hose are crosslinked by radiation. A plant for the production of SiC fibers by radiation crosslinking technique is operating by Japan Carbon Co. Ltd. Radiation vulcanized natural rubber latex gloves are used in nuclear power plants. Total production value of these products in 1997 was estimated to be about ¥ 200 million.

2.1.2 EB curing

Radiation curing of resins with low energy electron accelerator is the environmentally friendly process because it is solvent free and energy saving process. Examples of commercial application of electron curing in Japan are precoated steel panels, precoated steel coils, tunnel interior panels, floppy discs, anti-fogging films, thermo-sensitive paper, and pressure-sensitive adhesive films. However, this technique has not been utilized as expected due to emerging of UV curing technique. Total production value of EB cured products was estimated to be about ¥3 billion.

2.1.3 Radiation graft polymerization

Radiation graft polymerization is known as one of the best methods to modify solid polymeric materials such as film, membrane, fiber, and cloth. Battery separators and super-clean-air-filters used in LSI factories are commercially produced by this technique. Total production value of radiation grafted products was estimated to be about ¥1 billion.

2.1.4 Radiation degradation

Fine powders of PTFE are produced by radiation degradation technique in Japan. Total production value of radiation degraded products was estimated to be about ¥500 million.

2.2 Radiation sterilization

The market for industrial sterilization of medical devices is around ¥472.8 billion. As shown in Fig. 2, 56% of sterilized medical articles are sterilized by Co-60 and 4 % by electron beams. Sterilization with high-energy electron accelerator of 5-10 MeV is increasing. Three 10 MeV electron linear accelerators are installed in Hogi Medical Co. Ltd. to sterilize medical clothes. Four 5 MeV electron accelerators are also operating as contract irradiators.

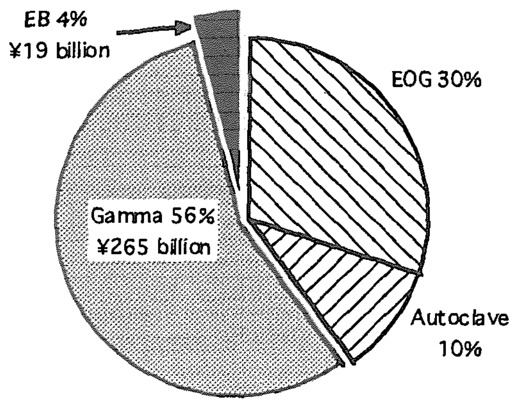

Fig. 2 - Share of sterilization methods

Packaging material and animal foods are sterilized by radiation, thought the amounts are not large as shown in Table 6.

Table 6 - Production Value of Radiation Sterilized Products 1997 (Unit: ¥100 million)

Field	Production Value
Medical Devices	2841
Packaging Materials	60
Animal Food	2

2.4 Food irradiation

Food irradiation was limited for the sprout inhibition of potatoes. The production value of the potatoes was ¥1.9 billion.

3. Future prospects of Radiation Processing of Polymers

Table 7 shows estimated relative productivity of EB machine (production value/number of operating EB machine). These data indicate that steady growth can be expected in crosslinking, but hard to growth in other processing.

Table 7 - Relative productivity of EB machine for Radiation Processing

Radiation Processing	Main Products	Number of EB Installed	Number of EB Operating	Production Value (¥billion)	Relative Productivity
Crosslinking	Radial Tires	28	17	1,018	59.9
	Wire/Cable	60	43	45	1.05
	Foams	16	8	18	2.25
	Tube/Film	14	12	17	1.42
Graft Polym.	Membrane	<5	2	1	0.5
EB Curing	Coating etc	48	<20	3	<0.15

3.1 Crosslinking

Most of the radiation crosslinked products are used in car industry. Cost reduction requirement from car companies to the parts suppliers is severe. There are competitive technologies for crosslinking. For example, the percentage of radiation crosslinked plastic foams in the total of plastic foams is only 2.5%. Radiation crosslinking technology has several advantages over the other technologies. However, cost of crosslinking by radiation is higher than the other crosslinking techniques. Reductions of the initial investment (price of EB machine) are desirable to advance the traditional radiation crosslinking technique.

Radiation crosslinking technique has been applied to solid products so far. Crosslinking of polymer in aqueous solution or dispersion will expand the radiation processing. Hydrogel prepared by irradiation of aqueous solution of synthetic polymers such as PVA and PVP are applied for wound dressing. The mechanical properties of the PVA hydrogel is improved by in incorporation of carrageenan. Though carrageenan degrades by radiation, carrageenan incorporated hydrogel by irradiation has an excellent mechanical properties. This fact is interesting from the standpoint of application of the hydrogel and radiation crosslinking of degradable polymers.

Example of radiation crosslinking of dispersed polymer in water is vulcanization of natural rubber latex. Natural rubbers (cis-l, 4-polyisoprene) dispersed in an aqueous medium as fine particles are crosslinked easily with low dose. Fig. 3 shows the recently developed RVNRL process. The process consists of five steps, (1) mixing latex with n-butylacrylate (vulcanization accelerator), (2) irradiating the mixture, (3) dilution, (4) addition of PVA, and (5) centrifugation.

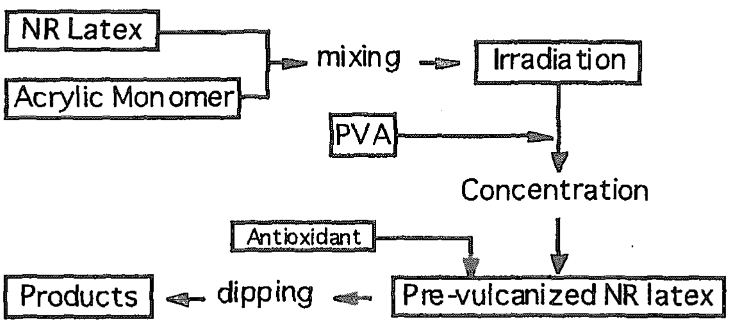

Fig. 3 - Process of radiation vulcanization of natural rubber latex

The resulting radiation vulcanized latex is used for the manufacture of latex products by a conventional coagulant dipping process. The radiation vulcanized latex does not contain dithiocarbamates, sulfur and zinc oxide that are used in the conventional vulcanization. In addition, radiation decomposes natural rubber proteins that cause serious allergy. Combination of dilution, PVA addition, and centrifugation of the radiation vulcanized latex reduces the amount of proteins of the rubber films to very low level by short term leaching. The radiation vulcanized latex has the following advantages over conventionally vulcanized NR latex with sulfur:

No fear of protein allegy
Absence of N-nitrosamines
Very low cytotoxicity

Easy degradation in the environment
Transparency and softness
Less formation of SO_2 when burned

Another promising crosslinking techniques that have not yet utilized are crosslinking of polymer blends at high temperature. Polymer material that has gradient distribution of crosslinking can be produced by irradiation of electron beams with adequate energy.

3.2 Graft polymerization

Besides radiation method, there are several graft polymerization methods. Most popular method is chemical initiator method. 540,000 tons of ABS resins are products by the chemical initiator method. Advantage of radiation graft polymerization is the modification of deep inside of arbitrary shape of product. Radiation method has limited uses to produce value added functional materials. Extreme reductions of the initial investment (price of EB machine) and to find proper products are necessary factors for the further promotion of radiation graft polymerization technique.

3.3 EB curing

EB curing has been facing with severe competition with UV curing. Extreme cost reductions of EB machine and EB curable resins are essential for the further encouragement of EB curing.

3.4 Degradation

Emerging application of radiation degradation technique is focused on natural polymers. Radiation degraded marine carbohydrates such as alginate, carrageenan, and chitin/chitosan have special biological activities. Plant growth promoter, antimicrobias, heavy metal suppressor will be produced from radiation degraded marine carbohydrates. Radiation degradation of pulp cellulose can significantly lower production costs and can provide critical environmental benefits in viscose industry.

3.4 Polymerization

Radiation-induced radical polymerization is hard to compete with conventional polymerization in terms of initial investment and quality of polymers. Undeveloped area of radiation-induced polymerization is high dose rate polymerization with electron beams. New polymer can be produced at high dose rate irradiation because cationic polymerization processs becomes predominant.

4. Conclusion

Present situation of radiation processing was reviewed. Very slow expansion is anticipated in the crosslinking of solid products, graft polymerization and EB curing. New generation of radiation processing will be crosslinking of polymers in solution and dispersion. Radiation degradation of natural polymers is expected to develop new area of radiation processing. Furthermore, remarkable progress in electron accelerator is necessary to support the radiation processing.