Electron Beam Processing for Industrial Applications

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ABSTRACT

High energy electrons from accelerators-both focused and scanned have been utilized for a number of applications in the fields of medicine, engineering, industry, environmental protection and research. Focused electron beams and bremsstrahlung x-rays are employed mainly in radiotherapy and industrial engineering applications. Scanned beams up to 10 MeV are utilized extensively for irradiating materials on large scale in industry, called as EB processing. High voltage linear accelerators like Cockroft-walton generators, Dynamitron etc. (DC machines) and RF linacs are beneficially used for these applications suitable in terms of robust design, cost and beam characteristics. The associated equipment and irradiation geometry are normally chosen specific to the application. Presently, processing of materials using high energy electron accelerators (200keV-10MeV) constitutes the largest commercial radiation application in the industry. World over, there are over 2000 accelerators operating in the wire/cable, heat shrinkable, surface curing and other related industries. These industrial type accelerators have the ability to deliver high doses at dose rates of the order of 10 kGy s⁻¹ (10¹⁰ - 10¹² Gy s⁻¹ in case of pulse accelerators) as compared to few Gy/s for ⁶⁰Co gamma irradiators. They can be operated continuously for 24 hours/day and have been in use for on-line processing of wires & cables, films, tyres etc. With the availability of high energy pulse accelerators (5-10MeV) operating at power range of 10-100 kW, coupled with x-ray generation systems, sterilization of medical products has become competitive to present ⁶⁰Co gamma sterilization.

I ELECTRON BEAM (EB) PROCESS AND PARAMETER EVALUATION

The upper limit in the energy i.e.10MeV for electrons and 7.5MeV for x-ray sources has been imposed for radiation processing applications to ensure that no radioactivity is induced in the irradiated material. The role of EB processing in industry has been growing due to the advantages such as: a) desired chemical / biological changes are induced at room temperature b) a much purer product is obtained since the use of chemical catalysts, initiators, fumigants etc, are eliminated or drastically reduced- hence environment friendly c) process larger throughputs at high dose d) ability to hook up to the industry for existing on-line processing e) energy efficient f) switch on & off

type radiation (unlike in gamma irradiators) - hence more safe and wide public acceptance.

The aim of the industrial processing using EB accelerators is to treat large quantity of products to the required dose levels uniformly, at fast line industrial (product conveying) speeds. In accelerators, unlike radiotherapy and engineering applications, the output electron beam is scanned and extracted through a thin foil so that a line source is formed. The product is made to pass under it perpendicular to the source. Uniform dose distribution is ensured by proper selection of the electron energy, thickness and product irradiation geometry. Even though the electrons have shallow penetration and has dose distribution (as shown in fig.1), because of the intense sources in the range of 10-500 kW power, it is possible to irradiate larger throughputs at higher doses.

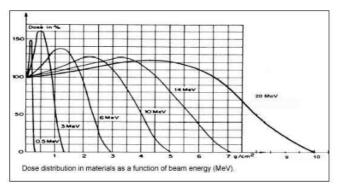


Fig.1 Dose distribution in materials as a function of beam energy

The main accelerator parameters of interest are the electron beam energy and current (beam current in case of DC accelerators; beam pulse & average current in case of pulsed beams). The energy decides the thickness of the product that can be uniformly irradiated while the dose rate at which the product can be irradiated depends upon the current. The thickness R which is called the *useful thickness* is defined as the depth at which the dose equals the surface dose. In order to evaluate this thickness, it is essential to obtain depth-dose curves as shown in figure 2 in the material for different beam energies. The useful thickness can be increased if the product is irradiated from both the sides as shown in figure 3.

A rough estimation of useful (process) thickness can be reached from the formulae given below.

 $E = 2.63 R_o + 0.32$ (one-side irradiation)

 $E = 1.19 R_p +0.32$ (two-side or double sided irradiation)

where E is the beam energy and R_p is the useful thickness of the material in g/cm^2 .

The process throughput T depends upon the beam power P, dose D and the beam utilisation efficiency η , using a suitable irradiation system and is defined in equation

 $T(kg/h) = 3600 P(kW) \eta / D(kGy)$

It is necessary to employ different irradiation methods and product transport systems depending upon the nature of products and their shapes and dimensions. Sometimes, it is also necessary to irradiate the product repeatedly to give a cumulative desired dose. For example finished wire/cable insulations are irradiated from both the sides using the *figure of eight* conveyor geometry. For bulk processing viz, medical products sterilization, food irradiation etc, carefully packed product boxes can be transported under the beam using linear conveyor with two & fro motion.

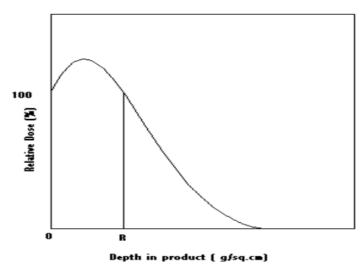


Fig. 2 Typical Depth dose curve for electron beam

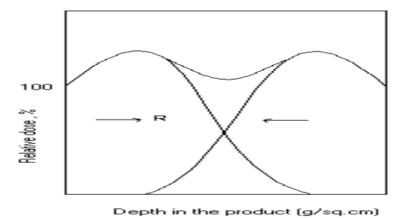


Fig.3 Typical shape of depth-dose curve when irradiated from both sides using electrons

II X-RAY MODE OF IRRADIATION

High energy electrons are made to impinge on heavy targets to produce intense X- rays (bremsstrahlung radiation). This radiation can be beneficially utilized for processing of materials. Studies have shown that such radiation with maximum energy and power, offers better dose uniformity and processing throughputs in comparison to the equivalent power of radioisotope source based irradiator. Thus, the accelerator can be used for high throughputs of thin products in EB mode; and large thick (inhomogenous) products in X-ray mode.

III APPLICATIONS IN ELECTRON BEAM PROCESSING

Different applications with required dose are mentioned in the following table 1. Some of the popular established applications include polymer modifications, color enhancement of gem stones, medical products sterilization. Other emerging applications like waste water treatment; flue gas treatment and food processing are gaining importance worldwide.

Table 1: Absorbed dose range required for some applications

Application	Dose required (kGy)
Disinfection	0.25-1.0
Food preservation	1.0-25.0
Medical Sterilization	20-30
Curing of coatings	20-50
Polymerization	50-100
Crosslinking of polymers	50-300
De-polymerization of PTFE	400-1000
Coloration of diamonds	~ in MGy levels

(a) Polymer Modifications Using Ebeams- Free radicals are produced when polymers are exposed to ionizing radiation like gamma ray, EB or X-rays. These active species are responsible for initiating chemical reactions leading to modifications like (1) formation of network in polymer chains called cross-linking (2) molecular weight reduction by chain scission called degradation and (3) polymerizing a monomer and grafted onto the base polymer chain called grafting. Simultaneous polymerization and cross linking is also possible as in the case of coatings or composites called as curing. However, the effect is different for different polymers and is intrinsically related to the chemical structures of the polymers. While cross linking is predominant in some polymers, degradation is predominant in others. Polymers with more hydrogen atoms on the side (e.g., polyethylene) tend to cross-link with radiation. Polymers with a methyl group (e.g., polypropylene), di-substitutions polymethacrylate) and per-halogen substitutions (e.g., polytetrafluoroethylene) would more likely undergo degradation with radiation. Aromatic polymers with benzene rings either in the main chain or on the side (e.g., polystyrene and polycarbonate) are usually radiation resistant. For some polymers, elevated temperature may increase the mobility of the polymer chains and make it

more favorable to cross-linking. Oxygen in the air usually assists the degradation more through a peroxide radical mechanism, so an oxygen-free atmosphere would usually be more favorable for cross linking.

- (b) Cross-linking Cross-linking is the most important effect of polymer irradiation and has the larger number of applications because it can usually improve the mechanical and thermal properties and chemical, environmental and radiation stabilities for both preformed parts and bulk materials. The following are some examples of applications.
- (i) Wire and Cable: The crosslinking of insulation on electrical wires and cables was one of the first practical applications of radiation processing. Polymers used in this application include polyethylene, polyvinylchloride, ethylene-propylene rubber, polyvinylidene fluoride, and ethylenetetrafluoroethylene copolymer. Product improvements obtained by irradiation include increased tolerance to high temperature environments and overloaded conductors, fire retardation, increased abrasion resistance and tensile strength, reduction in cold flow,

- increased resistance to solvents and corrosive chemicals as well as some other important characteristics. Irradiated wires are commonly used in automobiles, military vehicles, aircraft, spacecraft and many other applications where high performance is required.
- (ii) Heat-Shrinkable Products: Thin-walled plastic tubing and plastic films are cross-linked to obtain the so-called "memory" effect from the cross-linked network. Radiation crosslinking fixes or stabilizes the original dimensions of the tubing or films. When the material is heated above the temperature where the unirradiated material would melt, it becomes elastic and can be expanded to at least twice its original dimension. When cooled, it maintains the expanded dimension but retains the "memory" of its original dimension. When heated again, it contracts to the original dimension. Polyethylene is commonly used for this application. Many commercial products have been developed. Some examples for tubing products are encapsulations for electronic components, bundles of electrical wires and exterior telephone cable connectors. The applications for films are mainly in the food industry, where heat-shrinkable wrapping material is used to make attractive, sealed packages. Modern packaging films use blends of several different polymers to provide desirable properties like clarity, toughness, oxygen exclusion and moisture retention.
- (iii) Rubber Tires: Automobile tire tread sections are irradiated to obtain partial cross-linking before the tire is assembled. This stabilizes their thickness during the final thermal curing process. It also prevents the steel belt from migrating through its supporting rubber layer. The result is a higher quality tire with more uniform thickness and better balance. This allows the tire to be made thinner to save material and reduce cost. A thinner tire also generates less frictional heating on the road. Dose requirements are in the range of 30 to 50 kGy.
- (iv) Plastic Pipes: Cross linked plastic pipes are used to distribute potable hot water and for floor and wall heating applications. The pipe may either be made entirely of polyethylene, or may be a composite pipe consisting of an inner layer of polyethylene to keep the water from contacting a middle layer of thin aluminum, which resists the water pressure, and an outer layer of polyethylene for abrasion resistance. Both the inner and outer plastic layers are irradiated simultaneously with electron beam. Cross-linking enhances the mechanical properties and the thermal stability

- of the pipes. Plasticized PVC pipes are also cross-linked with radiation.
- (v) Plastic Foams: Plastic foam is made by mixing a foaming compound with the basic polymer and then heating the mixture to release gas bubbles emanating from a nitrogencontaining foaming agent in the plastic material. Polyethylene, ethylene vinlyacetate copolymer and polypropylene are suitable materials. A typical foaming agent is azodiacarbonamide or nitrogen.

Radiation cross linking allows the use of higher expansion temperatures and simplifies the control of the expansion process. Applications include foamed insulation in coaxial cables, gaskets, coated tapes, floor backing, helmet liners, athletic safety pads, bra cups, automobile seat padding and jewelry case liners.

Orthopedic devices such as hip joints are usually made of ultra high molecular weight polyethylene (UHMWPE). Radiation cross-linking can significantly improve the wear resistance of the surface these devices.

- (c) Curing: Curing is a combination of polymerization and cross-linking initiated by radiation from monomers and oligomers. Major advantages of radiation curing include reduction or elimination of volatile organic compounds (VOCs) and faster curing. Radiation curing of coatings, inks and thin adhesives usually only requires low energy electron beams. The following are applications for medium to high beam energies.
- (i) Composite Materials: Advanced composites, such as carbon fiber reinforced polymer resins, have become very important materials that are used for a wide range of applications because of their excellent mechanical properties and low weight. Conventionally, the composites have been cured by thermal means, which employ autoclaves or ovens and high temperature to accomplish the chemical reactions of curing (i.e., polymerization and cross-linking of the polymer resin). EB curing has many important advantages over the traditional thermal curing, e.g., faster cure time, lower (ambient) temperature curing (which significantly reduces internal stress), capability to cure large parts, simplified tooling, improved material handling, reduced VOC emission and better process control. Typical resins are acrylated epoxies and EB curing may be accomplished with either a free-radical mechanism (no initiator needed) or a cationic mechanism (initiator required). Doses are typically in the range of 100 to 200 kGy. The main potential applications are in automotive and aerospace industries.

- (ii) Adhesive Bonding of Thick Components: There have already been examples of EB curing of adhesives for the bonding of large composite structures for aerospace and automotive applications. Compared with conventional thermal curing, EB curing of adhesives has many environmental and processing advantages such as reduction or even elimination of organic solvents (VOCs), faster curing, elimination of time constraints (due to the long life of EBcurable adhesives), fewer processing steps, reduced cost, elimination of autoclave/oven processing, reduced residual stress, prevention of de-bonding of dissimilar materials and "spot welding" type of bonding by beaming at specific areas.
- (d) Degradation: Some polymers that undergo degradation upon EB processing include polytetrafluoroethylene (PTFE), polypropylene (PP) and cellulose. Although degradation usually brings about deterioration of mechanical properties of polymers and needs to be avoided in many cases (e.g., radiation sterilization), some good applications have been found for chain scission of polymers by radiation.
- (i) Particle Size Reduction for Fine Powders: A well-known example of applications for degradation is the making of fine PTFE powders. PTFE has a high G value for scission and can be readily degraded to lower molecular weight by radiation. One of the results of the degradation of PTFE is the much higher brittleness of the material. This effect is used to convert scrap PTFE into fine particles or micronized powder. The unirradiated scrap is too tough, doughy and slippery to grind, but the irradiated material can be ground readily.
- (ii) Melt Flow Rate: Adjustment. Another effect of degradation is the increase of the melt flow rate (MFR) of the polymer. In particular, polymers can be intentionally degraded by radiation in air to improve the process ability for extrusion, etc. Irradiated polymers can be blended with unirradiated polymers to adjust the melt flow and improve the process ability, for example producing a range of MFR for PTFE that it is high enough for the polymer to be melting process able but low enough so that the polymer was is too brittle to process. Irradiated PP can be mixed with unirradiated PP, and the degree of degradation may be controlled so that mechanical properties are not significantly deteriorated, yet melt flow advantages are obtained.

(e) Grafting: Radiation-initiated grafting is known to be a very good method for surface modification of polymer materials. The surface properties of polymers can be modified by graft copolymerization with different monomers. Grafting can be accomplished by irradiation on common polymers such as polyethylene, polypropylene and fluoropolymers. Most work has been done on polymer films, membranes, fibers and natural and synthetic textiles. Examples include grafting of acrylonitrile, maleic anhydride, styrene, N-vinylpyrrolidone acrylic acid and various acrylate monomers on polyethylene and fluoropolymers. Other examples are the bonding of styrene on cellulose, vinyl pyridines on wool and p-nitrostyrene on polyethylene, polypropylene and polyvinyl chloride. Hydrophilic properties can polymers. be imparted to hydrophobic Biocompatibility of various polymers can be improved in this way for medical uses. Ion exchange membranes and fuel cell/battery separator films can be made by grafting styrene onto porous fluoropolymer (e.g., polyvinylidene fluoride) membranes followed by sulfonation.

IV OTHER APPLICATIONS

EB accelerators have been in use for lifetime control studies in semiconductor power devices. The advantages of this technique include precise control of defects through proper dose and dose rate, convenient process, rectification in defect control by annealing and re-irradiation.

Applications viz. Medical products sterilization, food irradiation, decontamination of waste water and sewage are great giants for commercial exploitation using high energy accelerators. Typically a 10 MeV electron accelerator is able to sterilize more than 90% of the medical devices being irradiated using gamma radiation.

- (a) Flue gas treatment: Low energy accelerators with high powers are being employed to irradiate SO₂ and NO_x along with CO₂ gases generated in large quantities by industrial power plants in the presence of ammonia to simultaneously remove SO₂ and NO_x gases and convert them into useful fertilizers as a by-product. Pilot scale studies have been completed in USA, Japan, Germany & Poland and industrial treatment plants are being set up.
- (b) Colour enhancement in gem stones: Significant color enhancement in the diamonds can be brought out by subjecting them to very intense electron beams, there by inducing defects so that substantial value addition can be achieved for the irradiated diamonds.

Table 2
Industrial EB processing applications by BARC-BRIT

S.NO.	Material (industry)	Application	Purpose
1	PE 'O' Rings	Cross linking	High temp. dimensional stability
2	Cable insulations	Cross linking	Better operating temperature and better heat resistance; improved aging characteristics; higher current rating etc
3	Automotive plastic components	Cross linking	Heat resistance; partial cross linking @selective locations of the components
4	HV Busbar electrical insulation	Cross linking	High temp. shape forming using vacuum mold technique; Heat Resistance; better aging; better arc resistance; anti-tracking;
5	Diamonds	Crystalline alterations	Colour enhancement
6	PTFE scrap	Degradation	Brittle; can obtain micro fine powder
7	Viscose pulp	Degradation	To reduce degree of polymerization from (DP); improved reactivity in rayon process
8	Automobile tyre	Pre-curing (improvement in green strength)	Dimensional stability during tyre buildup process; reduced curing time; less scrap; increased throughput better rolling resistance
9	Nylon components	Cross linking	Reduced water uptake and better shelf-life and improved mechanical properties. The material is suitable as railway liners

V CONCLUSION

DAE played a major role in the promotion of the EB technology in Indian industry. Several industrial applications have been developed and demonstrated at BARC-BRIT Complex using a 2 MeV/ 20kW industrial type pulse linear accelerator during the last decade, as tabulated in table 2. Also, an Electron Beam Centre (EBC) has been set up installing indigenously developed EB accelerators (10MeV and 3 MeV at Kharghar, Navi Mumbai) and another 10 MeV EB accelerator by CAT, Indore.

Thanks to the initiative from DAE, the technology has been successfully picked up by the Indian industry. During the last ten years, around seven EB machines have been installed by the wire & cable manufacturers in India and beneficially utilizing them to process several industrial products. Many more are on the way.

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