# Electron Beam Crosslinking of Polyolefin Films for Various Packaging Applications

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**Abstract:**

Radiation crosslinking comprising of gamma rays from a $Co^{60}$ source and even high energy electron crosslinking from > 1 MeV accelerators have been commercial since 1960's. These applications were mostly for the wire and cable industry, rubber tires, and some high barrier shrink film applications for meat packaging introduced by Cryovac. Since the development of low voltage electron beam accelerators in the < 300 kV range, in particular in the 125kV range the use of EB crosslinking has found new applications and markets particularly in the packaging industry. What are these markets, and what properties are achieved by electron beam irradiation of polyolefin films used in packaging will be presented. In addition theory of electron beam crosslinking will be discussed in detail.

**Introduction:**

Polymers when irradiated either by gamma rays from a $Co^{60}$ source or high energy electrons generated by electron accelerators either crosslink or undergo chain scission depending on the chemical structure. Actually both processes take place simultaneously, and depending on the chemical structure either crosslinking or chain scission becomes the rate limiting step and thus the end result of the irradiated polymer. Crosslinking usually results in molecular weight increase and is directly proportional to the dose of irradiation. The molecular weight increases with dose till a 3 dimensional network is formed, making the polymer thermoset. When chain scission reaction pre-dominates then the molecular weight decreases with dose resulting in reduction of the polymers mechanical properties. Following Table : 1 indicates which polymers crosslink or chain scission. [1]

## Table: 1

## Predominant Processes in Some Irradiated Polymers

| Cross-Linking | Chain-Scission |
|---|---|
| Polyethylene | Polyisobutylene |
| Polystyrene | Polypropylene |
| Natural Rubber | Polyvinylidine chloride |
| Polyvinyl chloride | Polytetraflouroethylene (TEFLON) |
| Polyamides | Cellulose (Paper) |

Radiation crosslinking of natural rubber for the tire industry and crosslinking of polyethylene for packaging have been used since the 1960's using high voltage 400 kV to 1 MEV type EB accelerators. Even for the wire and cable industry, radiation crosslinking to provide temperature resistance was the favorable curing option instead of thermal crosslinking using peroxides.

There has been significant work and lot of commercial activity in radiation crosslinking of polyolefins especially polyethylene films for packaging applications. Properties of ordinary polyethylene film made by the bubble process were significantly enhanced by electron crosslinking and are as shown in Table: 2.[2]

## Table: 2

## Effect of Irradiation on Properties of Oriented Polyethylene

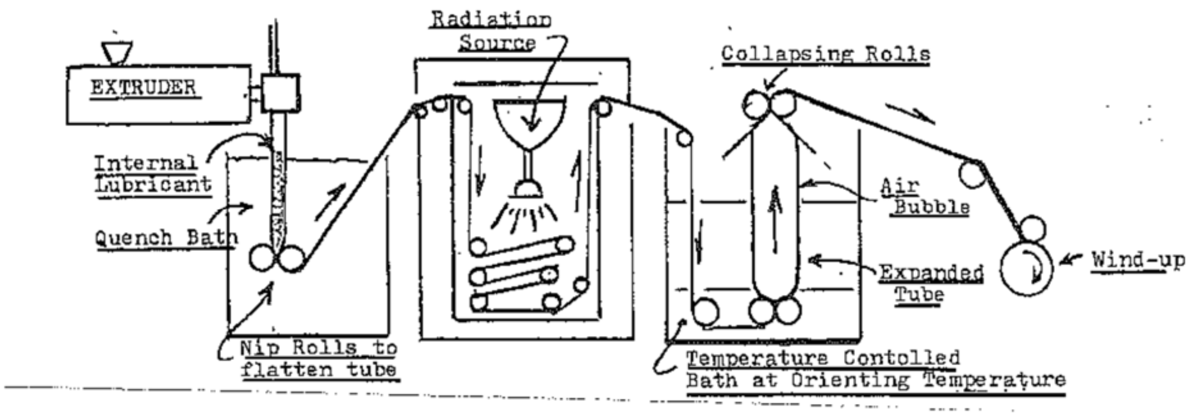
| | Irradiated | Not Irradiated |
|---|---|---|
| **Specific Gravity gm/cc** | **0.916** | **0.916** |
| **Tensile Strength psi**<br>**At 22 C**<br>**At 93 C** | <br>**8000-16000**<br>**1500-3000** | <br>**1500-3000**<br>**100-200** |
| **% Elongation** | **100-200** | **600** |
| **Heat Seal range C** | **150-300** | **110-150** |
| **% Shrinkage 98 C** | **80** | **60** |

As can be seen from the above table that EB irradiation provided significant amount of enhanced physical properties required for heavy duty high shrink bags for meats/chicken and poultry packaging.

The process is as shown in Fig:1. The extruded thick walled tube is irradiated using high energy 1 MEV type accelerator before being oriented in a bubble form. The irradiation step crosslinks the polymer molecules, then it is bi-axially stretched and oriented. The irradiation imparts the memory affect to the polymer and thus resulting in higher shrink ratios. The crosslinking affect increases of the molecular weight of the polymer thus resulting in higher temperature resistance, broader heat seal range and enhanced mechanical properties as seen above Table: 2. Copolymerizing of EVA copolymers and EB crosslinking results in excellent shrink bags. Electron beam crosslinking has 2 major advantages FDA approval, and no chemical residual contaminants. These advantages result in greater than 90% of frozen turkey bags packaged in high barrier EB cross linked PE films.

Figure: 1

Process of Biaxially Orienting EB irradiated Polyethylene film




**EB Crosslinking of Polyethylene Chemistry:**

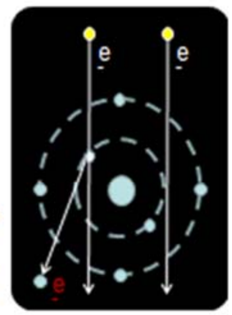
Polyethylene molecules upon absorbing the electrons form free radicals. These free radicals are postulated to be formed on adjacent chains accompanied by the loss of hydrogen molecule or and is known as the hydrogen abstraction process. Hydrogen gas is liberated upon crosslinking and the polymer radicals combine readily to form a crosslink as shown in the following Figs 2A 2B & 2C forming a 3-dimensional network is formed.

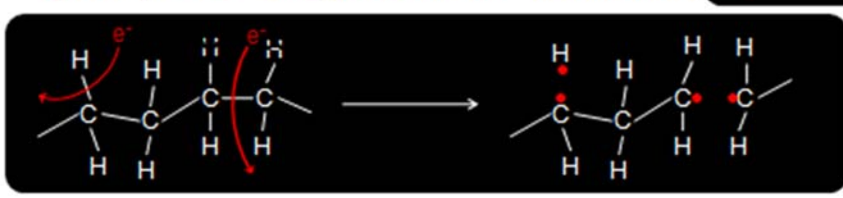
**Figure: 2A 2B & 2C**

**Electron Beam Crosslinking of Polyethylene Mechanism**

## Reaction -Generation of Radicals-

- Electron(from electron beam) collides with the atomic nucleus and the electron in the material.
- These electrons cuts each bonds (C-H, C-C etc), then the radicals





## Reaction -Basic Reaction-

- Basic Reaction (PE)

Generation of radicals

$-CH_2-CH_2-CH_2- \rightsquigarrow -CH_2-CH_2-\dot{C}H- + H\bullet$

$-CH_2-CH_2-CH_2- \rightsquigarrow -CH_2-\dot{C}H_2 + \dot{C}H_2-$

Termination reaction and Movement of radicals

$H\bullet + H\bullet \longrightarrow H_2$ , $-CH_2-\dot{C}H_2 + \dot{C}H_2- \longrightarrow -CH_2-CH_2-CH_2-$

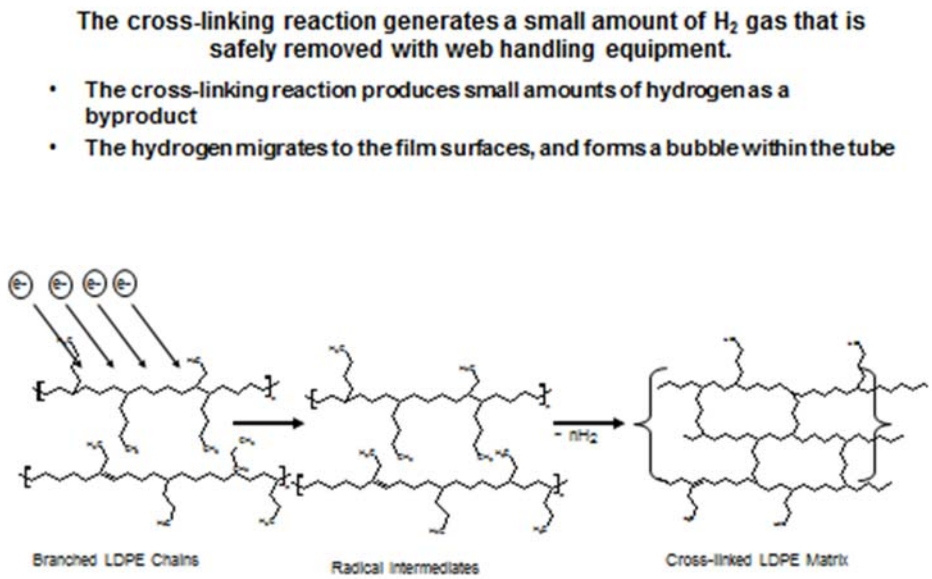
$-CH_2-CH_2-\dot{C}H- + H\bullet \longrightarrow -CH_2-CH_2-CH_2-$

$-\dot{C}H-\dot{C}H-CH_2- \longrightarrow -CH=CH-CH_2-$

$-CH_2-CH_2-\dot{C}H- + H_2 \longrightarrow -CH_2-CH_2-CH_2- + H\bullet$

$-CH_2-CH_2-CH_2- + H\bullet \longrightarrow -CH_2-\dot{C}H-CH_2- + H_2$

54




**Low Voltage Electron Beam Cross linking Applications:**

**High Barrier Shrink Film Bags**:

High barrier shrink bags were introduced to increase the shelf life of the products that were packaged in it. These high barrier shrink bags containing 3 layers of film were manufactured by the double bubble process[3] as shown in Fig: 3. These layers contained PVDC (polyvinylidine copolymer) having typically the following structure:

Structure:

Outer Layer = 48 microns (18% EVA + LDPE)

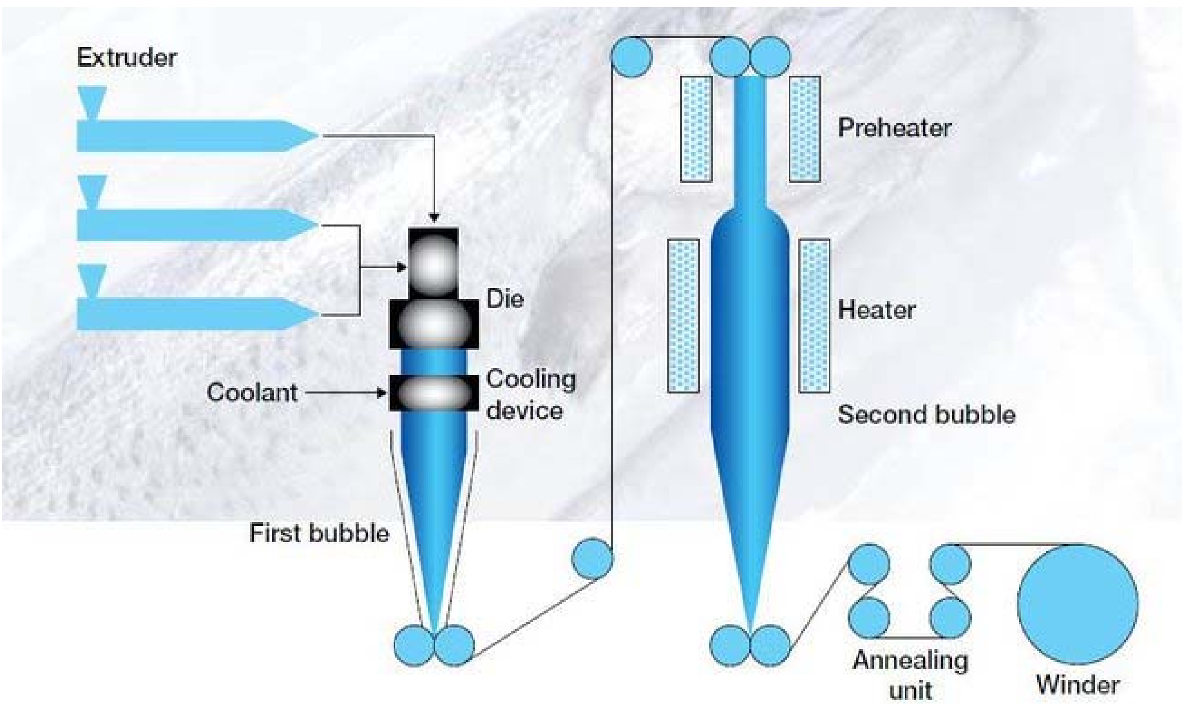
Middle Layer = 7 microns (PVDC)

Inner Layer = 8 microns (18% EVA + LDPE)

After the second bubble the wall thickness is typically around 63 micrometers. The PVDC layer provides the required oxygen barrier properties, oxygen transmission rates of 8-10 cc/$m^2$/24. EB crosslinking is required to increase the outer layer heat resistance to avoid burn through, at the same time restrict EB absorbance to the PVDC layer and the inner sealant layer. EB irradiation to PVDC causes discoloration, and EB irradiation to the inner sealant layer causes crosslinking and increases its melt index and thus reduced seal strength. Both these properties are not desirable.

**Figure 3:**

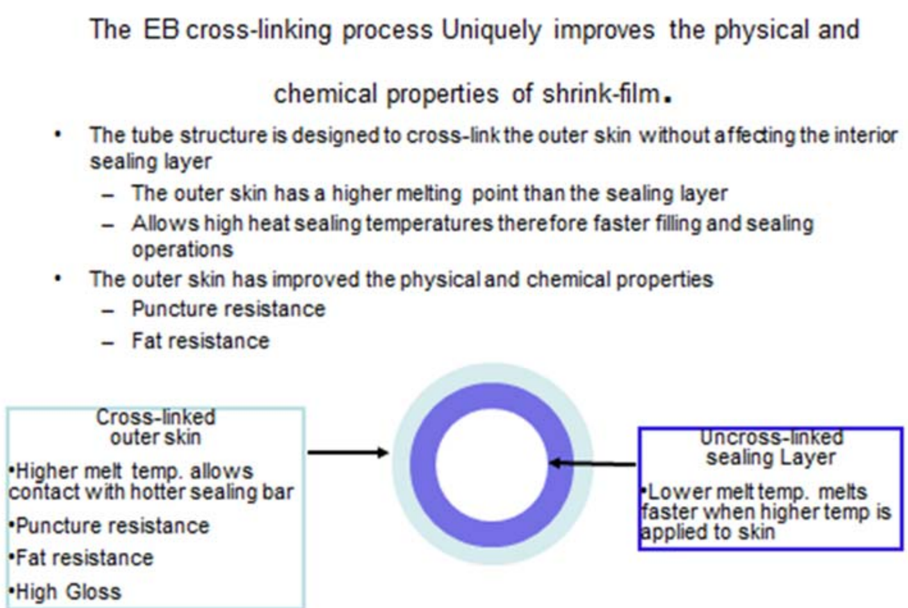
**High Barrier Shrink Film Bags Double Bubble Process Using 3-Layers**




The efficacy of controlling the depth of electron penetration using low voltage EB units [4,5] to the outside layer to achieve the desired crosslinking is as shown in Fig: 4.

**Figure: 4**

**Desired properties with EB Crosslinking using low voltage EB accelerators**




By operating the EB equipment at 90 -100 kV and a dose to cure of 4-6 Mrads temperature resistance to the outer (EVA+LDPE) layer is increased to 220 C by crosslinking it. While the inside sealant layer is un-cross linked and having a lower melt index and provides required seal strength. Also the dose to the PVDC layer is reduced. Other benefits of EB crosslinking is avoid cold shrinkage. Utilizing split rollers one EB unit is used to simultaneously irradiate both sides of the shrink bags. For example a 26 inch wide shrink bag goes into the EB gets irradiated on the top layer of the bag. The bag comes out then goes over turn bar gets irradiated on the other side and gets wound up. A 54 inch Low voltage EB unit is commonly used for this application.

**High Barrier Skin Packaging:**

The use of high barrier skin packaging already very common in Europe is gaining market acceptance in North America. As shown in Fig: 5 mostly meats, cheese, poultry, seafood products are the common foods packaged in this way. The high vacuum barrier film settles around the product like a skin without compromising the product structure. It provides the required safe and secure seal preventing contamination and leakage, at the same time maintaining the natural appearance of the food product. The materials of the skin film are designed to seal various types of trays.

**Figure: 5**

**Meat Packaged using electron beam crosslinked high barrier skin film**

The skin films are typically 80 to 150 microns thick, with the bulk of the market requiring 100 microns.

The structure of the film is as follows:

Structure: Typical 100 microns (100 grams/$m^2$) (5 layers)

Surlyn Ionomer

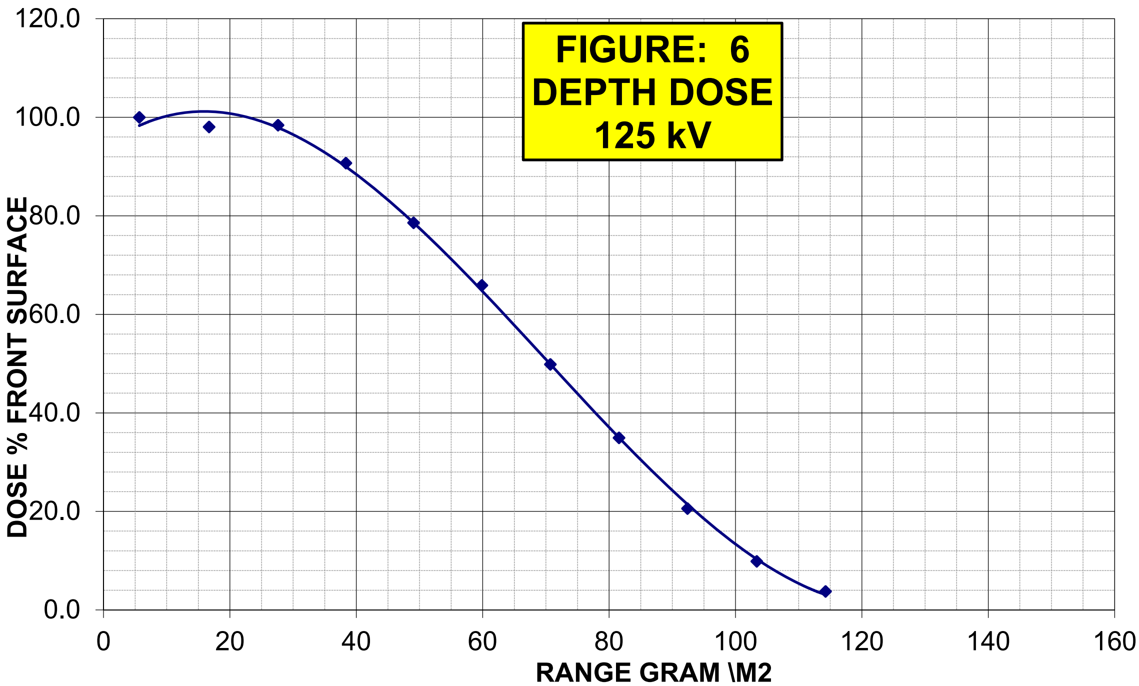
Tie Layer

EVOH 44%

Tie Layer

Inside Sealant layer (LDPE/EVA)

Ethlylene vinyl alcohol (EVOH) provides the required oxygen barrier typically of < 10/cc/$m^2$/24 hrs to provide the shelf stability and avoid meat going rancid because of oxygen contamination. Low voltage electron beam crosslinking of the outer ionomer layer provides the required temperature resistance of > 200 C to the ionomer. This layer is in direct contact with the heating surface. While the inside sealant layer is not EB treated and seals to the tray at a lower temperature providing a hermetic seal. Low voltage 125kV operation of the EB unit restricts penetration to the inside sealant layer as shown in Fig: 6 (DD125kV) providing essentially no dose to the sealant layer.




**Non-barrier shrink films for packaging**:

This application usually is a 3 layer structure of lldpe/lldpe/lldpe. The thickness of these films is in the 12-18 microns and the typical application is shrink films for packaging as shown in Fig: 7. EB treatment using low voltage provides better shrink properties and temperature resistance to avoid burn through.

**Figure: 7**

**Non-Barrier Shrink Films for Packaging**


**Conclusions:**

Use of low voltage electron beam less than 125 kV operating range for crosslinking polyethylene based films for packaging applications is growing. Especially for high barrier packaging either for shrink bags or skin packaging electron beam crosslinking provides advantages for processing purposes. Longer shelf life to reduce waste, sustainable packaging mandating lower energy consumption is paving the path for use of these smaller energy efficient electron beam accelerators. Moving forward use of EB technology either to crosslink film or initiate in situ polymerization for packaging will grow.

**References:**

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