Modification of Polymer Substrates using Electron Beam Induced Graft Copolymerization

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Introduction

Low energy electron beam (EB) systems with accelerating potentials up to 300 kV have been used in industrial processes for more than 30 years. Most of the systems feature a self-shielded design meaning the systems include all shielding needed to prevent emission of secondary x-rays as the substrate is transported in and out of processing zone. [1] The most common substrates are flexible webs; however, systems designed to transport flat and even 3-dimesional objects are now known.[2]

Electron beams are a form of ionizing radiation meaning that the accelerated electrons have enough energy break chemical bonds in organic materials including polymers. The most common result of the breaking of chemical bonds is the formation of free radicals. EB applications take advantage of processes resulting from the formation of these radicals. EB processes can be classified by the effects resulting from the formation of free radicals which include: (A) curing, (B) crosslinking, (C) scission, and (D) grafting.[3] These processes are illustrated in Figure 1.

EB curing occurs when the radicals which are formed initiate the polymerization of monomers and oligomers. Acrylate functional materials are most commonly used because of their high reactivity. Curing is usually associated with the rapid conversion of liquid ink, coating, or adhesive to a solid crosslinked polymer layer. EB curing is used in variety of printing, packaging and industrial applications.

EB crosslinking occurs when the radicals which are formed recombine with each other. Crosslinking usually starts with a polymer material and results in the joining of adjacent polymer chains to form a three dimensional network. A relatively small number of crosslinks can often have a large impact on the thermal and mechanical properties of a polymer. Common application for low energy EB crosslinking include: (1) processing of polyethylene films to provide heat shrink properties for packaging application,[4] and (2) processing of pressure sensitive adhesives to improve heat resistance and shear properties.[5]

EB scission occurs when the radicals which are formed fail to recombine and are terminated by reactions with oxygen and/or hydrogen abstraction. The net result of EB scissioning of a polymer is a reduction in the molecular weight. Industrial processes for EB scissioning are less common than curing or crosslinking. An example of scissioning is the processing of polytetrafluoroethylene (PTFE) to make low molecular fragments for use in waxes and

lubricants. [7] Most polymers undergo both crosslinking and scissioning and the process that predominates depends on chemical structure and morphology of the polymer. Scissioning can be applied to biopolymers and is used kill bacteria and other pathogens in EB sterilization processes.

EB induced graft copolymerization (EIGC) occurs when radicals formed in and on a polymer substrate become a site for initiation of monomer polymerization. The net result is that two dissimilar polymers are covalently joined to form a new copolymer material. EB grafting is less well known than curing or crosslinking but is an important process for creation of new functional materials. The EB grafting process and applications are the subject of the discussion in this paper.
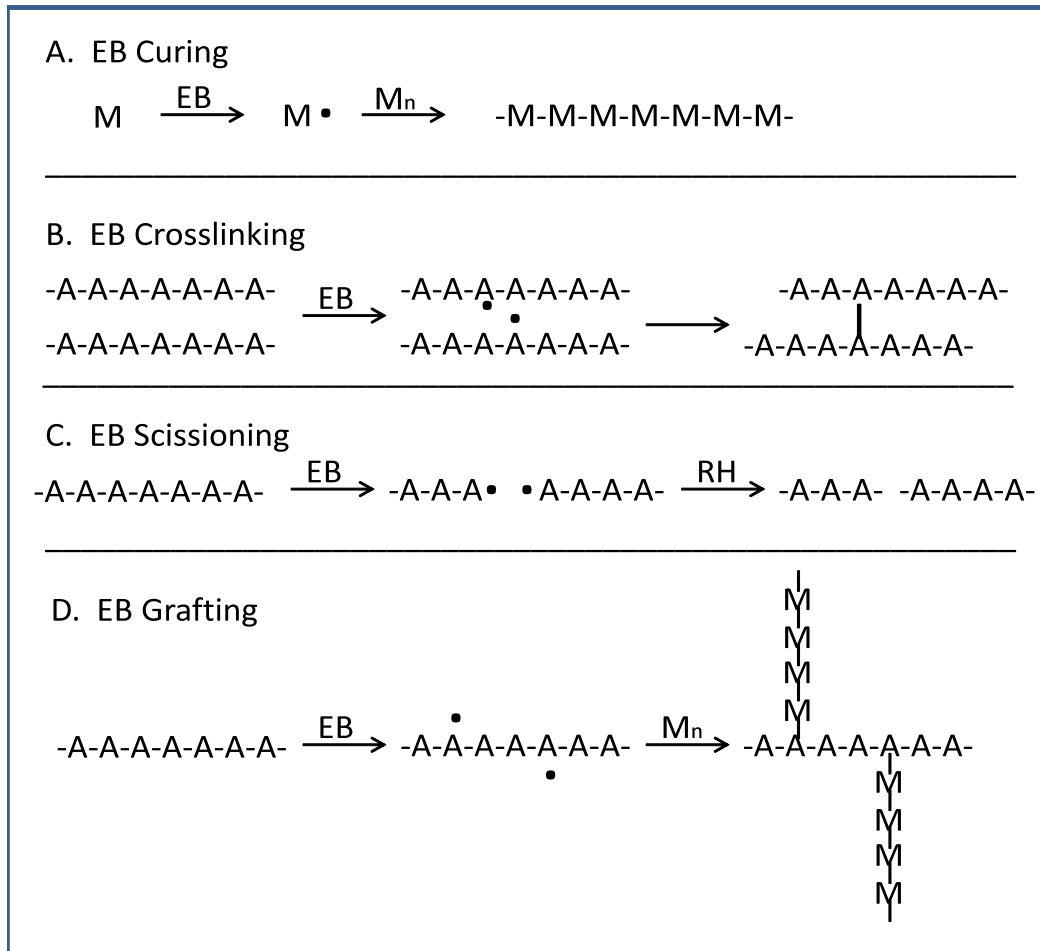
A. EB Curing

$$M \xrightarrow{EB} M\bullet \xrightarrow{M_n} \text{-M-M-M-M-M-M-M-}$$

B. EB Crosslinking

-A-A-A-A-A-A-A-
-A-A-A-A-A-A-A-
$\xrightarrow{EB}$
-A-A-A-A-A-A-A-
-A-A-A-A-A-A-A-
$\longrightarrow$
-A-A-A-A-A-A-A-A-
-A-A-A-A-A-A-A-

C. EB Scissioning

-A-A-A-A-A-A-A-A- $\xrightarrow{EB}$ -A-A-A• •A-A-A-A- $\xrightarrow{RH}$ -A-A-A- -A-A-A-A-

D. EB Grafting

-A-A-A-A-A-A-A-A- $\xrightarrow{EB}$ -A-A-A-A-A-A-A-A- $\xrightarrow{M_n}$ -A-A-A-A-A-A-A-A-

Figure 1. Electron beam induced polymer reactions: (A) curing , (B) crosslinking, (C) scissioning, (D) grafting.

EB Grafting Process

EIGC has several advantages over other grafting methods. They include:

1. Ability to ionize polymers that have limited reactivity in chemical processes
2. Clean non-chemical method to generate polymer radicals
3. Consistent controlled process
4. Low energy usage
5. Scalable from slow to fast process speeds
6. Scalable from narrow to wide webs
7. Easy integrated into complete process lines

Many common low cost polymer substrates such as polyethylene and polypropylene are very unreactive and lack functional groups that can be used for chemical grafting. EB can easily ionize these polymers creating radical sights for grafting. Because these polymers are normally unreactive they can also benefit greatly in performance and value as a result of EIGC. The number of radical sites created is proportional to the EB dose applied to the polymer substrate. Once the optimum dose is determined it can be maintained at a very constant level as the EB dose is automatically controlled with increases or decreases in line speed. The output of the equipment itself is also very consistent with little variation over very long periods of operation. The process can also be scaled using EB systems available from under 0.4 to over 3.0 meters wide (Figure 2). The EB systems are also compact typically occupying only 2 to 4 meters of space in the web direction. This facilitates integration into a process line.
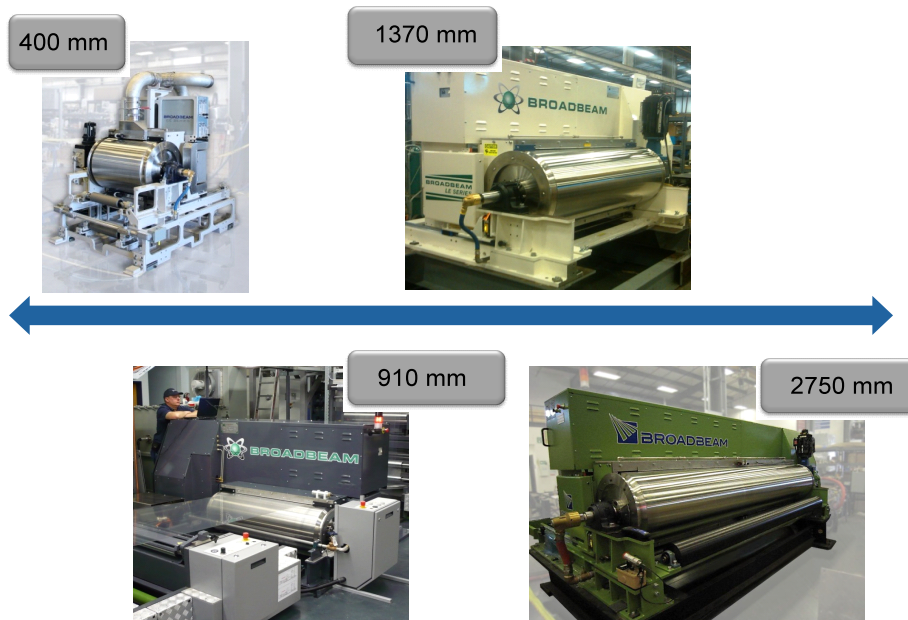

Figure 2. EB Systems

The depth of EB energy deposition into materials is controlled by the accelerating potential of the equipment and the elemental composition and density of the material being irradiated. This can be very accurately predicted by Monte Carlo simulations.[7] Most organic polymers show very similar energy deposition characteristics. The net result is that energy deposition is well predicted by the density of the polymer alone. A plot of the relative dose versus the basis weight (weight per unit area) of the polymer essentially factors out the density and provides a very useful tool to determine energy deposition as function of the material basis weight. Figure 3 shows the energy deposition for systems operating from 100 to 300 kV. A material with a basis weight of 20 g/m^2 will receive a very uniform dose from the front to back surface using an accelerating potential of 150 kV or more. Materials up to 400 g/m^2 will get a relatively uniform ($\pm$ less than 20%) dose from the front to back using a potential 300 kV. Another way look at this is to consider a thick material (for example 1.0 mm with a density $1.0 = 1000$ g/m^2). EB energy deposition can be controlled in this case from less than 20 microns to more than 400 microns into the material. This is very useful for controlling the location of the radicals that are formed and the resulting grafting that occurs. An interesting aspect of this is that low density materials such as micro-porous membranes and fabrics (woven or non-woven) can be functionalized on internal surfaces since the air voids within these materials have very little electron stopping power. The same depth/dose curves can be used to predict energy deposition in low density materials as long
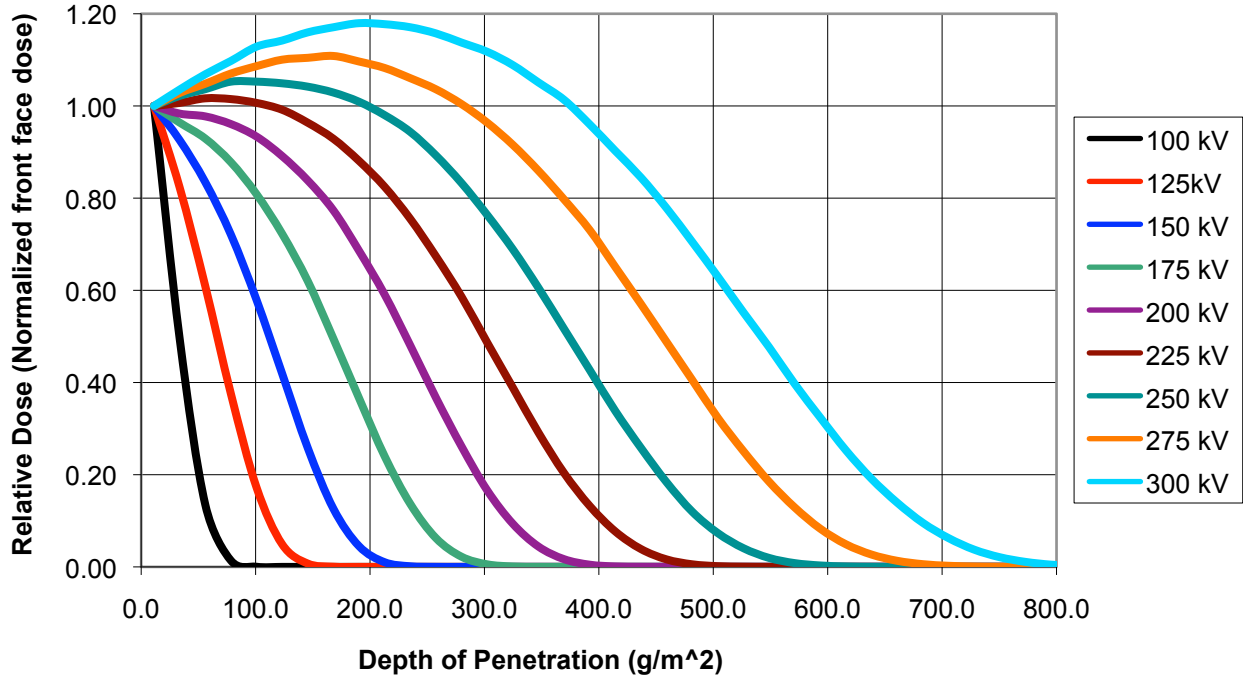

Figure 3. EB energy deposition in materials.

as the materials have a uniform density on a microscopic scale (ie, the average basis weight is about the same for any given spot on the material). Note, although the energy deposition in materials can be accurately predicted, the actual yield of radicals that are formed is highly dependent of the type of polymer being used.[8]

EIGC may be performed by two main methods: (1) simultaneous irradiation or (2) pre-irradiation methods. These are illustrated in Figure 4.

In the simultaneous irradiation method, the polymer substrate is coated or saturated with neat monomer or a monomer solution. The substrate/monomer combination is then irradiated to initiate polymerization of the monomer. This may be followed by a washing process that removers uncured monomer or polymer which is not grafted to the substrate. An optional thermal drying step may be used to evaporate residual wash solvent from the graft copolymer substrate.

A disadvantage of the simultaneous irradiation method is the formation of homopolymer which is not grafted to the substrate. This can be minimized by using relatively dilute monomer solutions, including inhibitors in the solutions, or minimizing the EB dose levels that are used. Some degree of homopolymerization may not be an issue as long as it is removed upon washing or is anchored well enough to the substrate to provide the desired functionality.

In the pre-irradiation method, the polymer substrate is irradiated to generate radicals. As long as the substrate is maintained in a vacuum or inert atmosphere the radials have a relatively long lifetime and can initiate polymerization of monomer which is subsequently brought into contact with the irradiated substrate. A washing process may be used to remove unreacted monomer. A thermal oven may be used to evaporate the wash solvent. Homopolymerization is less of an issue with pre-irradiation compared to simultaneous irradiation methods.

In an alternate version of the pre-irradiation method, the polymer substrate may be irradiated in air forming either peroxy or hydroperoxy groups. Grafting is then initiated by decomposition of the peroxides into radicals at elevated temperature in the presence of a monomer.

With all methods the main process factors used to control EIGC are: (1) EB voltage, (2) EB dose, (3) type of solvent used to dilute the monomer, (4) monomer concentration, (5) temperature and, (6) dwell time for grafting reaction. [9]
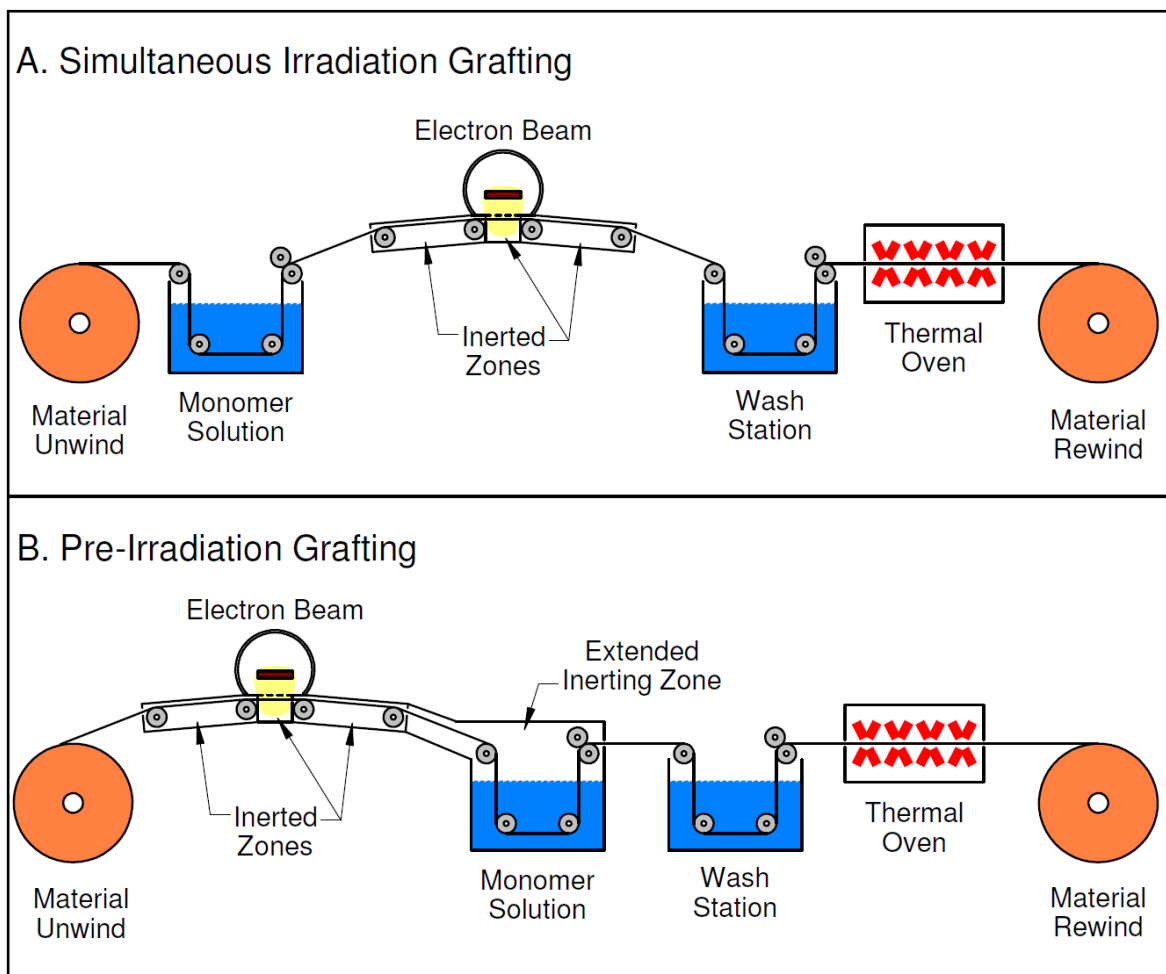
Figure 4. EGIC methods: simultaneous irradiation (A), and pre-irradiation (B).

Polymer Substrates

A wide variety of polymer substrates may be used for EIGC. The majority are synthetic polymers such as polyethylene (PE), polypropylene (PP), polyamides (PA), polyether sulfone (PES), poly(vinylidenefluoride) (PVDF), poly(tetrafluoroethylene) (PTFE) and poly(ethylene-co-tetrafluoroethylene) (ETFE). Additional graft copolymers originate from modified natural backbone polymers such as cellulose, starch, alginate and chitosan. From a morphological point of view, the polymer substrates may be in form of beads, gels, fibers, fabrics, films, and membranes.[10]

Graft Copolymers

There are a wide variety of graft copolymers which can be formed by EGIC. A broad classification would be neutral and ionic copolymers. Ionic copolymers may be subdivided into

anionic, cationic, and bipolar types. The monomer used for grafting determines the type copolymer which is formed (Figure 1D). A list of sample monomers that have been used in EGIC are shown in Table 1. A monomer such as a perfluoroacrylate will produce highly fluorinated graft side chains which results in a very hydrophobic copolymer. Acrylamide monomer by contrast gives a polar graft side chain resulting in hydrophilic copolymer. Acrylic acid produces graft side chains containing carboxy groups. The acid groups may be neutralized to form the corresponding metal salt which then may be medium for exchange with other metal cations.

The monomer itself may provide the desired properties when copolymerized on the polymer substrate. Another option is to subject the copolymer to a post grafting reaction where the side chain is chemically converted to give the desired functionality. An example is the use of gycidyl (meth)acrylate which produces epoxy functional side chain groups. The epoxy groups can be reacted with other materials including phenols, amines, phosphoric acid, and amino acids (Table 1) to give the desired properties.[10] In most cases the goal is to start with a very inert polymer such as PE, PP, PVDF, or PTFE and produce active or contrasting properties in the grafted copolymer.

Table 1. Monomers Used for the Formation of EIGC

Monomer	Post Grafting Reaction	Copolymer Character
Perfluoroacrylate	none	Neutral hydrophobic
Acrylamide	none	Neutral hydrophilic
Acrylic acid	none	Cation exchange
Vinyl benzyl trimethyl ammonium chloride	none	Anion exchange
Styrene	sulfonation	Cation exchange
Glycidyl (meth)acrylate	phenol	Neutral aromatic
Glycidyl (meth)acrylate	Triethyl amine	Anion exchange
Glycidyl (meth)acrylate	Phosphoric acid	Cation exchange

| Glycidyl (meth)acrylate | Amino acid | Bipolar |

Applications

There are many applications for copolymers produced by EB grafting. Examples include:

1. Specialty fabrics (woven or non-woven) with modified properties such as water repellence or water absorption[11]
2. Reinforcing fiber for composites where enhanced bonding properties between the fiber and matrix resin results in higher perfomace properties[12]
3. Plastic films with enhanced adhesion properties such as print receptivity or enhanced bonding of multilayer structures[11]
4. Production of media used for separation and purification purposes

The use of radiation induced grafting for the production of separation media is an active area of research and development and was the subject of a recent review article.[10] The separating media may be in the form of beads, gels, fibers, fabrics, and membranes. For commercial purposes the media may be packaged in many different configurations including tanks, columns, modules, and cartridges.

There are a wide variety of industrial separation and purification applications that include:

1. Water treatment
2. Environmental
3. Chemical industry processing
4. Food processing
5. Battery and fuel cell separators
6. Biotechnology and biomechanical application

Sample applications from published literature are listed in Table 2. The variety of applications are very broad and include the recovery of toxic and high value metals from waste water [18-21] and a biomedical application for the purification of a racemic mixture to give the enantiomer with the desired pharmaceutical activity.[22]

Conclusions

EIGC is a very versatile method for the production of specialty graft copolymers. EB provides control of depth and concentration of radials in and on polymer substrates. The selection of monomers and post grafting chemical transformations allows the production of copolymers with desired functionality. EIGC allows the production of copolymers tailored for specific end-use application. Low energy electron beam equipment is well suited to integration in commercial EIGC production lines.

Table 2. Literature Examples of EIGC for the Production of Separation Media

Polymer Substrate	Grafting monomer/reaction	Application	Ref.
PVDF film	Sodium styrene sulfonate	Fuel cell separator membrane	13
PVDF film	Acrylic acid and sodium styrene sufonate	Improved hydrophilic membrane properties	14
Hydrogels	Vinyl functional water soluble polymers	Review that includes the use of EB to form hydrogels for use in multiple applications	15
Polyimide composite membrane	4-vinyl pyridine	Separation of benzene from cyclohexane	16
Non-woven fabric	Ionic monomer followed metal oxide nano-particle immobilization	Removal of ozone from air	17
HDPE hollow fiber	Gycidyl methacrylate followed by sufonation or amination	Salt production from sea water	18
Polyester/nylon fabric	Acrylic acid	Recovery of copper and chromium from waste water	19
PP, PVDF, and PTFE membranes	Gycidyl methacrylate followed HCl an NaSH to graft thiol groups	Recovery of gold from waste water	20
PP non-woven fabric	Acrylonitrile	Uranium recovery from sea water	21
PE hollow fibers	Gycidyl methacrylate followed by amine and bovine serum albumin treatment	Chiral separation of therapeutic agents for use in pharmaceuticals	22

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