INDUSTRIAL APPLICATION OF ELECTRON BEAMS for GRAFTING AND VULCANIZATION

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1. INTRODUCTION

The high energy ionizing radiation interacts with materials to produce ionization and excitation. The resulting species can further react to give free radicals. Polymer radical (R•) is formed when polymer (P) is irradiated.

$$P \rightsquigarrow P^*$$

$$P^* \longrightarrow R_1\bullet + R_2\bullet \qquad (1)$$

$$R_3\bullet + H\bullet \qquad (2)$$

The polymer radicals thus formed are so active that react with each other or monomer (M).

$$R_3\bullet + R_3\bullet \longrightarrow R\text{-}R \qquad (3)$$

$$R_3\bullet + M \longrightarrow RM\bullet \qquad (4)$$

The reaction (3) is known as crosslinking of polymer by recombination of the polymer radicals. The reaction (4) is the initiation step of graft polymerization which occurs when monomers interact with polymer radicals.

$$RM\bullet + nM \longrightarrow RM_{n+1}\bullet \text{ (graft copolymer)}$$

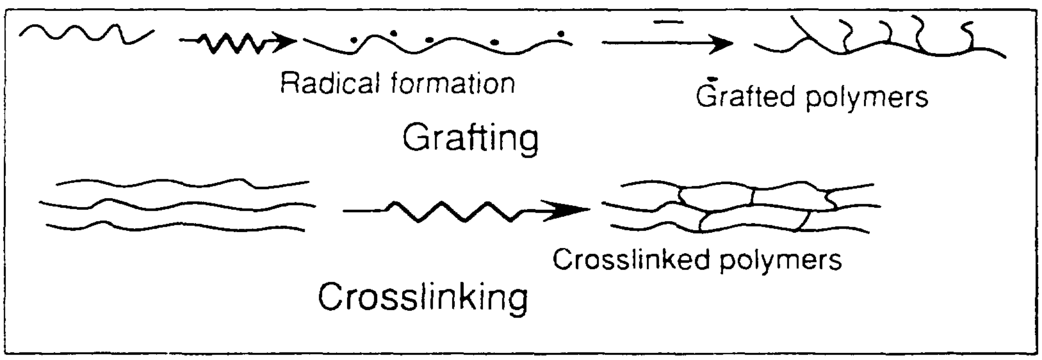

Fig. 1 Radiation grafting and crosslinking

2. RADIATION GRAFT POLYMERIZATION

Polymer radicals formed by irradiation of polymer (A) can react with monomer (B), resulting in graft chains. The structure of a graft copolymer can be illustrated as follows:

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-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A (Trunk polymer)
  |               |
 B-B-B-B         B-B-B-B (Branch polymer)
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Since a graft copolymer A_nB_m contains long sequences of two different monomer units A_n and B_m the graft copolymer may combine some of the characteristic properties of both polymers A_n and B_m.

Table 1 Modification of material by radiation graft polymerization

Trunk polymer	Monomer	Effect attained
Polyethylene	Acrylic acid	Ion-exchange properties
Polyethylene	vinyl phosphonate oligomers	Non-flammability
Poly(vinyl chloride)	Hydrophilic monomer	Anti -staining
Polyolefin	Hydrophilic monomer	Anti-static, Anti-fogging

The radiation-induced graft polymerization can be classified into the following two techniques:

(1) Direct or Simultaneous irradiation method
irradiation of mixture of a trunk polymer and monomer

(2) Pre-irradiation method-grafting initiated by trapped radicals
pre-irradiation of a trunk polymer, post-contact with monomer

Typical example of the direct irradiation method is the preparation of MG latex. Grafting of methyl methacrylate on to natural rubber is performed in NR latex. Usually γ-rays are used for this purpose because penetration of γ-rays is so large that a large amount of latex can be irradiated. Electron beams can be used for the preparation of MG latex by using a special irradiation vessel described later.

Generally radiation graft polymerization is used for the modification of solid polymeric materials such as film, membrane, fiber and cloth. From a practical viewpoint, the pre-irradiation method is preferable because of the negligible formation of homopolymers and easier control of degree of polymerization.

The yield of grafting by radiation depends directly on the efficiency of radical trapping. Radicals are trapped in crystal phase. Three types of radical are formed in PE by radiation, alkyl radical ($-CH_2-CH-CH_2-$), allyl radical ($-CH=CH-CH-$) and peroxy radical ($-HC-O-O\bullet$). The graft polymerization depends mainly on alkyl radical. In general, the life time of the trapped radicals is much longer at low temperatures. Accordingly, irradiation at low temperature increases the radial yield. In addition, storage temperature of the irradiated trunk polymer affects the decay of radicals. It is preferable to store the irradiated polymers at low temperature. Oxygen is known to destroy trapped radicals because it converts radicals into peroxide radicals of which reactivity with monomer is lower than that of former radicals. Therefore it is essential to irradiate at low temperature under inner atmosphere and keep it under the same conditions before graft polymerization.

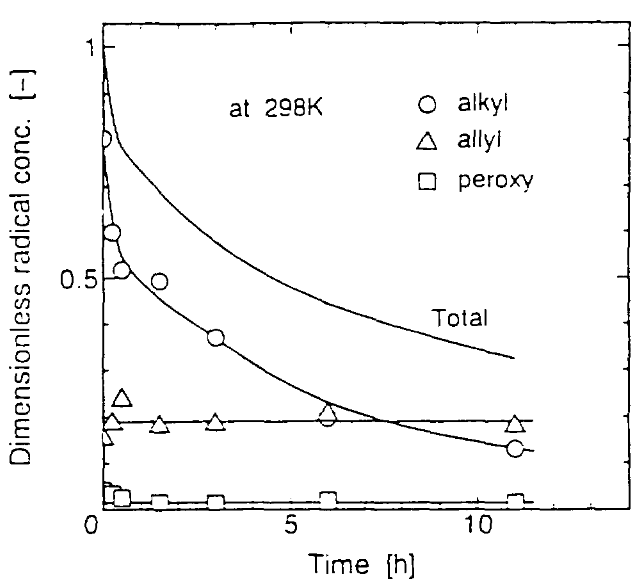

Fig. 2 Decay of PE radicals in air

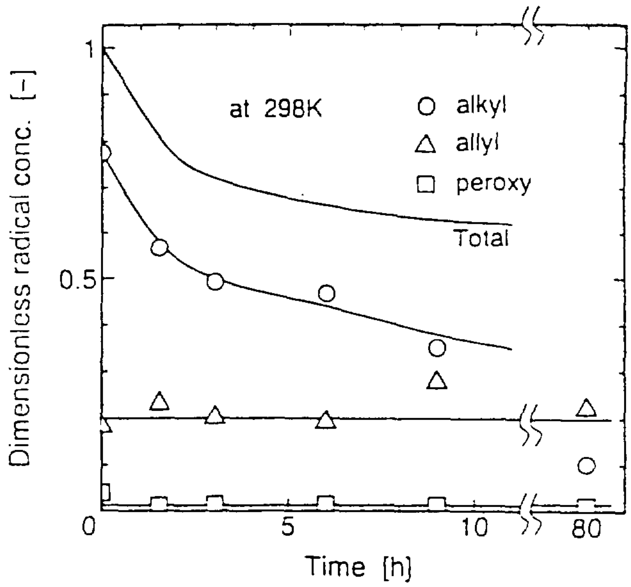

Fig. 3 Decay of PE radicals in nitrogen atmosphere

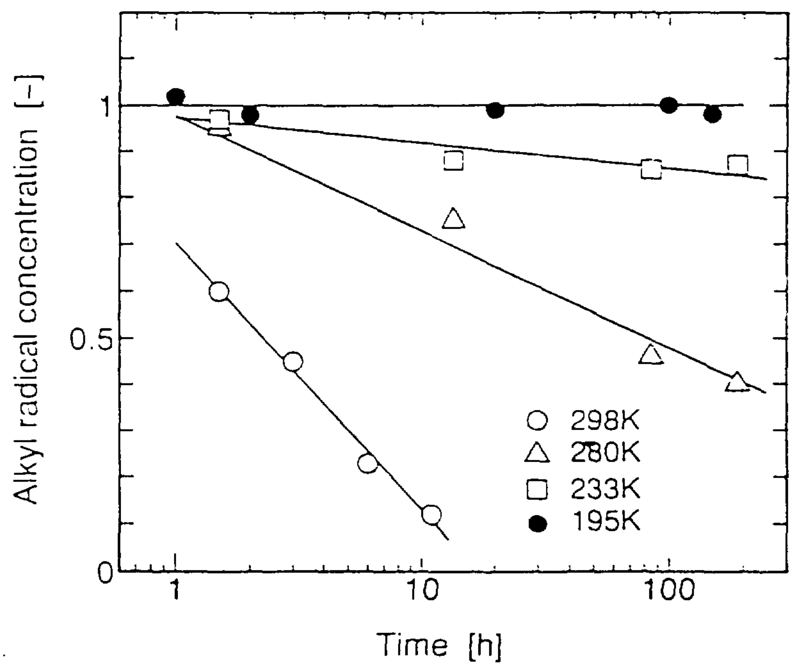

Fig. 4 Effect of storage temperature on decay of PE alkyl radicals in air

The principal advantages of the radiation-induced graft polymerization as a method of polymer modification can be summarized as follows.

(1) any type of polymers can be modified regardless of shape, size and phase.

(2) grafting can be carried out from gaseous, vapor and liquid monomer.

(3) initiation rate can be regulated simply by selection of dose rate, irradiation time etc.

(4) products free from remains of initiating agent or catalysis can be produced.

2.1 Industrial application of radiation grafting

Application of radiation for the synthesis of graft copolymers has been investigated in great depth. In spite of this extensive work only a rather low level of commercialization has been achieved. However, the situation will soon change and there will be growing industrial interest in radiation grafting.

A. Ion exchange membrane for a battery separator

Membranes based on polyethylene (PE) with polyacrylic acid are produced on an industrial scale and used as separators in electric batteries. Direct irradiation method of PE and acrylic acid is adopted in USA and China. Japanese company uses pre-irradiation method developed by JAERI. PE substrate is irradiated with EB to 200 - 300 kGy under inner atmosphere at low temperature to produce radicals. Then the substrate is immersed in acrylic acid solution to perform graft polymerization. The rate of grafting increases with increasing grafting temperature but the final percentage of grafting decreases.

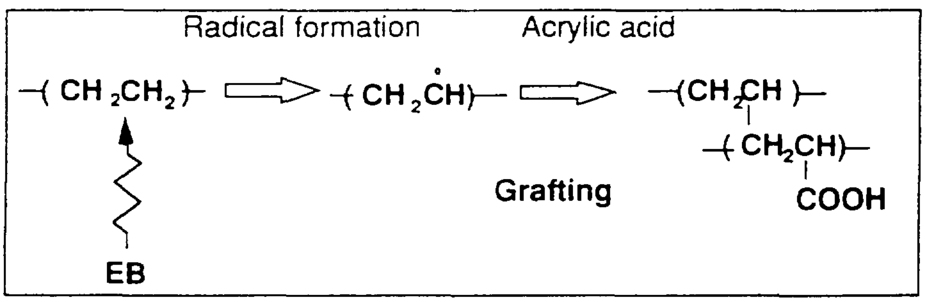

Fig. 5 Graft polymerization of acrylic acid on polyethylene

B. Ammonia adsorbent

Fibrous adsorbents containing sulfonic acid groups for the removal of ammonia gas have been developed. Large amount of ammonia can be absorbed by the graft copolymers compared with a commercial absorbent.

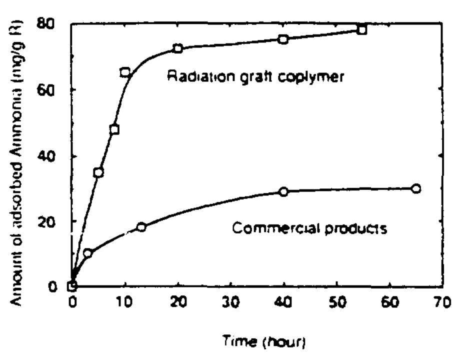

Fig. 6 Ammonia absorbing rates of graft product and commercial product

C. Non-flammable PE foam

The direct radiation grating of vinyl phosphonate oligomers has been successfully adopted to give non-flammable properties to polyethylene foam. The foams were immersed in oligomers solution, then irradiated with electron beams. Low viscosity of the oligomer solution is favorable for impregnation of the oligomer. Dilution of the oligomer with adequate solvent is essential to control the concentration of oligomer impregnated in the foams. The self-extinguishing properties was introduced by the grafting of the oligomers.

2.2 R&D on radiation grafting

The radiation graft polymerization can be applied for obtaining functional materials by converting the resulting graft chains into functional chains. Typical example is the uranium adsorbents from sea water, prepared by the radiation grafting of acrylonitrile onto polyethylene fibers. By the treatment with hydroxyl amine the nitrile groups were transformed into amidoximic ones.

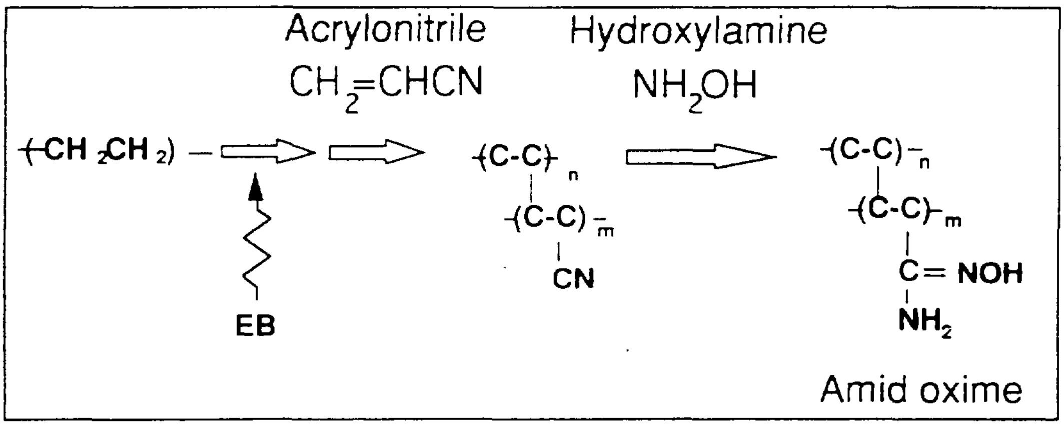

Fig. 7 Synthesis of amidoxime group containing functional materials

The concentration of U in seawater is strangely constant at 3.3 mg/m^3 and the total U in seawater amounts to 45 billion tons. This value is almost thousandsfold larger than the terrestrial resources of reasonable concentrations. The main U species in seawater is the stable anionic tricarbonate-uranyl complex. Among various chelating resins amidoxime-group containing resins have attracted much attention for recovering U from seawater due to their uranyl ion adsorption and permeation characteristics.

3. RADIATION VULCANIZATION OF NATURAL RUBBER

The process of crosslinking of rubbery or elastomeric materials is termed vulcanization. Radiation vulcanization of natural rubber (NR) latex (RVNRL) means crosslinking of natural rubber (cis-1,4- polyisoprene) dispersed in the form of microscopic particles in an aqueous medium. Recently a new RVNRL has been developed through RCA program. The radiation vulcanized

(RV) NR latex having the following advantages over conventional sulfur vulcanizates due to the absence of dithiocarbamates, sulfur or zinc oxide that are essential chemical for the conventional sulfur vulcanization.

(1) absence of carcinogenic N-nitrosamines

(2) very low cytotoxicity

(3) low emission of SO_2 and less formation of ashes

(4) transparency and softness (low modulus)

(5) degradability in the environment

Usually RVNRL is carried out with γ-rays. RVNRL with EB is not popular due to its low penetration into NR latex. High energy EB was used to overcome the problem of low penetration. A pilot plant having with a linear electron accelerator having a mean power of 10 kW and energy of 6 MeV was installed in France. NR latex was irradiated continuously by flowing in the form of thin layer by using a latex circulating pump. The capacity of vulcanization was 1 ton of NR latex per hour. 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. However, this flow method was not applied in industry due to some technical difficulties of circulating system.

TRCRE has developed an irradiation system of RVNRL in batch system that is more simple and convenient than flow system. NR latex is irradiated in a vessel with stirrer (Fig. 8). A low energy EB (250 - 300 keV) can be used for RVNRL with this system. However, the significant disadvantage of low energy EB is the very low penetration level, only several hundred μm in latex, depending on energy. Therefore the stirring during irradiation is the important factor to achieve homogeneous irradiation. The shape and speed of stirrer should be determined carefully.

This system can be used for radiation grafting of MMA onto NR in latex phase. Control of the temperature of latex will be a key factor to obtain MG latex with acceptable quality.

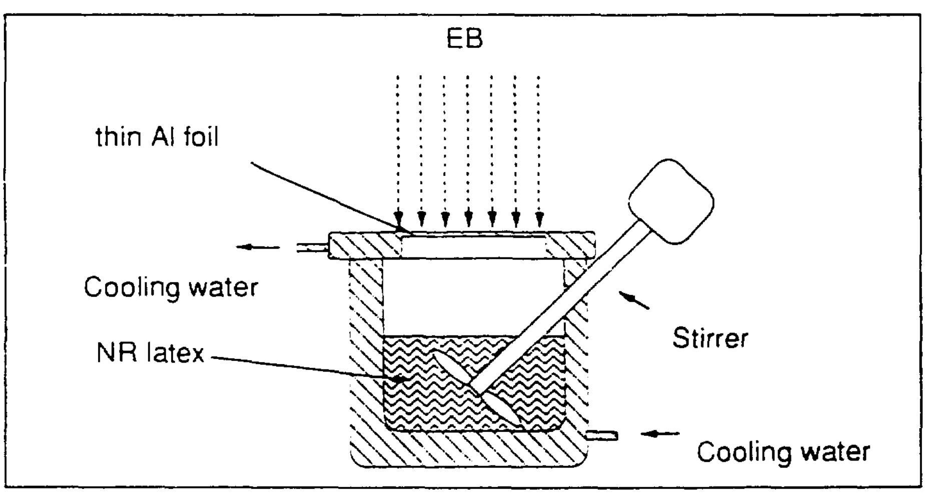

Fig. 8 Irradiation system with EB

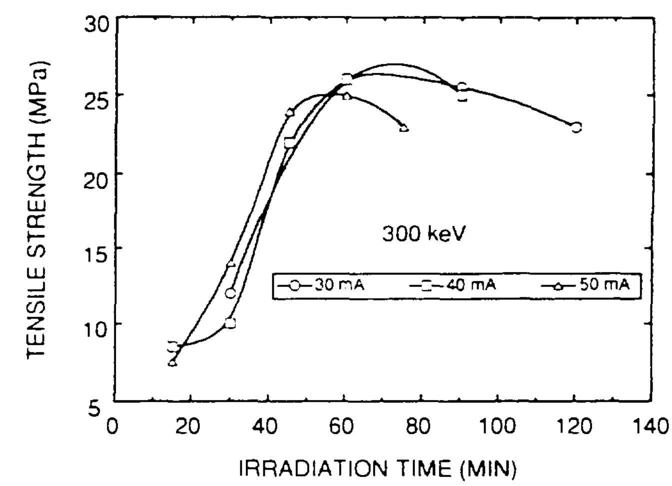

Fig. 9 RVNRL with 300 keV EB-effect of beam current
NR latex without sensitizer

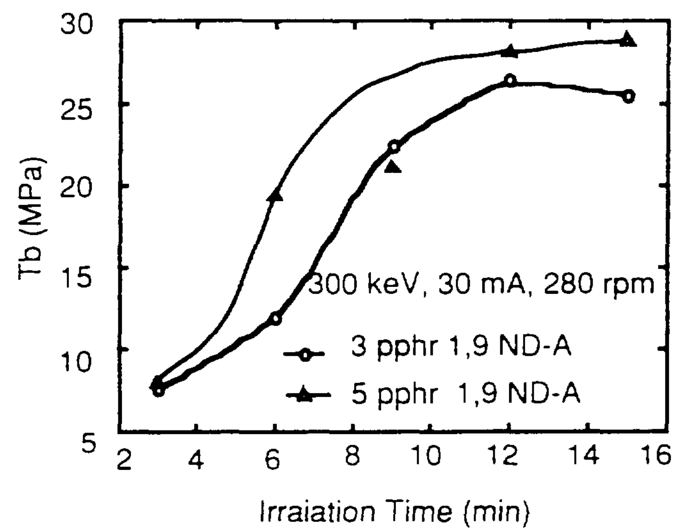

Fig. 10 RVNRL with 300 keV EB-effect of sensitizer
1,9 ND-A : 1,9-Nonanendiol diacrylate

The cost of irradiation with a low energy EB will be lower than that with γ-rays because the bio-shielding is net required for low energy EB.

4. CONCLUSION

Applications of EB for grafting have not yet used widely compared with radiation crosslinking and curing technologies. However, this technology for production of unique value added materials will be spread soon. New direction of utilization of low energy EB in NR producing countries such as Indonesia and Malaysia will be the production of MG latex and RVNRL. The lower initial investment and higher total production rate of EB process compared with γ-ray process are important factors for commercial application. Close cooperation between a national radiation processing laboratory and private sector should be carried out for the development of these technologies.