2. Trend and Future of Radiation Processing of Polymers

K. MAKUUCHI

Takasaki Radiation Chemistry Research Establishment, JAERI

1233 Watanuki, Takasaki, Gunma, 370-1292 Japan

1. INTRODUCTION

Today five major Asian countries are cooperating with Takasaki Radiation Chemistry Research Establishment (TRCRE) in the field of radiation processing. It was 1980 when TRCRE was involved in cooperation with Asian countries. After 20 years, now we are going to enter a new ear of research cooperation. To make a fresh start we have to bind together by common interest and understanding on radiation processing. I will try to summarize and generalize our experience in cooperation with Asian countries for 20 years to create and develop a new cooperation strategy.

2. RADIATION PROCESSING OF POLYMERS

Figure 1 illustrates the radiation processing of polymer. Main processes are polymerization of monomers, crosslinking and degradation of polymers, graft polymerization and curing. Among them radiation-induced polymerization is not commercialized in Japan. This is believed that the polymers produced by radiation-induced polymerization have non-unique properties compared with those produced by conventional polymerization.

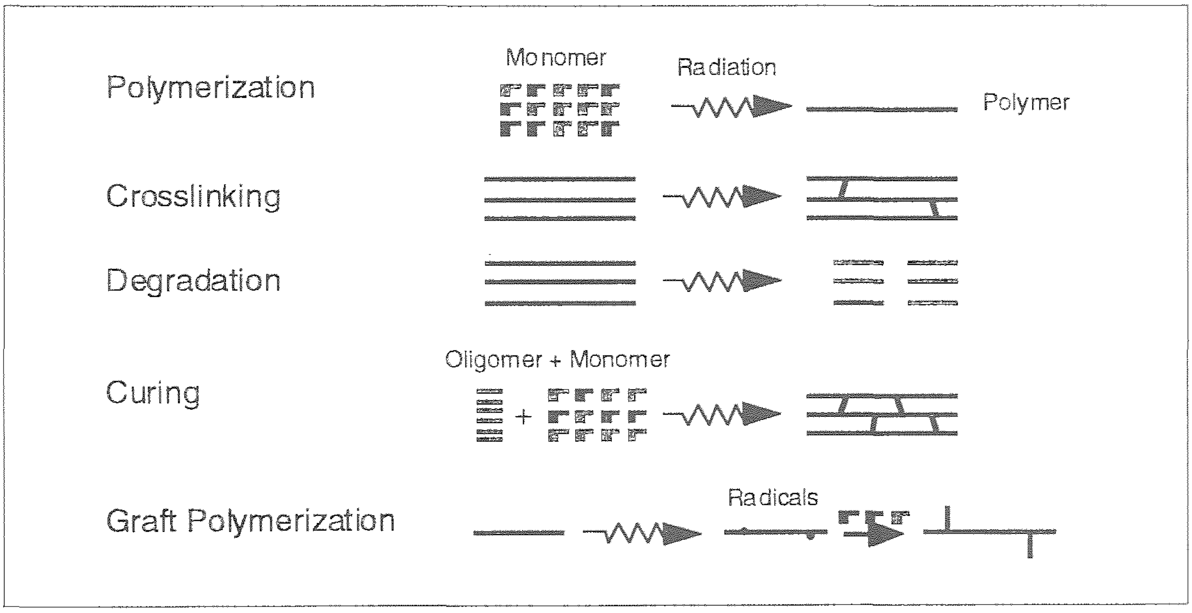

Fig. 1 Radiation processing of polymers

Table 1 indicates estimated economic scale of radiation technology in Japan, 1997. Most of radiation processes use electron accelerator. Table 2 shows the number of installed electron accelerator.

Table 1 Economic Impact of Radiation Processing in Japan, 1997

Process	Typical Products	Radiation	Output (M$)
Crosslinking	Radial tires	EB	1,0100
	Wire/Cable	EB	450
	Plastic Foams	EB	170
	Heat Shrinkable Tube	EB	160
	Others	EB	5
Degradation	PTFE Solid Lubricants	γ-rays、EB	5
Curing	Paper Coating	EB	30
Graft Polymerization	Battery Separator	EB、γ-rays	10

Table 2 Radiation Processing using EB in Japan

Process	Products	Installed EB
Crosslinking	Wire/Cable	60
	Tire	28
	Plastic Foam	16
	Heat Shrinkable Tube	14
	Heat Shrinkable Film	no data
	Vulcanization	no data
	SiC Fiber	1
	Paper Battery	1
	Hydrogel	1
Curing	Coatings, etc	48

2.1 Crosslinking

Radiation-induced crosslinking of polymer has been playing the leading role of radiation processing. This is the commercially most important area of radiation chemistry of polymers. The advantages of radiation crosslinking are rapid, easiness of control, cost effectiveness.

The main chemical issue related to the radiation crosslinking is that of enhancing the crosslinking and reducing the oxidative degradation during irradiation. Usually polyfunctional monomers such 1, 6-hexanediol diacrylate and trimethylolpropane triacrylate are used to enhance the crosslinking. For the reduction of the oxidative degradation the high dose rate irradiation is effective. This is one of reasons to use electron beams for crosslinking. Most of the radiation crosslinked products are used in automobile and electronic appliances such as TV sets, VTR and audio disc players. However, there are other methods to crosslink wire/cable. Comparison between the radiation method and other methods are shown in Table 3.

Table 3 Comparison of Crosslinking Technologies for Wire/Cable

Technological Aspect		Radiation	Peroxide	Silane
Applicable polymer	PE	○	○	○
	PVC	○	×	×
	Rubber	○	○	×
	Fluoropolymer	○	×	×
	Flame retarded	○	×	×
Processability		○	△	○
Compound shelf life		○	△	×
Rate of crosslinking		Large	Medium	Small
Uniformity of crosslinking		Depend on EB energy	Non-uniform	Uniform
Cost of compound		Low	High	High
Cost	Small scale	161	145	133
	Medium scale	127	127	118
	Large scale	100	115	109
Quality	Electric properties	◎	○	△
	Heat stability	○	○	△
	Appearance	○	×	△
Equipment		Complex	Simple	Simple
Initial Investment		High	Medium	Low

Heat shrinkable tubes and sheets are used for covers of distributing lines terminals, joint covers of telecommunication lines, protection of fuel pipe line, wrapper of foodstuffs and so on.

Five tire manufacturers are using electron accelerators for radiation crosslinking of tire components. Electron accelerator is used to crosslink the components partially to increase their green strength and to decrease their surface tackiness. The EB irradiated components are easier to mold and vulcanize without large deformation at high temperature and pressure.

A plant for production of heat-resistant silicone SiC fibers was constructed in Japan. The process consists of radiation crosslinking of polycarbosilane (PCS) fibers and heat treatment of the PCS. PCS fibers are irradiated up to 10-15 MGy by a 2 MeV EB under He gas atmosphere, then the fibers are converted to SiC at high temperature (ca 1,800 K) in Ar gas. The tensile strength and Young's modules are 2.5 GPa and 250 GPa, respectively. This technology was developed by TRCRE and transferred to the company through Research Development Cooperation of Japan (JRDC).

Poly(vinyl alcohol) hydrogel has been developed by TRCRE in cooperation with BATAN PAIR. This technology was transferred to one of a biggest medical device company (Nichiban Co. Ltd.) through JRDC. Wound dressings by this hydrogel are under clinical test.

2.2. Degradation

Irradiation of polytetrafluoroethylene which belongs to the radiation degradation polymers causes such an embrittlement that it can be crushed down to a medium particle size by grinders. The obtained fine powders are widely used as dry lubricants. Irradiated butyl rubber is also reused. Thus the degraded polymers by radiation contribute to recycling of used polymers. The radiation degradation technique will be useful for material and chemical recycling.

Recently, radiation degradation of cellulose has been applied for the viscose rayon production. Also degradated polysaccharides have been found to act as plant growth promotor. Radiation degradation of polysaccharides has a possibility to produce bioactive materials such as plant growth promoter and antibacterial. The details will be reported in this Proceeding.

2.3 Radiation graft polymerization

Two radiation-induced graft polymerization methods can be used for the modification of polymers, direct or simultaneous irradiation method and pre-irradiation method-grafting method. From a practical viewpoint, the pre-irradiation method is preferable because of the negligible formation of homopolymers and easier control of degree of polymerization.

Acrylic acid grafted polyethylene fibers are used as battery separator. The radiation graft polymerization can be applied for obtaining functional materials by converting the resulting graft chains into functional chains. Thus this technique can be applied for the preparation of adsorbents for various pollutants from waste water or air.

There are several non-radition process of graft polymerization. Table 4 summarizes the comparison between radiation and other graft polymerization. The principal advantages of the radiation-induced graft polymerization as a method of polymer modification may be freedom of trunk polymer selection. Inside of a complicate shaped substrate can be modified only by radiationgrfat polymerization.

Table 4 Comparison of Graft polymerization technologies

	Initiation			
	Radiation	UV	Plasma	Chemical
Polymer	No limit	Limited	Limited	Limited
Shape of substrate	No limit	Limited	Limited	Limited
Surface Grafting	No limit	No limit	No limit	No limit
Inside Grafting	No limit	Limited	Limited	No limit
Monomer	No limit	No limit	No limit	Limited
Industrial Operation	Proven	Not Proven	Not Proven	Proven
Initial Investment	Large	Small	Medium	Small

2.4 Radiation curing

The original meaning of curing is a mere physical change from a liquid state to a solid state. The radiation curing means a radiation-induce polymerization of prepolymer-monomer mixture to form three dimensional network (crosslinking) involving a radical polymerization between double bonds in the prepolymer and monomer. The radiation curable prepolymers generally are low - to medium molecular weight mono- or multi functional unsaturated materials such as unsaturated polyesters and acrylated prepolymers. The prepolymers, being generally highly viscous or almost solid, are necessary to be diluted with monomer(s) to have a working viscosity. Usually electron beams are used for the radiation curing. The features of radiation curing can be summarized as follows.

(1) Non-polluting and solvent free
(2) Low energy requirements
(3) Rapid cure
(4) Application versatility
(5) Enhanced product durability
(6) Low temperature operation
(7) Small space requirements
(8) Single component coating (excellent storage stability)

The disadvantages of radiation curing are high initial investment and running cost. Thus more economical curing method using UV is more popular in the world. Table 5 shows the comparison of several curing methods. It looks difficult to promote the radiation curing if the price of EB machine and resins are not reduced.

Table 5 Comparison of Curing Processes - Coating

	EB	Thermal	UV
Atmosphere	Nitrogen	Air	Air
Cure Time	sec	sec -min	sec
Solid % in Paint	100%	< 50%	100%
Coating Thickness	depend of EB energy	no limit	0.1mm
Effect on Substrates	radiation damage	shrinkage	non
Paint Cost	high	low	high
Energy Requirement	1	100～500	3～30
Investment	high	high	low

2.5 Prospect of Radiation processing of polymers

Prospect of Radiation processing of polymers is shown in Table 6. The radiation chemistry of polymers has been applied in industries in the world from the economical point of view. Further development of the radiation chemistry of polymers will depend on the world concerns about environment conservation. The contribution of radiation chemistry of polymers will be (1) production of functional polymers for purification of environment, (2) reducion of solvent and energy, (3) production of recyclable polymers and (4) production of environmentally degradable polymers.

Table 6 Future of Radiation Processing

Process	Prospect
Crosslinking	Steady growth
Graft polymerization	Sever competition with other methods
Curing	Sever competition with UV Curing
Degradation	Growth in Natural polymers
Polymerization	Need new application field

3. INTERNATIONAL COOPERATION OF TRCRE

The first involvement of the TRCRE in the RCA Program was the RCA Workshop on Food Irradiation held in 1979. The next big event in the TRCRE was the RCA Group Training Course on Industrial Applications of Isotopes and Radiation Technology in 1980. TRCRE has led the radiation processing activities of the UNDP/RCA/IAEA program that started in 1982. Cooperation of the TRCRE with the RCA covers food irradiation, radiation crosslinking, radiation vulcanization of natural rubber latex, EB curing, radiation treatment of flue gas, radiation treatment of municipal sludge, radiation dosimetry and radiation engineering. The TRCRE is acting as one of the centers of RCA for learning advanced knowledge and scientific discovery in the field of radiation processing. Cooperation of the TRCRE to the UNDP/RCA/IAEA Project on the Industrial Application of Isotopes and Radiation Technology included

1. installation of pilot plants of RVNRL and EB Curing at BATAN
2. long term expert services to the UNDP Project Office at BATAN PAIR
3. training of scientists and engineers from the RCA member states
4. expert services to the member countries
5. hosting several types of meeting for coordination and planing of the RCA activities
6. developing new RVNRL process

The support of the TRCRE to the UNDP/RCA/IAEA Environmental Project from 1992 to 1996 was enhanced to promote the environmentally friendly technology for preservation of the environment. Eleven Regional Training Courses were hosted by the TRCRE and totally 156 participants trained. Now the radiation processing becomes popular technology in the RCA member states as the results of these RCA programs. In addition, the remarkable contributions of the TRCRE are the commercialization of food irradiation in several RCA member states, establishment of new RVNRL process and the promotion of radiation treatment technique of flu gas. Four pilot plants of RVNRL and one big demonstration plant of flue gas treatment were built in the RCA region.

The main objective of the previous RCA program on the radiation processing was technology transfer of the established technologies to the private sectors in the RCA member states. Several technologies have been introduced to the RCA member states as shown in Table 7. Radiation crosslinking facility of wire/cable was installed in Malaysia, tires in Philippines and plastic foams in Thailand. The resultant products are assembled in automobiles and electrical appliances for export. Some technologies in the table are transferred by Japanese company. Characteristic of radiation processing in Japan can be abstracted as follows: Major Process is the radiation crosslinking. End users of radiation crosslinked materials are car Industry and electrical appliances industry. Oversea Japanese factories intend to import crosslinked materials from Japan. Radiation crosslinking facility will be installed directly by Japanese company if there is enough market.

Table 7 Radiation Processing in Asian Countries (EB Technologies)

Country	Technology
China	Heat shrinkable Tube, Wire/Cable
Korea	Heat shrinkable Tube, Wire/Cable, Tires
Indonesia	Tires
Malaysia	Wire/Cable, Heat shrinkable Film
Thailand	Plastic Foam, EB Sterilization
Philippines	Tires, EB Sterilization

Bilateral cooperation between TRCRE and BATAN began in 1984 to supplement the RCA Project. The international cooperation of TRCRE with Asian countries has been expanded to include the multilateral RCA project and bilateral cooperation with BATAN, OAEP, MINT, CNN and VINATOM. Table 8 summarize previous Cooperation Program of TRCRE with Asian countries. Several meetings have been held to discuss about research cooperation in Asian countries. These countries are suffering economic recession. What we learned through the economic crisis is that the weakness of assembling industry and importance of original technology based on the indigenous products. After due consideration we reached the following basic strategy of the cooperation. The objective of the research cooperation should be development of original technologies for environmentally friendly process and products. The technology should be based on the indigenous natural resources of the region. Based on this strategy, TRCRE started new research cooperation program from 1998. The present programs are listed in Table 9.

Table 8 Previous Research Cooperation of TRCRE

System	Counterpart	Subject
IAEA/RCA	RCA Member Countries	Food Irradiation
		Radiation Processing
		Environmental Preservation
JAERI Bilateral Cooperation	BATAN	Graft Polymerization
	MINT	Agrowaste
	OAEP	Sludge Treatment
	CNNC	Radiation Processing

Table 9 Present Research Cooperation of TRCRE

System	Counterparts	Subject
JAERI	BATAN	RV of Fresh NR Latex

Bilateral Cooperation

	MINT	Starch Modification
	CNNC	Radiation Processing
	OAEP	Silk Modification
	VINATOM	Polysaccharides
IAEA	RCA Member Countries	Natural Polymer
		RV NR Latex film
		Agrowastes

4. FUTURE RATIONADI PROCESSING IN ASIA

Asian countries are rich in natural resources such as polysaccharide, hydrocarbons and proteins. The promising radiation technologies for the natural polymers will be degradation and crosslinking. It has been revealed that radiation degradation of polysaccharides has potential application as biological active materials. Good examples are plant growth promoter from the radiation decomposed Na-Alginate and anti-fungal from irradiated chitosan. It was also known that addition of polysaccharide into water solution of synthetic polymer followed by irradiation enhances mechanically properties of hydrogel. A new area of radiation processing of natural polymers can be develop by research cooperation among Asian countries. A model of Bio-regionism by radiation processing is illustrated in Figure 2. Irradiation and modification facility will be installed at the Center of the region. Low energy electron accelerator will be suitable for the key facility of the Center. The advantages of low energy electron beams (LEEB) are listed in Table 10.

Table 10 Comparison between Co-60 and Low Energy EB

	Co-60	Low Energy EB
Initial investment	High	Low
Irradiation cost	High	Low
Efficiency	Low	High
Utilization technology	Developed	Under developing

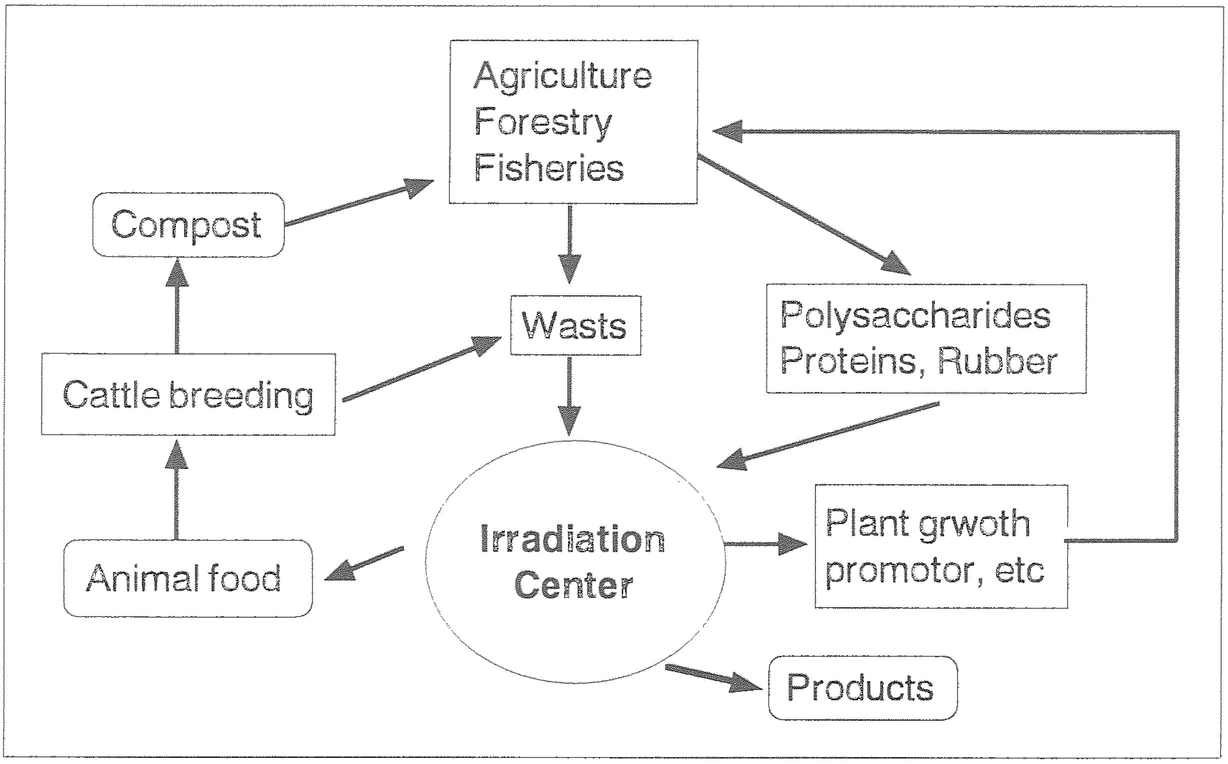

Fig. 2 Regional development by utilization of natural resources in Asia

Utilization of LEEB should be developed by the international research cooperation. The objectives of the research are (1) development of utilization technology of LEEB and (2) development of indigenous products with LEEB. Low energy electron beams can be applied in many purposes as follows:

1) Liquid irradiation technology
    - Vulcanization of NR latex
    - Modification of molecular weight of polysaccharide
    - Emulsion polymerization
2) Powder irradiation technology
    - Sterilization of spices, cosmetics and pharmaceutical
    - Sterilization of surface contamination of medical devices
3) Film/Sheet irradiation technology
    - Production of hydrogel dressing
    - Immobilization of bioactive materials