

RADIATION PROCESSED MATERIALS: DOSE-RATE EFFECTS

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Industry has accepted electron beam (EB) radiation processing in many diverse areas. With the advent of high current, high voltage accelerators, which now enable X-ray processing, greater attention has been paid to dose-rate effects for commercial applications. Dose-rates have been found to significantly affect the polymerization of monomers and oligomers used in coatings, adhesives and as impregnants. The rates by which polyolefins, that are predominately saturated, respond to ionizing radiation is dependent upon the structure of comonomers and upon crystallinity. This is shown both for semi-crystalline thermoplastic and amorphous elastomeric materials. Adroit formulating can also alter the kinetics of radiation responses. The balance between concurrent propensities to scission and to crosslink can be shifted through both proper polymer/material grade selection and formulation. X-ray processing now affords a means to control dose-rates. Examples of the use of controlled dose-rate X-ray curing are shown for monomeric wood impregnants and for matrix systems used in fiber reinforced composites. Dose-rate has also been found to be significant for the radiation tolerance of thermoplastic olefins used in the medical device area. The historic equivocation of gamma, X-ray or bremsstrahlung, and electron beam processing, as found in much literature, no longer holds for many commercial materials.

I. INDUSTRIAL RADIATION PROCESSING

On a world-wide basis, there are >1400 high current (typically >10's of milliamps), EB accelerators used in manufacturing. This does not include accelerators used in research facilities, as ~550 Van de Graaff generators and low current linear accelerators, linacs.⁽¹⁾ There are also ~160 gamma facilities dedicated mainly to medical device sterilization and to some treatment of food.⁽²⁾ Table I highlights the major segments of the EB industrial radiation processing business based on accelerator voltage, with electron penetration being expressed on an equal-entrance—equal-exit basis (surface dose = dose on exit from material) in unit density materials. Industrial accelerators are limited to a maximum of 10 MV so as to preclude inducing any radioactivity in the target material.

The pie chart of Figure 1 illustrates the market breakdown by major end-use categories.

TABLE I. EB industrial market segments

Market Segment	Typical Voltage	Electron Penetration
Surface Curing	80 – 300 kV	0.4 mm
Shrink Film	300 – 800 kV	2 mm
Wire & Cable	0.4 – 3 MV	5 mm
Sterilization	4 – 10 MV	38 mm



Figure 1. Industrial EB accelerator end-use markets

Cobalt-60 sources can be downsized into small laboratory units. As a result a good deal of research has been conducted using this source. Likewise, within the research community, investigators have greater access to low current electron beams, such as Van de Graaff generators, which operate in the pico-amp range, orders of magnitude lower in beam current than industrial equipment, and linacs. For the most part, investigators have not availed themselves of the high current EB facilities that are available on a toll processing basis. Appendix Table A-I lists the processing facilities in North America which have high current industrial accelerators. Similar facilities are available in Europe, in South America and in Japan and elsewhere in Asia.

Heretofore, industrial radiation processing has been bracketed by the dose-rates attainable either from Cobalt-60 sources or from high current electron beams. With the advent of high current, high voltage accelerators (700 kW at 7 MV or 300 kW at 5 MV), the known inefficiencies of

the conversion of electron beams to X-radiation, which ranges between 8% and 12% for energies between 5.0 MeV and 7.5 MeV, can be compensated for with much higher beam currents.^(3,4) This renders X-ray processing as a viable alternative to the use of the radioactive Cobalt-

60 source. Table II compares some of the basic properties of electron beams, X-rays and gamma radiation. Figure 2 illustrates that the depth of X-ray penetration from an electrically sourced accelerator is comparable to that of gamma radiation from a radioactive source.

Table II. Alternative Sources of Ionizing Radiation

	Electron Beams	X-rays	Gamma Rays
Power source:	Electricity	Electricity	Radioactive isotope (mainly Cobalt-60)
Power activity:	Electrical on-off	Electrical on-off	5.27 year half-life
Properties:	Electrons mass = 9.1×10^{-31} kg	Photons $\lambda = 3 \times 10^{-10}$ m	Photons (1.25 MeV) $\lambda = 1 \times 10^{-12}$ m
Emission:	Unidirectional (can be scanned and bent by magnets)	Forward peaked	Isotropic (cannot be controlled)
Penetration:	Finite range	Exponential attenuation	Exponential attenuation
Maximum penetration: (industrial purposes; entrance = exit at unit density)	38 mm from 10 MeV	~ 400 mm	~300 mm
Dose-rate:	360,000 kiloGray/hour 100 kGy/s	960 kiloGray/hour 0.27 kGy/s	10 kiloGray/hour 2.8×10^{-3} kGy/s

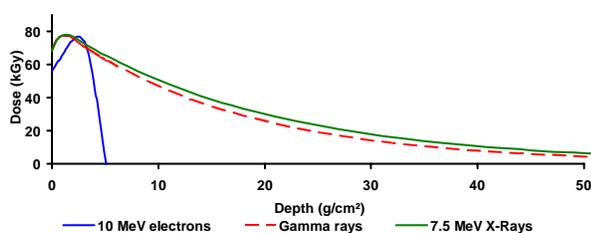


Figure 2. EB, gamma and X-ray penetration

Of consequence to industry is the five-fold difference in dose-rates between electron beams generated by high current accelerators and that of radioactive gamma sources. Most industrial EB uses involve high speed production operations in which product is transported in front of a beam in a continuous manner, often at hundreds of meters per minute. Gamma operations tend to be batch or shuffle and dwell type operations.

II. Material Effects at the Atomic Level

When a material is impinged by either an accelerated electron that is traveling near the speed of light or by short wavelength, high frequency photons (as ~ 0.1 nm at 10^{18} Hz for X-rays or ~ 0.001 nm at 10^{20} Hz for gamma radiation), a cascading stream of secondary electrons is generated. The velocity of the impinging electrons is determined by the acceleration voltage and dictates the penetration and consequent depth at which secondary

electrons can be effective.⁽⁵⁾ For X-rays and gamma radiation, the depth of penetration is practically the same, as illustrated in Figure 2. In industrial processing, the rate at which these secondary electrons are generated for EB is controlled by the beam current of the accelerator. For impinging gamma radiation, the rate is fixed by the decay rate of the radioactive isotope, Cobalt-60. The rate for impinging X-radiation can also be controlled by the voltage and consequent conversion efficiency of the accelerated electrons hitting a high atomic number target, most often tantalum (as illustrated in Figure 3) as well as by the beam current. Thus, dose-rates for X-rays are controllable. They differ from the dose-rates of gamma radiation by about one order of magnitude. X-rays are attenuated in a controlled direction and are not a panoramic source of radiation as are radioactive materials as Cobalt-60. Being so targeted, there is less loss of emitted energy due to divergence of the radiation. Within a material, the secondary electrons have nearly immediate effects, transporting through the material and creating ionizations and excitations in $\sim 10^{-16}$ of a second and free radicals at $\sim 10^{-13}$ of a second. Radiation chemistry thus involves a very direct use of energy transport into a material, not subject to the time dependence of heat transfer and the development of states of molecular vibration required in historic thermal processes where

diffusion controlled reaction events, once temperature is reached, happen in $\sim 10^{-5}$ seconds.⁽⁶⁾

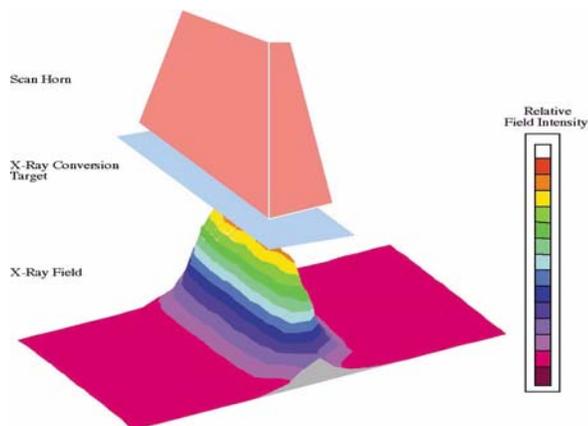


Figure 3. Controlled attenuation of X-rays

Of interest in radiation processing is the effect on carbon based materials. Major segments of the industrial radiation market (Figure 1) rely upon the positive effect that ionizing radiation has on the most inexpensive, commercial commodity polymer, polyethylene (PE). Many irradiated wire and cable formulations and all of the heat shrinkable films are based on PE. Elastomers used in tires are also hydrocarbons as are most of the monomers and oligomers used in surface curing applications. The atomic structure of carbon lends itself to many useful molecular configurations. Carbon forms covalent bonds with other carbon atoms and with some key substitutive groups, such as halides and oxygen. The double bond conformation of carbon is also important in a number of materials used in industry. Carbon is amenable to radical formation by acceptance of an electron, going from C to C[•], with an unpaired electron.

III. Molecular Effects

The effects of ionizing radiation on materials can be illustrated through the determination of “G” factors, that is the event yield per 100 eV of energy imparted to a material. In radiation processing there are often concurrent and competing reactions of crosslinking or polymerization (Gx) and of chain scissioning or disproportionation (Gs).⁽⁷⁾ The secondary electrons generated within a material are indiscriminate in terms of which atoms they bombard or where they hit. G factors are determined by the relative changes in material solubility when exposed to radiation. Gx is often indicated to be at the onset of gel formation.⁽⁸⁾

III.A. Effects on polymers

The crosslinking of polyethylene represents the most significant and greatest market value in radiation processing. Major areas of use for crosslinked PE include heat shrinkable tubing and heat shrinkable food packaging films, wire insulation, and closed cell foams. Crosslinking takes place in the amorphous regions of semi-crystalline homopolymers through the creation of free radicals which combine carbon atoms on adjacent PE molecules and link them by covalent bonding. Hydrogen is liberated. The crystallinity, comonomer type and content all influence the response of high molecular weight PE (>150 melt index) to radiation and the dose required to attain grade specific properties.⁽⁹⁾ The dose required to crosslink PE can be reduced by the incorporation of small amounts ($\leq 5\%$) of multi-functional monomers, such as triallyl cyanurate (TAC) or trimethylolpropane triacrylate (TMPTA).

While isotactic polypropylene homopolymer (PP) will chain scission when exposed to ionizing radiation, incorporation of these same monomers (TAC or TMPTA) into an impact grade of polypropylene copolymer (~6% ethylene content) rendered such material crosslinkable.⁽¹⁰⁾ The dominance of Gs in polypropylene was shifted to a dominance of the Gx factor. The scissioning of PP is exacerbated by a long lived trapped methide radical which can distort implications of accelerated aging tests. The adroit use of stabilizer systems has produced radiation tolerant materials that are used in the manufacture of medical devices which are to be subjected to radiation sterilization. The hindrance of the scission process itself has been found to be sufficient to permit crosslinking with EB or X-ray exposure at typical sterilization doses of 25 kGy, but not for gamma radiation of the same material at the same dose, as shown in Table III. Both the EB and X-ray have higher dose-rates and are notably less deleterious on polypropylenes intended for use in medical device manufacture.⁽¹¹⁾

Table III. Radiation Tolerant Polypropylene Copolymer Formulation

Source	Dose	Dose-rate	Elongation	Response
Control	none	----	100%	----
Gamma	25 kGy	2.8×10^{-3} kGy/s	30%	Scissioned
Gamma	50 kGy	2.8×10^{-3} kGy/s	2%	Scissioned
X-ray	25 kGy	3.3×10^{-2} kGy/s	420%	Crosslinked
X-ray	50 kGy	3.3×10^{-2} kGy/s	20%	Scissioned
EB	25 kGy	100 kGy/s	410%	Crosslinked
EB	50 kGy	100 kGy/s	500%	Crosslinked

The molecular architecture of halogen containing polymers dictates their response to ionizing radiation. Polyvinyl chloride (PVC) will chain scission. However, if formulated with multi-functional monomers (TAC or TMPTA), PVC will crosslink, as is commonly done in

producing radiation crosslinked wire insulation. Polyvinylidene chloride (PVdC), with two chlorine atoms on the same carbon, chain scissions. In contrast, polyvinylidene fluoride (PVdF), which has two fluorine atoms on the same carbon, crosslinks even without additives.⁽¹²⁾ An alternating copolymer of ethylene and tetrafluoro-ethylene (ETFE), radiation crosslinks. The segments of ethylene and tetrafluoro-ethylene alternate in sequence along the polymer backbone (an alternating copolymer) and are not, as are other copolymers, random. Polytetrafluoro-ethylene (PTFE) and similar highly halogenated polymers, such as polychlorotrifluoro-ethylene, also chain scission. Scission takes place in the amorphous regions of these polymers.⁽¹³⁾ A copolymer of tetrafluoro-ethylene and hexafluoro-propylene (FEP) will crosslink if irradiated at slightly elevated temperatures. If FEP is irradiated at >80C, crosslinking takes place, not degradation and Gx dominates over Gs.⁽¹⁴⁾

In 1933, the B. F. Goodrich Company obtained a patent on the use of radiation to crosslink natural rubber (polyisoprene), which has 100 mol per cent unsaturation.⁽¹⁵⁾ Polybutadiene and copolymers of butadiene, like styrene-butadiene (SBR) and butadiene-acrylonitrile (NBR) rubber also radiation crosslink. Ethylene-propylene rubbers (EPR's) are copolymers of ethylene and amorphous propylene segments that can be radiation crosslinked if the ethylene segment itself is sufficiently high, ~70%. Terpolymers with a pendant diene (EPDM's) are more radiation responsive. The radiation response depends upon the diene type and content. EPDM's made with ethylidene norbornene are more responsive than ones made with 1,6 hexadiene.⁽¹⁶⁾

Polyisobutylene (PIB) is often used to illustrate the chain scissioning of hydrocarbon polymers. The copolymer of isobutylene and a small mol per cent (1% to 3%) of isoprene, butyl rubber (IIR), also chain scissions. Butyl rubber can be crosslinked in thermo-chemical processes through the isoprene segments. When the isoprene comonomer is halogenated, either with bromine or chlorine, there is a double bond shift in the isoprene segment. Formulating with halogen acceptors renders halo-butyl compositions that will radiation crosslink.⁽¹⁷⁾ Bromo-butyl has been found to be preferable to chloro-butyl for use in the partial radiation crosslinking of tire innerliners. The carbon-bromine bond energy is slightly less (87 kCal/mole) than the carbon-chlorine dissociation energy (103 kCal/mole). If the halogen is stripped from the isoprene, that is dehydrohalogenated, the resultant copolymer has a conjugated diene structure which in itself, even at these low molar concentrations, is fully radiation crosslinkable.⁽¹⁸⁾ Thus, within one family of polymers (PIB), shifting the comonomer structure renders materials that are scissioned by irradiation (Gs dominant) into those which can crosslink (Gx dominant).

III.B. Reactive monomers and oligomers

In the fast growing use of EB processing in the converting industry, many monomers and oligomers are used which have terminal vinyl functionality. Acrylate esters and a diverse array of acrylated oligomers form the basis for many radiation curable inks, coatings and adhesives. Oligomers, typically viscous liquids <10,000 molecular weight, are made with mid-blocks of other moieties, such as urethane, epoxy or acrylic structures, as illustrated in Figure 4.^(19,20)

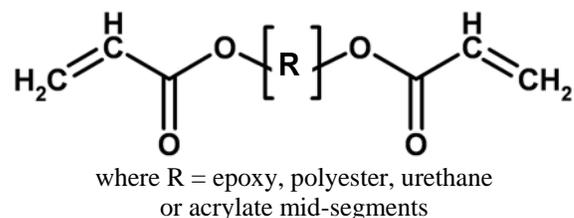


Figure 4. Acrylated Oligomers Used as Precursors in Radiation Curing

In this technology, it is well known that the use of di- and tri-functional monomers promotes polymerization and crosslinking. Many formulations will include some tri-functional monomer, such as TMPTA, to do this. The kinetics of these reactions were studied using photo-differential scanning calorimetry, wherein an ultraviolet (UV) light source was used to expose materials to radiation and the exotherm determined.⁽²¹⁾ As with the use of tri-functional monomers in converting PP and PVC to crosslinkable materials and to enhance the dose response of polyethylenes, these very reactive monomers also enhance the dose response of monomers and oligomers used in ink, coating and adhesive formulations.

However, in some systems monofunctional acrylates by themselves are preferred because of very specific end-use properties they impart. One such case is the use of hydroxyl-ethyl acrylate (HEMA) as a wood impregnant. This monomer has been found to enter the cell walls of wood and to impart dimensional stability to wood during humidity cycling. Initial tests using vacuum impregnated wood and a 5 MV electron beam showed that it took >100 kGy to complete the in-situ polymerization of the HEMA monomer. Multiple passes had to be used and care taken so as not to volatilize the monomer during processing. Using a lower dose-rate X-rays from a 3 MV EB, it was found that only 25 kGy was sufficient to fully polymerize and crosslink the monomer into wood blocks as thick as 16 cm. The heat from the exotherm from the acrylate polymerization generated a wood surface temperature that exceeded what would be expected solely from the energy input of the X-rays. Thus, an auto-catalytic acrylic polymerization was induced. Once polymerized and

crosslinked within the wood, the HEMA impregnant could not be extracted.⁽²²⁾ The lower dose-rate of X-rays permitted the classic initiation, propagation and termination steps to take place, whereas with high dose-rate EB processing both disproportionation and chain termination occurred, as a result of the excess of radicals.

In the manufacture of pressure sensitive adhesives, monofunctional acrylate monomers with alkyl groups between C₄ and C₈ have been found to be effective in developing radiation cured adhesives which have excellent balances of tack and holding power. It has been proposed that a novel pulsed linac be used to sustain the propagation step during EB polymerization and crosslinking of these monomers.⁽²³⁾ However, the use of such pulse-beam technology is not warranted. A similar monofunctional monomer, iso-decyl acrylate, C₁₀, was polymerized and crosslinked using a standard low-voltage laboratory EB unit. At 125 kV, 15.2 m/minute under beam speed and in a nitrogen inerted atmosphere, this monomer did not polymerize when exposed to ~45 kGy in a single pass nor in a second pass at the same high beam current (a total of ~90 kGy). When the beam current was dropped to ~1 ma and the dose allowed to accumulate with multiple passes (10), gelation and a tough tacky film was observed at a cumulative dose of ~45 kGy. A hard, tough film was produced at ~90 kGy (20 total under-beam passes). The under beam residence time needed for systems dependent solely on monofunctional monomers could be increased by aligning multiple low-voltage EB units in parallel along the direction of under beam travel.⁽¹⁾ Given the lower cost of these EB units, which are already in the market, this presents a viable option for in-line curing of materials that are based entirely on monofunctional monomers. Figure 5 shows such possible low-voltage EB alignment.

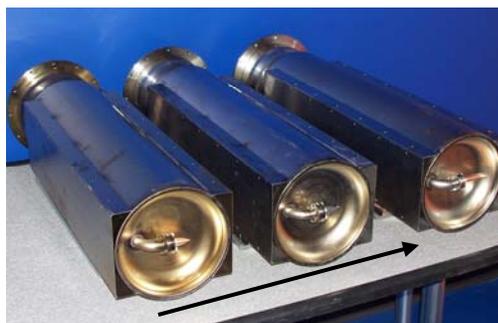


Figure 5. Low-voltage EB units sequenced in parallel

IV. Future considerations

While many radiation responses may be dose-rate independent, some specific instances have been observed in which dose-rate is of significant consequence, such as

in the polymerization and crosslinking of monofunctional monomers and in the response of some industrially significant polymers, such as polypropylenes designed for use in medical devices. One can also postulate that there may be a dose-rate effect on the scissioning of the DNA backbone of living materials, bioburdens. Studies of the X-ray response and cell survival conducted for therapy treatment indicate that a linear quadratic model is more predictive of cell death (and by implication bioburden elimination) for one step exposure, as can be had from an EB or X-ray source (A), than the traditional use of linear extrapolation model which is more applicable to step-wise radiation (B) as is incurred in the shuffle-and-dwell systems of gamma radiation processing, Figure 6.⁽²⁴⁾

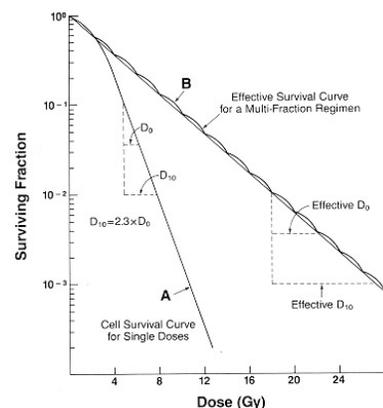


Figure 6. Survival curves for radiation exposed cells

Contemporary techniques in molecular biology, such as the polymerase chain reaction (PCR), can be used to verify the elimination of bioburden contamination. Such techniques are accepted in forensic studies, but not yet used in the area of medical device sterilization. PCR can rapidly amplify surviving cells to 10⁶ multiples. This is the same order of magnitude as sterility assurance levels, SAL (10⁻⁶). Now measurements can be made in regions which heretofore were based solely on extrapolation or derived from models. Implementation of these techniques may reduce the dose requirements needed to attain sterility assurance and thereby reduce the overall product-cost of medical devices.

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Appendix

Table A-I. North American EB radiation processing service facilities

<u>Facility</u>	<u>Location</u>	<u>Beam energy</u>	<u>Beam power</u>
BeamOne	Denver, CO	10 MeV	15 kW
	Lima, OH	10 MeV	18 kW
	San Diego, CA	2 x 10 MeV	18 kW each
E-Beam Services			
	Cranbury, NJ	10 MeV	50 kW
	Cranbury, NJ	5 MeV	150 kW
	Lafayette, IN	1.5 MeV	75 kW
	Lebanon, OH	5 MeV	150 kW
Electron Technologies			
	South Windsor, CT	1 MeV	20 kW
Iotron			
	Port Coquitlam, BC	10 MeV	60 kW
NeoBeam			
	Middlebury, OH	5 MeV	150 kW
Radiation Dynamics			
	Edgewood, NY	3 MeV	90kW*
Sterigenics			
	Bridgeport, NJ	10 MeV	190 kW*
	Gaithersburg, MD	3 MeV	75 kW
Steris			
	Libertyville, IL	5 MeV	80 kW

*X-ray capability