Preparation and Submission of a Manuscript for the Proceedings of the International Topical Meeting on Nuclear Research Applications and Utilization of Accelerators

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1. Introduction

Japan is a pioneer for application of electron accelerators. In 1963 the Takasaki Radiation Chemistry Research Establishment (TRCRE) of Japan Atomic Energy Research Institute (JAERI) was established to be fully devoted for research and development of radiation processing using electron accelerators and Co-60.

The first industrial application of electron accelerator in Japan was achieved to produce heat resistant wires by cross-linking polyethylene insulators in 1971. Since then industrial applications of electron accelerator have continuously grown in production of varieties of value added polymers, sterilization of medical supplies and environmental protection with collaboration with the Takasaki Radiation Chemistry Research Establishment.

The paper describes current status of industrial use of electron accelerator and R/D approaching commercial application in Japan.

2. Electron Accelerators with Different Energy Ranges

In Japan there are 248 electron accelerators used for industrial applications and 148 for research and development.

Electron accelerators with different energy ranging from 100 keV to 10 MeV are used for different purposes as shown in Table 1. Accelerators with medium energy ranging of 300 keV to 3 MeV are most commonly used for industrial applications. Low energy accelerators are designed as self-shielded equipment to save cost of shielded irradiation room and mostly used for surface coating, printing and grafting application. High energy accelerators of 3 MeV to 10 MeV are mainly used for sterilization of medical products, and for radiation services for a variety of products.

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3. Industrial Applications of Electron Accelerators

(1) Environmentally Friendly Coating and Printing

Major applications of low energy accelerator are curing of surface coating and printing at very high speed. Electron beam (EB) curing is more environmentally friendly because it converts solvent into polymer coating without emission of volatile organic solvents to environment.

The EB curing is also energy saving due to elimination of evaporation of solvent which is essential process for conventional coating technology. The EB curing is being increasingly used in coating and printing industry because of superior quality of products, such as high scratch resistance and hardness as well as high speed and large production capacity.

Challenges of EB curing technology are to develop reliable and low cost accelerator of lower energy of 30 to 100 keV, and less expensive coatings and inks. In case of transparent coatings, UV curing is competitor to EB because UV is less expensive. Penetration range of

UV is very limited in pigmented coatings, and quality of finished product of UV curing is lower than that of EB.

(2) Cross-linking of Polymeric Materials for Upgrading Properties

Application for radiation induced cross-linking of polymers is most widely used in a variety of industries, such as automobile tires, wire/cable and heat shrinkable materials.

① Wires and cables

All major wire and cable companies in Japan are using several electron accelerators each for production of heat, flame and chemical resistant wires. Radiation cross-linking is only technology commercially used to produce such a high quality wires used for automobiles, home appliances, equipments and plants where wires are exposed at temperature higher than normal one.

Distinct advantage of radiation technology is to cross-link wire insulators at room temperature and solid state at high production rates. Challenge for this application is cross-linking of thicker insulators for large diameter cable using high energy accelerator.

②Automobile tires

In Japan more than 90% of automobile tires are produced by partial cross-linking of rubber using electron accelerator. Major tire companies are using electron accelerators to irradiate rubber sheets before molding them into tires. Radiation cross-linking of rubber sheet does not need sulfur for vulcanization and provides high speed continuous processing at room temperature.

③Heat shrinkable sheets and tubes

Memory effect of electron beam cross-linked polymers is commercially used in Japan to produce heat shrinkable materials. Heat shrinkable tubes are used for insulation of electrical junctions. Heat shrinkable sheets are used for food packaging and protection of metal pipes from corrosion.

④Foamed plastics

In order to produce foamed products, polyethylene sheets containing chemical forming agents are irradiated by electron beams to be cross-linked.

Cross-linking is needed to produce individual stable foam in molten polyethylene in foaming process. The foamed products are used a variety of applications such as packing, mats, automobile components and floating jackets.

⑤ Hydrogel wound dressing

More recently production of radiation cross-linked PVA hydrogel wound dressing has been commercialized in Japan using low energy electron accelerator in continuous process as shown in Fig. 1. The hydrogel dressing is much more patient friendly because heeling of wound is faster than gauge, and patient has no pain when dressing is peeled off.

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(3) Radiation Grafting for Production of Functional Polymers

①Battery separator

Radiation grafting is first used for industrial application in Japan long time after Chapiro first reported the unique technology in 1950's. The JAERI, TRCRE developed technology to produce long life battery separators 1,2). Thin polyethylene film irradiated by electron beams to form long lived radicals on its backbone. Then, acrylic acid is grafted on the radicals in solution. The continuous process of grafting reaction was developed in collaboration with Yuasa Battery Co. to produce homogeneously grafted and smooth shaped thin membrane. The produced membrane separator has better chemical resistance and much longer life time than conventional membrane. The membrane is exensively used in Japan for battery production.

②Deodorant and air cleaning fabrics

Deodorant and air cleaning fiber by removing ammonia are commercially produced in Japan by radiation grafting of polyethylene fiber. These products are used for cleaning air for LSI fabrication rooms, and deodorants. Industrial plant of continuous grafting of polyethylene fiber using self-shielded electron accelerator of 300 keV is shown in Fig. 2.

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(4)Emerging Applications of Accelerator for Polymeric Materials

① Super heat resistant silicone carbide fiber 3)

Silicone carbide (SiC) fiber with excellent heat resistance is produced in Japan by electron beam cross-liking of polycarbosilane (PCS). First, molten PSC is extruded to fiber and then cross-linked by electron beams of 10 MGy in helium gas followed by pyrolysis in argon at 1500 C to detach hydrogen. In conventional process PSC fiber is cross-linked by thermal oxidation. Therefore, produced SiC contains oxygen to make heat resistance lower. Electron beam cross-linked SiC can maintain high tensile strengthen up to 1700 C while thermally cross-linked SiC up to 1200 C. The EB produced SiC has light density of 2.7 g/cm$_3$, high mechanical strength of 30 t/cm$_2$ and excellent heat resistance up to 1700 C being used as ceramic composites for different applications, such as outer wall of space craft. Commercial production scale is in the range of ten tons per year and will be increasing.

② Cross-linked Polytetrafluoroethylene (PTFE) 4)

PTFE is highly radiation degradable at normal temperature. However, at high temperature of 330-340 C slightly above its melting point in inert gas PTFE was found to be cross-linked by electron beams. The cross-linked PTFE has excellent wear resistance 1000 times higher than non-cross-linked one, and increased radiation resistance by two orders. The products are commercially used for sliding parts, roller and bearing. Production scale is about 10 tons per year.

③ Fuel Cell Membrane 5)

In Japan new fuel cell membranes are being developed in Japan Atomic Energy Agency (JAEA) by grafting polystyrene on commercially available polymer films such as PTFE, PFVd, PE and PP using low energy electron beams or ultraviolet light followed by sulfonation. Although irradiation of polymer films is limited in the surface less than 2 micron to avoid radiation damage of polymers, grafting reaction can extend whole region of 200 micron thick film. This technology produces poly-electrolyte fuel cell membrane with proton conductivity higher than 0.06S/cm with excellent chemical and mechanical properties.

④ Metal adsorbent produced by radiation grafting

Grafting functional polymer chain on polyethylene irradiated by electron beams can produce adsorbent of selected metals. JAEA has developed absorbent selective to uranium by grafting acrylnitrile onto polyethylene to be converted to amidoxime group. By pilot scale operation using this adsorbent in Mutsu Bay, 1kg uranium was successfully collected from sea water. For assurance of uranium supply in Japan for nuclear power, recovery of uranium from sea water is an option in future if it is economically competitive.

Metal adsorbent application is also being tested for recovery of rare metal, such as scandium and vanadium from hot-spring water of Kusatsu Hot Spring by pilot plant.

4. Electron Accelerator for Radiation Sterilization

Efficient sterilization of medical products and food packages including PET bottles is new and growing application of accelerator in Japan.

Co-60 radiation facilities are still major tool for sterilization of medical products. There is, however, a trend in Japan to use high energy electron beams of 10 MeV replacing Co-60 due to increasing concern about assurance of Co-60 supply, and improvement in the quality of high energy electron accelerator.

Recently sterilization of PET (polyethylene telephtalate) bottles for drinks by electron accelerator has been commercially used in Japan replacing chemical sterilization because of advantages of simplicity, reliability and low running costs. Sterilization capacity of plant with an accelerator of 300 keV is as large as 600 bottles of 500 ml. per minute. Plastic food packages are also commercially sterilized by electron beams.

5. Environmental Protection by Removing Pollutants by Electron Accelerator

(1) Cleaning Flue Gases from Fossil Fuel Burning Power Station

In1972 JAERI, TRCRE first demonstrated by continuous flow type plant of 60Nm3/h that 600-900 ppm of SO2 and 80ppm NOx were removed by 80% and 90%, respectively with absorbed dose of 40 kGy. Following the demonstration, extensive basic research was conducted to elucidate reaction mechanism of SO2 and NOx removals by radiation. 6) In 1993 collaboration of Ebara Corporation, JAERI Takasaki and Chubu Power Co. successfully demonstrated in large scale pilot plant of 12,000 m3/h removing 94% of SO2 and 80% of NOx in exhaust gases from high sulfur heavy oil burning power station.

In 1997 Ebara Corporation then constructed a commercial scale plant in Chengdu in China to remove SO2 and NOx with capacity of 300,000m3/h flue gas containing 1800ppm SO2 and 400 ppm NOx from coal burning power station of 90MW. Two units of electron accelerator of 800 keV x 400mA were used. The plant was successfully operated to achieve its design performance to remove 80% and 20% at the absorbed dose of 4 kGy.

Ebara Corporation constructed a commercial plant for cleaning exhaust gas from high sulfur oil burning power station of 220MW of Chubu Power Co. in 1998. During test operation of the plant, Ebara faced serious problems of continuous operation of 6 large capacity electron accelerators of 800keV x 500mA due to break down of power-supply. Similar power source break down happened for electron accelerator of 300 kW in Poland for the plant in Pomorzany power station, but solved by reducing energy from 800 keV to 700 keV to achieve successful continuous operation7).

Major issues for design and installation of industrial scale plant are well described by Chmielewski, A. in the recent IAEA publication entitled with ‘Radiation Processing: Environmental Protection’. Experience in Japan indicates the sensitive components are electron accelerator and ESP for continuous operation of industrial plant for appropriate period of time without break down. Manufacturing reliable large capacity electron accelerator from 500 to 1000 kW at reasonable cost is the most crucial challenge for future expansion of this technology in industrial use.

(2) Removals of Dioxin from Municipal Waste Incinerator Flue Gas 8)

Control of dioxin content in flue gas of waste incineration plant has been much stricter (from 80 ng/m3 to 1 ng/m3) in Japan in 2002. The pilot plant with capacity of 1000 m3/h was installed in the waste incineration plant of Takasaki city for removing dioxin from flue gas. By using one self-shielded electron accelerator of 300 keV x 40mA, 90% dioxin could be removed with 14 kGy.

(3) Removing Bad Smell of Gas from Plant of Drying Sewage Sludge

In Nanao city a mobile electron accelerator is used to remove bad smell from drying process of sewage sludge at waste water treatment plants for 2,000 inhabitants. Capacity of

plant is to clean gas flow at the rate of 360-400 m3/h using accelerator of 125 kV, 7.5 mA. The mobile irradiator is used for 3 waste water treatment plants.

(4) Removals of VOC by Electron Beams 9)

Some volatile organic compounds (VOC) such as benzene, formaldehyde and trichloro-ethylene are hazardous for human. JAEA group has found that trichloro-ethylene of 300 ppm can be decomposed completely with 10 kGy, and formaldehyde of 1500ppm can be effectively decomposed in much shorter time than that by catalytic thermal decomposition. Aromatic VOC such as benzene and xylene are stable against radiation and not easily decomposed.

6. Trends and Challenges of Electron Accelerator Application in Japan

(1) Trends

In Japan there is a trend of increasing application of high energy accelerator for sterilization of medical products replacing Co-60 irradiators due to increased cost and shortage of Co-60. Installation of low energy accelerator is increasing for curing of coating and printing for saving energy and environmental protection. Installation of low energy accelerator for sterilization of PET bottles and food packages is foreseen to increase.

Export of medium energy accelerators to Asian countries is increasing due to expansion of accelerator application in industry in developing countries.

Research and development aiming to develop new applications using electron accelerators including environmental protection and functional polymers are actively carried out at research institutes such as JAEA, industrial firms, and universities in Japan.

(2) Challenges

Electron accelerator application technology is still not well known by industries in terms of its distinct advantages over conventional processes. Dissemination of information and possible cooperation in applications of electron accelerator with potential end-users should be further enhanced.

In order to expand applications of low energy accelerators for curing coatings and printings which are more environmentally friendly, fast development of low cost accelerator with energy ranging 20-30 keV should be an important challenge.

Application of electron beams for environmental protection, such as cleaning flue gases and waste water is one of the most important fields to meet socio-economic needs. Development of accelerators with large capacity and reliability for one year continuous operation is extremely important for promotion of this important application.

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