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# Introduction to Electron Beam Processing

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Industrial application of electron accelerator(EB) started in 1960 with production of heat shrinkable film using EBG(from GE). After that, manufacturing technique of accelerators has progressed rapidly, and various types of EB machines are used for commercial applications today. Radiation effects used in industries are classified into physical, chemical and biological ones. EB applications in polymer industries are mainly based on the chemical effects, i.e., crosslinking and graft-polymerization for modification of polymer materials.

Radiation sterilization of medical products is based on biological effect, and now a big application field of radiation. In this field, Co-60 have been used as radiation source so far. Recently high energy electron accelerators have been developed and introduced in industries.

## 1. A general features in the irradiation of polymers

Radiation can affect the molecular weight of polymer in two ways; increase by linking polymer molecule [cross-linking] and decrease by main-chain degradation [scission]. The principal chemical reactions are as follows:

**Excitation**

$$P \rightarrow P^*$$

**Scission**(main-chain degradation, free radical formation)

$$P^* \rightarrow R_n\cdot + R_m\cdot$$

**Crosslinking**(termination)

$$R_n\cdot + \quad R_m\cdot \;\rightarrow\; R\text{-}R$$

where **P** is polymer; $\mathbf{P}^*$ excited polymer; $\mathbf{R_n}\cdot$, $\mathbf{R_m}\cdot$, **R·** polymer radicals; **R–R** crosslinked polymer.

Small chemical changes induced by radiation cause large changes in the physical properties of some polymer. This is very important in the radiation chemistry of polymer, and lead to industrial application of radiation processing of polymer.

Although cross–linking and degradation may occur to some extent simultaneously, one of them must predominate. Table 1 shows classification of polymers(1), the predominant reaction for pure polymers irradiated in the absence of oxygen is shown.

## 2. EB machine

EB machines are classified by an energy of the electron beam as;

**·Low energy accelerator**

Non scanned and radiation self–shielding types are typical, and the energy range is 150–300 keV(300–500kW). The high voltage terminal of the machine is connected to the power supply by a flexible cable. Typical industrial applications are curing of coatings, of printing inks, of adhesives and crosslinking of thin plastic films.

**·Medium energy accelerator**

Various types have been developed in the energy range of 0.3 to 5MeV, i.e., Cockcroft & Walton, Dynamitron, Insulating Core Transformer type and resonant transformer type, etc. To prevent associate X–rays, thick concrete shielding surrounds the irradiation room. These EB machines are now used in industries with power up to 200 kW, and main applications include crosslinking of plastics, vulcanization of rubber and modification of polymers.

**·High energy accelerator**

Above 5MeV EB machine, 10MeV linear electron accelerators are now used in industries for sterilization of medical products, etc. As several megawatts of klystron tubes are required to produce the acceleration field, the output of power is about 20 kW in maximum.

## 3. Application of EB machine in industries

A number of EB machines have been installed in Japan as shown in Fig.1(2). As indicated from this figure, the number of machine for research & development is increasing with high rate. These are almost low energy machines that are introduced in industries. This means there is à large latent need for low energy EB uses in future.

EB applications in industries are for modification of polymer materials using mainly radiation crosslinking effects, i.e., for production of heat-resistant wires/cables, and heat shrinkable tubes/sheets, and for paint curing. Production of battery separator is an example of application of radiation graft-polymerization. This radiation technology is a unique technology for introducing of various functions to various shape materials such as films, fibers and hollow fibers.

Radiation processing using oxidation effects may be promising for application to removal of pollutants in flue gases and waste water. Considering application to environmental preservation technologies, on the other hand, a large mass treatment ability is needed generally, that is large energy output of radiation source are necessary. So uses of Co-60 sources are limited actually, we have to suppose to use large electron accelerators for environmental preservation.

## 4. Engineering of EB Processing

When EB machines are used in radiation processing, there are a few engineering problems.

The first is that the penetration range(reaction zone) of EB in materials is very thin, so thick materials can not be treated by EB. In sewage sludge disinfection treatment by EB, for example, most important technology is how to make a thin layer of sludge. The pilot plant test of composting of sewage sludge was carried out in JAERI/Takasaki(3). In this case, sludge cakes are irradiated by EB for disinfection followed by fermentation. The raw sludge was transported from a reservoir to a flat nozzle by a sludge pump. The sludge thickness was adjusted to be 6 mm for 2MeV EB irradiation. It was proved that continuous disinfection can be performed.

The second is that the dose rate in the range(reaction zone) is very high, so high rate treatments of thin layer material are required. In EB treatment of waste water such as aerobic decomposition of organic pollutants, for example, it is necessary to remove the wastewater quickly from the reaction zone, and effective oxygen supply is required during irradiation. If design of irradiation vessel using EB is not adequate, irradiation will be continued after consuming up of pollutant or oxygen in the reaction zone, which lead to a low efficiency of energy utilization. Fig. 2 shows a dual–tube type bubbling column reactor for aerobic treatment of waste water using EB(4). The reactor is composed of an outer tube and an inner tube. EB comes from the top, and the surface portion of water in the range will be reaction zone. Air or oxygen gases are introduced in the inner tube from the bottom. So waste water go up in the inner tube by airlift, and led to the reaction zone and flow down in the annular portion before dissolved oxygen is consumed completely by irradiation. Oxygen is effectively supplied to the liquid in this oxygen absorption zone in the inner tube.

The third is that EB irradiation of thick insulating materials accumulates electric charges in materials that lead to break of materials, so EB processing is not applied for crosslinking of thick electric cables.

## 5. Dosimetry of EB

Radiation processing has grown rapidly in the field of polymer modification, sterilization of medical products, etc. Radiation dosimetry, measurement of absorbed radiation energy in target materials, is very important for quality control of the processes. There are many kinds of dosimeters as shown in Table 2(5). Dosimetry is also important to transfer the process from the laboratory to the production stage.

For dosimetry in electron beam processing, film dosimeters are used mainly. The absorbed dose is evaluated on the changes of optical density induced by radiation. In some film dosimeters such as alanine film dosimeter, dose is determined by the number of free radicals produced by irradiation using ESR.

CTA(Cellulose triacetate) dose meter developed in JAERI is useful as routine a dosimeter in radiation processing, especially for EB processing. It has linear response with dose up to 150kGy. CTA film is in the form of long tape(thickness: 0.125 mm, width:8 mm). Using this film, it is possible to trace automatically the dose distribution along the CTA tape as shown in Fig.3(6). CTA dose meter is manufactured also in sheet form. So, microbeam scanning type dose reader makes it possible to give two dimensional dose profiles.

## 6. Safe Operation of EB machine

With increasing reliability and availability of the EB machines, their merit over gamma sources has been recognized: variable energy ranges, high utilization efficiency, large outputs. There are no generation of radiation, in principle, when beam current was switched off. Safety system in EB irradiation facilities, however, is very important for proper operation. Because the occurrence of substantial dose rate in the irradiation field under the beam scanner, due to dark current from the beam acceleration tube is not unexpected, even when the beam current is off(7,8,9).

## 7. Recent topics on EB Processing under Development

### (1) Two pilot-scale tests for EB treatment of exhaust gases(10,11)

The pilot test for flue gas from coal-burning boiler was carried out under the joint research of JAERI, Chubu Electric Power Company and Ebara Corporation until 1993. The plant was constructed in the site of Shin-Nagoya thermal power plant of Chubu Electric Power Company in Nagoya. The capacity of the pilot plant is 12,000Nm$^3$/h. Gas is cooled at the cooling tower to 65 °C. After adding $NH_3$, the gas is led to irradiation vessel and irradiated by electron beams of 800 kV. Irradiated gas is led to the electrostatic precipitator and bag filter to remove byproducts; ammonium sulfate and ammonium nitrate.

The pilot test for EB treatment of incinerator gas was also carried out under the joint research of JAERI, Matsudo-city and NKK. The capacity of the pilot plant at Matsudo-city is 1,000 Nm$^3$/h. The gas is irradiated by EB(900kV) under spray of $Ca(OH)_2$ slurry. Irradiated gas is led to the bag house to remove calcium sulfate, chloride, and nitrate.

### (2) Development of high efficient various absorbents

Radiation-induced grafting is effective for introducing a new functional group to various forms of existing polymeric materials such as sheet, fiber or hollow fiber. This technology is going to be introduced to an industry for producing a high efficiency filter for clean rooms in semiconductor device factories. Fibrous or film materials are irradiated by EB or gamma ray to produce active points on the surface, and contact with monomers. Then graft polymerization occur on the active points. By functionalization such as sulfonation or quaterniza-tion, for example, functional group contained resins are obtained.

Table 3 shows examples of functional materials, which are produced using radiation-induced grafting. Various functional groups can be introduced by changing grafted monomer. There are battery separators, absorbents for toxic gases, functional hollow fiber membrane as Co absorbent and absorbent for U from sea water. Co ion absorbent is a functional hollow fiber. Polyethylene hollow fibers are irradiated by EB, and GMA(Glycidyl methacrylate) is grafted on/in fibers. Grafted chains are treated by IDA(Iminodiacetic acid)(12,13). Uranium absorbent is a chelating resin containing amidoxime groups which are introduced on fibrous or nonwoven polypropylene by EB grafting technology(14).

**(3) Development of super heat resistant ceramic fiber**

The SiC fiber "Nicalon" from Nippon Carbon Co. Ltd. has been manufactured from polycarbosilane(PCS). The SiC fiber is prepared by melt spinning of PCS, infusible treatment by oxidation curing, and pyrolysis as shown in Fig. 4. The heat resistance of this fiber is around 1200C, because the fiber contains oxygen in the process of curing by thermal oxidation. New SiC fibers were synthesized from polycarbosilane fibers by electron beam irradiation curing(crosslinking). In this process, PCS fibers are irradiated by an electron beam with dose rate of 2-5kGy/s up to 15MGy in He atmosphere. The cured PCS fibers were heat-treated in Ar gas up to about 1500K. Heat resistance of SiC fiber with low oxygen content less than 0.5wt% is about 2000K. Comparing with "Nicalon", the new fiber with low oxygen content is improved by 500K(15,16).

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## Table 1 Classification of Polymers

| Crosslinking Type | | Degradation Type | |
|---|---|---|---|
| Polyethylene | $-CH_2-CH_2-CH_2-CH_2-$ | Polyisobutylene | $-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}$ |
| Polypropylene | $-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-$ | Poly α-methylstyrene | $-CH_2-\overset{CH_3}{\underset{C_6H_5}{C}}-CH_2-\overset{CH_3}{\underset{C_6H_5}{C}}-$ |
| Poly(vinyl chloride) | $-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-$ | Polymethacrylates | $-CH_2-\overset{CH_3}{\underset{COOR}{C}}-CH_2-\overset{CH_3}{\underset{COOR}{C}}-$ |
| Polystyrene | $-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH}-$ | Polymethacrylamide | $-CH_2-\overset{CH_3}{\underset{CONH_2}{C}}-CH_2-\overset{CH_3}{\underset{CONH_2}{C}}-$ |
| Polyacrylate | $-CH_2-\underset{COOR}{CH}-CH_2-\underset{COOR}{CH}-$ | Polytetrafluoro ethylene | $-CF_2-CF_2-CF_2-CF_2-$ |
| Polyacrylamide | $-CH_2-\underset{CONH_2}{CH}-CH_2-\underset{CONH_2}{CH}-$ | | |

## Table 2 Characteristics of Various Dosimeters

| Dosimeters | Principle | Big dose by EB | Dose range (Gy) | Dose rate (Gy/h) |
|---|---|---|---|---|
| Ionization chamber | Iionization in gas | X | 1 - $10^3$ | 1 -3x$10^5$ |
| Calorimeter | absorbed energy | G | $10^2$– $10^5$ | $10^4$– $10^7$ |
| Frick dosimeter | $Fe^{2+}$ to $Fe^{+3}$ | F | 5x10 - 2x$10^3$ | 1 - $10^7$ |
| Celium d. | $Fe^{+4}$ to $Fe^{+3}$ | F | $10^3$– $10^6$ | 1 - $10^7$ |
| Alanine d. | radical formation | F | 10 - $10^5$ | 1 - $10^7$ |
| PMMA d. | coloration | F | $10^4$– $10^6$ | $10^3$– $10^7$ |
| CTA d. | coloration | G | $10^4$–3x$10^5$ | $10^2$– $10^7$ |
| Radiachromic d. | coloration | G | 7x$10^2$– $10^5$ | 1 - $10^7$ |
| Blue cellophan d. | decoloration | G | $10^4$–2x$10^5$ | $10^2$– $10^7$ |
| Themoluminescence d. | color center form. | F | 1 - $10^4$ | 1 - $10^7$ |
| Glass d. | coloration | F | 2x$10^2$– $10^4$ | 10 - $10^7$ |

G : good F : fair X : bad

## Table 3 Synthesis of Various Absorbent by Radiation Graft Polymerization

| Substrates | Monomers | Treatment & Functional Groups | Utilizations |
|---|---|---|---|
| Polyethylene Films (25μ m) | Acrylic Acid $CH_2CHCOOH$ | Alkali Treatment -COOK or -COONa | Battery Separators |
| Nonwoven Poly-propylene(1–20μ m ) | Styrene | Sulfonation $-SO_3H$ | Absorbents for Toxic Gases($NH_3$, $H_2S$) |
| Polyethylene Hollow Fiber(id:0.62mm) | Glycidyl Metha-acylate(GMA) | Iminodiacetic Acid (IDA) $-N(CH_2COOH)_2$ | Functionalized Hollow Fiber Membrane Co Absorbent |
| Fibrous or Nonwoven Polypropylene (1–20μ m) | Acrylnitrile $CH_2CHCN$ | Amidximation with Hydroxyamin $-C(NOH)(NH_2)$ | Absorbents for U from Sea Water Heavy Metal Ions |

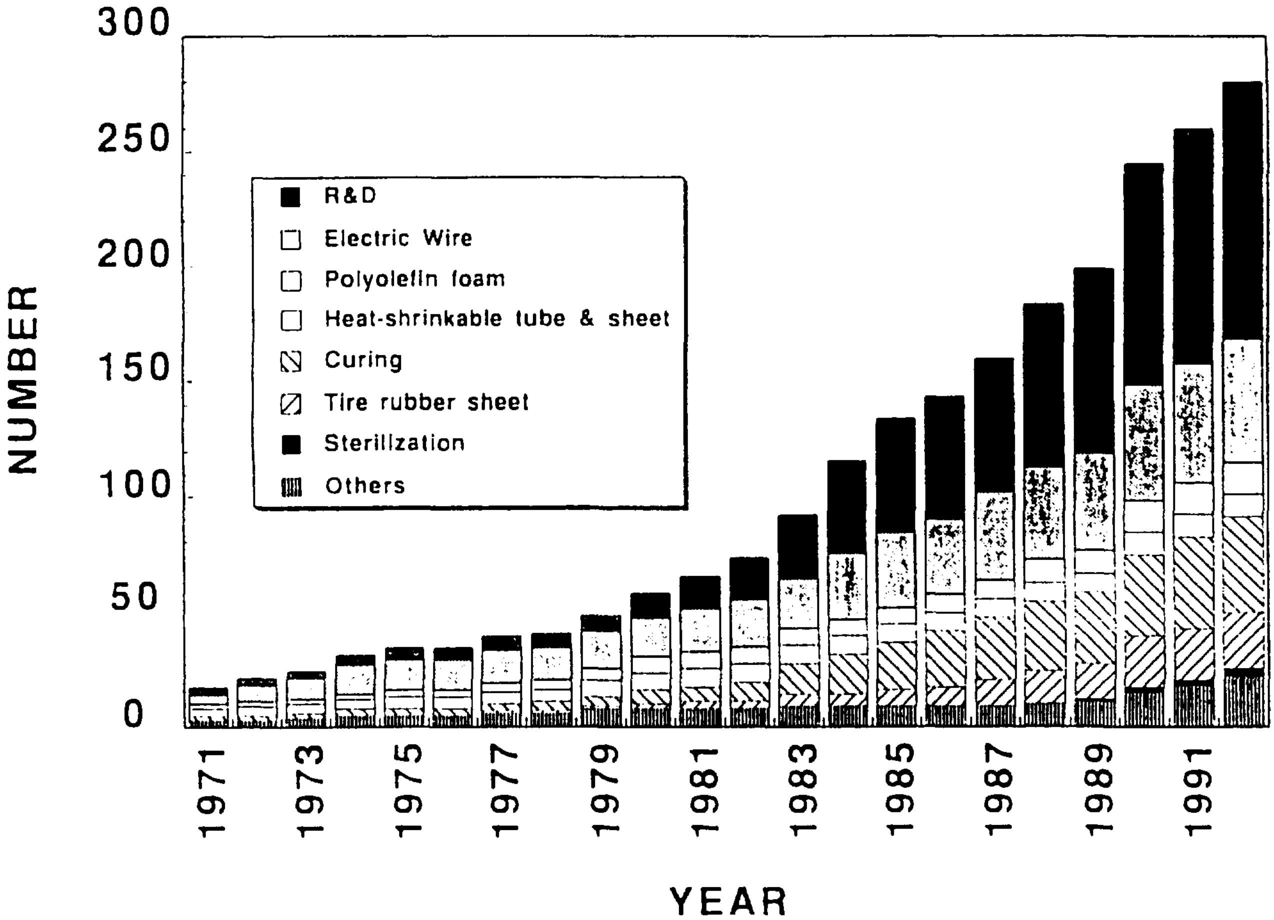


**Fig. 1 Number of EB Machine in Japan**

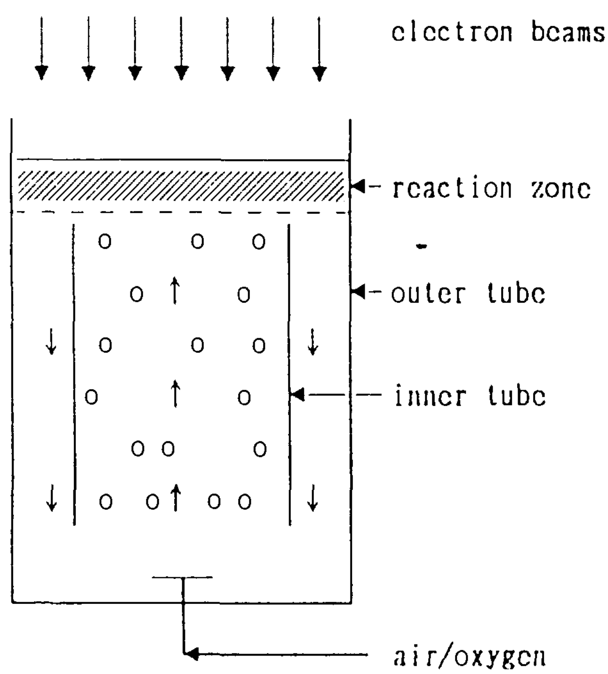


**Fig. 2 Dual-Tube Bubbling Column Reactor**

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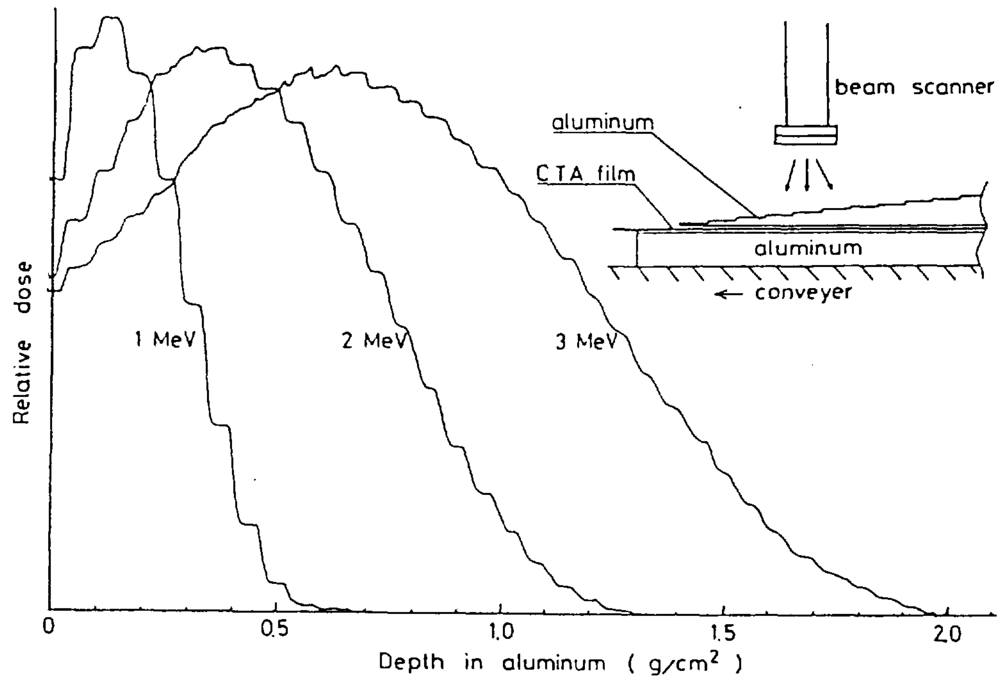


**Fig. 3 Dose Distribution Measurement Using the CTA Tape**

A long strip of CTA tape is inserted between a wedge-shaped aluminum absorber graded stepwise with a slight gradient and thick aluminum plane.

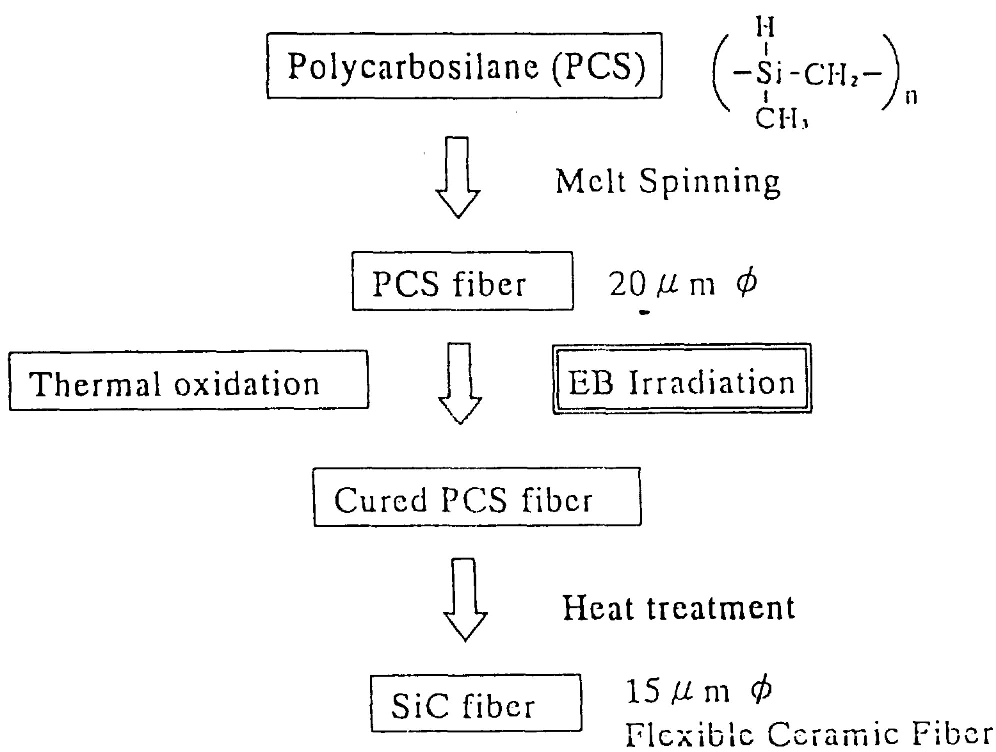


**Fig. 4 Process of SiC Fiber Synthesis from Polycarbosilane**