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**ATOMIC ENERGY  
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**L'ENERGIE ATOMIQUE  
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**RADIATION PROCESSING IN THE PLASTICS INDUSTRY:  
CURRENT COMMERCIAL APPLICATIONS**

**TRAITEMENT PAR IRRADIATION DANS L'INDUSTRIE DES MATIERES PLASTIQUES:  
APPLICATIONS INDUSTRIELLES ACTUELLES**

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**Pinawa, Manitoba R0E 1L0**

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RÉSUMÉ

L'interaction du rayonnement ionisant et des substrats organiques pour produire des changements physiques et chimiques utiles est la base de l'industrie de traitement par irradiation des matières plastiques. Les accélérateurs à faisceaux d'électrons (EB) dominent l'industrie; toutefois, pour quelques petites applications, on se sert du rayonnement gamma.

Les cinq catégories générales de produits correspondant à plus de 95% de la capacité mondiale de traitement par irradiation dans les accélérateurs à faisceaux d'électrons pour la production des matières plastiques, sont les suivantes:

- (1) les isolants de fils et câbles (34%);
- (2) les films, tubes et tuyaux thermorétractables (34%);
- (3) les revêtements traitables par irradiation (12%);
- (4) les produits en caoutchouc (10%);
- (5) la mousse de polyoléfine (5%).

Au total, 6,1% de la fabrication annuelle de ces produits aux États-Unis est traitée aux faisceaux d'électrons.

La capacité de production des États-Unis correspond à 59% de la capacité totale mondiale de traitement aux faisceaux d'électrons de 20,5 MW (1984) suivie de celle de l'Europe (16%) et de celle du Japon (15%). Il y a 469 à 479 accélérateurs aux faisceaux d'électrons dans le monde entier lesquels servent à la production des matières plastiques et du caoutchouc.

Le taux de croissance moyen annuel (TCMA) de traitement aux faisceaux d'électrons des matières plastiques au Japon, de 1977 à 1987, a été de 13,3%. Il est passé de 20% au cours de la période 1977-1981 à 6,4% au cours de la période 1984-1987.

La réticulation par irradiation des isolants de câbles électriques (puissance nominale de câble de  $\geq 75$  kV), feuilles épaisses de polyoléfine et caoutchouc ( $\geq 15$  mm) et tubes à paroi épaisse est l'une des applications possibles d'un système à faisceaux d'électrons de 5 à 10 MeV. On peut traiter économiquement, aux faisceaux d'électrons, d'autres produits tels que les revêtements, films et isolants de fils à l'aide d'un accélérateur de 5 à 10 MeV s'il est possible d'irradier simultanément plusieurs couches de chacun de ceux-ci. Deux catégories générales de produits nécessitant une étude plus poussée pour déterminer le potentiel du traitement aux faisceaux d'électrons à haute énergie sont les matières plastiques moulées et les matériaux composites.

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ABSTRACT

The interaction of ionizing radiation with organic substrates to produce useful physical and chemical changes is the basis of the radiation processing industry for plastics. Electron beam (EB) accelerators dominate the industry; however, there are a few small applications that use gamma radiation.

The five general product categories that account for over 95% of the worldwide EB capacity used for plastics production are the following:

- (1) Wire and cable insulation (34%);
- (2) Heat-shrinkable film, tubes and pipes (34%);
- (3) Radiation-curable coatings (12%);
- (4) Rubber products (10%); and
- (5) Polyolefin foam (5%).

A total of 6.1% of the yearly production of these products in the United States is EB treated.

The United States accounts for 59% of the total worldwide EB capacity of 20.5 MW (1984), followed by Europe (16%) and Japan (15%). There are 469 to 479 individual EB units worldwide used for the production of plastics and rubber.

The average annual rate of growth (AARG) for the EB processing of plastics in Japan, from 1977 to 1987, was 13.3%. The AARG for Japan has decreased from 20% for 1977 to 1981, to 6.4% for 1984 to 1987.

Radiation cross-linking, of power cable insulation (cable rating  $\geq 75$  kV), thick polyolefin and rubber sheet ( $\geq 15$  mm), and thick-walled tubing is one of the potential applications for a 5- to 10-MeV EB system. Other products such as coatings, films and wire insulation may be economically EB-treated using a 5 to 10 MeV accelerator, if several layers of the product could be irradiated simultaneously. Two general product categories that require more study to determine the potential of high-energy EB processing are moulded plastics and composite materials.

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## 1. INTRODUCTION

The interaction of ionizing radiation with organic substrates to produce useful physical and chemical changes is the basis of the radiation processing industry for plastics. Radiation processing can often be economically substituted for more conventional thermal and chemical processes.

Several factors have increased the number of commercial radiation applications in industry over the last 30 years. These factors include the following:

- (1) Availability of powerful electron accelerators and large gamma radiation facilities,
- (2) Improved understanding of radiation chemistry, and
- (3) Increasing costs for competitive processes.

Table 1 lists the various industrial accelerators and their manufacturers.

The general principles of the several accelerator designs will not be described in this paper but can be found in Schuler, 1979. The radiation sources for the plastics industry are dominated by electron beam accelerators dedicated to the production of specific products. Table 2 reviews the major electron accelerator types, giving their designed beam voltage and current ranges (Peters, 1984; Cleland, 1981).

Gamma radiation from contract facilities is used for some small plastics applications when either very high penetration is required or when high-dose rates are not necessary. Electrons are less penetrating than gamma rays, but with power levels up to 200 kW, product throughput for industrial electron beam facilities can exceed even conventional industrial processes. The required penetration and product throughput dictates the required radiation source. Figure 1 illustrates the differences in penetration for X-rays and electron beams (EB) (McKeown, 1985).

This paper summarizes radiation processing in the plastics industry. Potential applications for high-energy (5 to 10 MeV) electron beam processing systems have also been reviewed.

## 2. COMMERCIAL ELECTRON BEAM PROCESSING

### 2.1 PRODUCT AND PROCESS DESCRIPTIONS

#### 2.1.1 Wire and Cable Insulation

High-performance wire and cable insulation, produced using radiation cross-linking techniques, was one of the earliest successful electron accelerator applications in the plastics industry (Singleton and Clabburn, 1986). In the last twenty years use of this method has grown, making it the largest radiation application for plastics production.

TABLE 1  
ELECTRON BEAM ACCELERATORS

Type	Manufacturers	Status/Features
<u>Electrostatic</u>		
Van de Graaff	High Voltage Engineering Corp., U.S.A.	Research machine; Voltage $\leq 28$ MeV
<u>Electromagnetic</u>		
Low Frequency- Capacitatively Coupled	- Emil Haefely and Co., Switzerland	Used in proton injectors
	- Nissin High Voltage, Japan	Commercially Active; Scanned beam; Voltage $\leq 3$ MeV
High Frequency- Capacitatively Coupled	- Radiation Dynamics Inc., U.S.A.	Commercially Active; Scanned beam; Voltage $\leq 5$ MeV; Dynamitron model
Low Frequency- Magnetically Coupled	- Durr - Polymer Physik, West Germany	Unknown. Commercial Activity; Unscanned beam
	- Durr Industries, Inc. U.S.A.	Unknown. Commercial Activity; Unscanned beam
	- D.V. Efremov Institute U.S.S.R.	Commercially Active; Unscanned beam; Aurora models; Electron III and IV
	- Energy Sciences, Inc. U.S.A.	Commercially Active; Unscanned beam; gas insulated; Electrocurtain models
	- High Voltage Engineering Corp., U.S.A.	Built on demand; Scanned beam; Insulated core transformer (ICI)
	- Nissin High Voltage, Japan	Commercially Active; Both scanned and unscanned beam types; Insulated transformer
	- RPC Industries U.S.A.	Commercially Active; Unscanned beam; Planar Cathode
	- AID Zirst France	Research machine; Toroid transfer; AID-TRELEC Model
	- Novosibirsk Institute U.S.S.R.	Research machine; Resonant transformer
Microwave Linear	- CCR-MeV Cassitron, France	Commercially Active
	- D.V. Efremov Institute, U.S.S.R.	Research machine
	- Haimson Research, U.S.A.	Custom built research machine
	- RPC Industries, U.S.A.	Custom built research machine
	- Siemens Ltd., West Germany	Medical applications
	- Applied Radiation Corp., U.S.A.	Unknown
	- Thomson CST., U.S.A.	Unknown
	- Varian Associates, U.S.A.	Medical applications



TABLE 2

COMMERCIAL ELECTRON BEAM ACCELERATOR SPECIFICATIONS:  
BEAM VOLTAGE AND CURRENT RANGE

Type of Accelerator (Manufacturer)	Beam Voltage Range (MeV)	Beam Current Range (mA)
<u>Electrostatic</u>		
- Van de Graaff: (High Voltage Engineering Corp.)	≤ 20	≤ 1.0
<u>Electromagnetic</u>		
- Low Frequency-Capacitatively Coupled: (Haefely; Nissin High Voltage)	0.5 to 3.0	≤ 30
- High Frequency-Capacitatively Coupled: (Radiation Dynamics Inc.)	0.4 to 4.5	35 to 100
- Low Frequency-Magnetically Coupled: (Durr-Polymer Physik; Durr Industries Inc.)	0.15 to 0.25	~ 100
(D.V. Efremov Institute: Aurora Models)	0.3 to 0.75	60 to 100
(D.V. Efremov Institute: Electron III and IV models)	0.3 to 0.7	10 to 20
(Energy Sciences Inc.)	≤ 0.3	≤ 300
(High Voltage Engineering Corp.)	0.3 to 3.0	25 to 100
(Nissin High Voltage)	0.5 to 0.75	100 to 200
(RPC Industries)	0.15 to 0.3	100 to 200
(AID Zirst)	0.15 to 0.5	50 to 200
(Novosibirsk Institute)	0.7 to 1.5	13 to 70
- Microwave Linear:		
(CGR - MeV Cassitron)	8 to 10	~ 2.5
(D.V. Efremov Institute)	4 to 40	Custom Design
(Remaining Manufacturers)	Custom Design	Custom Design

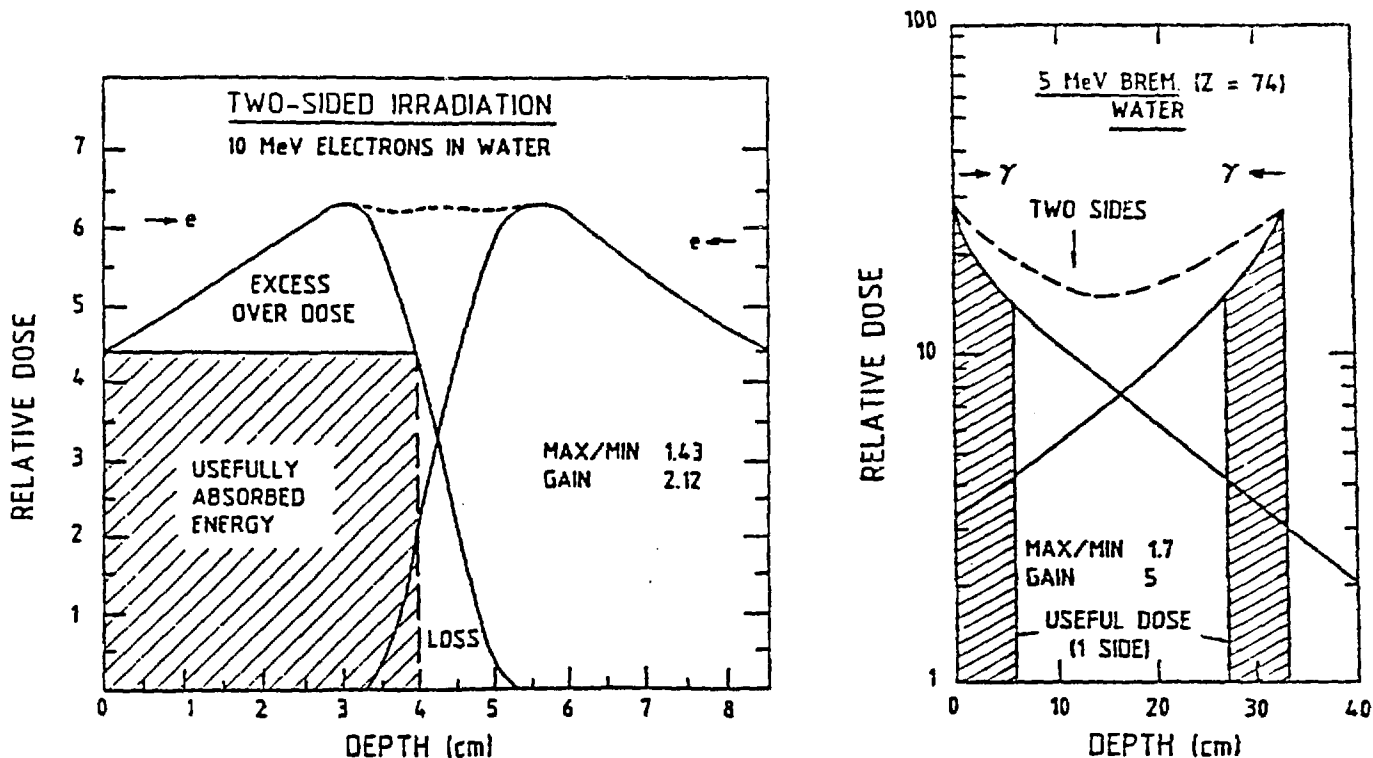


FIGURE 1: Penetration Depth Profile for X-rays and Electron Beams

Macromolecule cross-linking has been done commercially by three methods (Finkel et al., 1984):

- (1) A chemical reaction between macro-radicals resulting from the interaction between polymer molecules and decomposition products from thermally unstable compounds.
- (2) A chemical reaction between reactive groups present in the macromolecules.
- (3) A recombination of macro-radicals produced in the polymer by high-energy radiation.

Polymer cross-linking increases shape stability at elevated temperatures, including temperatures above the polymer melting point. Cross-linking polyethylene raises its maximum service temperature from 105 to 135°C (Singleton and Clabburn, 1986). Cross-linking also improves solvent resistance, environmental stress cracking resistance, and some mechanical properties. Electron beam processing of wire and cable insulation can be done in air when the appropriate resin formulation is used.

Radiation cross-linking of polymers has several advantages over the other cross-linking methods. Table 3 illustrates the comparison of radiation cross-linking with the most common alternative method: chemical cross-linking (Singleton and Clabburn, 1986; Finkel et al., 1984; Barlow et al., 1981).

There are some disadvantages of using radiation cross-linking techniques for wire and cable insulation. The most important drawback is the current practical limit for the insulation thickness, typically about 2.5 mm in unit density material at a 1.5-MeV beam voltage (Bly, 1981). The advent of EB accelerators capable of delivering high beam powers ( $\geq 100$  kW) at beam voltages of up to 5 MeV has increased this thickness limit to about 15 mm. Figure 2 illustrates the required insulation thickness and EB energy for the present range of power cable ratings.

These higher voltages have exposed some processing problems with cross-linking power cable insulation: insulation foaming, electrical discharge breakdown and cable rigidity (Bly, 1981).

Insulation foaming is caused by the accumulation of heat and the emission of gases, mainly hydrogen (Sasaki et al., 1979). The amount of foaming is dose-dependent and, therefore, can be avoided by incorporating accelerating or cross-linking agents into the polyethylene to reduce the required radiation dose. Discharge breakdown is the result of accumulation

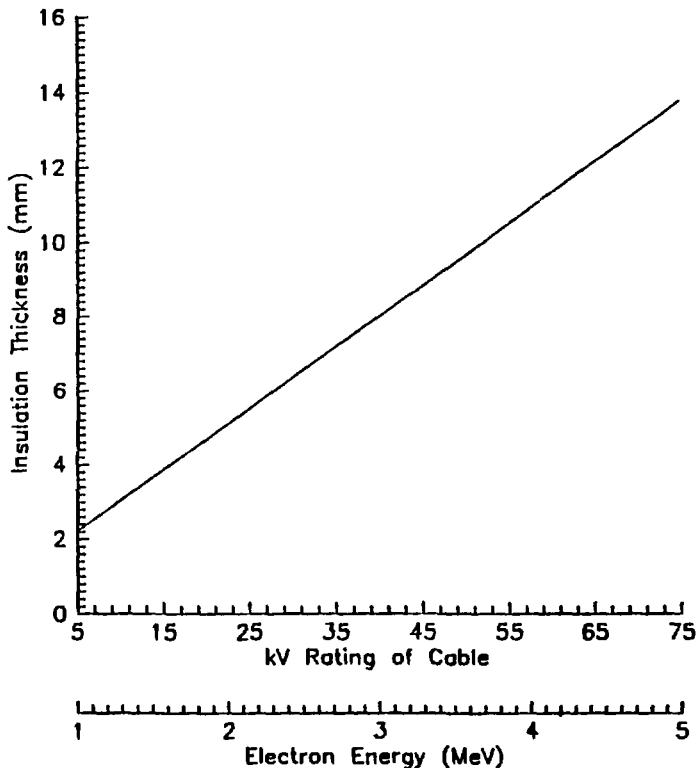


FIGURE 2: Insulation Thickness Specifications and Required EB Energy over the 5- to 69-kV Range for Power Cables (Association of Electrical Illuminating Companies).

TABLE 3

COMPARISON OF RADIATION CROSS-LINKING AND CHEMICAL CROSS-LINKING  
FOR WIRE AND CABLE INSULATION

---

Comparison	Radiation	Chemical
Cross-link Density	- Uniform; closely controlled	- Can be variable because of temperature fluctuations
Product Quality	- Defect-free materials can be obtained  - No residual chemicals	- Microvoids and bubbles can be formed  - Residual chemicals may be beneficial or harmful
Production	~ 300 m/min (extrusion)  - Process can be shutdown quickly  - Off-line process  - Room temperature process  - No lower insulation thickness limit  - Maximum insulation thickness depends on the beam voltage and the source design	~ 100 m/min (extrusion)  - Difficult to control accurately  - In-line method  - Can be at elevated temperatures  - Impractical for thicknesses less than 0.5 mm  - $\geq 2.5$ cm is a common insulation thickness

---

of excess charge and it is promoted by the addition of some cross-linking agents (Sasaki et al., 1981). Proper selection of the cross-linking agent, such as dipropargyl succinate or trimethylpropanetriacrylate, can suppress discharge breakdown, while still preventing foaming (Sasaki et al., 1981). Sufficient beam voltage for complete penetration to a grounded conductor, along with an appropriate compounding formulation, may avoid both the discharge breakdown and foaming problems (Bly, 1981).

The rigidity of power cables makes them unsuitable for bending; therefore, a multiple pass design is impractical (Bly, 1981). Many studies have explored this problem and several systems have been proposed, including a rotary technique, multiple accelerator designs (Bly, 1981) and a circular magnet system (Uehara, 1977).

High accelerator powers in combination with the usually low thermoconductivity of polymers complicates heat removal techniques (Finkel et al., 1984). Foaming is not the only result of heat accumulation; the final mechanical properties of the insulation may also be affected. Fractional irradiation, where the required dose is applied in segments with natural or forced heat removal between irradiations, usually provides appropriate cooling of the insulation for systems using high-power accelerators (Finkel et al., 1984).

Another disadvantage of radiation cross-linking is the difficulty in matching the wire diameter and coating construction to the beam's geometry to obtain the most effective use of the beam. Multiple passes are usually required, making such systems either expensive or not feasible for thick wires that cannot be bent sufficiently for multipassing.

Low-density polyethylene (LDPE) is the most popular polymer for wire and cable insulation followed by poly(vinyl chloride) (PVC). Other polymers used to a lesser degree include ethylene-propylene copolymer (EPM), ethylene-propylene-diene copolymer (EPDM), neoprene, chlorosulfonated polyethylene, nitrile, isoprene, styrene-butadiene rubber (SBR) and silicone elastomers. Each of these general polymer systems can be cross-linked with either chemical or radiation techniques. The actual formulations for chemical and radiation-curable compounds are, however, very different. Radiation-curable compounds must be specifically formulated to take advantage of the economics offered by electron beam processing (Barlow et al., 1981). Merely removing the peroxide from an established recipe and adding a radiation sensitizer does not make a radiation cross-linkable compound. Several developmental steps have to be followed, including selection of (Barlow et al., 1981):

- (1) The base resin, chosen for its ease of cross-linking and ease of acceptance of a specific filler;
- (2) Appropriate radiation cross-linking sensitizers or promoters that may economically reduce the required radiation dose for the selected base resin;
- (3) An antioxidant that has either a beneficial or negligible effect on cross-linking efficiency and does not degrade the physical properties of the compound over time. Antioxidant selection is

much more critical for radiation-cured systems than for peroxide-cured compounds (Barlow et al., 1981); and

- (4) Secondary additives, such as fillers, flame retardants and release agents that do not interfere with the cross-linking mechanism of the base resin.

For example, the following six steps were used to develop the YR19505 flame-retardant radiation curable compound for the U.S. Industrial Chemical Company (Barlow et al., 1981). An ethylene vinyl acetate (EVA) copolymer was selected as the base resin because it was more readily cross-linked than polyethylene or ethylene-ethyl copolymer. Copolymers are also more easily filled than homopolymers. No cross-linking promoter was used because it was not cost effective. The antioxidant selected is proprietary information. The flame retardant was alumina trihydrate. A coupling agent, vinyl alkoxy silane, was also used to improve the bonding between the filler and the resin to obtain satisfactory physical properties.

Table 4 shows some of the present radiation applications for high performance wire and cable (Singleton and Clabburn, 1986). Radiation cross-linking can achieve or enhance the listed properties in properly formulated polymer systems.

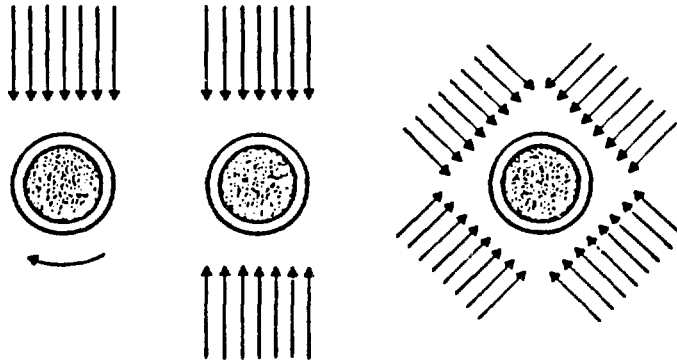
TABLE 4  
APPLICATIONS OF IRRADIATED POLYMER INSULATION

Application	Required Properties
Automobile Wires	<ul style="list-style-type: none"><li>- Abrasion resistance</li><li>- Cut through resistance</li><li>- Improved thermal stability</li><li>- Fluid resistance</li></ul>
Aircraft Wires	<ul style="list-style-type: none"><li>- Small size</li><li>- Light weight</li><li>- Non-flammability</li><li>- Thermal stability</li><li>- Resistance to fuel and lubricants</li></ul>
Locomotive Power and Control Wires	<ul style="list-style-type: none"><li>- High-temperature rating</li><li>- High-current rating</li><li>- Overload capacity</li><li>- Hot oil and grease resistance</li><li>- Flexibility</li></ul>

The irradiation method, including under-beam equipment, is an important variable when considering radiation cross-linking for wire and cable insulation. The configuration of the radiation sources, the beam voltage and the core arrangement all require careful attention to insure

acceptable dose uniformity, beam utilization, product quality and throughput (Bauerlein and Bickel, 1981).

Figure 3 illustrates the three general irradiation methods for wire insulation and tubes to provide uniform cross-linking (Bauerlein and Bickel, 1981). A three-sided design is being researched for irradiating thicker substrates (Bly, 1981).



1-sided

2-sided

4-sided

FIGURE 3: General Irradiation Methods for Wire and Cable Insulation

Figure 4 shows the most frequently used two-sided irradiation configurations using a single electron beam accelerator (Finkel et al., 1984).

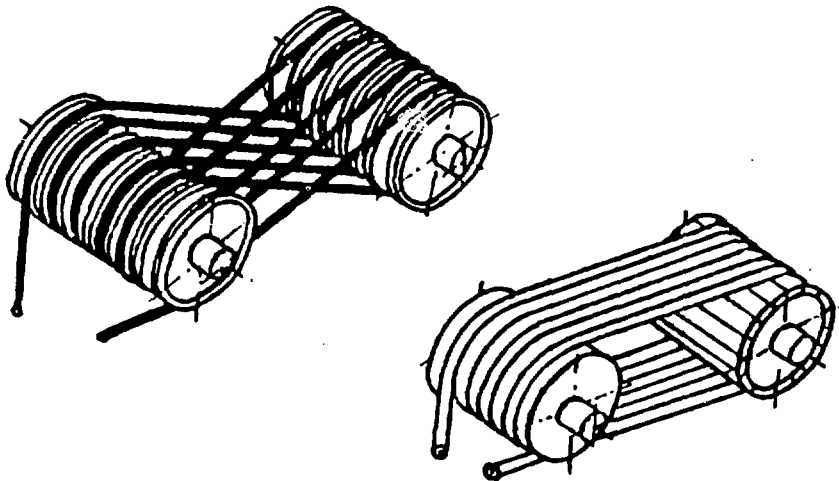


FIGURE 4: Typical Wire and Cable Conveyor Systems

The core runs transverse to the scan direction in a "figure 8" or "race track" arrangement. The advantages of these methods include the following:

- (1) The simplicity of the system;
- (2) The conveyor speed can be controlled to vary the absorbed dose and cooling intervals;
- (3) There is nearly 100% utilization of the beam for the "race track" arrangement;
- (4) The product diameters can be changed on the same equipment without interrupting the production process; and
- (5) The elimination of excessive tension on the wires, preventing product deformation and breakage.

The primary disadvantages include the following:

- (1) The many passes required, especially for small gauge wire, to effectively utilize the electron beam. Fewer passes are needed for conveyor designs running the core longitudinally to the scan direction (Bauerlein and Bickel, 1981). Irradiation of several cores simultaneously also increases the beam utilization, but makes coupling of the EB unit to the core production line impractical.
- (2) The requirement that the core has to be shifted through the full scanner width to insure adequate dose uniformity in the insulation. Rotating the wire is the surest method to provide uniform circumferential irradiation with one EB accelerator; however, the product handling and control systems can be complicated and expensive.

Several other twin-irradiator designs have also been studied and commercially used for wire and cable insulation. These designs are usually four-sided irradiations with the EB units offset by 90 or 180°. Such facilities have wire conveyor systems similar to the single EB unit designs. The required beam voltage decreases for each of the twin irradiators as compared to a single irradiator, and the overall manufacturing rate usually doubles by using the twin design. The 180° offset design does require the core to be rotated to guarantee a uniform circumferential dose.

### 2.1.2 Heat-Shrinkable Sheet, Film and Tubes

Irradiation cross-linking can be used to impart "elastic memory" to a semicrystalline polymer. Figure 5 illustrates this unique effect of radiation processing (Ota, 1981).

Normal polyethylene has both crystalline and amorphous regions, and the polymer shape is maintained by the molecular chain entanglement. When the polyethylene is heated above its melting point the crystalline regions disappear and each molecule can move in random directions. Radiation cross-linking, usually at a dose of 200 to 300 kGy (Ota, 1981) and primarily in the amorphous region of polyethylene, prevents the molecules from flowing at temperatures above the melting point and produces a polymer that tolerates deformation. When polyethylene is cooled in a deformed



shape, the produced crystalline regions maintain the shape even when the deformation force is released. When the deformed polyethylene is heated again, the crystalline regions again disappear and the product returns to its non-deformed shape.

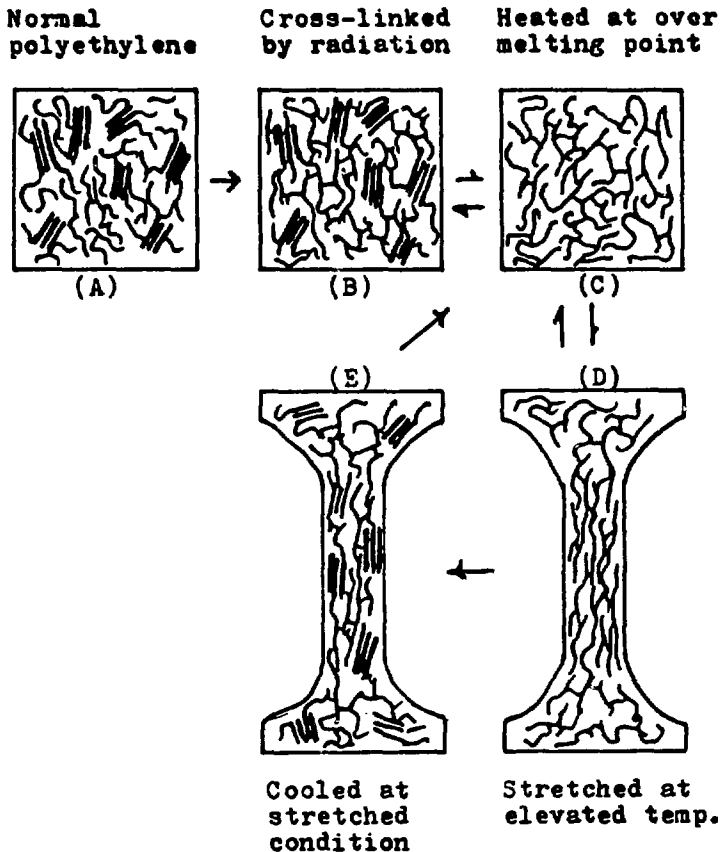


FIGURE 5: Principle of Heat-Shrinkable Material

Many polymers can be rendered heat-shrinkable, particularly polyolefins and some fluorocarbons. Heat-shrinkable tubing or moulded parts provide mechanical and/or chemical and/or electrical protection. Products include the following:

- (1) A substantial shrink wrap film market for packaging produce and meat;
- (2) Fully sealed electrical connectors that meet the wire insulation specifications;
- (3) Corrosion protection systems; and
- (4) High-voltage power cable terminal protectors. The product must withstand extremes of climate, electrical stresses and surface discharges during the lifetime of the cable.

High-density polyethylene, low-density polyethylene and ethylene copolymers are usually used for shrinkable products. These polymer systems usually include antioxidants, flame retardants and coloring agents.

Heat-shrinkable tubings are usually produced by one of two methods: an extrusion method or a sheet-wrapping method. Conventional extruders are used for the first method. Beam voltages of 1 to 3 MeV are normally required for irradiating polyolefin tubing. The beam voltage range for sheet production is 0.5 to 3.0 MeV.

Tubes up to 2.5 cm in diameter are usually irradiated continuously with a conveying system similar to that used for the irradiation of wire and cable insulation. Tubes up to 30 cm in diameter have been successfully irradiated on a commercial scale using various equipment designs. Uniform circumferential irradiation is required for tubing in order to get a smooth extension.

The most common expansion methods for heat-shrinkable tubing are the differential pressure method (Figure 6) and various mechanical methods (Figures 7 and 8) (Ota, 1981).

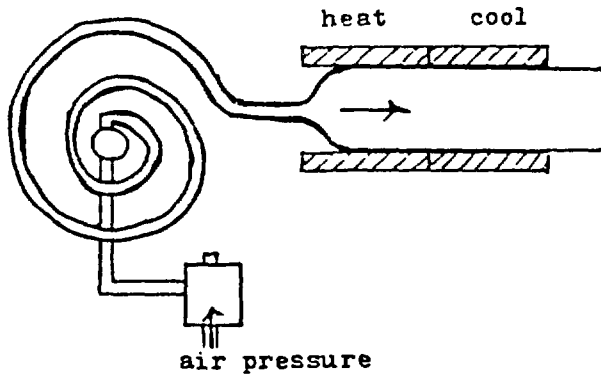


FIGURE 6: Differential Pressure Expansion Method

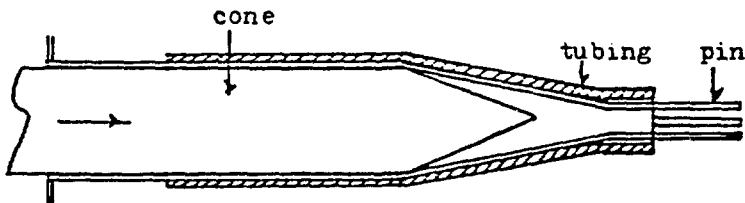


FIGURE 7: Mechanical Expansion Method: Cone Design

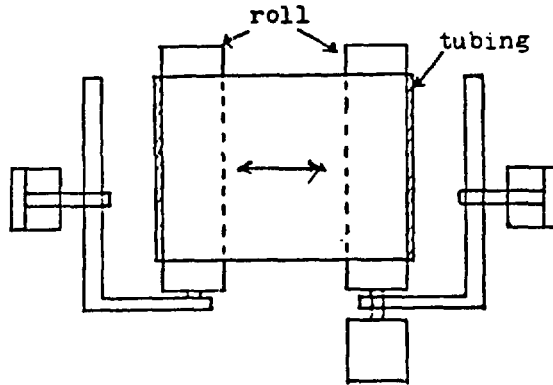


FIGURE 8: Mechanical Expansion Method: Roller Design

Air pressure is supplied to one end of the tubing for the general differential pressure method. The tubing is first heated in a die to expand it, then cooled to maintain the expansion. The usual expansion ratio is 1.5 to 2.5 times. Many specific equipment designs use modifications of this general principle.

Heated tubing can also be expanded using guide pins and a wedge cone (Figure 7). After expansion of up to 3 to 4 times, the tubing is cooled and the cone is withdrawn.

Rotating rollers can also be used to expand tubing (Figure 8). This method was designed to manufacture tubing with large diameters, 60 to 100 cm. In this method the tubing reduces its length in the process.

The sheet-wrapping method produces tubing from irradiated stretched polyethylene sheet or film as shown in Figure 9 [Ota, 1981].

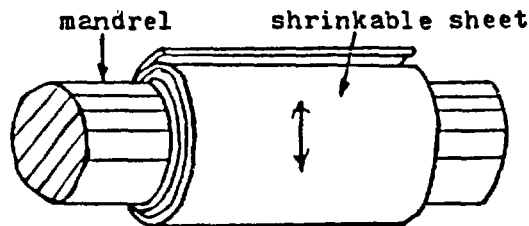


FIGURE 9: Sheet-Wrapping Method

The polyethylene is wrapped around a mandrel and the system is heated above the polyethylene melting point. The sheet layers adhere to each other forming the tubing. The tubing is cooled and removed from the mandrel.

Heat-shrinkable sheet or films are produced using standard manufacturing techniques for the unirradiated product. Films are less than 0.25-mm thick and sheets are thicker than this limit. The sheets or films are formed by various extrusion methods or by calendering (Rodriguez, 1982). The sheets or films are irradiated ( $\leq 300$  kGy), heated above the melting point, mechanically stretched to the desired expansion ratio using various equipment designs, and then cooled to produce the heat-shrinkable product.

### 2.1.3 Rubber and Elastomers

Electron beam processing in the rubber industry is used primarily for cross-linking certain polymers, providing "green strength" through a partial vulcanization of components of radial tires (Mohammed and Walker, 1986). Green strength is the cohesive strength that allows an essentially uncured, polymer-based composition to deform uniformly under stress without sagging or nonuniform thinning.

Electron beam vulcanization is usually accomplished continuously on-line, following extrusion or calendering operations. Full vulcanization for tire manufacturing is a potential application, but it is not presently used commercially. Most of the accelerators used by the rubber industry have beam voltages of 1 to 5 MeV (Mohammed and Walker, 1986). Full vulcanization is used in other elastomer applications. Full vulcanization doses usually range from 50 to 250 kGy and depend on the polymer system and the type of radiation sensitizer. Sensitizers are usually multi-functional monomers. Unsensitized natural rubber may require a dose as high as 400 kGy to fully vulcanize.

A number of elastomers have been cross-linked using radiation, attesting to the versatility of this processing method. These elastomers include ethylene-propylene rubber, isobutylene-isoprene, natural rubber, nitrile, polybutadiene, neoprene, silicone and styrene-butadiene rubber (SBR) systems. The notable exception to this list is butyl rubber, a major component in several tire brands. Butyl rubber degrades upon irradiation; however, this degradation can be prevented by halogenation (Mohammed and Walker, 1986).

The major advantages of using EB processing for elastomer production include the following (Sonnenberg, 1983):

- (1) Reduced energy requirements and manufacturing costs compared to conventional vulcanization methods;
- (2) Improved form stability, enabling rigid tolerances to be met for tire assembly;
- (3) Increases in the synthetic rubber content that reduce the product cost but not the product strength; and
- (4) Product assembly can be more easily automated.

The current major applications for EB processing of elastomers are the following:

- (1) Partial cross-linking of tire components such as innerliner stock, body plies, sidewalls, chafer strips, veneer strips and tread ply skims for improved physical properties and to give dimensional stability during tire assembly and final vulcanization (Mohammed and Walker, 1986);
- (2) Production of single-ply rubber sheet for roofing applications. This on-line, full vulcanization application, for typically calendered or extruded 1.14- to 1.52-mm-thick sheets, eliminates the need for talcing to prevent sticking of the sheets during rolling. The production rates are high and the sheets can be rolled immediately after processing; and
- (3) Conveyor belt and transmission belt components.

#### 2.1.4 Polyolefin Foam

Foam produced from radiation cross-linked polyethylene is a tough resilient product, with significantly better mechanical and chemical properties and heat resistance, compared to polystyrene and polyurethane foams (Singleton and Claburn, 1986). This technique was commercially developed in Japan in 1969. The foaming process can be separated from the forming stage since the cross-linked polyethylene will not flow at the temperatures required to decompose the blowing agent. The foaming process can also be controlled more accurately and the foam pore size can be regulated. The high melt strength of the irradiated polyethylene increases the expansion ratio to up to 40 times the initial volume. The general process steps for producing radiation cross-linked polyethylene foam are the following (Peters, 1984):

- (1) Mixing the foaming agent, usually azodicarbonamide, with the polyethylene and appropriate additives;
- (2) Extruding the mixture into a sheet;
- (3) Irradiating the sheet to between 20 and 50 kGy;
- (4) Heating the sheet to decompose the foaming agent and soften the sheet so the foam structure can be established; and
- (5) Cooling the sheet and cutting it into the desired shapes.

Radiation cross-linked foam products are finding increasing use in packaging and cushioning applications, specialty insulations and various electronic products. Radiation-cured foam tubing is being produced commercially. Incorporation of flame retardants has also opened markets in the automotive, appliance and construction industries.

#### 2.1.5 Coatings and Adhesives

Radiation curing of coatings and adhesives is usually a polymerization application using low-energy EB or ultraviolet equipment. Electron beam voltages are usually in the 100- to 300-keV range, but have gone as high as 1 MeV (Rie and Berejka, 1986).

The advantages of this radiation curing technique are the following:

- (1) Formulations solidify by chain addition polymerization along with a high degree of cross-linking. Thermally-cured coatings contain diluent solvents that are driven off by heating to cure the material. These solvents are considered pollutants and their emission must be controlled at added expense. Radiation-cured coating, because of their highly cross-linked networks, have improved chemical and thermal resistance.
- (2) Curing is at ambient temperatures, allowing heat-sensitive substrates such as polyethylene, polypropylene, polystyrene, wood and low quality paper to be printed or coated without detrimental effects. Radiation curing is more energy efficient and produces less thermal pollution.
- (3) Curing is very quick, increasing production throughput. This increased production often makes radiation curing more economical than other systems.

The disadvantages of this radiation curing technique are the following:

- (1) The material costs are high, which must be made up by the savings in energy and process costs. The relative cost of radiation-curable materials is decreasing; however, as the production volumes increase and there is more commercial competition in the formulations market.
- (2) There is an inferior adhesion of some coatings compared to conventional materials. This is due to a lack of solvent wetting and heat, which promote physical bonding to the substrate. Many current formulations have eliminated this disadvantage and radiation cured coatings can be used for most applications.
- (3) Formulating can be more difficult. The required resin viscosity may not be attainable using the common acrylic diluent monomers because of the needed required cure rate, volatility and toxicity problems.

Coating formulations for electron beam applications usually contain a base oligomer, diluent monomers, cross-linking monomers and stabilizers (Rie and Berejka, 1986). Adhesion promoters, surfactants, fillers and pigments may also be added. Oligomers contribute adhesion, toughness and flexibility to a cured coating although allowing good pigment dispersion and coating application characteristics. Typical oligomers used for radiation curable formulations include unsaturated polyesters, polyester acrylates, urethane acrylates and epoxy acrylates (Hausman, 1980). Diluent monomers such as tetrahydrofurfuryl methacrylate and 2-phenoxyethyl acrylate are usually monofunctional. They are added to a system to decrease the viscosity without excessively retarding the cure rate. Cured monofunctional monomers are soft, linear thermoplastics. Cross-linking monomers are either

difunctional or multifunctional monomers that cure very rapidly. Tripropylene glycol diacrylate and trimethylol propane triacrylate are typical cross-linking monomers. Stabilizers, such as hydroquinone, scavenge free radicals to prevent premature polymerization.

The established applications for EB-radiation curing of polymer coatings include the following (Rie and Berejka, 1986):

- (1) Pressure-sensitive adhesives used with a variety of substrates such as glass, plastics, ceramics and metals. These adhesives can be produced and used with less cost compared to the conventional solvent-based, water-based or hot melt technologies. Radiation-cured adhesives are easy to use, allowing automatic dispensing. The cure is rapid and energy requirements are low.
- (2) Overprint coatings or varnishes for paper, paperboards, plastics and metal products. These coatings protect the printed surface with a high gloss finish. Final products include paper cartons, record album jackets, books and magazine covers, and paper and vinyl laminates.
- (3) Magnetic media coatings. Electron-beam curing provides the required cure speed to eliminate surface contamination problems experienced by other coating methods. The resulting coating is highly cross-linked and wear resistant.

There are several ultraviolet applications as well, including vinyl flooring coatings, metal decoration, photo-polymer printing plates, printed circuit boards, microcircuitry, screen printing, wood finishing and optical fibre coatings (Rie and Berejka, 1986).

There are several coating application methods, depending on the product being coated. Screen printing uses a stencil to produce tightly controlled, reproducible patterns. Direct roller coating is a method used for relatively uniform substrates. Curtain coating has the coating material pumped continuously into an applicator head, forming a continuous vertical curtain of material. The product to be coated is passed through the curtain. Curtain coatings produce a very uniform and smooth film on substrates of various thicknesses without altering the equipment. Spraying methods can also be used to apply coatings. More complete descriptions of these coating methods can be found in Rie and Berejka (1986).

#### 2.1.6 Miscellaneous

Several small commercial electron beam applications have been identified in the plastics industry. Some of these applications presently have a limited market while others are being actively developed.

- (1) Composite Materials: Various substrates including concrete, wood and ceramics have been combined with multifunctional oligomers and monomers to produce construction materials with improved physical and mechanical properties (Czvikovszky, 1985). The monomers are usually vacuum-impregnated into the substrate and then radiation polymerized. The only significant commercial application for this

process is the production of parquet wood flooring, containing 10 to 15% methylmethacrylate (MMA) (Peters, 1984). Hardwoods such as red oak, are used for flooring because they have lower monomer loading limits compared to softwoods (Barclay, 1986). Polymer impregnation improves the hardness, abrasion resistance and compressive strength of the wood (Barclay, 1986).

Wood-plastic composite production is usually considered a gamma-ray application, although EB accelerators are beginning to be used as their beam voltages increase.

Coral, impregnated with MMA and irradiated to a dose of 30 kGy, has been used for decorative products in Japan (Peters, 1984). The compressive, impact and bending strengths are all significantly improved by this application.

Research is being done on radiation curing of fibre-reinforced composites (Czvikovszky, 1985) and concrete-polymer composites, particularly in the U.S.S.R (Peters, 1984). These products have not yet found their way to the marketplace.

- (2) Polyethylene Irrigation Pipes and Hot Water Pipes: Radiation cross-linking of polyethylene pipe provides superior environmental stress cracking resistance and can save on material costs (Mellberg, 1978). Companies that produce radiation cross-linked polyethylene pipe can offer performance warranties several years longer than producers of unirradiated pipe.
- (3) Teflon<sup>TM</sup> Degradation: Irradiation doses of 60 to 100 kGy degrades tetrafluoroethylene (Teflon<sup>TM</sup>) enough that it can be easily powdered for: spray lubricants, release agents for moulds, thickening agents and non-sticking kitchenware (Peters, 1984). Contract facilities are usually used for irradiating Teflon<sup>TM</sup>. Most of the irradiated Teflon<sup>TM</sup> is produced in the U.S.S.R. and Japan (Peters, 1984).

## 2.2 PRODUCT SUPPLIERS AND ELECTRON BEAM SOURCES

### 2.2.1 Worldwide

Table 5 shows the worldwide breakdown of commercial EB units used in the plastics industry (Peters, 1984).

The high-energy systems ( $\geq 500$  kV) make up about 75% of the total, excluding machines manufactured in the U.S.S.R.

Figure 10 illustrates the estimated breakdown of the worldwide commercial production of plastics using EB processing (Peters, 1984; Mizusawa and Klempen, 1987).

Cross-linking of wire and cable insulation and cross-linking heat-shrinkable films and tubing are the two major EB-production processes, each with about 28% of the worldwide EB capacity. The other major products are



TABLE 5

BREAKDOWN OF THE WORLDWIDE COMMERCIAL EB UNITS  
USED IN THE PLASTICS INDUSTRY (1984)

EB Unit Manufacturer	Estimated Number of Commercial Units
<u>Low-Energy Systems</u>	
Durr	10
Energy Science Inc.	80-85
Haefely	1
RPC	10
<u>High-Energy Systems</u>	
CGR-MeV	2
High Voltage Engineering	150
Nissin High Voltage	62
Radiation Dynamics	90
Others	4-9
Subtotal	407-419
U.S.S.R. Manufactured	60
Total	469-479

coatings and adhesives (10%), rubber products (8%) and polyolefin foam (4%). The large percentage of production unaccounted for, 17%, is primarily from the U.S.S.R. (5%) from which there is little published data and the United States (10%) where a lot of the information is proprietary.

These EB-capacity percentages can be subdivided by country, as shown in Figure 11.

The United States produces the largest percentage of the major products, with about 59% of the total worldwide EB capacity in 1984, followed by Europe (16%) and Japan (15%). The data used to produce Figures 10 and 11 are given in Table 6 (Peters, 1984; Mizusawa and Klempen, 1987).

The estimated total EB capacity in 1984 was about 20.5 MW with 469 to 479 individual EB units.

The worldwide growth rate of the EB-processing industry for the production of plastics is very difficult to calculate because of the unavailability of the required data. Japan is the only country where enough data has been published to study their EB-processing growth rate. This analysis is described in Section 2.2.4.

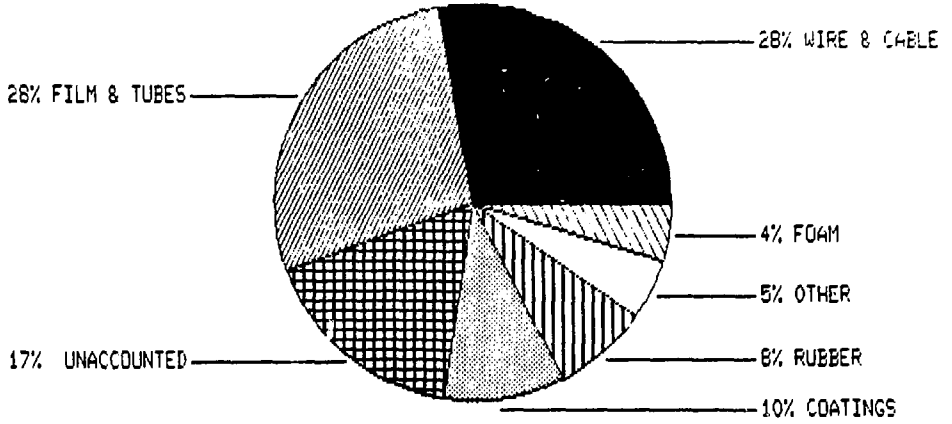


FIGURE 10: Estimated Breakdown of the Worldwide Commercial Production of Plastics Using EB Processing (1984)

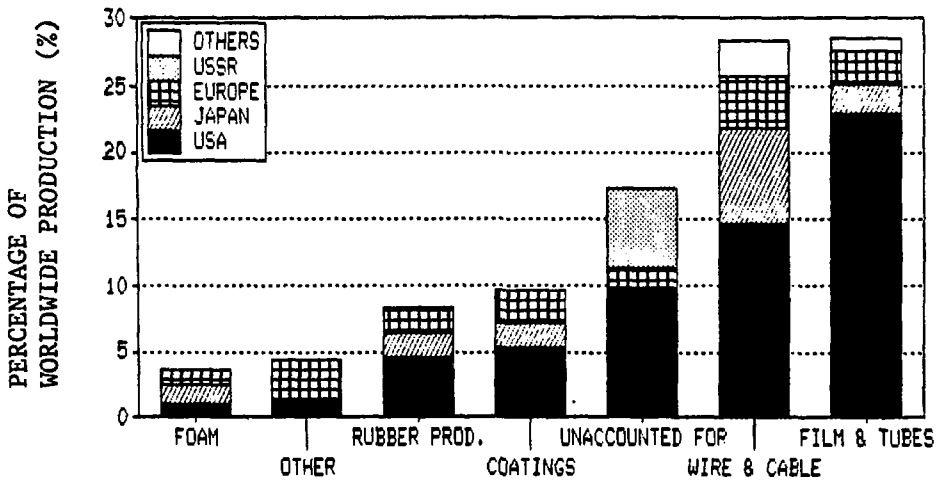


FIGURE 11: Estimated Breakdown By Country of the Worldwide Commercial Production of Plastics Using EB Processing (1984)

TABLE 6

ESTIMATED BREAKDOWN OF THE WORLDWIDE COMMERCIAL PRODUCTION OF PLASTICS  
USING EB PROCESSING (1984)

Product	United States		Japan		Europe		Other		Total	
	kW	No. of Units	kW	No. of Units	kW	No. of Units	kW	No. of Units	kW	No. of Units
Wire and Cable Insulation	3000	50-60	1465	27	785	17	560 <sup>(1)</sup>	10	5810	104-114
Polyethylene Foam	200	5	338	10	200	5	-	-	738	20
Cross-Linked Film, Pipe and Tubes	4700	92	456	7	500	11	205 <sup>(2)</sup>	3	5861	113
Rubber Products	950	15	356	10	350	7	50 <sup>(3)</sup>	1	1706	33
Coating	1100	16	410	6	465	7	-	-	1975	29
Other (Contract)	200	7	61	2	650	10	-	-	911	19
Unaccounted For	2000	55	-	-	330	36	1200 <sup>(4)</sup>	60	3530	151
Total	12 150	240-250	3086	62	3280	93	2015	74	20 531	469-479
% of Total	59	52	15	13	16	20	10	15	100	100

- (1) The ten units are found in Australia (1), Brazil (2), Mexico (2), Taiwan (2), Korea (1), China (1) and Other (1).
- (2) The three units are found in Taiwan (1), Korea (1) and China (1).
- (3) The unit is found in Canada.
- (4) The estimated EB capacity and number of units in the U.S.S.R.

2.2.2 United States

Figure 12 illustrates the breakdown of the EB processing industry for plastics in the United States as of 1984.

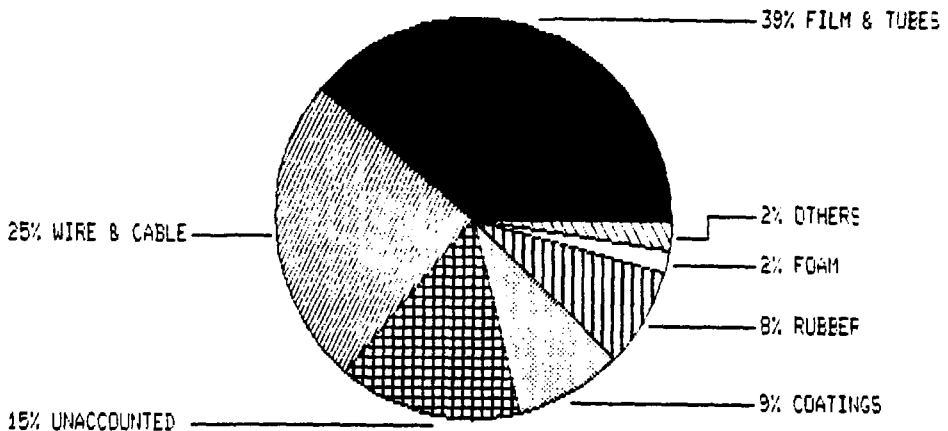


FIGURE 12: Estimated Breakdown of the Commercial Production of Plastics Using EB Processing in the United States (1984)

Cross-linking of film, tubing, tape and pipes dominates the industry with 39% of the total EB capacity of about 12.15 MW (Peters, 1984). The major producer of heat-shrinkable film is the W.R. Grace Company (Cryovac) in South Carolina. W.R. Grace has at least 45 EB units for film production. Most of these units are 500 kV accelerators produced by High Voltage Engineering (HV). The beam current is probably 100 mA (Peters, 1984). The major producer of cross-linked tubing and pipe is Raychem in California, with about 20 EB units. Most of the systems, manufactured by Radiation Dynamics Incorporated (RDI), have beam voltages between 500 and 1500 kV and beam currents ranging from 50 to 100 mA. Raychem does have 5 units with beam voltages greater than 1500 kV (1 @ 4.5 MeV; 4 @ 1.5 to 3.0 MeV).

Wire and cable insulation is the next major product manufactured with EB, accounting for 25% of the United States EB capacity. Several companies have more than one EB unit. The Western Electric Company of Georgia has six RDI units (500 kV, 100 mA) to lead the industry, based on published data. There is, however, a large number of EB units unaccounted for (23 to 35%) that are being used for the production of wire and cable insulation (Peters, 1984).

The radiation-curable coating industry with 9% of the United States EB capacity is lead by the 3M Company with a total of 4 commercial EB units at various locations. These units are used to produce magnetic tape, pressure-sensitive adhesives and coated paper. The majority of the accelerators used for coatings, including those owned by the 3M Company, are electro-curtain designs built by Energy Sciences Incorporated (ESI). The beam voltages are less than 300 kV and the beam currents are less than 300 mA.

The U.S. tire manufacturers, Firestone and Goodyear, use the majority of the 8% of United States EB capacity to produce rubber sheets for radial tire manufacturing.

Radiation cross-linking of polyolefin foam, accounting for only 2% of the United States EB capacity, is lead by the Voltek Company of Massachusetts with 4 EB units. The specific facility details for Voltek are proprietary.

Table 7 (Peters, 1984) gives all of the available information on the commercial EB units located in the United States as of 1984. Very little recent information has been published.

### 2.2.3 Europe

Figure 13 shows the breakdown of the European EB processing capacity for the production of plastics (Peters, 1984; Stachowicz, 1987).

Cross-linking wire and cable insulation accounts for 24% of the European EB capacity, followed by contract facilities (20%), heat-shrinkable film and tube production (15%), radiation-curable coatings (14%), rubber sheet production (11%) and polyolefin foam cross-linking (6%). About 10% of the EB capacity can not be accounted for.

TABLE 7

UNITED STATES COMMERCIAL FACILITIES (1984)

General Product Category	Company/Location	No. of EB Units	EB(1) Manufacturer	Available Facility Details	Comments
Cross-linking Wire and Cable Insulation	Champlain Cable, Vermont	3	3 RDI	3 @ 1.8 MeV and 50 mA	
	General Cable, California	3	?	?	
	GMC - Electromotive, Michigan	1	?	?	
	ITT Suprenant, Massachusetts	3	3 HV		
		3	3 HV		
	Judd Wire, Massachusetts	2	2 HV		
	Northern Telecommunications, Michigan	2	2 ESI		
	Rockbestos Co., Connecticut	3	3 RDI	probably 1 @ 550 kV and 100 mA 1 @ 1.0 MeV and 20 mA 1 @ 3.0 MeV and 20 mA	
	Sammor Co., Pennsylvania	1	RDI		
	Western Electric, Georgia	4-6	3 RDI probably 3 HV	3 @ 500 kV and 100 mA ?	
EB Facilities and Beam Power Unaccounted For	23-35	-	1250 to 1900 kW		
Polyolefin Foam	Brand Rex, Connecticut	1	?	?	
	Voltek, Massachusetts	4	?	?	
	EB Facilities and Beam Power Unaccounted For	?	?	?	
Heat-Shrinkable Film	W.R. Grace, South Carolina	45	40 HV 2 RPC 3 ?	Most are 500 kV, 100 mA ? ?	
	Dupont, Indiana	5	2 ESI 2 HV 1 ?	250 kV, <300 mA 500 kV, 100 mA ?	
	Album Graphics, Illinois	1	RPC	<300 kV Scanned Beam	Overprint Varnish and Album Cover
	Bixby International, Massachusetts	1	ESI	250 kV, <300 mA	Bonding of Flocking
	Brook-Willamette, Oregon	1	HV	300 kV, 90 mA Scanned Beam	Wood Finishing
Hampton Paper, Pennsylvania	1	ESI	250 kV, <300 mA 54" Paper Width	Paper Coatings	

**TABLE 7 (concluded)**

General Product Category	Company/Location	No. of EB Units	EB <sup>(1)</sup> Manufacturer	Available Facility Details	Comments
Coatings	James River Paper, Wisconsin	1	?	?	Paper Coatings
	King-Seely, Massachusetts	1	ESI	250 kV, <300 mA 60" Paper Width	
	Universal Wood, Kentucky	1	ESI	250 kV, <300 mA 54" Product Width	Particle Board Filling and Coating
	3M, Various Locations	4	probably ESI	250 kV, <300 mA	Magnetic Tape and Disks; Pressure-Sensitive Tape, Coated Paper
	Others	5	Some ESI	?	?
Rubber Products	Firestone; Unknown Locations	2	2 RDI	1 MeV; probably 70 mA	Radial Tire Sheet
	Goodyear Tire and Rubber, Unknown Location	1	?	?	Radial Tire Sheet
	EB Facilities and Beam Power Unaccounted For	~2	?	~140 kW	?
Cross-linked Tubing, Tape and Pipe	Raychem, California	20	14 RDI 6 ? 1 @ 4.5 MeV, 4 @ 1.5 to 3 MeV (Menlo Park)	most 500-1500 kV probably 50 to 100 mA	Tubing
	Alpha Wire Corp., New Jersey	1	?	?	Tubing and Tape
	Electronized Chemical Corp., Massachusetts	3	3 HV	1 @ 750 kV, 100 mA 1 @ 10 MeV, 50 mA 1 @ 3.0 MeV, 30 mA	Shrink Tube
	Essex International, Indiana	2	2 RDI	1 @ 1.5 MeV, 50 mA 1 @ 400 kV, 100 mA	Shrink Tube and Tape
	Radiation Irrigation, California	1	?	?	Pipe
	Windsor Nuclear Corp., Connecticut	2	2 HV	Van de Graaff;	Shrink Tube, Drum Gaskets
	EB Facilities and Beam Power Unaccounted For	8-13	?	both 3.0 MeV, 1 mA ~500 - 650 kW	
	Other	Columbia Research Corp., North Dakota	1	?	2.5 MeV, 40 kW
Energy Science Inc., Massachusetts		2	2 ESI	250 kV, <300 mA	Pilot Plant Units
IRT Corp., San Diego, California		3	?	Linacs at <15 MeV	Contract Radiation
RAI Research, Happausa, New York		1	HV	500 kV, 25 mA	Battery Separators
Radiation Dynamics Industries, New York		1	RDI	?	Drum Gaskets, Contract Radiation

1  
24  
1

(1) RDI: Radiation Dynamics Industries  
 HV: High Voltage Engineering Corporation  
 ESI: Energy Science Incorporated  
 RPC: RPC Incorporated

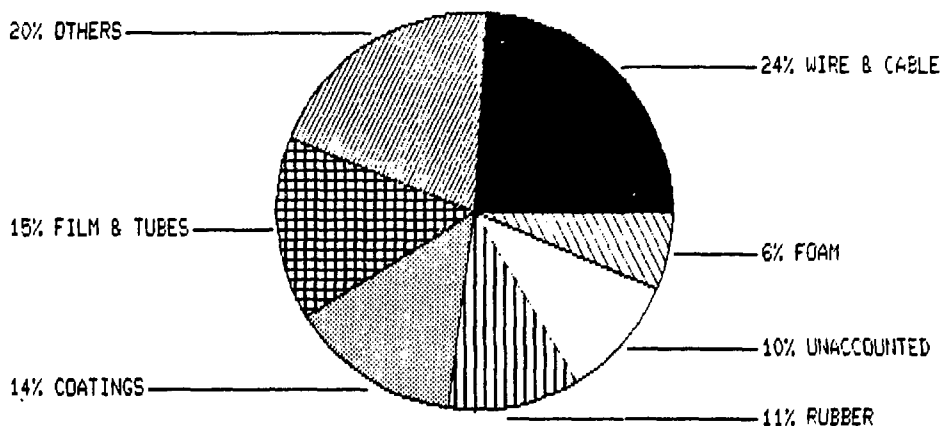


FIGURE 13: Estimated Breakdown of the Commercial Production of Plastics Using EB Processing in Europe (1984)

The Sieman Company of West Germany, with 5 EB units, has taken a leading role in the cross-linking of wire and cable insulation, but insulation is also EB cross-linked in France, England and Switzerland. The contract facilities are located throughout Europe and range in size from a 500 kV, 50-mA RDI unit in West Germany to a 10 MeV, 10-kW unit in Riso, Denmark. The production of heat-shrinkable film is lead by Cryovac (W.R. Grace), as it is in the United States, with 9 EB units, most of them being 500- to 1000-kV accelerators manufactured by High Voltage Engineering (HV). Wood panel production uses the majority of the European EB capacity for radiation curable coatings, although no one company dominates the market place. Most of the accelerators used for coatings are Energy Science, Incorporated (ESI) designs (250 kV,  $\leq$  300 mA). Table 8 gives all of the available information on the commercial EB facilities in Europe for the production of plastics (Peters, 1984; Stachowicz, 1987).

#### 2.2.4 Japan

Wire and cable insulation cross-linking dominates the Japanese EB-processing industry with 47% of the commercial EB capacity dedicated to the production of plastics, as shown in Figure 14. (Mizusawa and Klempen, 1988; Sakamoto and Mizusawa, 1981).

The EB capacity, devoted to the other major EB-produced materials, ranges from 15% for heat-shrinkable film and tubes to 11% for cross-linked polyolefin foam.

TABLE 8

EUROPEAN COMMERCIAL EB FACILITIES (1984)

General Product Category	Company/Location	No. of EB Units	EB <sup>(1)</sup> Manufacturer	Available Facility Details	Comments
Cross-linking Wire and Cable Insulation	Acome, France	2	?	1 @ 1.0 MeV, 15 kW 1 @ 500 kV, 20 kW	
	AEG - Telefunken, West Germany	1	RDI	1.5 MeV, 37.5 kW	
	British Industrial Plastics, England	1	?	?	Some PE Foam also
	Sieman, West Germany	5	some HV	?	
	Studer Wire and Cable, Switzerland	1	?	?	
	Huber and Suhner, Switzerland	1	?	?	
	EB Facilities and Beam Power Unaccounted For	~5		~250 kW	
Polyolefin Foam	BASF, West Germany	1	?	?	
	EB Facilities and Beam Power Unaccounted For	2-4	?	<160 kW	
Heat-Shrinkable Film, Tubes and Tapes	Cryovac - several locations	9	most HV	500 - 1000 kV	Film
	Inst. of Nuclear Chemistry & Tech., Poland	2	?	1 @ 2 MeV, 20 kW 1 @ 2.2 MeV, 20 kW	Film and Tubing
	Raychem, Denmark	1	CGS-MeV	10 MeV Linac	Tubing and tape
	West Germany	1	RDI	4 to 5 MeV	
Coatings	Bruynzel, West Germany	1	ESI	250 kV, < 300 mA	Wood Panel Coating
	Novatel, Netherlands	1	ESI	250 kV, < 300 mA	Wood Panel Coating
	Parisot, France	1	ESI	250 kV, < 300 mA	Wood Panel Coating
	Svedex, Netherlands	1	ESI	250 kV, < 300 mA	Wood Panel Coating
	Theuma, Belgium	1	ESI	250 kV, < 300 mA	Wood Panel Coating
	Volkswagon, West Germany	1	Durr	150 kV, 100 mA	Metal Wheel Coating
	Other: France	1	?	?	Inks and Coating of Packages
	Rubber Products	Michelin, France	2	2 HV	?
WKP, West Germany		2	2 HV	?	Rubber Tire Sheet
EB Facilities and Beam Power Unaccounted For		~3	?	~150 kW	
Other	Beta-Gamma; West Germany	2	RDI	1 @ 500 kV, <50 kW 1 @ 3.0 MeV, <150 kW	Contract Radiation
	Capri Centres d.E. Tudes France	1	?	300 kV, 30 kW	Textile Grafting
	CAPRIC, France	1	CGS-MeV	7 MeV, 7 kW linac	Contract Radiation
	National Laboratory, Denmark	2	?	1 @ 10 MeV, 10 kW 1 @ 400 kV, 20 kW	Contract Radiation
	Viritech, England	2	?	1 @ 1.5 MeV, 75 kW 1 @ 4.5 MeV, 90 kW	Contract Radiation
	EB Facilities and Beam Power Unaccounted For	~6	?	?	

(1) RDI: Radiation Dynamics Industries  
 HV: High Voltage Engineering Corporation  
 CGS-MeV: CGS-MeV Company  
 ESI: Energy Science Incorporated  
 Durr: Durr-Polymer Physik



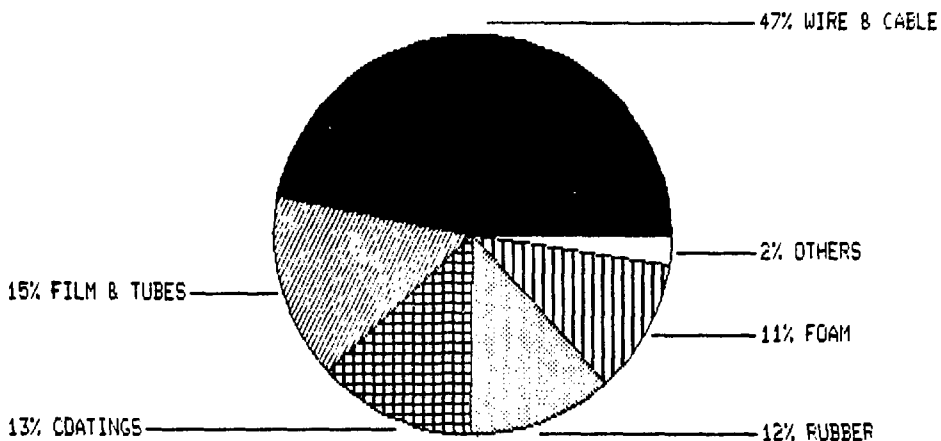


FIGURE 14: Estimated Breakdown of the Commercial EB-Processing of Plastics in Japan (1987)

Table 9 gives the available information on the commercial EB-processing industry in Japan (Mizusawa and Klempen, 1988; Peters, 1984).

The Nissin High Voltage Company supplies virtually all of the Japanese EB units. The Sumitomo Electric Industry leads the production of radiation cross-linked wire and cable insulation with 5 EB units totaling 152 kW. Most of the details of the EB facilities used for producing heat-shrinkable film and tubes, coatings, rubber products and polyolefin foam are unavailable.

The yearly breakdown, from 1977 to 1987, of the Japanese EB capacity is given in Table 10 (Peters, 1984; Mizusawa and Klempen, 1988). The growth rate of the Japanese EB-processing industry has been calculated from this data. Such complete information is not available for the United States or the European industries, making similar calculations impossible.

The average annual rate of growth (AARG) for the entire industry over the last 10 years, including EB units for research and development, has been 13.3%. When this 10-year period is divided into three segments, the AARG decreases from 20% for 1977 to 1981, to 6.4% for 1984 to 1987.

The AARG for the five major product categories, over the 1977 to 1987 period, is the following:

- |                                      |       |
|--------------------------------------|-------|
| (1) Wire and cable insulation:       | 11.6% |
| (2) Polyolefin foam:                 | 19.3% |
| (3) Heat-shrinkable film and tubing: | 16.4% |

TABLE 9

JAPANESE COMMERCIAL EB FACILITIES (1987)

General Product Category	Company/Location	No. of EB Units	EB <sup>(1)</sup> Manufacturer	Available Facility Details	Comments	
Cross-linking Wire and Cable Insulation	Dainichi Nihon Cable Co.	1	?	50 kW		
	Fuji Kura Cable Works	1	?	11 kW		
	Furukawa Electrical Co.	3	NHV	2 @ 50 kW 1 @ 33 kW		
	Hirakawa Cable Works	1	NHV	23 kW		
	Hitachi Cable Co.	2	NHV	1 @ 50 kW 1 @ 50 kW		
	Oki Electric Cable	1	?	52 kW		
	Showa Cable Works	1	?	33 kW		
	Sumitomo Electric Ind.	5	NHV	4 @ 23 kW 1 @ 60 kW	Some PE foam also	
	Taisho Electric Ind.	1	NHV	50 kW		
	Tokai Electric Wire Co.	1	NHV	33 kW		
	Tokyo Electric Co.	1	NHV	60 kW		
	Yazaki Cable Works	2	NHV	1 @ 50 kW 1 @ 23 kW		
	Others	6	NHV	1 @ 50 kW 1 @ 60 kW 2 @ 52 kW 1 @ 33 kW 1 @ 23 kW		
	EB Facilities and Beam Power Unaccounted For	4	probably NHV	≈750 kW		
	Polyolefin Foam	Sekisui Chemical Ltd.	2	?	?	
		Sumitomo Co.	2	?	?	
		Toray Co.	?	?	?	
EB Facilities and Beam Power Unaccounted For		7	?	≈438 kW		
Heat-Shrinkable Film and Tubing	Hosokawa Yoko Co.	?	?	?	Films and Packaging Materials	
	Nitto Electric Co.	?	?	?		
	UBE Industries	?	?	?	Tube and Film	
	Asahi Co.	?	?	?		
	EB Facilities and Beam Power Unaccounted For	7	?	≈456 kW		
Coatings	Eidai Industry Ltd.	1	NHV	600 kV, 100 mA	Plywood Coating	
	Mitsubishi Rayon Co.	1	?	500 kV, 65 mA	Sheet Metal Coating	
	Nippon Steel	1	?	?	Coil Coating	
	Suzuki Motor Co.	2	?	2 @ 300 kV, 100 mA	Paint Coating	
	EB Facilities and Beam Power Unaccounted For	10	?	≈307 kW		
Rubber Products	Bridgestone Co.	1	NHV	1 MeV, 100 mA		
	Toyo Co.	1	NHV	1 MeV, 100 mA		
	EB Facilities and Beam	6	probably NHV	340 kW		
Other		2	?	61 kW (total)		

(1) NHV: Nissan High Voltage Co.

- (4) Coatings: 12.0%
- (5) Rubber products: 26.8%

Again, if this time period is divided into three segments, the AARG's of the products usually decrease from the 1977 to 1981 period to the 1984 to 1987 period. The only product where this trend is not seen is radiation-curable coatings, where the AARG rose from 3.9% during 1977 to 1981, to 27% from 1981 to 1984 and then decreased to 8.8% from 1984 to 1987.

TABLE 10

YEARLY BREAKDOWN OF JAPANESE EB CAPACITY BY INDUSTRIAL APPLICATION

Application	1977			1981			1984			1987			Average Annual Rate of Growth of EB Capacity (%)										
	Quantity (kV) (K)	No. of Units Total (%)	Average EB Unit Power (kV)	Quantity (kV) (K)	No. of Units Total (%)	Average EB Unit Power (kV)	Quantity (kV) (K)	No. of Units Total (%)	Average EB Unit Power (kV)	Quantity (kV) (K)	No. of Units Total (%)	Average EB Unit Power (kV)	1977-81	1981-84	1984-87								
Wire and Cable Insulation	575	48	12	39	48	1000	40	20	33	50	1465	42	27	32	54	1724	41	31	28	56	15	14	5.6
Polypropylene Foam	75	6	2	6	38	270	11	7	12	39	338	10	10	12	34	438	10	11	10	40	38	7.8	9.0
Heat-Sealable Film and Tubing	100	8	3	10	33	340	14	8	13	43	456	13	7	8	65	456	11	8	6	65	36	10	0
Curing of Coatings	150	12	2	6	75	175	7	2	3	88	356	10	10	12	36	459	11	15	14	31	3.9	27	8.8
Rubber Products	50	4	1	3	50	290	11	6	10	46	410	11	6	7	68	540	13	8	7	68	55	12	9.6
Other	25	2	1	3	25	50	2	2	3	25	61	2	2	2	31	61	1	2	2	31	18	6.8	0
Subtotal	925	80	21	67	2125	85	45	74	25	3096	88	62	73	18	3678	87	74	67	23	23	13	6.0	
Research and Development	230	20	10	33	25	375	15	15	26	25	425	12	23	27	18	553	13	35	33	16	11	4.3	9.2
<b>TOTAL</b>	<b>1225</b>	<b>100</b>	<b>31</b>	<b>100</b>	<b>2500</b>	<b>100</b>	<b>60</b>	<b>100</b>	<b>25</b>	<b>7511</b>	<b>100</b>	<b>85</b>	<b>100</b>	<b>18</b>	<b>4231</b>	<b>100</b>	<b>109</b>	<b>100</b>	<b>16</b>	<b>20</b>	<b>12</b>	<b>6.4</b>	

1. The subtotal and total values are the average growth rates for the EB processing industry.

2.2.5 Other Countries

Figure 15 illustrates the EB capacity breakdown for the other countries using EB processing to manufacture plastics (Peters, 1984; Mizusawa and Klempen, 1988, Laisier, 1986).

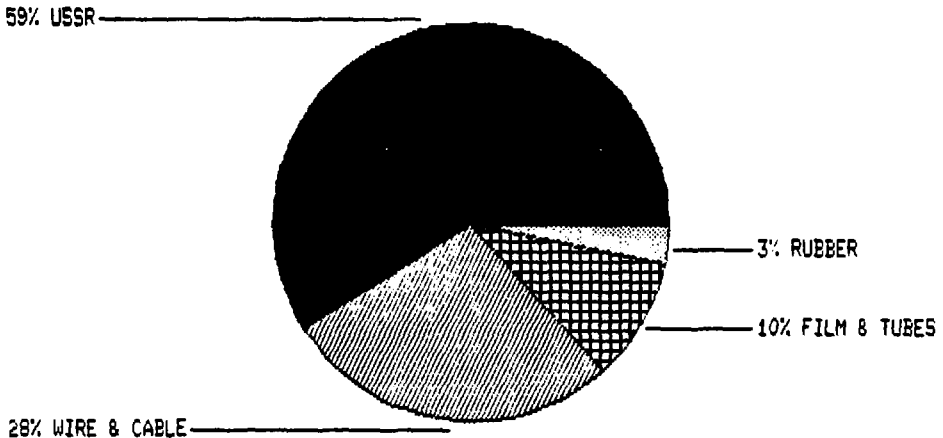


FIGURE 15: Estimated Breakdown of the Remaining Worldwide EB Capacity for Plastics Production. (1984)

The U.S.S.R. electron-beam processing industry accounts for 59% of the remaining EB capacity. The specific products manufactured in the U.S.S.R are unknown, except that cross-linking of wire and cable insulation dominates the industry (Peters, 1984). The remaining 41% of EB capacity available to other countries is divided between wire and cable insulation (28%), heat-shrinkable film and tubes (10%), and rubber sheet (3%).

Table 11 gives the available information on the other EB units.

TABLE 11  
OTHER COMMERCIAL EB FACILITIES

Location/Company	No. of EB Units	EB Manufacturer	Available Facility Details	Comments
Australia	6	1 RDI 5 ?	?	Wire and Cable Insulation
Brazil	2	RDI	1 @ 10 MeV, 1kW	? Wire and Cable Insulation
Canada	2-3	RDI		
Shaw Pipe and Cable, Toronto;	1		2 MeV; 60 kW	Wire and Cable Insulation
Cryovac, Toronto	1	?	?	Heat-Shrinkable Film
Northern Telecom	1 ?	?	?	
China	2	?	40 kW total	Wire and Cable Insulation; some Tubing
Korea	2	?	146 kW total	Wire and Cable Insulation; some Tubing
Mexico	2	RDI	?	Wire and Cable Insulation
Taiwan	3	?	335 kW total	Wire and Cable Insulation; some Tubing

2.3 PRODUCTION INFORMATION

Table 12 gives the estimated yearly production in the United States of the major product categories that use EB processing (Peters, 1984; Leaversuch, 1987).

TABLE 12  
ESTIMATED PRODUCTION OF PLASTICS USING  
EB PROCESSING IN THE UNITED STATES (1986)

Product	Total Product (Mg x 10 <sup>5</sup> )	EB-Processed Total (Mg x 10 <sup>5</sup> )	% EB Processed
Wire and Cable Insulation	4.3	1.1	25.0
Film	18.2	1.2	6.5
Tubes and Pipes	18.2	0.95	5.0
Coatings	5.9	0.41	6.9
Rubber	13.2	0.36	2.7
Foam	12.6	0.09	0.7
Total	72.6	4.41	6.1

The United States market was selected for this calculation because all of the required data were readily available and the U.S. is the major supplier of EB-processed products. The percentage of product that is EB-treated ranges from 0.7% for foam to 25% for wire and cable insulation, with the average for these five product categories being 6.1%.

2.4 POTENTIAL APPLICATIONS FOR HIGH-ENERGY ELECTRON BEAM PROCESSING SYSTEMS

A potential application for a 5 to 10 MeV, EB-processing system in the plastics industry must manufacture a high value-added product and/or have a very high production rate to economically justify the capital expense of the EB unit. The obvious starting point is to identify potential applications by investigating the existing commercial products that are manufactured using EB processing.

Radiation cross-linking of power cable insulation ( $\geq 75$ -kV cable rating), thick polyolefin and rubber sheet ( $\geq 15$  mm) and thick-walled tubing and pipe are the only products presently manufactured by EB treatment where a 5- to 10-MeV accelerator may be both useful and economical. (Bly, 1981; Sasaki et al., 1981; Mohammed and Walker, 1986). The other commercial products, wire insulation, polyolefin foam, heat-shrinkable film and tape, and radiation-curable coatings are all "thin applications" that can be produced with the less expensive, lower energy EB units. Many of these products may, however, be EB treated in several layers simultaneously, making a 5- to 10-MeV accelerator economical, based on the increased production capacity of the system. Each of these applications will have to be considered in detail to determine the potential of high-energy EB processing for the existing EB-manufactured products.

Two general product categories in which EB processing could have many potential applications are moulded plastics and composite materials. Each of these applications has thick substrates to be polymerized and cross-linked, and they could take advantage of the increased production rates provided by the high-energy EB process as compared to the conventional thermal or chemical curing process. The major process hurdle is the increase in temperature of the component as a result of EB treatment. Researchers continue to seek methods to lower the required radiation dose to polymerize various polymer formulations and, therefore, reduce the temperature rise (Zagorski, 1985). Techniques to raise the thermoconductivity of polymers by the use of fillers, additives and blending with other polymers is also being researched. If suitable processing systems and resin formulations can be designed, there may be no limit to the number of potential applications for high-energy EB processing in the plastics industry.

### 3. GAMMA PROCESSING FOR PLASTICS

Plastics production using gamma irradiation is very limited. The only application of any significance is wood-plastic composites: the impregnation of wood with monomer followed by irradiation to polymerize the monomer. About  $7.5 \times 10^7$  GBq of  $\text{Co}^{60}$  in four facilities was dedicated to wood-plastic composite flooring production worldwide in 1983 (Peters, 1984). Polyacrylamide, a thickening agent for cosmetics, is also produced using gamma irradiation (Ransohoff, 1981; Mellberg, 1978). The major disadvantage of gamma irradiation as compared to electron beam is the decreased dose rate and thus the low production capacity of gamma facilities. Oxygen can also be a free radical scavenger, preventing the radiation polymerization reaction in some resin formulations (Tamura, 1981). Oxygen would, therefore, have to be removed from around the component being irradiated. The major advantages of gamma irradiation as compared to EB are its penetration and that the low dose rates enable the irradiated components to remain at or near ambient temperature, eliminating the need for forced air cooling.

Gamma processing in the plastics industry is small and considered unimportant by many (Peters, 1984). The potential for new applications for gamma processing is also considered to be limited.

### 4. CONCLUSIONS

1. The five major product categories that account for most of the worldwide EB capacity used in the plastics industry are the following:

- (1) Wire and cable insulation;
- (2) Heat-shrinkable film and tubes, and cross-linked pipe;
- (3) Rubber sheet for tire production;
- (4) Polyolefin foam; and
- (5) Radiation-curable coatings.

2. In 1984, there were about 500 individual EB units worldwide: 75% of them being considered high energy systems ( $\geq 500$  kV).
3. Cross-linking of wire and cable insulation, and cross-linking heat-shrinkable film and tubing are the two major EB processes, each accounting for about 28% of the worldwide EB capacity (1984). The other major products are coatings and adhesives (10%), rubber sheet (8%) and polyolefin foam (4%). A total of 17% is unaccounted for.
4. The United States accounts for 59% of the worldwide EB capacity (1984), followed by Europe (16%) and Japan (15%). The estimated total EB capacity in 1984 was 20.5 MW.
5. The W.R. Grace Company (Cryovac) of South Carolina dominates the worldwide production of heat-shrinkable film, accounting for about 35% of the total EB capacity in the United States and 10% in Europe ( $\approx 54$  EB units in 1984). Cryovac also has an EB processing facility in Toronto.
6. Raychem of California leads the cross-linked tubing and pipe production with about 20 EB units worldwide.
7. The average annual rate of growth (AARG) for the EB-processing industry for plastics in Japan, from 1977 to 1987, was 13.3%. Similar calculations for the United States and Europe were not possible because the required data were unavailable.
8. The AARG of the EB-processing industry for plastics in Japan has decreased from 20% for 1977 to 1981, to 6.4% for 1984 to 1987.
9. The AARG for the EB processing in the five major product categories, in Japan from 1977 to 1987 period are:

(1) Wire and cable insulation:	11.6%
(2) Polyolefin foam:	19.3%
(3) Heat-shrinkable film and tubing:	16.4%
(4) Coatings:	12.0%
(5) Rubber products:	26.8%
10. A total of 6.1% of the yearly production of wire and cable insulation, film, tubes, pipes, polymer coatings and foam ( $72.6 \times 10^5$  Mg) in United States is EB treated ( $4.41 \times 10^5$  Mg).
11. Twenty-five percent (25%) of the yearly production of wire and cable insulation in the United States ( $4.3 \times 10^5$  Mg) is EB cross-linked ( $1.1 \times 10^5$  Mg).
12. Radiation cross-linking of power cable insulation (cable rating  $\geq 75$  kV), thick polyolefin and rubber sheet ( $\geq 15$  mm), and thick-walled tubing and pipe are the only products presently manufactured in significant quantities by EB treatment for which a 5- to 10-MeV EB unit may be both useful and economical.

13. Other "thin products" such as coatings, films and wire insulation may be EB-treated economically using a 5- to 10-MeV EB unit, if several layers of the product can be treated simultaneously.
14. Two general product categories in which EB processing could have many applications are moulded plastics and composite materials. The major process hurdle—temperature rise of the substrate during irradiation—must be overcome to realize these potential applications.
15. Gamma processing is only a very small part of the total radiation processing industry for the production of plastics.

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