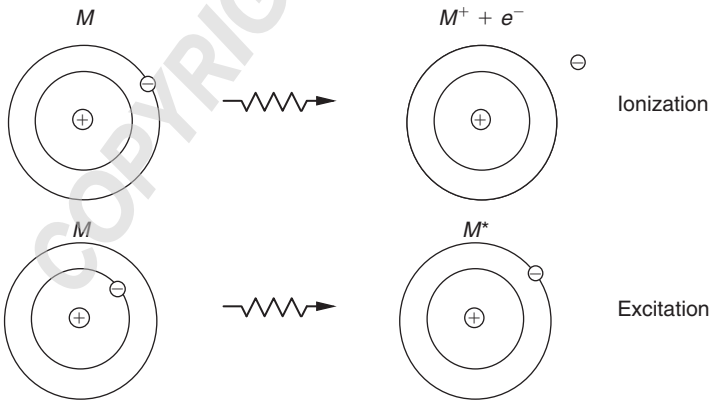
1 Basic Concepts of Radiation Processing

1.1 RADIATION SOURCES

Radiation processing of polymer materials involves subjecting the polymers to the irradiation, usually in a continuous mode, for modifications of the polymers to improve properties for industrial purposes. The main irradiating sources for the purpose of radiation modification of polymer properties include γ-rays from radioactive isotopes such as Co-60 (^{60}Co), electron beams from electron accelerators, and X-rays converted from electron beams [1]. γ-Rays, electron beams, and X-rays have important differences, but they all transfer energy to the atoms of the irradiated material. When the transferred energy is higher than a particular orbital electron, the electron is ejected and the atom is ionized. When the energy is not high enough for ionization, the electron is raised to an upper energy level, resulting in excitation (Scheme 1.1).



SCHEME 1.1 Ionization and excitation.

Radiation Processing of Polymer Materials and Its Industrial Applications, First Edition.
Keizo Makuuchi and Song Cheng.

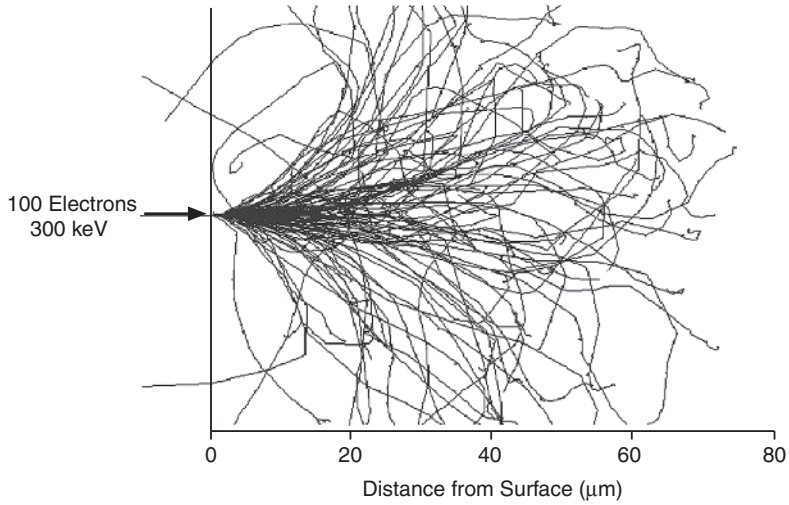


FIGURE 1.1 Monte Carlo simulation of tracks of 100 electrons with 300 keV energy injected into water, calculated with EGS4 code. (Courtesy of Dr. Fukuda, M.)

The ionizing potential for most molecules is <15 eV, while the energies of industrial irradiators range from 100 to 10 MeV, so ionization is the main process. The electron generated by ionization, called the secondary electron, ionizes and excites another molecule upon colliding with it. Ionization and excitation repeat until the energy is lost to the point at which it is lower than the ionizing energy of the molecule. Figure 1.1 illustrates the tracks of 100 electrons with an initial energy of 300 keV when they are injected into water. The ionization and excitation produced by these electrons proceed like an avalanche [2].

The ionized and excited species created by irradiation would induce various reactions, but it is important to point out here that materials irradiated under energies <10 MeV do not have radioactivity.

1.1.1 γ-Ray

As high-energy electromagnetic radiation, γ-rays generated by radioactive decay interact with the molecules of the matter they irradiate through secondary electrons. The typical energy of γ-rays is a few hundred electron volts (eV), higher than the energy of ultraviolet (UV) light and slightly higher than that of X-rays. γ-Rays ionize matter by three main processes: the photoelectric effect, Compton scattering, and pair production. In the wide energy range of 100 to 1 MeV, Compton scattering is the main absorption mechanism, in which an incident γ-photon loses enough energy to eject an electron in an atom of the irradiated matter, and the remainder of its energy is emitted as a new γ-photon with lower energy.

Although decay from other isotopes, such as cesium-137 (^{137}Cs), also produces γ-rays, ^{60}Co is the most commonly used radiation source for industrial

uses. Radioactive ^{60}Co slugs or pellets are made from sintered powders of the stable isotope of cobalt-59 by welding and then nuclear reaction (for a period of 18 to 24 months) through absorption of neutrons in a nuclear power reactor:

$$\text{Co-59} \xrightarrow{\text{Neutrons}} \text{Co-60}$$

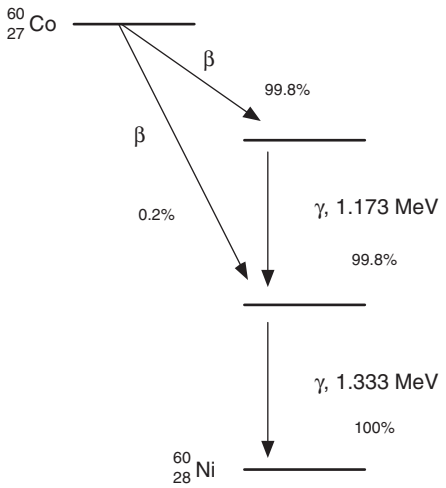
The slugs or pellets are encapsulated in small corrosion-resistant steel cylinders to make source "pencils," which can be transported safely in bigger stainless-steel containers, which shield the radiation. Cobalt-60 decays into the excited-state nickel-60 isotope, emitting one negative β particle with a half-life of $\sim$5.27 years. The excited state nickel-60 further decays into stable nickel-60, emitting two photons with energies of 1.173 and 1.333 MeV, respectively (Scheme 1.2).

In industry, the amount of the radioisotope is indicated by the unit for radioactivity, Curie (Ci): 1 Ci of a radioisotope disintegrates at 3.7×10^{10}/s. A γ-ray of 2.506 MeV is emitted by each disintegration. Thus the radiation power of 1 Ci of ^{60}Co is calculated as:

$$1\,\text{Ci}\ {}^{60}\text{Co} = 3.7 \times 10^{10}/\text{s} \times 2.50\,\text{MeV} = 3.7 \times 2.5 \times 10^{16}\,\text{eV/s}$$
$$= 3.33 \times 10^{21}\,\text{eV/h} = 0.0148\,\text{W}$$

So the power of 1 MCi of ^{60}Co is equivalent to 14.8 kW.

γ-Irradiation using a ^{60}Co source has a low dose rate, or dose absorbed by the matter per unit time (on the 10^{-3} kGy/s order of magnitude). The dose rate



SCHEME 1.2 Radioactive decay of ^{60}Co.

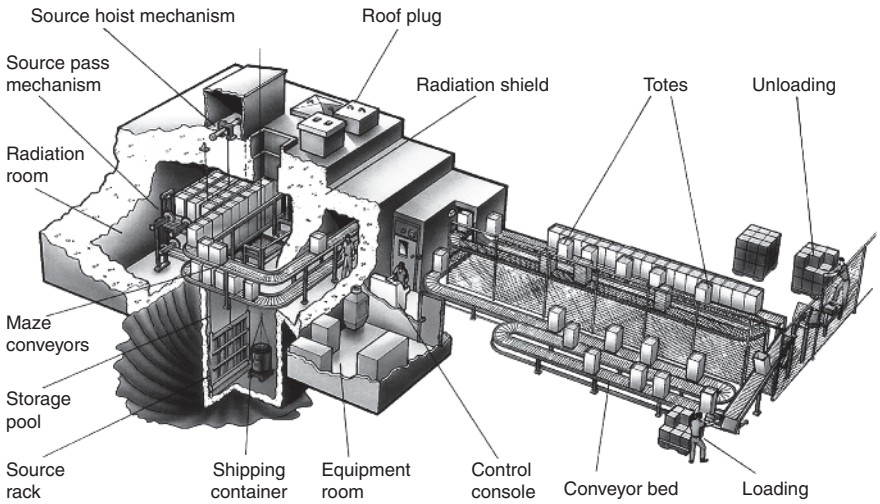


FIGURE 1.2 Layout of typical wet storage γ-irradiation facility. (Reprinted with permission from Nordion, Inc.)

of γ-rays is much lower than that of electron beams. This is a limiting factor for the throughput of radiation processing with γ-rays.

A ^{60}Co γ-irradiation facility for industrial processing consists of an irradiation room, source storage room, source hoist device, materials transport and handling system, control station, safety interlock system, and radiation shielding, etc. The ^{60}Co source on a source rack (usually rectangular) is raised to be in the irradiation room during the irradiation of products and lowered to the storage room underneath the irradiation room floor, usually in a deep water well (wet storage), to sufficiently shield the radiation and to allow personnel to work in the irradiation room. The majority of the world's γ-irradiators use a rectangular source rack and wet storage. The materials transport and handling system takes the product in and out of the irradiation room. The whole facility is shielded by maze concrete walls. Figure 1.2 shows the layout of a typical γ-irradiation facility [3].

Compared to electron beam irradiation, γ-irradiation has high penetration, which gives it advantages for irradiating bulky products with large volumes or odd shapes. However, the absorbed dose of γ-rays within the irradiated material decreases exponentially with the increase of the depth into the matter following the equation:

$$I_t = I_0 e^{-\mu t}$$

where I_t is the intensity of the γ-rays after passing through the thickness, t, into the material; I_0 is the initial intensity; and μ is the linear absorption coefficient. The attenuation reduces the dose uniformity across the matter. Figure 1.3

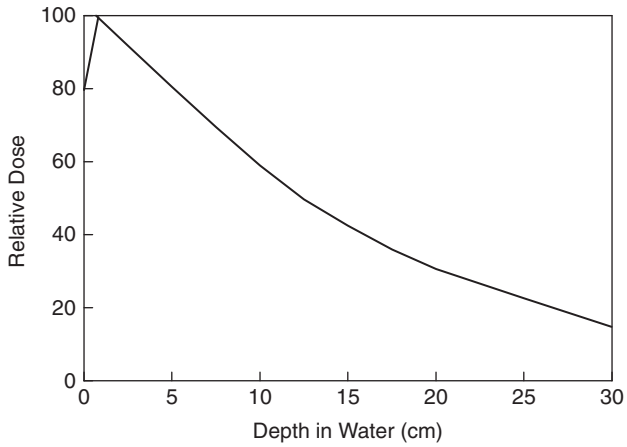


FIGURE 1.3 Percentage absorbed dose of ^{60}Co irradiation in water as a function of depth. (Reprinted with permission from Ref. 4.)

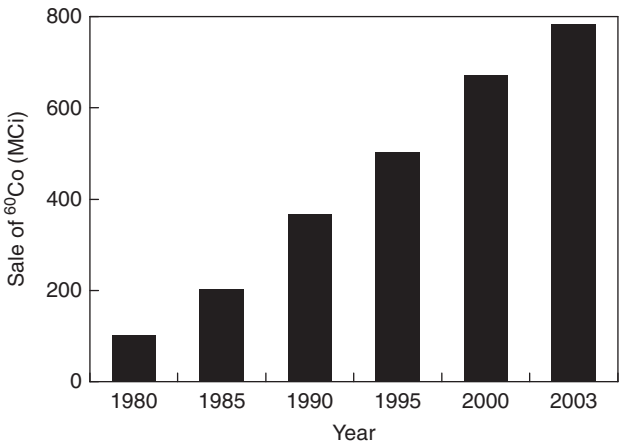


FIGURE 1.4 Accumulative worldwide sale of ^{60}Co for radiation processing from 1985 to 2003. (Reprinted with permission from Ref. 3.)

shows the percentage of absorbed dose of ^{60}Co irradiation in water as a function of depth [4].

γ-Irradiation using a ^{60}Co source has a low-energy consumption density, so the dose rate, or dose absorbed by the matter per unit time, is low (on the 10^{-3} kGy/s order of magnitude). The dose rate of γ-rays is much lower than that of electron beams. The power of a ^{60}Co irradiator is thus very low (only 1.48 kW for a 100 kCi source). This is a limiting factor for the throughput of the radiation processing.

Over the past 50 years γ-rays have been widely used for radiation processing. Figure 1.4 shows the growth of accumulative worldwide sale of ^{60}Co for

radiation processing from 1985 to 2003 [3]. There were about 160 γ-irradiation facilities in the world in 2008. An IAEA survey indicated that about 30% of the world's γ-processing facilities irradiate polymers for property improvement [5].

1.1.2 Electron Beam

An electron beam (EB) can be produced by energizing and accelerating a stream of electrons through an electromagnetic or electrostatic field. Industrial electron accelerators are composed of an electron gun, accelerating tube, power source system, control system, vacuum system, beam window, and scanner. Several types of electron beam accelerators are commercially available and are used as radiation sources for industrial processing. The acceleration can be carried out by either direct current (DC) power or radiofrequency (RF) power. The energy source is usually a high voltage DC power supply. Different methods are used to transfer alternating current (AC) power to the rectifier stages, including series or parallel inductive coupling and series or parallel capacitive coupling. The electrons are generated from a thermionic cathode at the negative end of the beam tube and accelerated toward the anode at ground potential. The cathode is typically a directly heated wire of tungsten. The beam current is usually controlled by varying the cathode temperature or by a grid with variable voltage placed in front of the cathode. The electrons gain kinetic energy continuously as they pass through the tube. After acceleration, the concentrated electron beams are scanned with an electromagnet. The beam diverges in an evacuated chamber (scan horn) and then passes through a thin metallic foil (beam window, usually made of a titanium alloy) into the air, with a small energy lost ($>$100 keV) through the window [6]. Low-energy accelerators may use nonscanning curtain to induct the beam out of the window. Table 1.1 summarizes the characteristics of EB accelerators with different technologies. Accelerators with DC acceleration have lower energy ($<$5MeV) but higher energy conversion and are bigger in size. Those with high-frequency resonant pulse acceleration have higher energy ($>$5 MeV) but lower energy conversion, and relatively small size. Figure 1.5 shows how a DC-type accelerator works. Summaries of the engineering aspects of these different accelerators can be found in a review by Cleland and Parks [6].

The strength of the EB as radiation is controlled by two factors: accelerating voltage and beam current. The energy of electrons is the same as the accelerating voltage. The energy of electrons affects their penetration into materials. The beam current determines the number of accelerated electrons: 1 ampere (A) of current has a flow of 6.3×10^{18} electrons per second. The total output of an electron beam is obtained by multiplying the accelerating voltage by the beam current. The commonly used electron energy ranges from 100 keV to 10 MeV and the power in the beam ranges from 0.5 to 200 kW.

Industrial electron accelerators are usually classified according to their energy levels. Low-energy accelerators have energies from about 80 to 300 keV. Medium-energy accelerators have a range of from about 300 keV to 5MeV.

TABLE 1.1 Types and Characteristics of Industrial Electron Beam Accelerators

Category	Type	Energy Range (MeV)	Characteristics
Electrostatic (DC) accelerators	Cockcroft–Walton	<5	Capacitive power supply, series-coupled system (1950s); low frequency, 60–80% energy conversion
	Schenkel	<5	Capacitive power supply, parallel-coupled system (1950s); RF power, low-energy conversion
	Insulating core transformer	<1	Inductive power supply, series-coupled system (1950s); simple structure, low-energy conversion
	Iron core at ground potential	<1	Inductive power supply, parallel-coupled system (1950s); high-energy conversion but low output power
	Dynamitron	5	Parallel-fed cascade generators (1960s); medium-energy and high-beam power; rugged, reliable, and adaptable
High frequency (RF) accelerators	Linear accelerator (Linac)	10	Electric field created by RF generator with standing waves (higher power) or traveling waves; electrons delivered in microsecond or nanosecond pulses (1990s); high-energy, low- to medium-beam power
	Rhodotron	10	Recirculating beam acceleration (2000s); high-energy and high-beam power; adjustable energy; capable of X-ray conversion

High-energy accelerators usually have energies >5 MeV, although for industrial applications energies >15 MeV are not used because radioactivity may be induced at that high level of energy. Radioactivity is negligible for most polymer materials treated with electron energies <10MeV, but may require attention for metallic parts irradiated with electron energies >10 MeV. Table 1.2 shows the

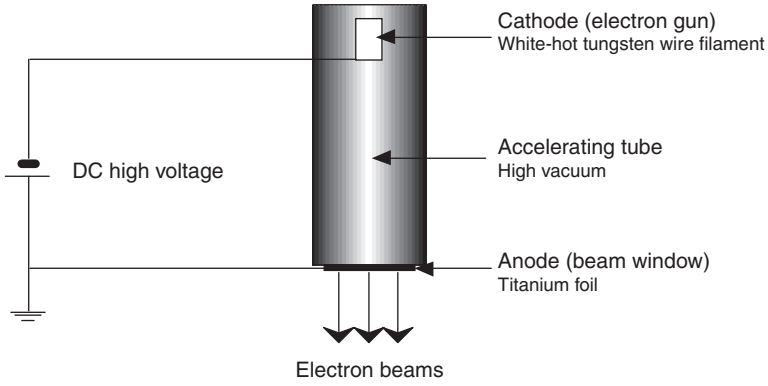


FIGURE 1.5 A DC-type accelerator.

TABLE 1.2 Characteristics of Electron Accelerators of Different Energy Levels

Type	Rating Range (MeV)	Features	Main Applications
Low energy	<0.3	Low penetration Easy shielding Small machine size	Surface coating Thin film crosslinking
Medium energy	0.3–5	Medium penetration	Crosslinking of plastic parts
High energy	>5	High penetration Heavy shielding	Sterilization, crosslinking, and degradation of polymers

characteristics of electron beam accelerators of different energy levels and Figure 1.6 compares the sizes of typical low-energy, medium-energy and high-energy electron accelerators.

In contrast to γ-rays, electron beams generated from an accelerator is monoenergetic. EB irradiators have much higher power than γ-irradiators. The average beam power ratings for modern medium-energy and high-energy accelerators can be up to 200 kW or even higher. The dose rate of EB irradiation, on the 100 kGy/s level, is orders of magnitude higher than that of γ-irradiation. However, because electrons have very small mass, EB has quick energy loss after interaction with the irradiated matter, so it has low penetration. The penetration depends on the EB energy, the density of the irradiated material, and the geometry of the products.

Figure 1.9 shows typical depth-dose curves for electron beams of different energies. The maximum absorbed dose is always at a small depth below the surface. The dose decreases quickly with depth after reaching the maximum. The optimal range of depth for effective irradiation, R(opt), is defined as the

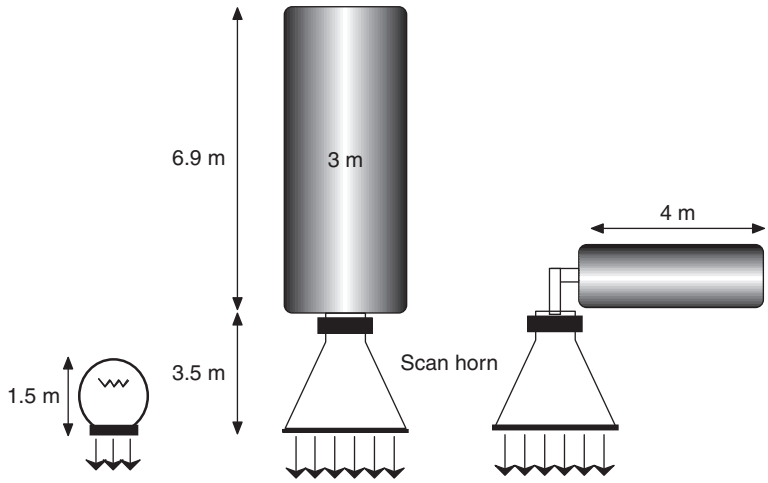


FIGURE 1.6 Relative sizes of typical electron accelerators.

depth at which the exit dose equals the entrance dose. $R(\text{opt})$ can be correlated with the incident electron energy E with sufficient accuracy for industrial applications by using the following linear equation:

$$R(\text{opt}) = 0.404E - 0.161$$

where the electron range values are in g/cm^2 and the electron energy values are in MeV [7]. As can be seen from Figure 1.7, the optimal penetration depth is <4 cm in a material with unit density even with the high electron beam energy of 10 MeV.

Figure 1.8 shows the increase of EB penetration in polyethylene (PE) with the increase of the EB energy, where in $R(50)$ is the depth at which the exit dose equals half the maximum dose, $R(50e)$ is the depth at which the exit dose equals half the entrance dose, and $R(p)$ is the depth at which the tangent line of the decreasing part of the depth-dose curve would extend to zero dose [7].

Double-sided irradiation is often carried out in commercial radiation processing for the purpose of obtaining better dose distribution either by successively irradiating one side and the other or by simultaneously irradiating both sides with two accelerators. Figure 1.9 shows the improvement of dose distribution of double-sided irradiation. Double-sided irradiation effectively increases the $R(\text{opt})$ from 3.8 to 9.2 cm for a 10-MeV accelerator irradiating a material with unit density.

An electron beam–processing facility includes the electron accelerator, material handling equipment, radiation shielding, ozone exhaust, and control

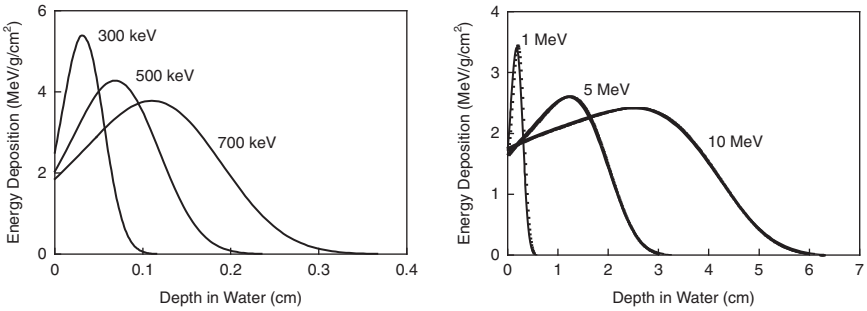


FIGURE 1.7 Dose distribution and penetration limit for electron beams of different energies.

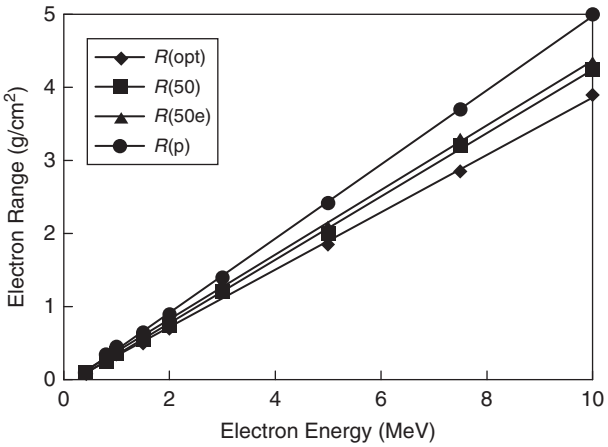


FIGURE 1.8 Electron beam penetration in polyethylene. (Reprinted with permission from Ref. 7.)

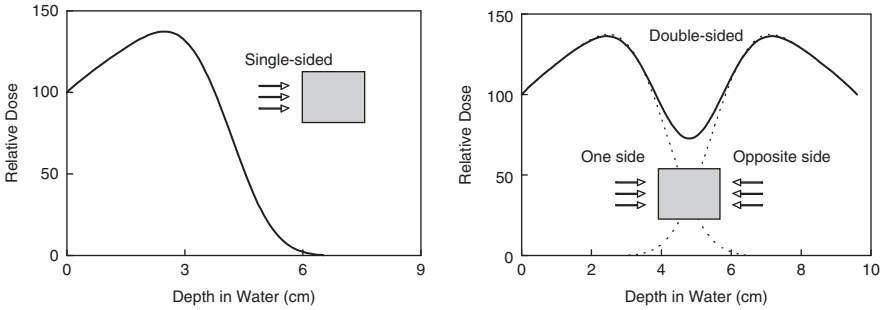


FIGURE 1.9 Dose distribution of double-sided vs. single-sided irradiation.

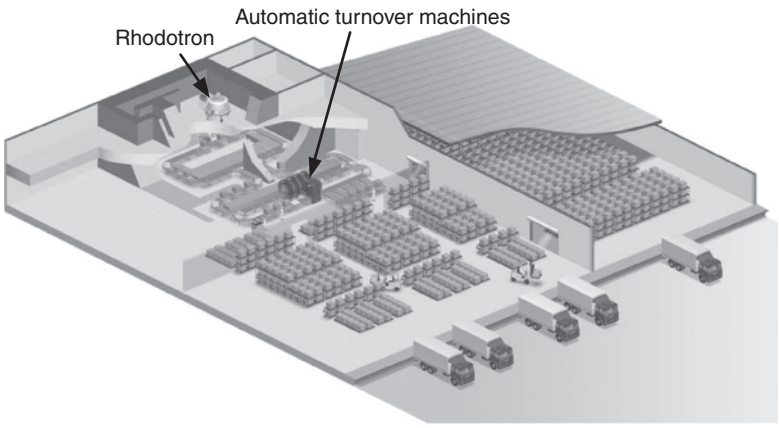


FIGURE 1.10 Layout of typical electron beam–processing facility with a Rhodotron accelerator. (Courtesy of Kansai Electron Beam Co., Ltd.)

system. For commercial applications, the most important characteristics of the accelerator are its electron energy and average beam power. The penetration of electrons in irradiated materials increases with their kinetic energy, while the processing rate increases with the beam power. Because of this, the modern high-energy, high-power electron beam accelerators such as the Rhodotron have tremendous advantages for industrial processing of polymer materials. The high throughput makes fast and continuous commercial processing possible and reduces the operation cost greatly. Figure 1.10 shows the layout of a typical EB-processing facility with a Rhodotron accelerator. The main facility consists of a Rhodotron, conveyor and automatic turnover machine for two-sided irradiation.

As of 2008, more than 13,000 electron beam accelerators had been installed and were being used all over the world; more than 1,400 high-current units were being used for radiation processing.

1.1.3 X-Ray

As discussed in the last section, despite its high power and high dose rate,EB has serious penetration limitations and is not suitable for processing thick products. Converting electron beams to X-rays can overcome the penetration limit, and the X-rays may provide more uniform dose absorption. However, because the electron beam to X-ray conversion process has low efficiency, X-ray irradiation has been made commercially feasible only with the more recent progress in advanced, high-energy and high-beam power electron accelerators.

When an electron beam is allowed to impinge on a target that is composed of a metallic material, the metal will absorb the electron beam and cause broad-spectrum X-rays in the form of bremsstrahlung radiation (photons) to be emitted from the target. The bremsstrahlung yield is determined by the atomic

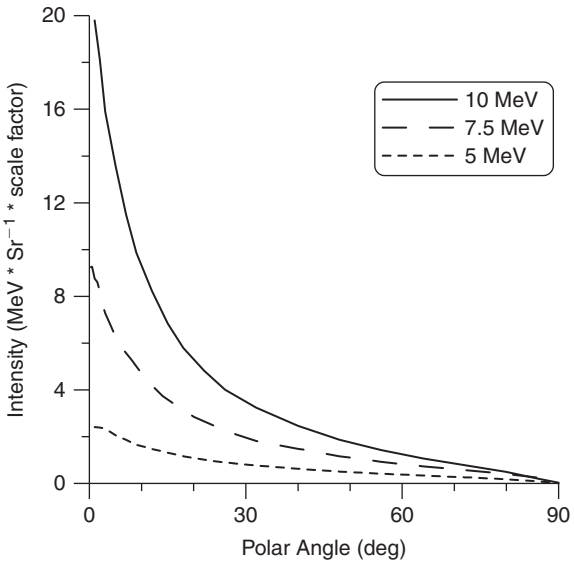


FIGURE 1.11 Angular distribution of X-rays at 5-, 7.5-, and 10-MeV incident electron energies. (Reprinted with permission from Ref. 8.)

number and thickness of the target and the energy and current of the incident electron beam. The higher the atomic number of the target, the higher the X-ray intensity. Lead, tantalum, tungsten, gold, etc. can be used as the target material, and tantalum is recommended for a high efficiency to cost ratio. Higher incident electron beam energy also gives a higher X-ray intensity. The X-ray yield has a distribution over the angle between observation and the incident electron beam. Figure 1.11 shows the calculated angular distribution of X-rays at three energy levels: 5, 7.5, and 10 MeV [8].

The bremsstrahlung photons are not monoenergetic but have a distribution over a range of energies. Figure 1.12 shows the spectrum of X-ray photon energies produced at the same three electron energies [8].

Penetration of X-rays in irradiated material is similar to those of γ-rays, but dose distribution may be more complicated. Figure 1.13 shows the computer-calculated dose distribution of X-rays in a 50 by 50 by 70 cm (height) high-density polyethylene (HDPE) phantom with a 7.5-MeV incident electron beam. It shows that the dose absorbed at the center of the stack is higher than the dose absorbed at the side edge of the stack, but it is lower than the dose delivered to the leading edge of the stack [8].

In terms of effects on polymer materials, X-ray radiation is more similar to γ-rays than to electron beams. Like γ-rays, X-rays have much deeper penetration into materials so the practical range of thickness that may be processed is much greater. However, because of the inefficient electron beam to X-ray conversion, the power and production rate of X-rays are greatly reduced and are much lower than that of electron beams. Although it may be higher than

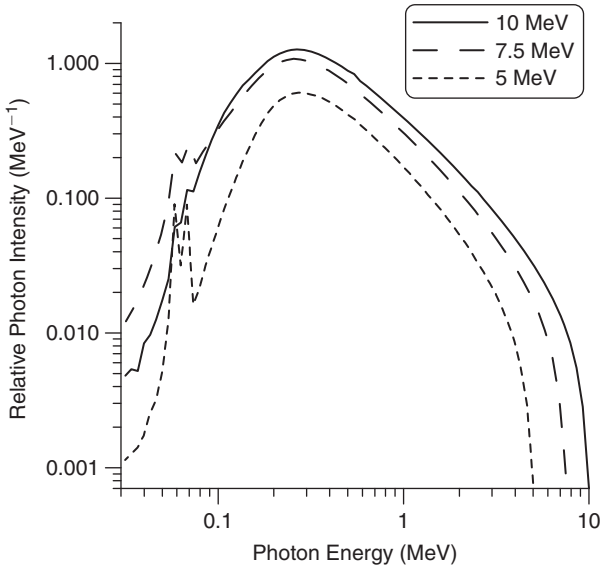


FIGURE 1.12 Calculated X-ray photon spectra for electrons with 5-, 7.5-, and 10-MeV incident electron energies. (Reprinted with permission from Ref. 8.)

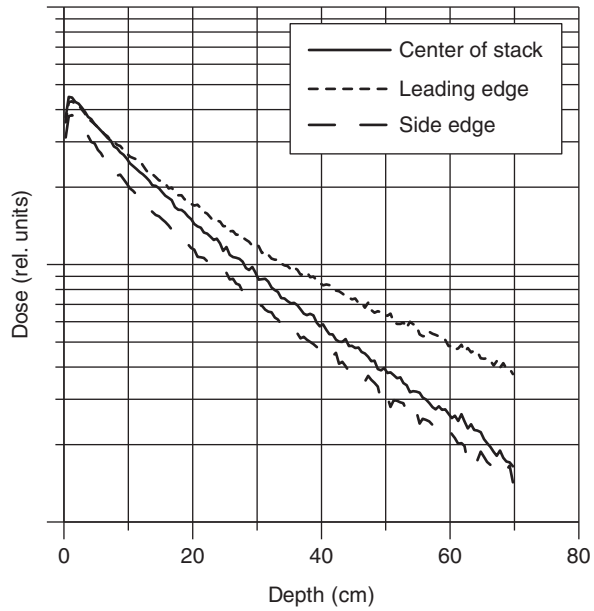


FIGURE 1.13 X-ray dose distribution in an HDPE phantom at 7.5 MeV incident energy. (Reprinted with permission from Ref. 8.)

TABLE 1.3 Comparison of Irradiation Technologies: γ-Ray, Electron Beam and X-Ray

Characteristic	γ-Ray	Electron Beam	X-Ray
Penetration	Strong, exponential attenuation	Limited range	Strong, exponential attenuation
Power (throughput)	Low	High	Low
Operating cost	Higher	Lower	Higher
Dose Rate	Low	High	Low
Power source	Radioactive isotope	Electricity	Electricity
Equipment	Easy to operate and maintain	Complicated to operate and maintain	Complicated to operate and maintain
Shielding	Continuous radiation requires more shielding	Can be turned on and off, less demanding in shielding	Can be turned on and off, less demanding in shielding
Source attenuation	Continuous attenuation requires regular addition of source	No attenuation	No attenuation

that of the γ-rays, the dose rate for X-rays is also orders of magnitude lower than that of electron beams.

Table 1.3 summarizes the characteristics of γ-rays, electron beams and X-ray technologies. Because of the higher throughput and lower operation cost, and because of the world's shortage of isotope sources, electron beams may have wider applications in polymer processing in the future. The implications of the differences in the three technologies will also be discussed more specifically for different applications in the corresponding chapters of this book.

1.2 RADIATION CHEMISTRY OF POLYMERS

1.2.1 Interactions of Ionizing Radiation with Polymers and Reactions Induced

The primary interactions of ionizing radiation with polymers include ionization, excitation, stabilization of electrons through the generation of hot electrons, ion neutralization, and free radicals. Free radicals are created either through scission of the main polymer chain or through the dissociation of the C-H side chain. The primary processes are shown Scheme 1.3.

The secondary reactions following the free radical generation include hydrogen abstraction, addition to double bond, recombination (crosslinking or branching), chain scission, oxidation and grafting, as shown in Scheme 1.4.

Monomers can also be polymerized by radiation as shown in Scheme 1.5.

Ionization	P	$\rightsquigarrow P^+ + e^-$
Excitation	P	$\rightsquigarrow P^*$
Thermal stabilization of electron	e	$\longrightarrow e_{th}^-$
Neutralization	$P^+ + e_{th}^-$	$\longrightarrow P^*$
Free-radical formation	P^*	$\longrightarrow R_1\bullet + R_2\bullet$
		$\longrightarrow R\bullet + H\bullet$

SCHEME 1.3 Primary processes (P = polymer, R = radical).

Hydrogene abstraction	$R\bullet + P$	$\longrightarrow RH + P\bullet$
Double-bond addition	$\bullet RCH{=}CH_2 + H\bullet$	$\longrightarrow RCH_2CH_2\bullet$
Crosslinking or branching	$R_m\bullet + R_n\bullet$	$\longrightarrow R_m{-}R_n$
Chain scission	$R\bullet$	$\longrightarrow R_k\bullet + R_l$
Oxidation	$R\bullet + O_2$	$\longrightarrow ROO\bullet$
	$ROO\bullet$	$\longrightarrow -C{=}O, -OH, -COOH$
Grafting	$R\bullet + M$	$\longrightarrow RM\bullet$
	$RM\bullet + nM$	$\longrightarrow RM_{n+1}\bullet$

SCHEME 1.4 Secondary reactions (M = monomer).

Radical formation	M or S	$\rightsquigarrow$ X•
Initiation	X• + M	$\longrightarrow$ XM•
Propagation	XM• + *n*M	$\longrightarrow$ XM_n•
Chain transfer	XM_n• + M or S	$\longrightarrow$ XM_n + X•
	XM_n• + P	$\longrightarrow$ P•
Termination	XM_n• + XM_m•	$\longrightarrow$ P
	XM_n• + P•	$\longrightarrow$ P

SCHEME 1.5 Radiation polymerization (S = solvent, P = polymer).

1.2.2 Different Responses to Radiation from Different Polymers

As discussed in the last section, when radiation from a γ-ray, electron beam, or X-ray source interacts with a polymer material, its energy is absorbed by the polymer material and active species such as radicals are produced, thereby initiating various chemical reactions. The fundamental processes that are the results of these reactions include

Crosslinking, where polymer chains are joined and a network is formed

Chain scission, where the molecular weight of the polymer is reduced through chain scission

Oxidation, where the polymer molecules react with oxygen via peroxide radicals (oxidation and chain scission often occurs simultaneously)

Long-chain branching, where polymer chains are joined but a three-dimensional network is not yet formed

Grafting, where a new monomer is polymerized and grafted onto the base polymer chain

When monomers are irradiated, polymerization can also be initiated. Radiation curing (as in the case of coatings or composites) is a combination of polymerization and crosslinking.

Different polymers have different responses to radiation, especially when it comes to crosslinking vs. chain scission. A parameter called the *G value* is widely used by radiation chemists to quantify the chemical yield resulting from the radiation. The *G* value is defined as the chemical yield of radiation in number of molecules reacted per 100 eV of absorbed energy. Table 1.4 shows the G values for crosslinking *G*(X) and chain scission *G*(S) for some of the common polymeric materials irradiated at room temperature without oxygen [9, 10]. Materials with *G*(S):*G*(X) ratios <1.00 are favored for crosslinking. Materials with *G*(S):*G*(X) ratios >1.00 tend to undergo degradation more. Materials whose *G*(X) and *G*(S) values are both low are more resistant toward radiation.

The different responses to radiation for different polymers are intrinsically related to the chemical structures of the polymers. Figure 1.14 illustrates some examples of chemical structures that correspond to crosslinking-type, degradation-type, and radiation-resistant polymers. Rough rules of thumb may

TABLE 1.4 ***G* Values for Crosslinking and Chain Scission for Some Common Polymers**

Polymer	Crosslinking $G(X)$	Scission $G(S)$	$G(S):G(X)$
Low-density polyethylene	1.42	0.48	0.34
High-density polyethylene	0.96	0.19	0.20
Isotactic polypropylene	0.16–0.26	0.29–0.31	1.1–1.5
Atactic polypropylene	0.4–0.5	0.3–0.6	0.7–0.9
Polymethylmethacrylate	<0.50	1.1–1.7	>2
Polytetrafluoroethylene	0.1–0.3	3.0–5.0	10
Natural rubber	1.3–3.5	0.1–0.2	0.14
Nylon 6	0.35–0.7	0.7	1.0
Nylon 6,6	0.5–0.9	0.7–2.4	1.4
Polyvinylacetate	0.1–0.3	0.06	0.2
Polyvinylidene fluoride	0.6–1.00	0.30–0.6	0.3
Polymethylacrylate	0.45–0.52	0.08	0.15
Polystyrene	0.019–0.051	0.0094–0.019	0.4
Polybutadiene	5.3	0.53	0.10
Polyisobutylene	0.05–0.5	5	>10
Butyl rubber	<0.5	2.9–3.7	>6

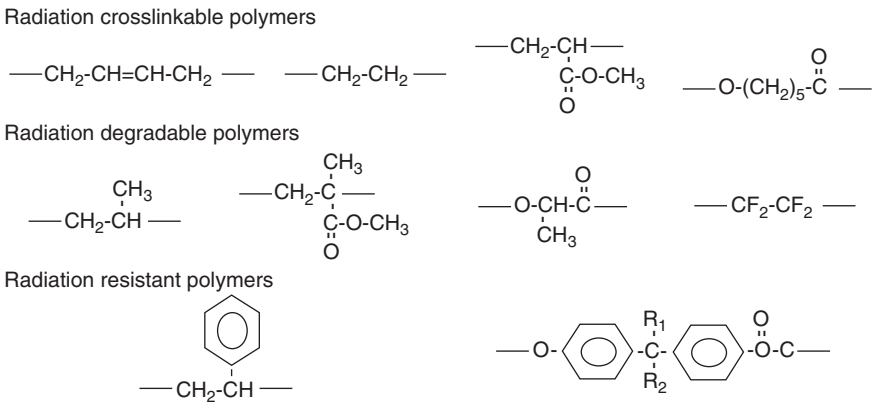


FIGURE 1.14 Examples of chemical structures of polymers with different responses to radiation.

be made from the examples. Polymers with more hydrogen atoms on the side (e.g., PE) tend to crosslink with radiation. Polymers with a methyl group (e.g., polypropylene), di-substitutions (e.g., polymethacrylate) and per-halogen substitutions (e.g., PTFE) 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.

Crosslinking and chain scission are two competing processes that always coexist under radiation. The overall effect depends on which of the two is predominant at a certain time. Whenever $G(X)$ is larger than $G(S)$, the overall result is crosslinking, and whenever $G(S)$ is larger than $G(X)$, the overall result is degradation. It should also be kept in mind that for a given polymer $G(X)$ and $G(S)$ both change with radiation conditions, such as the absorbed dose and the temperature. For the relationship with the radiation dose, both $G(X)$ and $G(S)$ increase with the increase in the dose. However, $G(S)$ for a polymer generally increases more than $G(X)$ does with increasing dose. Therefore, there can be three different scenarios for the relationship between the polymer molecular weight (MW) and the radiation dose, as shown in Figure 1.15. When $G(X)$ of a polymer is much greater that $G(S)$, the MW continuously increases due to continuous crosslinking, but the MW will level off because $G(S)$ will increase faster. When $G(X)$ is greater, but not much greater than $G(S)$, $G(S)$ will eventually catch up with $G(X)$, and the MW will show a turning point, with the overall reaction changing from crosslinking to degradation. Continuous degradation will occur when $G(S)$ is greater than $G(X)$.

$G(X)$ and $G(S)$ also depend on irradiation conditions, such as temperature and atmosphere. For some polymers, elevated temperature may increase the mobility of the polymer chains and make it more favorable to crosslinking. Oxygen in the air usually assists the degradation more through a peroxide radical mechanism (oxidative degradation), so an oxygen-free atmosphere is usually more favorable for crosslinking. A good example is PTFE, which undergoes degradation readily under ambient conditions, but can be crosslinked at elevated temperatures ($>$ melting temperature $= 315°C$) in an oxygen-free atmosphere (Fig. 1.16).

The different reactions that radiation incurs on a polymer bring about different effects on the physical properties of the polymer. Crosslinking normally enhances the mechanical properties and thermal stability of the polymer, while

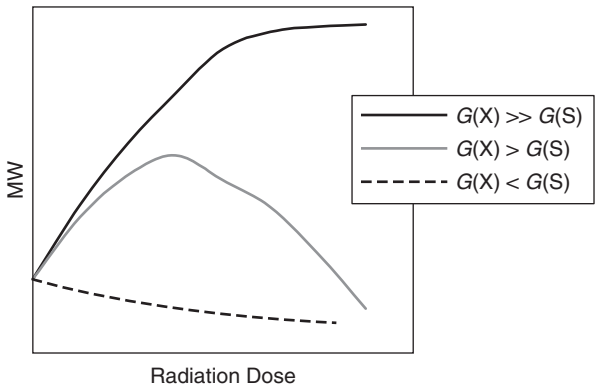


FIGURE 1.15 Relationship between MW of polymer and radiation dose.

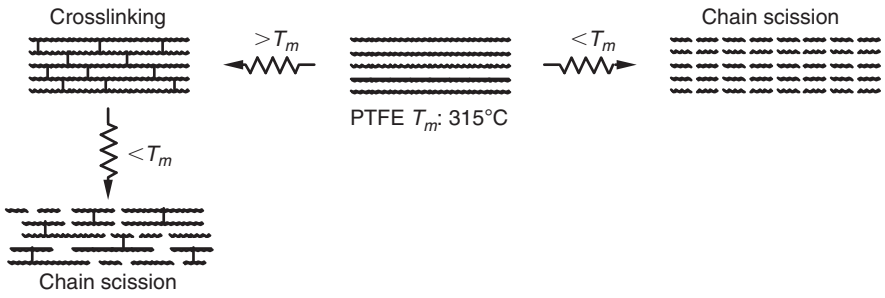


FIGURE 1.16 Degradation and crosslinking of PTFE under different conditions.

reducing the melt flow and increasing the viscosity of polymer solution. Chain scission, on the contrary, deteriorates the mechanical integrity and thermal resistance. It increases the melt flow and decreases the viscosity of polymer solution. Oxidation may give rise to discoloration and brittleness and introduce carbonyl-containing functional groups to the polymer. Long-chain branching brings modification of rheology and hence processability of the polymer. Grafting is used to endow the polymer with new properties through newly grafted functional groups. In the following chapters, we discuss the details of how these reactions, with their different impacts on the polymer properties, can be used for practical and commercially beneficial, industrial applications.

1.3 ADVANTAGES AND DISADVANTAGES OF RADIATION PROCESSING

Compared with chemical processes to modify polymer properties with similar reactions but by using chemicals, often with heat, radiation processing of polymers has both advantages and shortcomings. The advantages include higher throughput because of faster processing, energy savings because of processing at room temperature, less sensitivity to moisture, significant reduction of volatile organic compounds because no solvent is used, and higher purity and lower toxicity because no or less toxic chemicals are needed.

Radiation processing of polymers also has a few intrinsic disadvantages. Although the daily operation cost may not be high, the irradiator system is typically expensive for decent industrial throughput and capacity, so it requires significant capital investment. The operational cost of radiation processing also depends heavily on the volume, so it can be significantly higher than chemical modification when the volume is not high enough. In some cases the properties achieved by radiation processing are still inferior to those that can be achieved by chemical modification. A lot of times it is very difficult for the polymer processor to make radical changes to their existing processes to incorporate the radiation processing. The lack of understanding and acceptance of radiation technology by the public is also an obstacle.

It is important that we should keep in mind that the chief competition to radiation processing is chemical modification. To realize true added value potential of radiation processing of polymers it is crucial to commercial success that radiation processing has to offer more advantages than disadvantages and reduce the cost for the same level of property improvements when compared to competing chemical modifications.

1.4 ENGINEERING OF RADIATION PROCESSING

The most significant issues for industrial radiation processing of polymers are irradiators, materials handling, dose and dose distribution, throughput, temperature, and atmosphere. Irradiators were discussed in an earlier section of this chapter. Other factors are discussed below.

1.4.1 Materials Handling

The main objectives for materials handling for radiation processing are to control the dose, use the radiation source efficiently, and facilitate the loading and unloading operations. A variety of product handling and conveying systems have been developed and applied for these purposes. For bulk polymers, belt, roller, cart, and overhead chain conveyors can be used. Special designs, such as a reel-to-reel handling system, are needed for irradiating wires, cables, tubing, etc. [6].

1.4.2 Radiation Dose and Dose Distribution

Dose and the distribution of dose across the material are probably the most important parameters for radiation processing of materials. *Radiation dose* is defined as the energy absorbed by the irradiated materials per unit mass. The SI unit for dose is the Gray (Gy), which is 1 J/kg. An old unit, rad, is still used sometimes ($1\,\text{rad} = 1/100\,\text{Gy}$ and $1\,\text{Mrad} = 10\,\text{kGy}$). Dosimeters are used in radiation processing to detect and measure the absorbed dose. Radiation dose is determined by measuring the physical or chemical change in the dosimeter and by establishing its relationship with the absorbed dose. Various types of dosimeters can be used, such as quartz fiber dosimeter, film badge dosimeter, thermoluminescent dosimeter, and solid state (MOSFET or silicon diode) dosimeter. Each type of dosimeter is suitable for a different dose range. Table 1.5 shows the ranges of doses that are suitable for various dosimeters classified according to the chemical materials they use.

For practical industrial radiation processing, minimum and maximum dose have to be determined. The minimum dose is what is required to achieve the desired effect, and the maximum dose is where downside effects begin to take place or where it becomes uneconomical (the processing cost generally being proportional to the dose). Table 1.6 shows the approximate ranges of required radiation dose for various applications.

TABLE 1.5 Suitable Ranges of Radiation Dose for Different Dosimeter Materials

Dosimeter Material	Change	Detecting Instrument	Suitable Range (Gy)
Alanine	Radical generation	ESR	$1–10^5$
PMMA (colorless)	UV light absorption	UV spectroscopy	$10^3–10^5$
PMMA (colored)	Visible light absorption	Vis spectroscopy	$10^3–5 \times 10^4$
Ferrous sulfate	$Fe^{2+} \rightarrow Fe^{3+}$	UV spectroscopy	10–400
Cerium sulfate	$Ce^{4+} \rightarrow Ce^{3+}$	UV spectroscopy	$10^3–10^5$
Cellulose triacetate	UV light absorption	UV spectroscopy	$10^4–4 \times 10^4$

TABLE 1.6 Ranges of Required Radiation Dose for Various Applications

Application	Required Dose (kGy)
Crosslinking of cables and wires	30–200
Production of heat-shrinkable materials	50–100
Degradation of PTFE for making micropowders	50–1,000
Prevulcanization of tires	15–50
Crosslinking of polymer foams	20–50
Preparation of hydrogels	50–100
Curing of coatings, composites, adhesives	30–200
Graft polymerization	50–200

The dose is not 100% uniform across the irradiated material. For electron beam processing, the dose distribution is a function of the energy of the electron beams, and the density and geometry of the product being processed. For electron beam energies >1 MeV, the relationship between the electron penetration depth and the electron beam energy and product density is:

$$\text{Penetration depth (cm)} = (0.524E - 0.1337)/\rho$$

where E is beam energy in MeV, and ρ is product density in g/cm^3.

As discussed earlier in this chapter and shown in Figure 1.9, a rule of thumb is that the effective depth of penetration (the *optimal depth*) for a particular product is generally considered to be the depth with equal entrance and exit doses.

Figure 1.9 also shows that with higher-beam energy the electron beam would have deeper penetration and more uniform dose distribution. This is one of the important advantages for high energy accelerators. Table 1.7 shows the values of optimal depth for EB penetration for different beam energies for flat materials with a unit density (1 g/cm^3). The values are greater for materials with a density (or apparent density) <1 g/cm^3 and smaller for materials with a density (or apparent density) >1 g/cm^3.

TABLE 1.7 Optimal Depth for EB Penetration for Different Beam Energy

	Optimal Depth	
Beam Energy (MeV)	Single-Sided[a] (cm)	Double-Sided[a] (cm)
5	1.7	4.2
10	3.3	8.3
12	4.0	10.0

[a]For unit density (1 g/cm^3).

The penetration limitation for EB may be a problem for thick parts and parts with complex geometry. X-rays or γ-rays may be used to overcome the penetration limitation but at the expense of throughput.

1.4.3 Throughput

The mass processing rate of electron beam processing can be inferred from the definition and unit of radiation dose. Radiation dose is defined as the amount of radiation absorbed by a material. The Standard International (SI) unit of dose is the Gray, which represents J/kg. Therefore:

$$1\ \text{Gy} = \text{J/kg} = 1\ \text{W (s/kg)}$$
$$1\ \text{kGy} = 1\ \text{kW (s/kg)} = 3{,}600 \times \text{kW (h/kg)} = 3.6 \times \text{kW (h/t)}$$

This means that 1 kW of absorbed irradiation can produce a dose of 1 kGy in 3.6 t/h if the utilization efficiency of the radiation energy is 100%. The actual production rate (mass throughput rate) is therefore given by the following equation, adding the consideration of utilization efficiency:

$$M/t = 3.6 \times f \times P/D$$

where M/t is the mass throughput rate in the unit of t/h, D is the required dose (in kGy), f the utilization efficiency (unit less), and P the beam power (in kW). So the mass throughput for electron beam is directly proportional to the beam power and inversely proportional to the required dose. Higher beam power has the advantage of supplying higher throughput, which is very important for commercial production.

1.4.4 Temperature Rise

Irradiation increases the temperature of the treated material because part of the absorbed energy is consumed as thermal energy. The temperature rise in irradiated materials is proportional to the absorbed dose. In the following equation, Δ is the temperature rise (in °C), D is the average dose (in kGy), and c is the thermal capacity (in J/g °C).

$$\Delta T = D/c$$

The thermal capacity of water is 4.186 J/g K, so the adiabatic temperature rise per 10 kGy of dose would be $1/4.186 = 2.39°C$. Other materials have lower thermal capacities and higher temperature rises. Table 1.8 lists thermal capacities and temperature rises per kGy of common plastics. Among polymer materials, polyethylene has the highest thermal capacity (2.30 J/g °C) and the lowest temperature rise (0.43°C/kGy). PTFE has the lowest thermal capacity (1.05 J/g °C) and the highest temperature rise (0.95°C/kGy). Similar data for common metals are given in Table 1.9. In general, metals have lower thermal capacities and higher temperature rises than plastics [11].

It should be noted that the temperature rise of lead plates exceed above its melting temperature (328°C) by high-dose rate EB irradiation of >69 kGy in an adiabatic condition. Irradiation of wires and cables sometimes causes a deleterious effect to insulating polymeric materials due to the heating of copper conductor.

With high-dose processes using high-power electron beams, the temperature rise usually has to be controlled by applying multiple treatments and allowing time for heat dissipation between exposures or by cooling the material during irradiation or in between the passes.

There are also cases in which elevated temperature (above the room temperature) is needed for the irradiation. Special design for heating is needed in those cases.

1.4.5 Atmosphere

When polymers are irradiated in air, oxidation may occur via peroxide radicals with the presence of oxygen and moisture (see Fig. 1.16 for PTFE). Oxidation

TABLE 1.8 Thermal Capacities and Temperature Rises per kGy in Common Plastic Polymers

Polymer	Thermal Capacity (J/g K)	Temperature Rise (°C/kGy)
PA 6	1.67	0.60
PA 66	1.67	0.60
Polycarbonate (max)	1.26	0.79
Polycarbonate (min)	1.17	0.85
Polyethylene	2.30	0.43
Polymethylmethacrylate	2.09	0.48
Polypropylene	1.92	0.52
Polystyrene	1.34	0.75
Polytetrafluoroethylene	1.05	0.95
Polyvinylchloride	1.34	0.75

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TABLE 1.9 Thermal Capacities and Temperature Rises per kGy in Common Metallic Elements

Elemental Material	Thermal Capacity (J/g °C)	Melting Temperature (°C)	Temperature Rise (°C/kGy)
Ag	0.235	962	4.26
Al	0.90	680	1.11
Au	0.128	1,064	7.81
C	0.71	—	1.41
Cu	0.38	1,085	2.63
Fe	0.44	1,536	2.27
Ge	0.32	937	3.13
Pb	0.13	328	7.69
Si	0.71	1,412	1.41
Ti	0.52	1,668	1.92
W	0.13	3,407	7.69
Zn	0.227	420	4.41

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will tilt the competition of crosslinking and degradation to favor degradation. For this reason, oxygen-free atmosphere (vacuum or dry inert gas) may be needed for some crosslinking, long-chain branching or grafting applications, especially when the polymer's $G(X)$ and $G(S)$ values are close to each other. Oxidative degradation may cause significant deterioration of crucial properties for some applications, and can be prevented by using an oxygen-free atmosphere.

1.4.6 Dose Rate

Dose rate, or how fast dose is delivered to the irradiated material, may also have significant effect on the result. For example, for the competition of crosslinking and oxidative degradation in air, higher dose rate is more favorable for crosslinking because less oxidation can occur in shorter time (due to the diffusion control for oxygen). Industrial electron beams have much higher dose rate than γ-rays, and the dose rate may be an important factor to consider when choosing between the two.

1.4.7 Radiation Processing Cost

The cost of radiation processing has two main components: capital investment of irradiator and operating cost of irradiation facility. The capital investment includes costs for the accelerator or irradiator, auxiliary equipment, monitoring and process control systems, material handling system, building including radiation shielding, project preparation, and other engineering needs. The capital investment costs are generally high for irradiation facilities, especially

EB or X-ray facilities with high energy or γ-ray facilities with high source strength. The operating cost of an irradiation facility includes depreciation of equipment and building, debt service, maintenance and spare parts, labor, administration, and utilities (electricity, water, air, etc.). The economics of running an irradiation facility depends heavily on the use of the irradiator. The operation cost per unit mass of products treated decreases with the increase of utilization rate, so finding sufficient volume to process is crucial.

Industrial applications of radiation processing of polymers will be discussed in detail in the following chapters.

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