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Worldwide developments in the field of radiation processing of materials in the down of 2lst century

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Abstract Developments regarding the radiation processing of materials are discussed in the paper. Radiation sources are briefly listed, showing recent achievements in the field. The main group of materials modified by radiation are synthetic polymers and rubber. Other applications are irradiation of semiconductors and gemstone colorization. New, growing fields of application are processing of natural polymers and nanomaterials.

Key words ionizing radiation • polymers • nanomaterials

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Introduction

Radiation processing was used early for polymer modification [3]. Regarding synthetic polymers and rubber, the well established industrial technologies exist. In recent years, natural polymers are being looked at again with a renewed interest because of their unique characteristics like inherent biocompatibility, biodegradability and easy availability [17]. A further progress in natural polymer processing is foreseen.

Nanotechnology is one of the fastest growing new areas in science and engineering [18]. Radiation is early applied tool in this area; arrangement of atoms and ions has been performed using ion or electron beams for many years. Radiation chemists in material processing followed in the past a similar approach as did chemists in general, namely, treatment in bulk. However, new trends of more precise treatment technology were followed as well; surface curing, ion track membranes and controlled release drug-delivery systems are good examples of such developments. The ability to fabricate structures with nanometric precision is of fundamental importance to any exploitation of nanotechnology.

Finally, radiation processing concerns gem stones colorization, development of high temperature resistant fibers (SiC) and semiconductor modification.

Radiation sources

The number of irradiators, working on the service basis or installed on-line is growing.

Gamma irradiators

The number of industrial irradiation units is approximately 160 [26], the world directory covering information on the 121 industrial and semi-industrial gamma irradiators prepared by Mehta [14] reports 17 new units commissioned in the years 2000–2002. The other directory which has been prepared by Nordion is listing 64 plants [15, 29]. Big irradiators with an activity over 3.7×10^{16} Bq comprise over 20% of the total number. New developments concern construction of the compact irradiators like that presented in Fig. 1.

The solution presented in Fig. 1 is based on the design of a continuous, product-overlap source type for handling system of products. The sources can be positioned in two independent racks allowing different dose rate delivery according to the products to be processed. The originality of the design is based on the rotating concrete door, that integrates the shielding system with the product handling system, permitting the input and output of the products in a continuous way, without the necessity to lower the sources and open the irradiator chamber to change the batch [2].

Electron accelerators

The total number of accelerators installed all over the world applied for radiation processing is close to 1200. Direct, transformer accelerators, single resonant cavity accelerators and microwave source powered linear accelerators have been found to be the most suitable for radiation processing [33]. The industrial development of accelerators is still in progress, not only due to new areas of application, but also because of demands of lower cost and more compact size machines [7, 8, 32, 33]. The low energy accelerator capability has not been explored fully up to now [1].

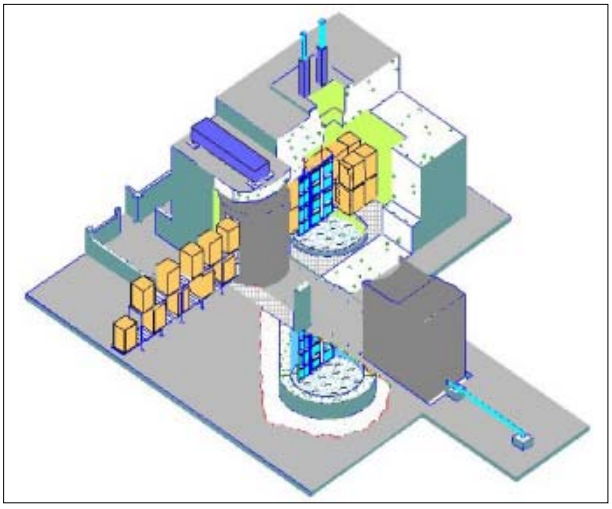

Fig. 1. Scheme of rotating door irradiator [19].

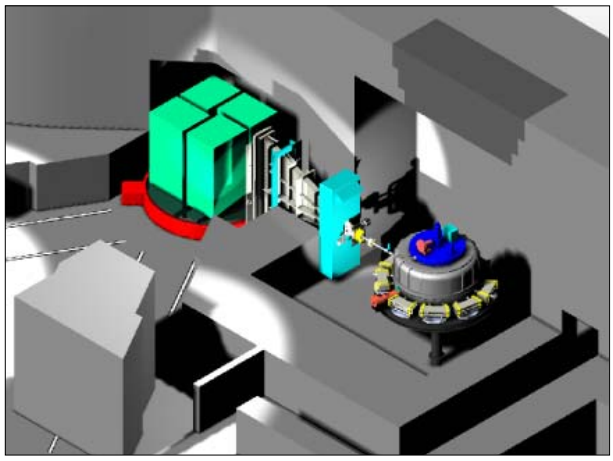

Fig. 2. Concept of high power e^-/X processing unit [16].

Electron beam units equipped with e^-/X converters

The concept of e^-/X conversion is known for years, a lot of R&D was performed in the field and some units were installed [27].

However, a breakthrough in technology is expected after implementation of the high power units which are already being tested (Jongen [16]). Commercial irradiators are being offered on the market (Cleland [15]). The concept of such irradiator based on Rodothron machine is presented in Fig. 2. The high power Rodothron accelerator (700 kW, 10 MeV) is used as electron beam generator. In the front of scanner, a water cooled target is installed. Conversion e^-/X takes place with a low efficiency equal to a few percent of the primary electron beam power, however, due to the good penetration of X-rays, the whole EU pallets can be irradiated. To achieve uniform dose distribution pallets are placed on the rotating table.

Radiation modification of materials

Chemical or material engineering mostly apply high temperature and/or high pressure processes for material synthesis/modification and quite often a catalyst is required to speed up the reaction. Radiation is the unique source of energy which can initiate chemical reactions at any temperature, including ambient, under any pressure, in any phase (gas, liquid or solid), without the use of catalysts [4]. However, the temperature rise factor should be considered when material is processed with high doses [8].

Synthetic polymers

Among irradiated materials, polymers are the most prominent ones. Therefore, changes in their structure may either be beneficial or undesirable. These facts are the reason why R&D concerning these materials is broad and most developments are foreseen in this area [24]. The application of radiation for modification of synthetic materials, mostly curing and crosslinking is a well-established technology [9].

Radiation crosslinking of wires and cables is the most active and largest area of radiation processing now. The radiation crosslinked wires and cables show excellent heat resistance (long-term thermal stability and short-term thermal stability) as well as abrasion resistance. The main markets for radiation crosslinking of wires and cables are actually those requiring performances of wires at elevated temperatures. Thus, a very well established market is the production of wire harnesses (assemblies of wires) for electronic instruments such as computers and audio-video instruments. Harnesses for automobiles is also a big market for radiation crosslinking. Radiation crosslinked heat resistant wires and cables are an essential component in the automobile engine room. Polyurethane covering the outside jacket of sensor cable for anti-lock brake system is also radiation crosslinked to improve the resistance against hot water. Insulating materials used in wires and cables crosslinked by radiation include PE, PVC, fluoropolymers and polyurethane. PVC consumption tends to decrease as compared to polyolefin due to the recent concerns relating to the carcinogenic nature of some plasticizers and the toxic halogen fumes generated on incineration. Polybutelene terephthalate (PBT), which is a plastic for electronic industry, can be crosslinked by radiation and lead free soldering materials can be applied in such a case. The temperature resistivity of such material is presented in Fig. 3 (Zyball [16]).

The polyethylene foam is used in a wide range of fields, such as automotive, buoyancy, flotation, insulation and packaging because it is easy to form and has superior heat insulation, flexibility and cushioning properties. In the foaming process, the melt viscosity suddenly decreases when it is heated above its melting point, in which case the gas generated from the foaming agent cannot be retained inside the resin. This makes it difficult to obtain foam with good expansion ratio, making it impossible to control the size and the number of cells. If crosslinking is used, more control can be exercised over the formation of cells with good control of nucleation and ultimate cell size. The manufacturing methods of crosslinking polyethylene foams are classified into two categories based on a type of crosslinking. One is chemical crosslinking by using peroxides as a crosslinking agent, and the other method is crosslinking by irradiation [5].

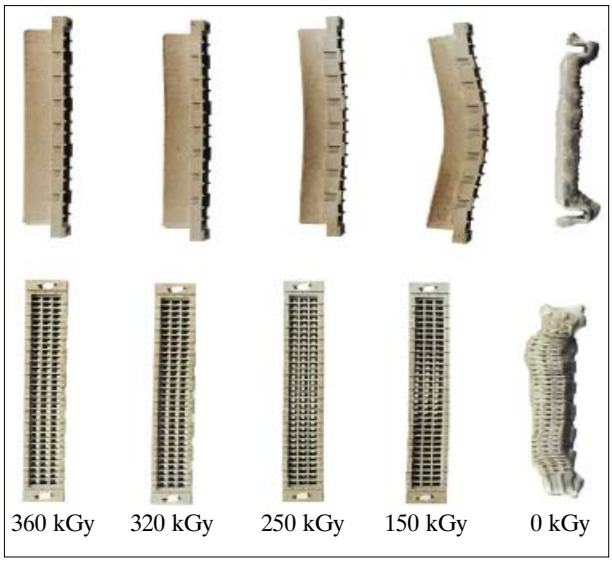

Fig. 3. Crosslinked PBT can be applied for electronic elements resistant to the higher temperature of soldering (300°C, 12 min) [16].

Rubber and natural latex

Various components of a tire include body ply, inner liner, tread, side wall and bead. These lead to the construction of green tires (raw tire), which are then being expanded into mould by inflation and vulcanized at high temperature and pressure. The displacement of cord fabric in body ply will give a fatal defect to the final products. This requirement prenecessitates the use of thicker plies in order to assure the adequate thickness of the final product. However, precise control of thickness is needed in the production of radial tires to reduce the weight of final tire. Thus, the radiation prevulcanized body ply will not decrease in thickness or be displaced during subsequent construction and vulcanization of the tire.

Typical electron accelerator used in the tire industry is low energy one like 500 keV, current 75 mA to 150 mA. Irradiation doses are 15–50 kGy. One accelerator can treat 30,000–50,000 plies/day [5].

In a conventional process, crosslinking or vulcanization is carried out by sulphur and heating. A small amount of the toxic substance nitrosamine, formed during vulcanization, remains in the product. Radiation vulcanization leads to products with improved mechanical properties as compared to sulphur or peroxide crosslinking. Technology of radiation vulcanization of natural rubber (NR) latex (RVNRL) was developed by Makuchi *et al*. [25]. The necessary dose for vulcanization is 15 kGy. The crosslinking sensitizer is *n*-butyl acrylate. The products are extremely safe due to the absence of *N*-nitrosamines. A low toxicity and a smaller amount of extractable proteins are the merits of the technology.

Natural polymers

The success of radiation technology for the processing of synthetic polymers can be attributed to two reasons, namely, the ease of processability in various shapes and sizes and secondly, most of these polymers undergo crosslinking reaction upon exposure to radiation. On the other hand, naturally occurring polymers were difficult to process and degraded when exposed to high energy radiation. Thus, the area of radiation processing of natural polymers largely remained unexplored and industrial applications have been difficult to achieve. In recent years, natural polymers are being looked at again with a renewed interest because of their unique characteristics like inherent biocompatibility, biodegradability and easy availability. Traditionally, the commercial exploitation of natural polymers like carrageenins, alginates, starch, etc. has been based, to a large extent, on empirical knowledge.

Formation of crosslinked polymer hydrogels from natural polymers and their derivatives offers new avenues for applications of such materials in many areas. The healing of wounds, specially burn wounds has been a challenging medical problem as such wounds take a long time to heal and need to be protected to prevent infection. A radiation processed wound dressing based on PVP, agar and polyethylene glycol is well established on the market. Naturally occurring polymers like alginates and carrageenins are known to possess excellent wound healing characteristics. In order to utilize the functional properties of these polymers for wound healing, a PVA based hydrogel containing naturally occurring polymers like agar and carrageenan has been developed and commercialized. An additional feature of these hydrogels is their usefulness in curing wounds of patients with diabetic ulcers which are otherwise difficult to treat. The PVP-carrageenin gel has an additional advantage of being a haemostatic agent which can be extremely helpful in many medical emergencies [17].

Cellulose

A lot of research work especially related to the use of radiation technology for minimizing the environmental pollution associated with the processing of natural polymers such as dissolution of cellulose in the viscose-rayon process was carried out [21].

As mentioned earlier, naturally occurring polymers or their derivatives undergo, under normal conditions of irradiation, a chain scission reaction.However, under suitable conditions, polymers such as carboxymethyl cellulose (CM-cellulose) or carboxymethyl starch can be crosslinked to form a hydrogel material [10]. This offers an opportunity to obtain non-toxic, additive free, totally biodegradable and biocompatible crosslinked hydrogels for many applications. This work has resulted in the development of a non-bedsore forming hydrogel mat based on radiation crosslinked CM-cellulose hydrogel. Carboxymethylcellulose (CMC) gave highly viscous solution when it was dissolved at a few percentages. Then the solution became a paste-like condition when it was homogeneously kneaded with water up to high concentration more than 10% as shown in Fig. 4. In the case of radiation processing in the past-like state, the crosslinking among CMC molecules takes precedence over the degradation. As a result, the biodegradable hydrogel could be obtained from polysaccharide derivatives.

This result implies that 20–30% solutions are effective to obtain CMC hydrogels by radiation processing. CMC hydrogels prepared by radiation-induced crosslinking of 10% CMC in water were practically applied to a bedsore prevention mat. Clinical studies revealed that no bedsore was observed in 178 subjects after their surgical operations by using CMC hydrogel mats. This result implies that the CMC hydrogel mats disperse the body pressure and the circulation of blood during the surgical operation is kept in the best condition. Hence, the CMC hydrogel mats were commercialized in Japan as “non-bedsore”. The waste of CMC gels can be converted into a fertilizer by degradation of bacteria in soil. The biodegradability is a big advantage of these crosslinked hydrogels.

Poly-lactic acid

Other interesting application is radiation crosslinking of poly-lactic acid (PLA). PLA is produced by the condensation polymerization of lactic acid obtained from fermentation of starch in polysaccharide group. The PLA is biodegradable, hard, and transparent polymer. However, PLA deforms its shape at the temperature above 60°C (the glass transition temperature of PLA is 60°C). Thus, crosslinking is considered effective to overcome this disadvantage for expanding the application of PLA. Generally, PLA predominantly undergoes the degradation under ionizing irradiation. It has been found that PLA was crosslinked in the presence of polyfunctional monomer, triallylisocyanurate (TAIC), as crosslinking agent (Fig. 5). The TAIC of 3 wt% in PLA is effective for the PLA crosslinking by irradiation.

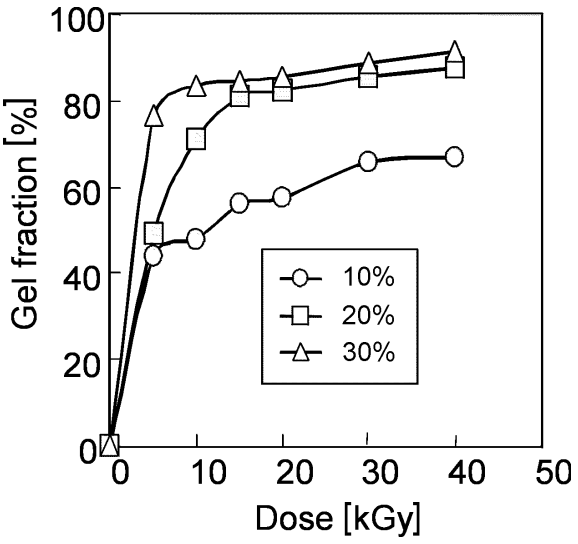

Fig. 4. Crosslinking of CMC at various concentrations [10].

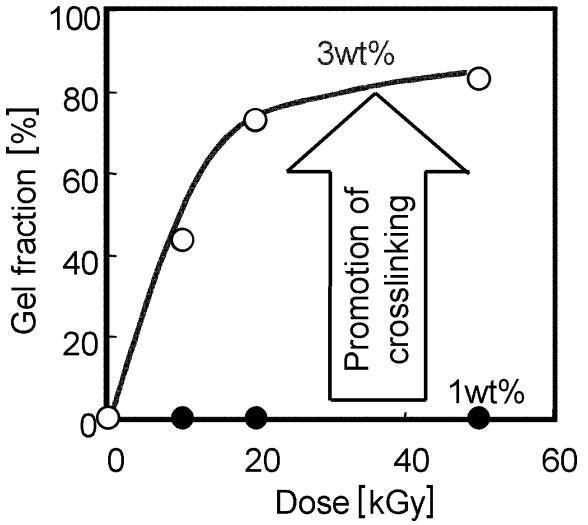

Fig. 5. Effect of TAIC concentration on crosslinking of PLA with irradiation [23].

The heat resistance of crosslinked polymer is dramatically improved and its deformation is not observed at temperatures higher than 200°C. The crosslinked PLA is applicable for manufacturing of biodegradable and transparent heat-shrinkable materials [23].

Chitosan

Chitin, poly[β-(1,4)-2-acetamid-2-deoxy-D-glucopiranose] is most abundant, next after cellulose, renewable natural polymer [27]. It occurs in the shells of marine crustfish, insects as well as some fungi wall cells. The chitosan, poly[β-(1,4)-2-amino-2-deoxy-D-glucopiranose] is a product of chitin deacetylation. Low solubility of chitin affects on its narrow range of practical application. Chitosan solubilized in the aqueous acid solutions, contrary to chitin, found several practical applications, especially in medicine, agriculture and wastewater pollution control. Chitosan is non-toxic (LD_{50} > 16 g per 1 kg of body weight), biodegradable polymer. The bioactivity is a specific property of this polymer. This phenomenon results from several processes such as biodegrability, membrane effect, polycationic character or stimulation of natural organism resistance.

Studies on the modification of molecular structure of chitosan forms by using different doses of γ-radiation (5–150 kGy) emitted from the ^{60}Co isotope were conducted. The results are presented in Fig. 6.

Chitosan is degraded by irradiation with radiation degradation yield of about 1.03 (scissions/100 eV) in solid state. Oligochitosan DP < 8 with 50% mass fraction can be obtained by irradiating a 10% (w/v) chitosan solution with gamma Co-60 radiation at a dose of 45 kGy for chitosan having initial M_v = 60.000. Irradiated chitosan exhibits a higher fungicidal effect than that of non-irradiated one. Furthermore, oligochitosan not only protects against diseases but also exhibits a growth-promotion effect for plants. Based on results obtained it can be considered that radiation technology is promising to produce oligosaccharides particularly oligochitosan used as biotic elicitor to enhance defense responses against diseases and as growth-promoter for plants. An example for products obtained by natural polymer radiation processing are sorbents utilized in wastewater treatment (Ciechańska [17]).

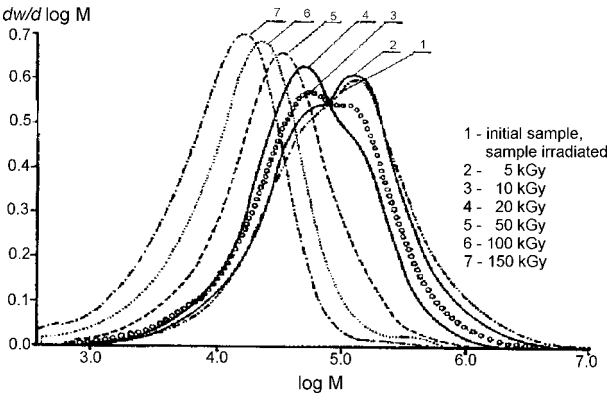

Fig. 6. Molecular weight distribution curves of chitosan degradated by ionizing radiation (Ciechańska [17]).

Much attention has been drawn to chitin and its deacetylated derivative – chitosan, due to its wide distribution in nature. Modification of carboxymethylchitin (CM-chitin) and carboxymethylchitosan (CM-chitosan) by gamma or EB irradiation results in obtaining hydrogels. The great concern in applications of those hydrogel in industry is recovery of metals from dilute solutions. Hydrogels of CM-chitin and CM-chitosan were obtained by EB irradiation of 40% CM-chitin and CM-chitosan pastes. The doses for CM-chitin and CM-chitosan were 75 and 100 kGy to obtain the hydrogels [31].

Depredated low MW chitosan is applied as a plant growth promoter [12].

Other applications

Semiconductors

Precise control over carrier lifetime is an essential factor in meeting the ever-increasing market expectations for power semiconductor device performance. Diodes and thyristors, in all power categories, which did not have the required switching and release times after diffusion, can be properly adjusted by irradiation, thus, saving them from rejection [11]. Proper adjustment of the switching time in the case of high-power bipolar semiconductor devices [28] gives remarkable electricity savings during operation of controlled devices, e.g. electrical engines. Sometimes both, electron and ion beam treatments, are being used in a combination to optimize switching characteristics. Electron treatment allows control over carrier lifetime throughout the device whereas the much more limited penetration of ions permits the carrier lifetime to be precisely changed in a specific region within the device. Electron doses range from 0.05 to 400 kGy and ion (e.g. proton and helium) doses from 1E9 to 1E13 ions/cm^2.

Gems

Of the various irradiation agents available, gamma rays are the preferred choice because they produce excellent uniformity of coloration, do not consume electrical power nor produce localized heating or induce radioactivity. With the exception of diamond and the possible exception of some blue turning topaz, the nature of the source is immaterial; the alteration produced is just the same as long as there is sufficient energy supplied by the irradiation. Typically, only one to 10 eV are needed. Though causes of color are diverse, in most cases the change involves a color centre.

All over the world, there are several irradiation contract facilities which convert colorless topaz into blue topaz using an EB processing system involving sometimes a combination of treatment in a reactor where some cooling period for radioactivity produced in gems is required. However, nature of all irradiations is proprietary. In semi-precious stones, transformations include conversion of beryls into yellow and green beryl, of quartz into yellow (citrine), dark brown (smoky),

purple (amethyst), topaz into imperial or blue topaz [30], spodumene into yellow or green, tourmaline (colorless) into pink red, zircon into brown to reddish and pearl into valuable brown, blue or black. It may be remarked that deep coloration of certain gems such as blue tourmaline and dark green emerald has been introduced with a judicious combination of heat and radiation.

Nanotechnology

Finally, nanotechnology is one of the fastest growing new areas in science and engineering. It is predicted to have a major impact on the manufacturing technology in 20 to 30 years from now. The subject arises from the convergence of electronics, physics, chemistry, biology and materials science to create new functional systems of nanoscale dimensions. Nanotechnology deals with science and technology associated with dimensions in the range of 0.1 to 100 nm. To achieve technological progress, firstly, the underpinning core science will need to be established. An interdisciplinary approach is required, bringing together key elements of biology, chemistry, engineering and physics. The development of appropriate interdisciplinary collaboration is expected to present challenges no less demanding than the science itself.

Therefore, such collaboration from the side of radiation chemists and physicists is needed as well. They are not newcomers in the field, arrangement of atoms and ions has been performed using ion or electron beams and radiation for many years. Talking about nanotechnology, we have in mind materials (including biological ones) and nanomachines. Molecular nanotechnology is perceived to be an inevitable development not to be achieved in the near future. In this context, self-assembly and self-organization are recognized as crucial methodologies. Radiation chemists in general, regarding materials processing, presented in the past a similar approach as did chemists, namely, treatment in bulk. However, new trends concerning a more precise treatment technology were observed as well: surface curing, ion track membranes and controlled release drug delivery systems are very good examples of such developments [6]. The last two products from this list may even fit into the definition of nanomachine: they control substance transport rate by their own structure properties. The fabrication of nanostructures yields materials with new and improved properties; both approaches, "top-down" and "bottom-up" can be studied. The ability to fabricate structures with nanometric precision is of fundamental importance to any exploitation of nanotechnology. Nanofabrication involves various lithographies to write extremely small structures. Radiation-based technology using X-rays, e-beams and ion beams is the key to a variety of different approaches to micropattering, synchrotron radiation is one of the tools [13].

Radiation effect on resists occurs through bond breaking (positive resist) or crosslinking between polymer chains (negative resist). Polymer is becoming better or less soluble in developer. This technique has already been commercialized. Due to the small wavelength of the 30–100 keV electrons, the resolution of electron beam nanolithography is much higher than that of optical lithography. To improve resolution, electron direct writing systems applying electrons with the energy as low as 2 keV are proposed to reduce electron scattering effects. Other studies concern formation and synthesis of nanoparticles and nanocomposites. Radiation synthesis of copper, silver and other metals' nanoparticles is studied [20, 22]. The solution of metal salts is exposed to gamma rays and formed reactive species reduce metal ion to zero valent state. Formation of aqueous bimetallic clusters by gamma and electron irradiation was studied as well. Metal and salt – polymer composites are synthesized by this method. Metal sulphide semiconductors of nanometric matrices are prepared using gamma irradiation of a suitable solution of monomer, sulphur and metal sources. These products find application in photoluminescent, photoelectric and non-linear optic materials. An interesting field of radiation nanotechnological application concerns the development of PC-controlled biochips for programmed release systems. Nano-ordered hydrogels based on natural polymers as polysaccharides (hyaluronic acid, agrose, starch, chitosan) and proteins (keratin, soybean) being pH and electric potential responsive materials for such biochips and sensors. To avoid regress in the further advance of radiation processing of natural polymers, the nanoapproach to these biological materials should be developed further. Their self-organization and functionalism depend on the basic fundamentals of the discussed science. The studies on natural rubber-clay composites and thermoplastic natural rubber-clay composites have given interesting results. Nanomaterials with high abrasion and high scratch resistance will find industrial application.

Conclusions

Radiation processing applying electron and ion accelerators, X-ray and gamma radiation is widely used in processing of materials and products. New fields of implementation are natural polymers and nanomaterials.

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