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## NANOSCALE AND NANOSTRUCTURED MATERIALS AND COATINGS

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# Application of Accelerated Electrons for Polymer Modification and Preparation of Composite Materials

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**Abstract**—Exposure to accelerated electrons makes it possible to change the properties of polymeric and composite materials on the surface and in a layer of a given depth. Ionization generates various reactive species, such as electrons, free radicals, ions, and excited molecules. These species can be used to initiate the formation of block and graft copolymers, latexes, and regular and irregular macromolecules and affect the functional properties of materials and their protective layers in a targeted fashion. Electron-beam technologies are being increasingly used in the design of improved and unique materials with desired properties of surface layers.

**Keywords:** electron accelerator, cross-linking, graft polymerization, copolymerization

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## INTRODUCTION

Exposure to ionizing radiation is a recognized and universal method to initiate chemical and physicochemical transformations (radiolysis) in polymers and monomers [1–3]. Radiolysis changes the properties of the substance owing to the formation of cross links (cross linking), scission of bonds in the main and side chains (degradation), the elimination and formation of double carbon–carbon bonds (variation in the degree of saturation), intramolecular bonding (cyclization), gas evolution, oxidation, and other effects. The known relationships of these processes make it possible to change the composition of surface layers in polymers and composites in a targeted way and impart improved and/or unique properties to them.

The main currently available tools for implementing radiolysis at a given depth are electrophysical instruments that are referred to as electron accelerators [4–6]. Technological accelerators generate a directed beam of accelerated electrons at a current density of up to 100  $\mu\text{A}/\text{cm}^2$  and an energy of up to 1.3 pJ (i.e., below the threshold energy of nuclear transformations). The service life of accelerators under conditions of continuous operation is more than 10 years. Recently, industrial accelerators with a beam power of up to 450 kW have been constructed; they are suitable for use in large-scale polymer plants. The rapid increase in the number and power of accelerators leads to a steady reduction in the cost of the energy produced by them.

Modification of surface layers and synthesis of film coatings using accelerated electrons (hereinafter, elec-

tron-beam machining (EBM)) is commonly used in all developed countries, primarily, in Japan, the United States, Germany, France, Canada, Belgium, the Netherlands, and the Republic of Korea [1–6]. Today, worldwide, more than 1500 technological electron accelerators are used only for polymer modification. Thus, in Japan, more than 200 industrial accelerators are used in polymer plants: for graft polymerization and curing of polymer coatings, modification of cable insulation, production of foamed plastic and heat-shrinkable products, and assembly and vulcanization of tires (Fig. 1). In particular, in Japan and Canada, more than 90% of the total volume of automobile tires is produced by means of EBM. Each year, the number of accelerators involved in the global polymer production increases by approximately 100 units.

In Russia, technological electronic accelerators have been developed and constructed at the Efremov Scientific Research Institute of Electrophysical Apparatus (St. Petersburg) and Budker Institute of Nuclear Physics, Siberian Branch, Russian Academy of Sciences (Novosibirsk). These large world-recognized manufacturers produced about 300 technological accelerators. Unfortunately, today, their products are used mostly abroad.

## PHYSICOCHEMICAL TRANSFORMATIONS DURING EBM

During EBM, highly reactive species—electrons, free radicals, ions (anion- and cation-radicals, carbanions, carbocations, etc.), and excited molecules—

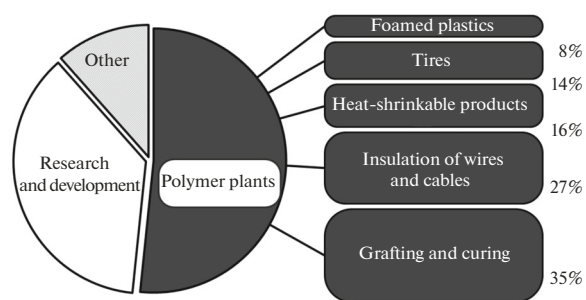


Fig. 1. Areas of application of accelerators in Japan.

are formed in the substance. Each of these species is capable of acting as an active site of polymerization [3]. Accordingly, radiolysis can provide polymerization of any monomers and their blends to form regular and irregular polymers, block copolymers, graft copolymers, and latexes. The polymerization mechanism (radical, ionic, or mixed) is determined by both the irradiation conditions and the nature of the monomer, impurities, and the relative yield of radicals and ions. It is only natural that the specific features of EBM are primarily manifested at the stage of initiation of chemical transformations.

Electron-beam machining is characterized by high energy efficiency [1–6], because the formation of reactive species under the action of accelerated electrons occurs with the highest efficiency [3]; in addition, the energy of a directed beam of accelerated electrons can be completely localized within a given layer (unlike, for example, the thermal energy). Electron-beam machining causes a variety of structural changes and reversible and irreversible changes in many physical properties [2]. This feature can be used to modify the surface layers in polymers and composites and prepare surface coatings.

Depending on the susceptibility to radiolysis, polymers are divided into two categories, namely, predominantly cross linkable and predominantly degradable (Fig. 2). Cross-linking efficiency depends on both the degree of crystallinity and the morphology of the polymer. Cross linking is dominant in the amorphous regions, where macromolecules are intertwined with each other and less rigidly fixed. In the crystalline regions, the thinner the lamellae and the denser their packing, the higher the cross-linking yield.

Cellulose, as a representative of degradable polymers, is converted to oligomers under the action of ionizing radiation (Fig. 3). Degradation radically changes the set of properties of the material [7, 8]: the solubility in aqueous media, the specific surface area, and the biodegradability increase, while the mechanical strength decreases. Preparations from irradiated cellulose exhibit a wide range of useful properties—they are used in the production of nitrocellulose and

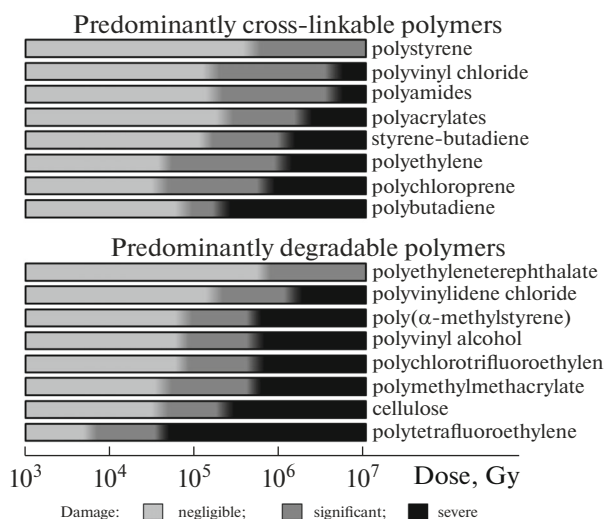


Fig. 2. Resistance of some polymers to ionizing radiation [3].

other ethers, varnishes, synthetic fibers (silk and wool), jet fuel, building materials, reinforced plastics, food additives, medicines, explosives, nanocellulose, etc.

Accelerated electrons activate discrete groups and bonds in the molecule and thereby make it possible to control the size and structure of the products. Owing to this feature, EBM is a very effective tool in nanochemistry and nanotechnology [9–13]. Electron-beam machining is used to design new-generation hybrid materials based on the integration of organic and inorganic features at the molecular or supramolecular level [14–18]. The synthesized hybrids exhibit unusual optical, electrical, magnetic, catalytic, biocidal, and mechanical properties. The demand for hybrid materials is particularly high in the production of biological and chemical sensors, nonlinear optical materials, laser media, selective membranes, catalysts, protective coatings, antistatic agents, etc. Using EBM, it is possible to synthesize polymer nanocomposites and nanogels with incorporated nanoparticles of metals (Ag, Au, Cu, Co, Ni, Pt, Pd, etc.) and oxides. In addition, composites based on graphene, graphene oxide, carbon disulfide, carbon nanotubes and fibers, silicates, zeolites, kaolin, titania, and other nanoobjects are also being designed. Electron-beam machining is commonly used for the thermal modification of the surface of metal products to improve their corrosion resistance and for the formation of protective polymer coatings.

Electron-beam machining opens up possibilities for the production of metallized and oxidized nanofilms, which have proved themselves in catalysis, microelectronics, the production of “smart” packaging materials, and micro- and submicrolithography. Nanophase components of vulcanized acrylate, epoxy, vinyl ether, and other matrices are used to enhance the mechanical properties of structural mate-

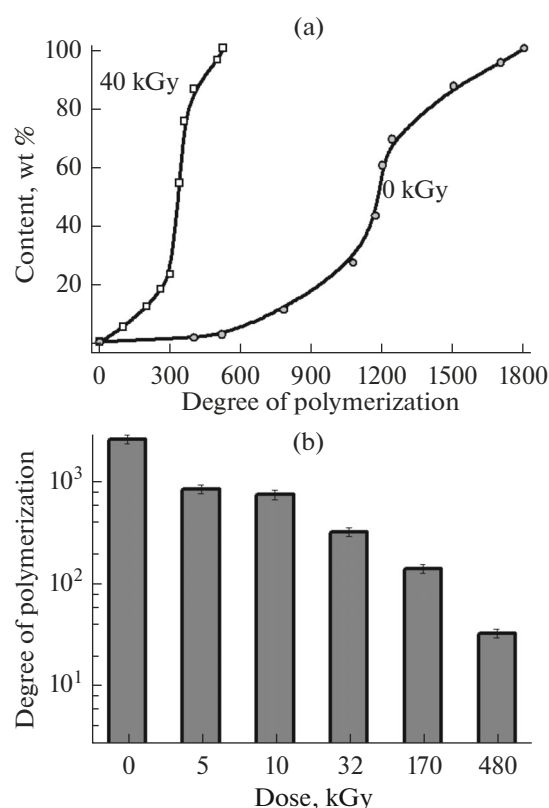
rials. Electron-beam machining is used for the direct modification of nanostructures and analysis of the induced changes in nanostructures. Cross linking and grafting by means of EBM are used to prepare nanowires exhibiting high magnetic resistance, self-cleaning surface coatings, catalytic complexes, dosimeters, nanoencapsulated preparations, semiconductor devices, gas sensors, thermal energy converters, and durable paint coatings.

### INDUSTRIAL MODIFICATION OF POLYMERS AND COMPOSITES

Electron-beam machining is the leader in the global trend of polymer modification technologies. During EBM, even relatively small doses of radiation can cause a significant change in the polymer properties [1–6]. The cross-linking effect caused by EBM is the basis for many processes, such as the modification of the polymer insulation of cables and wires; the production of reinforced and heat-shrinkable films, tubes, and shaped objects; the production of foamed plastics; the vulcanization of polysiloxane rubbers for the production of self-adhesive electrical insulating materials; the production of heat-resistant polyethylene pipes; the machining of automobile tire workpieces; and the modification of wood and mineral powders.

For example, polyethylene insulation subjected to EBM can operate at 150°C and withstand a short-term heating up to 350°C [3]. For this reason, the EBM of the polyolefin insulation is commonly used in the manufacture of cables and wires around the world. The EBM method is used, in addition to the cross linking of polyethylene and polyvinylchloride insulations, for the cross linking of an insulation of chlorosulfonated polyethylene, polyvinylidene fluoride, ethylene–tetrafluoroethylene or ethylene–propylene copolymers, etc.

Electron-beam machining is applied in the production of reinforced and heat-shrinkable shape-memory polymer products (films, tubes, tapes, bags, gaiters, shaped containers, and packaging containers) [1–6, 19]. To this end, a polymer product is initially irradiated to a dose that is slightly lower than the gelation dose; after that, it is heated to the melting point of the crystalline regions and stretched; next, the stressed polymer is cooled to increase the crystallinity. Typically, doses of 100–300 kGy are used (1 Gy = 1 J/kg). The polymer treated by this method preserves the spatial network of bonds in the “memory” and, after reheating, tends to restore the original shape. If an item is placed into this product before reheating, then, after heating, the product forms a tight-fitting shell on the item. Heat-shrinkable products are in demand for electrical engineering, electronics, food industry, shipbuilding, instrument engineering, aircraft construction, and some other areas [1–6, 19]. Polyethylene foam crosslinked by means of EBM is also commonly used. Heat- and corrosion-resistant polyeth-



**Fig. 3.** (a) Molecular weight distribution and (b) dependence of the degree of polymerization of cellulose on the absorbed dose.

ylene pipes, reinforced-plastic pipes for hot-water supply, and polyethylene lining of metal pipes are also modified by means of EBM [6, 20].

Electron-beam machining is applied for the vulcanization of film coatings on artificial leathers, vulcanization of natural rubber latex, and, in particular, in the production of self-adhesive electrical insulating tapes and rubber–glass fabrics based on polyheterosiloxane rubber. The vulcanizate of this rubber is capable of undergoing autohesion and adhesion at room temperature; the dose used in the process is 100–130 kGy. The resulting tapes are efficient up to 250°C and exhibit high water and freeze resistance. An even lower dose—50–70 kGy—is sufficient for the preparation of self-adhesive rubber–glass fabrics [3].

Electron-beam machining is used to vulcanize a cable insulation based on polysiloxane and carbon-chain rubbers, extruded tubes, and sealing parts for automobiles. In the tire industry, EBM is used for surface preirradiation of treads, carcasses, sidewalls, and other products before assembly, shaping, and thermal vulcanization. This pretreatment makes it possible to increase the cohesive strength of the raw rubber blends, replace a portion of the natural rubber with a synthetic rubber, reduce the total duration of tire man-

ufacturing by 20%, and significantly decrease the fraction of rejected products [1–6].

Electron-beam machining causes changes not only in mechanical and thermophysical properties, but also in some electrical characteristics, such as electrical conductivity, dielectric permeability, dielectric loss tangent, and electrical strength [1–6]. Thus, the dielectric permeability and dielectric loss tangent of polytetrafluoroethylene increase during EBM in the air. The electrical conductivity of polyvinyl chloride increases owing to radiolytic dehydrochlorination. In contrast, cross linking of polyester resins leads to an abrupt decrease in electrical conductivity. Polyethylene cross linked by EBM preserves high resistivity at high temperatures: the electrical strength of unirradiated polyethylene decreases with increasing temperature, whereas the following relationship is observed for irradiated polyethylene: the higher the absorbed radiation dose, the less the decrease in the electrical strength.

A change in the electrical properties during EBM is attributed to the formation of excess mobile charge carriers (electrons, holes, ions, etc.), which can be trapped by structural or chemical traps for some time. After the cessation of irradiation, the steady-state induced electrical conductivity slowly decreases. At room temperature, this process takes a few minutes to a few tens of hours depending on the polymer type. The change in electrical conductivity is reversible at low doses of ionizing radiation and irreversible at relatively high doses.

For a number of polymers (polyethylene, polypropylene, etc.), EBM leads to a change in their ability to undergo recrystallization and a decrease in the degree of crystallinity [3]. At room temperature, crystallites in polyethylene are eliminated at a dose of 35 MGy; however, this dose can be significantly decreased by heating; thus, the irradiation of a polyethylene melt causes a rapid decrease in the degree of crystallinity and an increase in the density of the spatial network and the melting point. In some cases, for example, in polytetrafluoroethylene irradiated at room temperature, the degree of crystallinity increases and achieves 94% at a dose of 80 kGy.

Composite polymer materials can be prepared using other radiolytic effects, such as variations in gas permeability, diffusion characteristics, and thermophysical properties; gas evolution; charge accumulation; and oxidation. For example, EBM of polyethylene leads to a decrease in the gas permeability coefficient (by three to four times at a dose of 1 MGy), thermal conductivity, and heat capacity (by about 15–25% at a dose of 6.1 MGy).

## ELECTRON-BEAM EMULSION POLYMERIZATION

Radiolysis provides a number of advantages over thermal or real emulsion polymerization.

—The possibility of polymerizing any monomers.

—This method does not require a real initiator; this feature provides the formation of a purer product and reduces the probability of chain termination on the initiator.

—The possibility of initiating at low temperatures; this feature weakens undesired secondary processes and contributes to an increase in the molecular weight and structural regularity of the polymer.

—Electron-beam machining generates radicals at a constant rate in all phases; this feature contributes to the acceleration of polymerization.

—The use of EBM in a pulse mode prevents chain termination owing to the entry of a second radical into a polymer particle that already has a free radical. Thus, it is possible to control the postpolymerization and obtain polymers with an exceptionally high molecular weight and provide an almost complete conversion of the monomer.

—Electron-beam machining affects—commonly increases—the stability of colloidal systems. This feature provides the occurrence of polymerization in the presence of extremely small amounts of an emulsifier and, consequently, the formation of more pure latexes.

—During EBM, hydroxyl radical OH, atom ·H, and hydrated electrons are formed in water; their chemical activity is higher than that of radicals arising from the decomposition of real initiators. This feature provides makes it possible to expand the set of monomers polymerized and grafted in latexes.

—Electron-beam machining exhibits a sterilizing and degrading effect; therefore, both the products and the waste are characterized by a low population of microorganisms and a lower content of harmful substances.

—Electron-beam machining provides a possibility of easily controlling the polymerization process, for example, owing to variations in the current, energy, and geometry of the electron beam.

## GRAFT COPOLYMERIZATION

Graft copolymerization is one of the most effective applications of EBM. It is used to modify many polymer materials (films, fibers, fabrics, molding powders, block copolymers, latexes, etc.) and minerals. The list of properties that can be improved or even re-imparted to various materials by means of EBM is extremely long. Thus, the following properties can be imparted to polyethylene: high adhesion to aluminum (grafting of acrylic acid), ion-exchange properties (grafting of acrylonitrile, acrylic acid, and some other monomers), and high radiation resistance (grafting of ace-

naphthene). In actual practice, graft polymerization by means of EBM is used to produce sorbents and flocculants; prepare creaseproof, fire-resistant, anti-static, hemostatic, thrombus-resistant, and biocidal fabrics; increase the chemical, thermal, mechanical, and light resistance; improve the oil resistance, dyeability, water repellency; etc. [1–6, 14–24].

Electron-beam machining is used to immobilize various preparations into polymeric products, for example, for medical purposes, in particular, enzymes, proteins, antigens, antibiotics, hormones, anticancer drugs, immune monitoring reagents, markers, and bacterial cells. In this case, two methods are used: (1) the formation of chemical bonds between the implanted particles and the substrate and (2) the capture of the implanted particles by the polymer matrix.

Electron-beam machining is commonly used to modify porous objects (wood, concrete, asbestos cement, etc.); to this end, the material is impregnated with monomers or oligomers and then polymerized by a beam of accelerated electrons. For example, after modification by means of EBM, the service life of parquet reaches 50 years and more. A similar technique is used to produce durable reinforced pipes, road slabs, floorings, pads, and drains of concrete, asbestos cement, expanded-clay concrete, tuff, and some other similar materials. In addition, EBM is used to strengthen ancient monuments made of wood, stone, bone, etc. [1–6].

### ELECTRON-BEAM CURING

Electron-beam machining is used to modify the surface of products of various shapes and purposes. This technique provides both the formation of a protective surface and the imparting of new functional properties to the material. In particular, irradiation with low-energy electrons is used to cure paint, decorative, magnetic, and current-conducting coatings; printing inks; and other materials on various surfaces (wood, metal, plastics, paper, leather, gypsum, asbestos cement, etc.) [1–6, 19–24]. This process is feasible owing to a number of advantages of EBM.

—The use of a directional electron beam provides a minimum energy consumption (ten times smaller than that provided by the thermochemical method).

—The EBM plants occupy significantly smaller production areas (fourfold and less).

—Electron-beam curing occurs much faster (and more efficiently) than thermochemical curing does; it ends in a few seconds.

—Electron-beam machining is conducted at room temperature; this feature is favorable for modifying thermosetting materials and improving working conditions (owing to a decrease in the amount of harmful fumes).

—The use of EBM provides a reduction in the consumption of raw materials and reagents, because this method does not require real initiators and catalysts.

—Electron-beam machining contributes to the grafting of polymer chains to the surface of the product; this feature significantly increases the coating strength.

### CONCLUSIONS

Electron-beam machining initiates structural and chemical transformations on the surface and in a given layer of the material owing to cross linking, degradation, variation in the degree of saturation of skeletal bonds, cyclization, cleavage and addition of functional groups, oxidation, and other processes. All these changes make it possible to produce new polymeric and composite materials with a desired set of properties in a targeted fashion. Owing to the broad range of advantages and unique features of the interaction of ionizing radiation with matter, EBM is an unsurpassed tool for nanochemistry and nanotechnology, which provides the formation of a variety of polymeric and hybrid nanomaterials with unique optical, electrical, magnetic, catalytic, biocidal, and mechanical properties. Therefore, electron-beam methods are increasingly being used throughout the world; they form the basis for advanced new-generation technologies for the production of polymer composite materials with improved and/or unique properties of the surface and surface layers of a given depth.

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