Electron beam irradiation treatment of textiles materials: a review

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Abstract
Electron beam irradiation technology has gained more attention as it appears to be a promising economically and environmentally sustainable alternative to traditional wet-chemical processing. It is an advanced approach that is clean, solvent-free, time-saving, and ecologically benign with acceptable handling and operation properties. This review provides a study of the latest literature on the technology of electron beam irradiation surface modification of textile. Considerable emphasis is also placed on the most novel applications of electron beam irradiation such as the functionalization of textile materials, which leads to the development of alternative sustainable techniques or revolutionary advanced materials soon.

Keywords Electron beam irradiation · Crosslinking · Curing · Grafting

Abbreviations

| Abbreviation | Description |
|--------------|-------------|
| EB           | Electron beam |
| EBI          | Electron beam irradiation |
| UV           | Ultraviolet |
| MeV          | Mega electron-volt |
| kW           | Kilowatt |
| EPS          | EB irradiation Processing System |
| DC           | Direct current |
| keV          | Kilo electron-volt |
| Gy           | Gray |
| kGy          | kiloGray |
| mA           | Milliamper |
| (DPC)        | Dip-pad-cure |
| XRD          | X-ray diffraction |
| TGA          | Thermogravimetric |
| ICP-OES spectroscopy | Inductively Coupled Plasma Optical Emission spectroscopy |
| XPS          | X-ray photoelectron spectroscopy |
| PDC          | Pad-Dry-Curing |
| UHMWPE       | Ultra-high-molecular-weight polyethylene |
| scCO2        | Supercritical carbon dioxide |

Introduction

Recent advances in the textile sector have concentrated primarily on both physical and chemical surface modifications of fabrics [1]. For many decades, the production of advanced materials has remained a significant challenge for all polymer and textile chemists. Moreover, the attempts to address this challenge are mainly focused on developing substitute/ modification-based solutions. However, the traditional chemical modifications of different polymers using strong alkaline or acidic agents are energy- and chemical-consuming [2–7]. Moreover, they pose potential health risks, harm the environment, reduce the technical life of the products, are often costly, and harm other fabric properties [1, 8, 9]. Instead, radiation approaches featuring low consumption of energy, no additives, ease of operation, and fast treatment speed could significantly efficiently modify the surface of textiles and promote dye adsorption, printing, fastness characteristics, coatings adhesion, and finishing agents adsorption [10–15]. Recently, electron beam technology has been used as a green replacement method for traditional textile wet processing, especially surface modification processes.
EB-irradiation (EBI) is a dry, pollution-free, and cool technology that eliminates the need for solvents and reagents used in wet chemical procedures. It provides advantages such as speedy processing, high flow rate, consistency, and environmental and labor protection while manufacturing [16–22]. EBI is widely used in several applications, inclusive of polymer and composite curing, polymer modification [23, 24] fiber surface modification [25], water purification [26], property improvement [21], and sterilization of medical tools and food science [27–29]. EBI units have provided the estimated US $85 billion value provided unique high-quality products for mankind in an environmentally friendly way. Pilot-scale EBI facilities have been established to indicate the application of this technology for the treatment of such pollutants effectively and efficiently [27].

**Electron Beam Irradiation (EBI)**

The (EBI) process is a flow of energetic electrons generated by an accelerator, for treating materials to modify their chemical and physical properties and improve the quality of the product [30, 31]. EBI is considered a pure energy carrier since the electron is one of the components in the atom. The interaction of accelerated electrons with polymers is categorized into three phases: physical, physicochemical, and chemical. During the physical process, the accelerated (primary) electrons gradually transfer their energy to the polymer substrate, resulting in the formation of short-lived reactive species (excited states, ions, and secondary electrons). Then, physicochemical process, in which these species are transformed into polymer radicals as shown in the next Eq. (1).

\[
AB + e^{-} \rightarrow AB^{+} + e^{-}
\]

(1)

The following is the chemical phase when the polymer radicals start a wide range of chemical reactions in the polymer. The chemical alteration of polymers caused by radicals mainly counts on the polymer constitution and the treatment parameters used throughout the EBI process [29].

**Advantages of EBI technology**

EBI application has the following characteristics:

1. The EBI has directivity and high processing efficiency: As the EBI exhibits excellent directivity to the acceleration direction, the rate of absorbed dose is perfectly large.

2. Extremely high energy utilization efficiency: This indeed owes to the fact that the absorbed energy in the chemical reaction is directly injected by EBI.

3. Catalysts are not required: The chemical reaction can be efficiency occurred by the direct-injected energy in the material.

4. Reaction control, operation, and maintenance are easy: Since the EBI system is an electric one, the reaction could be simply initiated or halted by turning on and off the switch, and the system is easily controlled by establishing several parameters [30].

   The rate of energy emitted of e-beam (the ratio of energy provided to the substance per unit length) is effectively larger and more efficient than that of other electromagnetic radiations including electric wave, visible light ray, UV, X-ray, and γ-ray since e-beam is a corpuscular ray [32–34] as shown:

   Gamma radiation: EBI is quite similar to gamma radiation in ionizing energy but varies in dose rates and penetration, however, EBI operation has other additional benefits. Gamma rays facilities have challenges including the management and maintenance of the radiation source capacity by replenishing it yearly. Furthermore, compared to gamma irradiators, EB accelerators offer a substantially higher efficiency (almost double) because of the directivity of the e-beam. In this regard, EBI is a more secure and inexpensive technique. [35]

   Ion beam: Since the emitted energy rate of the ion beam is excessively higher than the e-beam, it has limited applications in the industrial sector [31].

   UV radiation: EBI has advantages over it due to the toxic ozone generated as a by-product whenever UV irradiation is applied in the air [36].

   Plasma radiation: Compared to plasma treatment for high adhesion strength of materials, the low-energy EBI possesses a higher ability of penetration. This owes to the fact that the plasma treatment process occurs near the surface. Moreover, the systemic plasma treatment for adhesion characteristics was indicated that the excess treatments result in creating a poor boundary layer and reducing the adhesion strength [37–39].

   In the textile modification, unlike other radiation methods such as plasma[40, 41], corona charges [42], or microwave radiation, [43] it was reported that the e-beam penetration occurred in the entire volume of the fibers, as well as, affected the whole portions of the fiber substructure [36, 44, 45].

5. Lower operation cost compared to some other radiation technology: Since the EBI accelerator does not require a source of radiation such as gamma radiation; the main cost of the radiation process comes from electricity.
In this regard, the actual cost associated with the EBI process is contingent on the total required dose for the product.

Overall, the procedure and expense of administrative regulations for EB accelerators are quite hassle-free and low-cost.

Electron beam accelerators

The main two properties of EBI accelerators in industrial processing are energy and current. The energy ranges of EBI that are used in the various industrial application are) 0.15 to 10 (MeV. The accelerators of EBI that are used in the industry usually have beam power (the product of electron energy and current) in a range from 5 to about 100 kW. However, many powerful accelerators (400 kW and higher) have been set up recently to display certain applications or for commercial irradiation.

Classification of EBI machines by the energy

Low energy electron accelerators: It generates electrons that have energies of 0.15 to 0.5 MeV. Generally, this kind of accelerator is constructed as a self-shielded system in production. They are mainly utilized to treat surfaces and irradiate coatings and polymeric films.

Medium electron accelerators: It generates electrons that have energies of 0.5–5 MeV at powers of up to 300 – 350 kW.

High energy electron accelerators: It generates electrons that have energies between 5–10 MeV. Such a type is a linear accelerator giving pulsed beams of up to 50 kW. They are used for sterilization of medical goods and applications of food treatment [30]. The applications of electron accelerators are summarized in Table 1.

EBI Processing System (EPS)

EPS is a system that exposes the EBI to a substance and a particular reaction, such as a chemical reaction. EPS is essentially the same as a Braun tube of a television and an X-ray tube of an X-ray system in terms of electrons production and acceleration, as seen in Fig. 1. The construction of a general scanning style EPS which is the electrostatic (direct current) acceleration technique is shown as follows.

1. A power-supply unit part to produce a high voltage direct current.
2. An acceleration component for producing and accelerating electrons.
3. The irradiation window and the scanning chamber scan the accelerated electrons to the required irradiation width and allow them to move through the atmosphere.
4. A vacuum device for maintaining the acceleration portion and scanning chamber at ultra-high vacuum.
5. Control unit for handling as well as controlling the whole equipment.
6. A transportation unit for the transporting of irradiated substances.

| Application     | Electron Energy (MeV) | Typical penetration (mm) for unit density product |
|-----------------|-----------------------|-----------------------------------------------|
| Surface curing  | (80 – 300)            | 0.4                                           |
| Shrink film     | (300 – 800)           | 2                                             |
| Wire & cable    | (0.4 – 3)             | 5                                             |
| Sterilization   | (3 – 10)              | 38                                            |

Fig. 1 Electrostatic accelerator and cathode-ray (TV) tube [31]

Fig. 2 Explanation of EBI generation (a) scanning type (b) non-scanning type [31]
7. A safety system that shields the x-ray and removes ozone produced by the interaction of e-beams with substances.

The high voltage DC system, the beam optics technologies for electron acceleration, and ultra-high vacuum technologies are examples of “unusual technologies” that are nonpopular in everyday life [31].

Types of Electron Beam Processing System (EPS)

EPS could be categorized as a scanning type and a non-scanning type. The variance between both types is attributed to the condition of water poured into the water tank via a showerhead as illustrated in Fig. 2. The scanning types have a little faucet and swing it for spreading water to the required place as illustrated in Fig. 2a. However, the non-scanning types have an enlarged faucet that covers the required region as illustrated in Fig. 2b. The non-scanning types are used on machines with low energy of 300 keV or lower due to the constructional limitation [31].

Industrial EB processing’s profitability, as well as its capacity to produce high-value-added products at a cheap cost, is predicated on high output throughput. Industrial EB production operations, such as crosslinking wire or cable jacketing, functionalization of textile materials, or curing coatings or printing inks, operate at hundreds of meters per minute [30]. To demonstrate this environmental advantage, consider comparing the total energy consumption required to create a specific quantity of product at a given coating weight, such as 20 g/m². Table 2 compares low-energy EB to a "high solids" solvent-based solution. The total energy required to air dry the solvent system is weighed against the energy required to operate the low-energy EB system. With the introduction of extremely high-current EB accelerators, electron beam power conversion to X-radiation can be employed as an alternative to the industrial usage of gamma rays.

Important factors for EBI processing

Factors are required to control the process for predicting the production and quality of the product:

Absorbed dose: It is the amount of energy that is absorbed by material from the operation deposited in a particular mass of the substance. The absorbed dose unit is frequently in gray (Gy). The absorbed dose is equal to the ionizing energy provided per unit mass of the substance. Requirements of absorbed dose for different manufacturing operations span a large range (0.1 to 1000) kGy. (10 to 150) kGy is required for most applications such as sterilization, polymerization, grafting, cross-linking while less than 3 kGy is required to control fungi, bacteria, or parasites.

Electron beam energy: EBI- energy plays an essential role since it is to controls of penetration of the energy into the substance. The penetration in the substance can be linearly increased by the incident energy [30].

Depth of penetration: The absorbed doses near the entrance surface are far higher in materials with higher electrons per unit mass, but the electron ranges are much smaller. The depth of penetration into different densities of materials is determined by multiplying the depth of the penetration calculated from the curves by the water density to the substance density. The penetration for various accelerating voltages to the penetration depth in a substance with a mass density equivalent to water is displayed in these curves. [34]

Line speed: Line speed displays the material processing rate under the beam. This factor significantly raises with the increase of the current of the beam and reduces with the width of the beam and absorbed dosage [30].

The application field of EBI in the textile industry

The action of EBI on polymeric materials promotes essentially two processes: cross-linking, that is, the formation of chemical links between molecular chains, and or degradation/scission of polymer chains, in which the polymer

![Electron beam irradiation effect on polymers](image)

Fig. 3 The effect of irradiation on polymers
structure is destroyed as shown in Fig. 3. Small chemical changes induced by radiation cause significant changes in the physical characteristics of the polymers. This is crucially important in the radiation chemistry of the polymer and leads to the industrial application of the radiation processing of polymer. Although cross-linking and degradation may take place to some extent at the same time, one of them must predominate [46–49].

For surface modification of fabric, radiations can remove impurities and poor boundary layers on the surface of the fabric and change surface characterization and topography [50, 51]. EBI induces the hemolytic cleavage of C–C and C-H bonds on the surface of polymers. The generated alkyl radicals are also unstable and undergo a complex series of reactions that result in cross-linking, chain scissions, oxidation, and the creation of C = C bonds [52, 53]. The interactions between e-beam and polymers or chemicals including cross-linking reaction, graft polymerization, curing (radical) polymerization, and scission don’t take place independently. However, some of them occur simultaneously, and a reaction with a comparatively high generation possibility results in the process.

Table 3 Recent reports of crosslinking by EBI of various fabrics

| Fabric       | Working condition | Cross-linked substance                      | Results                                                                                         | Year | Ref  |
|--------------|-------------------|---------------------------------------------|-------------------------------------------------------------------------------------------------|------|------|
| Polypropylene| 0.001×10¹⁹ to 1.5×10¹⁹ (e cm⁻²) | _                                           | • Improve wettability and dyeability                                                            | 2010 | [54] |
| Wool         | 0~400 kGy         | _                                           | • Increase in color strength                                                                   | 2015 | [44] |
| Polyester    | 260 kGy           | Hyperbranched quaternary ammonium salts (QAS-HPs) | • The original elongation at first improved, and then, a monotonous reduction was obtained. Some fluctuations in the amount of the S-oxidized species as S-sulphonate, cystine monoxide, cysteic acid, cystine dioxide | 2020 | [55] |
| Polypropylene| 0~300 kGy         | _                                           | • Significant improvement in hydrophilicity efficiently and its durability towards washing. High antibacterial activity 100% S. Aureus and 90.84% E. Coli O157:H7 within 30 min of contact time | 2021 | [7]  |

Based on the preceding, the following may be summarized: A cross-linking process is a polymerization reaction that occurs between polymers to increase their molecular weight. Graft polymerization: A polymerization process that connects polymers to create a functional monomer with additional activities. Radical polymerization: A polymerization reaction in which radicals are generated in a substance with a lower molecular weight by irradiation and then polymerized.

Crosslinking polymerization reaction

Crosslinking is the polymerization reaction between polymers to enhance the physical characterization of the polymer, including heat resistance, by uniting intermolecular and creating 3D structures as illustrated in Fig. 4. Systems with acceleration voltages ranging from 500 keV to 3 MeV and e-beam currents ranging from (50 ~ 100) mA are employed as EPS. This technology was applied to manufacture a heat-resistant electric wires insulator, heat-resistant sheets, and films, textile surface modifications, heat shrinkable tubes, etc. [31]. In textile materials, considerable studies have grown up around the theme of EBI cross-linking to enhance the properties of the fabric. We presented some of them below in Table 3:

Payamara et al. [54] investigated the effect of electron bombardment with the energy of 10~40 keV and various periods into polypropylene (PP). PP exhibited significant changes in its physical and chemical characterization by EBI processing. The results showed an amenable modification of PP surface characterization after EBI processing and improvement in the wettability, dyeability, and printability
through forming (-O–H) and (C = O) groups on the PP surfaces. Also, the result of dyeing with basic dyestuff for treated fabrics showed a relative increase in color strength. (SEM) results of treated samples showed a rougher surface compared to the untreated with the increase of the absorbed dosage of electron bombardment.

Porubská et al. [44] investigated the effect of accelerated EBI with absorbed doses of 0–400 kGy in the air on wool fabric. At a higher absorbed dose, the α-helix was shifted from the majority into the minority non-monotonously. More than 220 kGy, the only creation of the cystine dioxide and cysteic acid was obtained. The improvement of the hydrocarbon groups showed a moderate creation of crosslinks at 250 kGy as well as the early stages of the breaking of the peptide chain were detectable at higher absorbed doses. The tensile break had no effect at all ranges of doses. However, the original elongation at first improved, after that, a monotonous reduction was obtained.

Another application of EBI on polyester (PET) was revealed by Zhang et al. [55] using EBI, the authors developed functionalized QAS-HPs as an antibacterial agent for PET fabrics. The findings of the water contact angle proved that the modified fabric with QAS-HPs via EBI demonstrated significant improvement in wettability. According to the washing durability findings, the cross-linked QAS-HPs on the PET fabric showed efficient and good washing stability. Within 30 min of contact time, the treated PET fabrics had high antibacterial activity, inactivating 100% S. Aureus and 90.84% E. Coli O157:H7. In this regard, this study presented a promising environmental finishing technique to produce a durable antibacterial polyester fabric depending on the numerous benefits of EBI on polymer modification.

A very recent investigation was employed by Abou Elmaaty et al. [7] (2021) that studied the dyeing characteristics of PP, nylon 6, and PET, with natural dyes, namely curcumin and saffron dyes which were pretreated using EBI as shown in

Fig. 5  Mechanism of dyeing treated synthetic fabrics using EBI. (a: PP, b: Nylon 6. c: PET) [7]
Fig. 5. The study demonstrated the effects of exposure doses (0–300 kGy) and different oxidation periods in the air on the synthetic fabrics. The optimum conditions were achieved at 300 kGy for an hour oxidation time. Significant enhancement in dyeability of the synthetic fabrics towards the natural dyes. Raman spectroscopy findings showed that the absorbance of the dye effectively occurred in the whole layers of the fabrics. Additionally, the dyeing procedure exhibited excellent coloration behavior and features, commercially acceptable leveling properties, and excellent results for durability and color fastness.

**Curing (radical) polymerization**

Curing is a polymerization reaction in low molecules as shown in Fig. 6. The radical polymerization reaction (polymerization reaction of low intermolecular) was used to cure a paint-coated film in the 1960s, and several paint manufacturers developed pilot plants.

However, thermochemical reactions necessitate energizing the molecules with thermal energy as an indirect injection of energy for the chemical reaction. In this application, EPS with low energy of 300 keV or less is mostly utilized. [31]. Electrons from the accelerator generate free radicals in polymerizable monomers leading to simultaneous polymerization and crosslinking of the monomer onto the substrate. Since EBI processing takes place at near ambient temperatures, drying of inks can be implemented even on heat-sensitive plastic substrates. The absence of extractable initiators in EBI curable inks and overprint systems allows the development of over-print materials. The studies presented in this review are listed in Table 4.

In 2005, Ibrahim et al. [56] studied surface modification of various fabrics including natural, blend, and synthetic fabrics surface-coated by a uniform thickness layer of 25 mm of an aqueous solution of (PVA) and (AA). EB curing for coating surface was performed at a constant exposure dose of 50 kGy. Results of all coated samples showed development in their water uptake, better hydrophilic and durability features of the coated formulation against the washing cycle. Furthermore, the study of the properties of color strength showed significant improvement for all fabrics towards basic and reactive dye. In 2005, El-Naggar et al. [57] investigated the pigment printing of cotton fabrics using formulations free of binders and thickeners using EBI as an alternative method to thermal curing. These formulations included (EG), (MMA), and (PMMA) oligomer as a base material, and pigment color. Results showed that printed cotton fabrics using EBI performed better color strength than the printed fabrics by the traditional thermal fixation at

| Table 4 Recent reports of Curing by Electron-beam Irradiation of various polymers |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Fabric          | Working condition | Formulation                      | Results                                                | Year  | Ref |
| Cotton, Cotton/ | A constant exposure dose of 50 kGy | -Polyvinyl alcohol (PVA) Acrylic acid (AA) | •All coated samples showed increases in their water uptake, better hydrophilic characterizations | 2005  | [56] |
| polyester blend |                 |                               | •Color strength properties results showed increases in color strength of all fabrics |                  |     |
| Nylon-6 fabrics |                 |                               | •Printed cotton fabrics using EBI showed better color strength than the traditional method at equal pigment color ratios | 2005  | [57] |
| Polyester       | Irradiation dose: (25, 50, 75,100) kGy | -Tetrahydrofurfuryl acrylate monomer -trifunctional urethane-methacrylate (TFUMA) oligomer | •Printed fabrics by EBI compared to traditional method obtained: •Higher color strength •Durable fastness properties | 2009  | [58] |
| Cotton          | Irradiation dose: (25,50,75,100) kGy | -Monomers (tetrahydrofurfuryl acrylate or hexane diol diacrylate), -Oligomers (trifunctional urethane methacrylate) | •Vat printing of cotton and polyester fabrics by EBI exhibited a much higher color yield than the traditional method | 2012  | [59] |
| Cotton          | range of 7–65 kGy | -3-(3'-acrylicacidpropylester)-5,5-dimethyl hydantoin | •Excellent biocide efficacy towards: 6-logs *Staphylococcus aureus* and *Escherichia coli* O157:H7 •Excellent regenerative properties •20% tensile loss | 2015  | [60] |
the same pigment color ratios. However, the pigment printing on cotton fabrics using EBI or thermal curing enhanced their crease recovery and mechanical characterization and displayed comparable durability characterization against fastness to washing, rubbing, and handling. In this regard, in 2009, Abdoua et al. [58] reported the pigment printing of polyester and cotton fabrics utilizing both formulation free from binders and thickeners and EBI as a replacement for thermal curing. These formulations include pigment colors and reactive chemicals (oligomers and monomers). TFUMA oligomer was utilized as a curable base besides ethylene glycol. Both fabrics were printed with these formulations then irradiated by EBI at different doses. Accelerated electrons generated by the EBI accelerator were applied to fix the pigment colors incorporated with these formulations to cotton and polyester fibers. The results proved that irradiated printed fibers by EBI obtained higher color strength and achieved durable fastness properties for roughness, rubbing washing, and perspiration of fabrics printed than those printed by traditional thermal curing. On the other hand, EBI was used as a green alternative method to overcome the difficulty of complicated several processes of the traditional vat dyeing in one step. In 2012, Hakeim et al. [59] investigated printing of vat dyes with curable formulations on cotton and polyester fabrics via EBI and reported conduction between the prints by EBI and steaming fixation in terms of color, and durability characterization. The used formulations contained only monomers (tetrahydrofurfuryl acrylate or hexane diol diacrylate), oligomers (trifunctional urethane methacrylate), and vat dyes. The optimum conditions by EBI achieved at (25/75 wt%) of monomer/oligomer ratio and exposure dose of 75 kGy at which the deepest color was obtained for both fabrics also, durability properties for rubbing, washing, and perspiration. For both fabrics, they proved that vat printing by EBI exhibited a much higher color yield than vat printing by the traditional approach and they got rougher surface than those printed by the traditional technique as well. The above discussion has indicated that the printing of cotton and polyester are reaching good color durability properties for roughness, rubbing, washing, and perspiration. In this regard, EBI was used as a green alternative method to overcome the difficulty of complicated several processes of the traditional vat dyeing in one step. In 2012, Hakeim et al. [59] investigated printing of vat dyes with curable formulations on cotton and polyester fabrics via EBI and reported conduction between the prints by EBI and steaming fixation in terms of color, and durability characterization. The used formulations contained only monomers (tetrahydrofurfuryl acrylate or hexane diol diacrylate), oligomers (trifunctional urethane methacrylate), and vat dyes. The optimum conditions by EBI achieved at (25/75 wt%) of monomer/oligomer ratio and exposure dose of 75 kGy at which the deepest color was obtained for both fabrics also, durability properties for rubbing, washing, and perspiration. For both fabrics, they proved that vat printing by EBI exhibited a much higher color yield than vat printing by the traditional approach and they got rougher surface than those printed by the traditional technique as well. The above discussion has indicated that the printing of cotton and polyester are reaching good color strength and fastness properties using EBI.

In the subsequent study [60], Li et al. synthesized and bonded 3-(3’-acrylacrypodyl)-5,5-dimethyl hydantoin onto cotton fabrics via the EBI approach. Upon application to household chlorine, the coated cotton fabrics can indeed be antibacterial. Chlorinated cotton was confronted with Staphylococcus aureus and Escherichia coli O157:H7 and demonstrated excellent biocide performance through deactivating 100% of the bacteria at contact times of 10- and 5-min. The measurements of the washing and UV irradiation have proven that modified fabric has excellent regenerative characteristics. The tensile loss has been approximately 20%, which is an acceptable antimicrobial treatment.

**Graft polymerization reaction**

Graft polymerization (polymerization reaction of a low molecule to polymer) is a polymer reforming technique that involves grafting different monomers onto the chain of the polymer for adding the characteristics of the monomer to the polymers, as illustrated in Fig. 7. In the pre-irradiation process, the monomer reacts with a polymer after the irradiation of EB to create free active radicals in the chain of the polymer, while in the coincidence irradiation approach, the EBI is irradiated when a monomer and polymer are present to produce graft polymerization simultaneously. Ion-exchange membranes and battery separators are manufactured using the pre-irradiation process. For this application, low energy-EPS of the range of)300–500(keV is the most widely employed. The studies of grafting presented in this review are listed in Table 5.

Graft polymerization reaction

Recently, several techniques have been presented to endeavor the modification of the natural fibers especially cotton fibers using EBI. Among these, in 2012, Chmielewska et al. [61] embedded silver NPs in the cotton matrix using EBI. It was found that both silver content and irradiation had an efficient effect on the thermal characteristics of cotton fibers. Modified cotton by Ag NPs demonstrates distinct antibacterial behavior against Gram-negative and Gram-positive bacteria, which could be defined by the variation in the cell membrane structure of both two bacteria. In 2016, Seino et al. [62] synthesized silver NPs immobilized on various fabrics using a radiochemical technique. A reduction reaction occurred when a high-energy EBI is irradiated into a solution of silver ions, resulting in metallic NPs. Small Ag NPs of 2–4 nm were discovered besides larger particles measuring more than 10 nm. Such nanoparticles are firmly immobilized on the surface of the support fabric without any requirement for a binder or surfactant. The number of silver NPs immobilized was found to be proportional to the water content of the supporting fabric, implying that radiochemical species created by water radiolysis, as well as radiochemical species produced by the irradiation supporting fabric itself, reduced silver ions. Even after a durability test that included washing the fabric 100 times, the silver NPs immobilized on the textile support fabric successfully improved antibacterial activity over a wide antibacterial range. In 2016, Jiang et al. [63] studied the preparation of
Table 5 Recent reports of grafting by Electron-beam Irradiation of various polymers

| Polymer           | Working condition | Grafting substance                                                                 | Results                                                                                                                                                                                                 | Year | Ref  |
|-------------------|-------------------|------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|------|
| Cotton matrix     | 25 kGy            | Silver nitrate (AgNO₃; purity 99.5%)                                               | •Good antibacterial behavior towards Gram-negative and Gram-positive bacteria                                                                                                                        | 2012 | [61] |
| Cotton            | 40 kGy            | Ag nanoparticles synthesized from AgNO₃                                             | •Improved antibacterial activity over a large antibacterial range even after the test of durability involving the washing of the fabric 100 times                                                                 | 2016 | [62] |
| Cotton, Rayon, PET, Nylon 66, Acrylic, PP, micro-fiber |                   |                                                                                     |                                                                                                                                                                                                        |      |      |
| Cotton            | 20 to 200 kGy     | fluoromonomer, 1H,1H,2H,2H-perfluoroocetyl acrylate (PFA)                           | •Good resistance to water and durability to washing after 10 cycles                                                                                                                                  | 2016 | [63] |
| Cotton            | Irradiation dose: |                                                                                     |                                                                                                                                                                                                        |      |      |
|                   | 10 kGy, in the air| glycidyl methacrylate monomer                                                        | •Excellent conductive network for the fabric                                                                                                                                                    | 2017 | [64] |
| Cotton            | Irradiation dose: |                                                                                     |                                                                                                                                                                                                        |      |      |
|                   | 0, 10, 25, 50 kGy | aqueous-alcoholic silver nitrate solution                                             | •UV-blocking,                                                                                                                                                                                          | 2018 | [25] |
| Cotton            | Irradiation dose: |                                                                                     |                                                                                                                                                                                                        |      |      |
|                   | 32.5 kGy          | Diethyl methacryloylphosphora-midate containing phosphorus and nitrogen              | •EB-modified cotton compared to PDC method has:                                                                                                                                                    | 2019 | [17] |
|                   |                   |                                                                                     | •Better flame retardancy compared with PDC-modified cotton                                                                                                                                    |      |      |
|                   |                   |                                                                                     | •Better tensile strength of irradiated cotton                                                                                                                                                 |      |      |
|                   |                   |                                                                                     | Both methods showed degradation of the modified cotton fabrics at lower temperatures and generated higher yields at 600 °C                                                                               |      |      |
| Silk              | Irradiation dose: |                                                                                     |                                                                                                                                                                                                        |      |      |
|                   | 20,40,60,80 kGy   | Methacrylamide (MAA)                                                                | •Improved the silk crease resistance                                                                                                                                                                 | 2003 | [65] |
|                   |                   |                                                                                     | The cross-linking with a catalyst produced higher crease resistance to the silk than without it                                                                                                   |      |      |
| Polyester         | reaction temp., 77 °C; monomer conc., 30 wt %; reaction time, 9 h | Acrylic acid (AA)                                                                  | •Improving in moisture regain and the water vapor permeability of the fabrics                                                                                                                      | 2003 | [66] |
| Polymer                          | Working condition                  | Grafting substance                                                                 | Results                                                                                                                                                                                                 | Year | Ref  |
|---------------------------------|------------------------------------|------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|------|
| poly(p-phenylene terephthalamide)| Irradiation dose: 0–450 kGy        | • Acrylic acid or/and (AA)                                                         | • Grafting with AA or AA/MA exhibited deeper color than the untreated one  
• Grafting with AA showed increasing in dyeability and low fastness to washing  
• Grafting with MA and AA showed increasing in colorfastness to washing | 2012 | [67] |
| Polyester                       | Irradiation dose:                 | • Acrylic acid (AA)  
• Acrylamide (AAM)  
• Dimethyl vinyl phosphonate (DMVP) | • Grafted PET with AAM and DMVP decreased the flammability  
• Grafted PET with AA enhanced the char-forming, anti-dripping and flammability characteristics  
• AAM and DMVP provided PET fabric with better flame retardation and thermal stability over 450 °C | 2014 | [68] |
| Polyester                       | 195 kGy                            | • Quaternary ammonium compound 2-dimethyl-2-hexadecyl-1-methacryloyethyl ammonium  
|                                 |                                    | bromide (DEHMA)  
• Acrylic acid (AA) | • Improved antibacterial efficacy towards S. Aureus and Escherichia coli (E. Coli O157:H7)  
• A slight degree of the breaking strength loss | 2018 | [69] |
| Polyester                       | 260 kGy                            | N-halamine precursor monomer 3-allyl-5,5-dimethyl hydantoin (ADMH) and acrylic acid  
|                                 |                                    | (AA) | • Higher antibacterial activity and inactivated 100% S. Aureus and E. Yeah. Coli O157:H7 within (1 and 5) min of contact  
• A slight decrease in tensile strength  
• UVA light stability revealed that the chlorine loading of the developed PET fabrics decreased with the duration of UVA exposure period | 2020 | [70] |
| Polyester                       | Irradiation dose:                 | • Commercially fluorine-based water and oil repellent (AG-E092) with perfluoralkyl  
|                                 | 0, 100, 200 kGy                    | groups (Rf groups)  
Acrylate monomers containing alkyl groups of different lengths using | • The treated fabrics with AG-E092 and acrylate monomer showed more hydrophobicity and oleophobicity  
• The EBI conditions showed no significant influence on durability owing to the effect of the binder added to AG-E092  
• AG-E092/ stearyl acrylate with or without EBI was found to preserve the wettability feature against washing and rubbing  
• by simply adding a long-chain alkyl group to a widely viable fluorine-based agent, Rf group mobility could be reduced, and the durability enhanced | 2021 | [71] |
| UHMWPE                          | ScCO₂: (30 MPa, 80 °C, 50 min)     | Trimethylolpropanetrimethacrylate (TMPTMA)                                        | • After scCO₂ and EB irradiation, the performance of UHMWPE fabric was changed  
• After EBI, the surface morphology of UHMWPE fibers significantly changed | 2018 | [72] |
superhydrophobic materials by grafting fluorine-containing hydrophobic agent, 1H,1H,2H,2H- (PFA) into the cotton fabric using both conventional dip-pad-cure (DPC) and EBI method as an eco-friendly technique. The modified cotton fabrics with both approaches exhibited good resistance to water and durability to washing. The adjusted cotton fabrics exhibited strong water repellency even after 10 washing cycles. The grafted fabrics also showed less bending rigidity and bending hysteresis than the control samples, suggesting that the PFA grafted cotton was softer. Via the EBI approach, the same results can be produced under lower temperatures and without an initiator, as compared to the conventional DPC method. In 2017, Krishnanand et al. [64] studied electro-conductive cotton fabric made by electroless silver deposition from a salt solution. Cotton fabric was first grafted polymerized with glycidyl methacrylate monomer via EBI, after that subjected to a chemical modification utilizing hydrazinium hydroxide solution, which serves as a reducing agent for metal deposition, as shown in Fig. 8. The XRD pattern showed that in situ produced Ag particles are nanoscale, with a typical size of around 41 nm. Metallic silver accounts for nearly 7.5 weight percent of the metalized fabric, according to the TGA plot. These are the results of hydrazine derivatives already present in the fibers reducing metal ions from their salt solution. The fabric’s surface resistivity decreases from (10 9 to 3.63) X/sq for metalized fabrics due to the deposited silver particles, which have an excellent conductive network. Although the conductive fabric preparation process sacrifices some flexibility and stretchability, as is common for coated textiles, the conductive network withstands washing for up to 15 cycles, indicating heavy metal particle adhesion to the fabric structure.

In 2018, Thite et al. [25] investigated the in-situ synthesis of silver particles cotton fiber, padded with different initial concentrations of an aqueous-alcoholic silver nitrate solution, followed by irradiating by various doses of EBI. The characteristics of the modified fabrics for the surface morphology with SEM showed that these a homogeneously dispersed on the surface of the sample and their dimensions fall in the nano range. The percentage of modified cotton weight was measured quantitatively by ICP-OES spectroscopy testing and was observed to be superior in the sample soaked with such a higher concentration of silver nitrate solution. It was demonstrated the variation of concentration range was more effective than the EBI doses. Silver particle deposition has also provided UV-blocking, color change, and antibacterial activities against two various microorganisms, S. Aureus and K. Pneumonia textile. It was confirmed that after 10 standard washing cycles, UPF and antibacterial properties were showed durability. This functional modification had no appreciable alter in the physical characterization of fabrics such as bending length and air permeability. In 2019, Liu et al. [17] synthesized

| Table 5 (continued) | Polymer | Working condition | Grafting substance | Results |
|---------------------|---------|------------------|-------------------|--------|
|                     | Polypropylene | Irradiation dose: 15,30,45,60,75 kGy | 1,4-dioxane and ClSO3H | Improve dyeability, Wash fastness ratings of 4–5 |
|                     | Polypropylene | Irradiation dose: 10 kGy | 2-vinyl-4,4 dimethylazlactonea (VDM) | The increase of carbon yields to 20% at 1000 C for the grafted samples compared to that of raw bocell |
|                     | Lycell | Irradiation dose: (100, 200, and 300) kGy | polyacrylamide (PAM) | The increase of the PAM concentration, the tensile properties of the modified fabrics were improved from 3.8 to 5.5 |
|                     |         |                  |                   | Stabilization significantly increased this yield to 55% |
|                     |         | Irradiation dose: (100, 200, and 300) kGy |                   | PAM grafted bocell fabrics at low EBI dose is extremely beneficial for the enhancement of mechanical characteristics |

superhydrophobic materials by grafting fluorine-containing hydrophobic agent, 1H,1H,2H,2H- (PFA) into the cotton fabric using both conventional dip-pad-cure (DPC) and EBI method as an eco-friendly technique. The modified cotton fabrics with both approaches exhibited good resistance to water and durability to washing. The adjusted cotton fabrics exhibited strong water repellency even after 10 washing cycles. The grafted fabrics also showed less bending rigidity and bending hysteresis than the control samples, suggesting that the PFA grafted cotton was softer. Via the EBI approach, the same results can be produced under lower temperatures and without an initiator, as compared to the conventional DPC method. In 2017, Krishnanand et al. [64] studied electro-conductive cotton fabric made by electroless silver deposition from a salt solution. Cotton fabric was first grafted polymerized with glycidyl methacrylate monomer via EBI, after that subjected to a chemical modification utilizing hydrazinium hydroxide solution, which serves as a reducing agent for metal deposition, as shown in Fig. 8. The XRD pattern showed that in situ produced Ag particles are nanoscale, with a typical size of around 41 nm. Metallic silver accounts for nearly 7.5 weight percent of the metalized fabric, according to the TGA plot. These are the results of hydrazine derivatives already present in the fibers reducing metal ions from their salt solution. The fabric’s surface resistivity decreases from (10 9 to 3.63) X/sq for metalized fabrics due to the deposited silver particles, which have an excellent conductive network. Although the conductive fabric preparation process sacrifices some flexibility and stretchability, as is common for coated textiles, the conductive network withstands washing for up to 15 cycles, indicating heavy metal particle adhesion to the fabric structure.

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a novel flame-retardant DMPP containing phosphorus and nitrogen. DMPP was grafted onto cotton fabric using EBI and PDC (pad-dry-cured) methods. SEM and XPS demonstrated that DMPP was efficiently grafted onto the cotton fabric. As demonstrated in SEM results, the modified cotton fabrics became irregular and rougher than control samples. The char length of EBI-modified cotton with a 35% concentration was 12.5 cm, while the char length of PDC–treated cotton was 17.1 cm, according to the LOI and vertical flammability tests. EB–modified cotton had a LOI of 30.2%, while PDC–treated cotton had a LOI of 28.7 percent. Both methods showed degradation of the modified cotton fabrics at lower temperatures and generated higher yields at 600 °C. In comparison to PDC–treated cotton, EBI–modified cotton has better flame retardancy, according to this report. Furthermore, irradiated cotton fabric has a higher tensile strength than PDC cotton fabric.

On the other hand, Liu et al. [65] studied EBI-grafted silk with (MAA) fabrics via EBI as an eco-friendly method. Two irradiation methods, pre-irradiation, and co-irradiation were compared, as well as certain parameters influencing the grafting degree were studied. Mechanical and physical properties including whiteness, breaking strength, and durability of grafted/ crosslinked silk samples were analyzed. The research reported a significant increase in the silk weight of the MAA silk graft through EBI. The co-irradiation grafting method has resulted in a marked increase in the degree of grafting compared with the pre grafting method; although there was a small change with the different dose rates used in this study, the degree of grafting increased dramatically with increasing irradiation dose. The presence of N2 in the atmosphere aids in the development of a higher degree of grafting. Silk crease-resistance was enhanced by EBI crosslinking with DMDHEU but cross-linking of radiation with a catalyst provided higher crease-resistance to the silk than without a catalyst.

Polyester fibers are exceedingly utilized in the textiles industry, which includes their modification with EBI technology. In 2003, He et al. [66] modified polyester fabrics by pre-irradiating via EBI in the air then grafted by (AA) without excluding oxygen to get a high water vapor permeability and great water-impermeability for PET. It was discovered that a longer reaction time, a higher reaction temperature, and a higher monomer concentration can all contribute to higher graft ratios, whilst the opposite is true of the influences of storage period and sulfuric acid on the grafting ratio. Mohr's salt allowed grafting at a lower temperature and can easily prevent homo-polymerization at sufficient concentrations. SEM analysis displayed clear and
vivid variations between the control and the grafted fabrics, which showed a layer of PAA grafted coating created on the surface of the fabrics. In 2012, Hirogaki et al. [67] investigated the modification of poly(p-phenylene terephthalamide) fiber by grafting of acrylic acid or/and (AA) methyl acrylate (MA) using EBI as shown in Fig. 9. The fabric treated with AA or AA/MA had a higher color strength than the unmodified one. AA demonstrated improvement in dyeability with a cationic dye. The colorfastness of the modified samples with only AA was poor, but the colorfastness of the grafted fabric with MA and AA increased.

In 2014, Ding et al. [68] investigated grafting of (AA), (AAM), and (DMVP) by EBI into polyethylene terephthalate (PET) fabrics via a high-energy electron accelerator. The effects
of exposure dose, as well as the concentration of monomer on the graft polymerization of PET fabrics, were demonstrated. Thermogravimetric analysis was used to evaluate the thermal activity of the grafted PET fabrics. The results demonstrated that the grafted PET fabric with AAM could boost its thermal stability. Furthermore, the whole copolymers displayed a more complicated thermal decomposition mechanism than ungrafted PET fabric. Grafted PET with AAM and DMVP decreased their flammability, based on the LOI values and the findings of the vertical flammability test. Grafted PET with AA, on the other hand, enhanced the char-forming property of PET fabrics, and thus conferred its anti-dripping characteristic. As a result, grafting with AA provided PET fibers anti-dripping characteristics and enhance flammability, whereas grafting with AAM and DMVP provided PET fabric with better flame retardation and thermal stability over 450 °C. However, in 2018, Zhang et al. [69] synthesized Quaternary ammonium compound (DEHMA) in order to be grafted onto polyester fabrics with (AA) via EBI technology. The grafted fabrics were soaked in the solution of AgNO₃ for further enhancing antibacterial properties as shown in Fig. 10. The antibacterial efficacy test displayed that the modified fabric deactivates all Staphylococcus aureus (S. Aureus) and Escherichia coli (E. Coli O157:H7) in 10 min. After coating PET fabric with Ag⁺, the antibacterial performance against S. Aureus improved efficiently. The EBI technique only results in a slight effect in the breaking strength loss of the modified PET fabric which is effectively acceptable in practical applications. With the above benefits, the modified PET textile will be extremely useful in the health care sector.

As illustrated in Fig. 11, grafting using N-halamine precursor monomer 3-allyl-5,5-dimethyl hydantoin (ADMH) and acrylic acid (AA) and irradiating with EBI is an effective and ecologically acceptable method for changing PET fabric for antibacterial and wet-ability qualities [70]. Both alkali pre-treatment and a hydrophilic monomer graft were used to achieve a high hydrophilic surface on PET fabrics. The findings of the contact angle test revealed that the application of alkali and grafted (AA) significantly improved the hydrophilicity of the PET fabric. Moreover, modified samples filled with Ag⁺ demonstrated better antibacterial activity and deactivated 100% S. Aureus and E. Yeah. Coli O157:H7 within 1 min and 5 min, respectively, of contact. The treatment of PET fabric by the EBI method resulted in a slight loss in tensile strength. The findings of the UVA light stability revealed that the chlorine loading of the treated samples reduced with the duration of UVA exposure time.

Shohbuke et al. [71] modified PET fabrics with a commercially available industrial-grade water/oil repellent agent
(AG-E092) and chemically pure acrylate monomer with an alkyl group using EBI pretreatment. In contrast, (AG-E092) treatment with no acrylate monomer was carried out using the conventional PDC process. (ATR-FTIR) and XPS measurement of the treated fabrics with (AG-E092) and acrylate monomer showed more hydrophobicity and oleophobicity. The contact angle between water and dodecane of the modified fabric increased to 129.4 degrees and 93.3 degrees, respectively, owing to adding the stearyl acrylate monomer. However, unexpectedly, the EBI conditions showed no significant influence on durability owing to the effect of the binder originally added to (AG-E092). AG-E092/stearyl acrylate with or without EBI was found to preserve the wet-tability feature against washing and rubbing. The finding demonstrated that by simply adding a long-chain alkyl group to a widely viable fluorine-based agent, Rf group mobility could be reduced, and the durability enhanced.

Dai and Shi [72] presented the grafting of (TMPTMA) into UHMWPE fibers via scCO₂ pretreatment before irradiating the fiber with EB. At five different doses of irradiation, considerable variations in gel quality, breaking strength, elongation at break, and creep rate emerged among UHMWPE fabrics. After scCO₂ pretreatment and EBI, the output of UHMWPE fibers was alerted to varying degrees. The gel content increased at first but decreased as the irradiation dose increased; the breaking strength reduced continuously; the elongation at break firstly showed improvement, then showed decreasing, while the creep rate initially reduced, then increased, before steadily decreasing. After irradiation, the surface morphologies of UHMWPE fibers changed dramatically. Multifunctional monomers boosted EBI crosslinking of UHMWPE fabric primarily by transferring macromolecular chains, which led to the creation of crosslinking networks between monomer polymers and macromolecules.
This procedure described the sensitized EBI crosslinking system of UHMWPE fabric in the existence of (TMPTMA).

PP is a highly crystalline polymer with a non-polar aliphatic structure that lacks any binding sites for traditional water-soluble dyes. For this reason, the EBI of PP was investigated in recent years. In 2009, Kim and Bae et al. [73] investigated dyeing properties of (PP) fabrics utilizing cationic dyes by EBI and sulfonic acid incorporation as shown in Scheme 1. With the treatment of EBI, results showed enhancement of dyeability due to functional groups such as carboxylate created on fabric substrates. Depending on the pH and absorbed dose ranges, the color strength is enhanced by pH increasing to alkaline conditions and increasing the absorbed doses (30~75) kGy. For PP, the incorporation of the sulfonic acid group boosted dyeability and was verified by ESCA analysis which determined certain color strength advantages over the only electronic beam. Eventually, for both EBI irradiated fabrics and sulfonic acid-incorporated fabrics, the fastness to wash of dyed fabrics with cationic dyes provided satisfactory ratings of 4~5.

However, Fontaine et al. [74] (2002) point out that the grafting of a functional monomer, namely (VDM) onto EBI (PP) films and fibers and subsequent reaction of the azlactone groups with different nucleophiles as shown in Scheme 2. Titration was used to assess the azlactone loading of PP-g-VDM film and fabrics. The grafted poly (VDM) chains, which were used as the peptide chain, were confirmed to be active for nucleophiles such as water, benzylamine, Jeff amine M6001, and benzyl amide (pbas). Sericin has been immobilized into PP-g-VDM fabrics. The findings showed that this method is ideal for creating permanently changed surfaces and that PP-g-VDM films and fabrics were utilized for deproteinization of aqueous solutions and in combinatorial chemistry as scavengers.

In 2021, Kim et al. [75] initially grafted Lyocell with (PAM) via EBI followed by subsequently fabric stabilizing and carbonizing as shown in Fig. 12. The findings revealed that the increase of carbon yields to 20% at 1000 °C for the grafted samples compared to that of raw lyocell. Moreover, stabilization significantly increased the yield to 55%. SEM demonstrated that the morphologies of modified fabrics substantially depended on the concentration of PAM. Accordingly, this has an impact on the mechanical characteristics of the modified carbon fibers. By the increase of the PAM concentration from (0.05 to 0.5) wt.%, the tensile properties of the modified carbon fibers were improved from (0.82 to 1.39) GPa. In this regard, grafted lyocell fabrics at a low EBI dose are extremely beneficial for the enhancement of the mechanical characteristics of lyocell-based carbon fibers.

**Conclusion**

This review has observed that EBI involved vital interactions between the electron beam and polymers or chemicals including cross-linking reaction, graft polymerization, and curing (radical) polymerization. On the other hand, EBI promotes fundamentally two processes in polymeric materials: cross-linking, which is the development of chemical linkages between molecular chains, and degradation/scission, which is the destruction of the polymer structure; both capable of replacing a chemical treatment for polymer modification. Moreover, in terms of cost and time, the electron beam is more efficient than the conventional methods and almost other radiation methods. Furthermore, EBI can be used with other treatment methods, such as biological treatment, to achieve better results. As a result, EBI is better suited for application prospects in the industrial ambit.

**Declarations**

**Conflict of interest** the authors declare no conflict of interest.

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