RADIATION PROCESSING OF COMPOSITES FOR ORTHOPAEDIC IMPLANTS

G. Popov, A.Avilov, V.Deruga, N.Popova, V.Rudychev,
Kharkov National University, P.O. Box 60, 61052 Kharkov, Ukraine

Abstract

Prime task for orthopedists and traumatologists is the development of new artificial materials for replacement of osseous tissue and cartilage defects, for functional rehabilitation of the injured locomotorium tissue after traumatic fractures and surgical interventions. Electron beam (EB) processing of polymer composites with bioactive ceramics was used for manufacture of new artificial materials for orthopedic implants. Experimental approaches and problems of EB processing for composites formation are discussed in the paper.

1 INTRODUCTION

The materials for reconstructive-restorative surgery of human locomotor ligaments must satisfy severe conditions about impermissibility of carcinogenic, blastomogenic, and allergenic effect on organism. They have not to be toxic or electrolytically active ones. Their mechanical properties must correspond to those for natural osseous tissue and cartilage. They have to stimulate the process of osteogenesis.

Now there is no artificial materials that completely satisfy all demands of medicine. The mechanical properties of human osseous tissue are very different from those of inert metal alloys currently used in artificial joints. This large mismatch in mechanical properties causes bone resorption or loss around the implant, as well as loosening of the artificial joint stem in the medullar cavity. Ultra high-molecular weight polyethylene (UHMWPE) used as a substitute for gristle is also rigid, it is not of sufficient wear-resistance, it has little adhesion to bone cement, that causes both increasing of volume of surgical operations and decreasing of a service life of the product.

All previously mentioned puts a task for searching of new materials for replacement of natural osseous and gristle tissues. Polymeric composites with bioactive ceramics are considered as the most appropriate candidates to this role. Our investigations deals with research and engineering studies of the use of EB processing of artificial materials for orthopedic implants. The investigations were performed in three main problem directions.

- Development of technological methods and processes of new composite materials formation for osseous tissue implants. The problem is the receiving of materials which have to possess mechanical and operating characteristics closed to those of natural osseous tissue and cartilage.
- Development of composite material (CM) for elastic elements of prosthesis that are simultaneously the elements of friction couple. The problems are the decreasing the friction coefficient in artificial joint and reducing the wearing rate of ultra high-molecular weight polyethylene (UHMWPE) construction element for endoprotheses.
- Radiation induced graft copolymerization of methylmethacrylate (MMA) monomer on surface of UHMWPE and composites based on it. The decided problem is the increasing adhesion of UHMWPE to bone cement.

2 EB PROCESSING OF COMPOSITES

The candidate CMs for implants were designed on a basis of reinforced polymers by various fibers and bioactive ceramics, which were treated by EB. The radiation-induced polymerization was fulfilled in compounds reinforced with various fibers such as carbonic, glassy, nylon, metallic ones, or their mixtures. As binding agents, vinyl monomers and oligomers, polyester and thermosetting resins were used. The following monomers and oligomers as well as their mixtures constitute the base of polymer matrices: MMA, ethyl methacrylate, butyl methacrylate, polyacril acid, oligomers on the base of unsaturated polyesters kind of TGM-3, PN-609-21M, Palatal A430, as well as the UHMWPE powder.

The EB irradiation of compounds in all processes was carried out by pulsed electron accelerator with energy range from 4 to 7 MeV, beam power up to 5 kW and absorbed dose in the range from 1 to 200 kGy [1, 2]. The spatial profile of electron beam intensity on the target surface was measured by an one-dimensional wire acoustic dosimeter. The absorbed dose distribution of electron beam into compound was measured by one dosimetric film inserted in parallel with EB between two contacted compounds. An equalization of electron depth dose distribution into one- and double sided irradiated compounds was conducted with help of simulation tools ModeRTL [3]. To provide the dose distribution with enhanced uniformity ~ 5 to10% special semitransparent filters for beam electrons were designed [4]. These filters partly overlapped the electron beam directed on irradiated samples, which mixed up transversally to electron beam direction. Radiation treatments and subsequent postradiation thermal treatment of composite materials were carried out in vacuum or in argon atmosphere. The postradiation treatment of polymer composites comprises artificial aging in thermostat at temperatures of 60 to 160 ^{0}C.

Detailed research of the radiation-induced polymerizing kinetics of monomer/oligomer systems in compounds was performed by measuring the following parameters: the coefficient of conversion K of monomer–oligomer system in compound, the temperature increase ΔT_P due to radiation induced heating, and the temperature increase ΔT_{PX} due to heat liberation in the course of exothermic radiation–induced by reaction of polymerization. The investigations of characteristics K, ΔT_P, ΔT_{PX} were performed depending on electron dose rate, absorbed dose of EB in compounds, type and concentration of reinforcing elements of compound, and external conditions of irradiation (temperature, pressure, irradiation environment –vacuum, air, inert gas).

It was experimentally shown:

- In the presence of reinforcing elements, the reaction of radiation-stimulated polymerization of monomer–oligomeric systems in compounds flows with increased rate as compared with block polymerization of pure monomers/oligomers.
- Molecular mass of polymer matrix in compound is in 1.5 to 2 times higher as compared with the case of block polymerization.
- Integral dose to be necessary for full completion of compound polymerization is in 1.5 to 4 times less as compared with the case of block polymerization.
- Process of radiation-induced polymerization is easy controlled and regulated by selection of mode of irradiation.

The technological modes of polymer composite materials formation were experimentally elaborated. By varying either the composition of the reinforcement and matrix polymer and EB processing regimes, we managed to obtain materials with modules of elasticity ranging from 10 to 40 GPa, bending strength 200 MPa and more, compressive strength 150 MPa and more, which satisfy the strength criteria of supporting elements of joints. These materials were experimentally tested as intraosseouse fixative devices.

3 EB PROCESSING OF UHMWPE

At present, the most of endoprotheses are using UHMWPE and metal alloys as materials for friction couple. Disadvantages of these materials are more high friction coefficient of hinged couple as compared with natural joint and a high value of wearing rate of elements made of UHMWPE. The wearing debris initiated an osteolysis which leads to implant loosening.

The production technique of material for elastic elements of prostheses to be simultaneously the elements of friction couples was elaborated. Cylinder and plate samples were made by hot molding or by shaping under pressure of UHMWPE powder (Tomsk, Russia) with molecular weight distribution 2.5-4.7 million grams/mole. The samples were made of pure UHMWPE and of UHMWPE reinforced by carbon, glass fiber, cord, and textile.

The radiation-induced crosslinking creates a 3-D network (gel phase) in the structure of UHMWPE as well as it is accompanied by occurrence of long term free radicals in bulk of PE. Free radicals can lead to destruction of UHMWPE due to oxidation processes which reduce the molecular weight of PE.

To reduce free radicals, EB processing of compound was carried out by two methods. In the first method, the radiation crosslinking of end samples of pure UHMWPE and of UHMWPE - based composite was conducted by pulsed EB, followed by the thermal annealing and slow cooling. In the second one, the hot samples in the temperature range 100-160 ^{0}C were treated by EB. The radiation treatment of compounds was conducted by EB with energy 6 MeV and absorbed dose in the range from 1 to 300 kGy. EB processing of UHMWPE was performed in vacuum, in medium of the air or an inert gas.

Crosslink density was determined by placing irradiated samples in hot xylene and measuring of gel and sole phases as well as by the use of Fourier Transform Infrared Spectroscopy (FTIR) technique [5]. In accordance with FTIR technique crosslink density was measured by a spectrophotometer as the ratio of trans-vinylene peak area at 965 cm^{-1} to the irradiation stable peak area at 2022 cm^{-1}. Presence of free radicals was determined by measuring of oxidation index as the ratio of carbonyl peak area at 1717 cm^{-1} to the stable peak area at 1370 cm^{-1}.

Wear rate was investigated on a stand for long-term examination which imitates work of hip joint. A friction couple consisting of a spherical insert of radiation-modified composite and a highly polished ball of stainless steel with diameter 32 mm was immersed in physiological solution or bovine serum and worked under cyclic loading up to 100 kg. The inserts were examined on wear in cyclic loading in the range of $5 \cdot 10^5$– $3 \cdot 10^6$ cycles by gravimetric method.

The investigations of variation of structural characteristics, friction coefficient, wear rate of polymer composite materials based on radiation crosslinking UHMWPE were carried out depending on the dose rate and an absorbed dose. As a result of investigations it was shown, that the minimum of oxidation index into irradiated samples is observed at a maximal dose rate and respectively at minimal irradiation time. The minimum gravimetric wear rate about 2 mg/(million cycles) and absence of free radicals had the pure crosslinked UHMWPE, which was irradiated by electron dose of 90 to 120 kGy at sample temperature of 120 to 150 ^{0}C in vacuum or in noble gas with subsequent thermal annealing. This value of wear rate is more than 20 time less in comparison with unirradiated samples.

4 GRAFTING OF MMA ON UHMWPE

In restorative surgery of joints many artificial implants are fixed to osseous tissue by bone cement. The basis of composition of bone cement is polymethylmethacrylate (PMMA) or other acrylic polymers. Implants from UHMWPE to be also used in restorative surgery have weak adhesion to bone cement. For increasing adhesion of UHMWPE to bone cement, the investigation and elaboration of operating regimes of radiation grafting of MMA monomer on surface of UHMWPE samples were performed.

The radiation induced graft copolymerization of MMA was carried out on the surface of UHMWPE plates to be preliminarily irradiated by 6 MeV EB in the air with subsequent heating in contact with solution of MMA monomer in methanol. This is so-called the graft copolymerization on the base of the post-effect. In this case, the copolymerization in a boundary layer on UHMWPE surface occurs at heating due to radicals. These ones are generated in the course of decomposition of peroxides and hydroperoxides appearing at irradiation. To prevent homopolymerization of MMA monomer, saline $Fe_2SO_4 \cdot 7\,H_2O$ was added in MMA solution.

The values of degree of the radiation grafting $\eta(mg/cm^2)=(P_{gr}-P_0)/S_{sample}$ were obtained experimentally in the range from 1 to 50 mg/cm^2. Where P_{gr} is the weight of the sample with grafted MMA after irradiation, P_0 is the weight of the initial sample of UHMWPE, S_{sample} is the full area of UHMWPE plate. Free radicals were extracted from UHMWPE plates after radiation grafting by artificial aging of heated samples.

The adhesion properties of UHMWPE samples with radiation induced graft copolymerization of MMA were tested by measurement of tensile bonding strength between UHMWPE and PMMA samples, which were connected together by bone cement "PALACOS R", GmbH Germany. The bone cement "PALACOS R" on 90% consists of PMMA. The tensile bonding strength between bone cement and UHMWPE samples with radiation-induced grafted MMA increased up to 80 time in comparison with samples without radiation grafting.

One of the features of new composites is the inclusion in their structure of biologically active ceramics in the form of powder or granules. The bioactive ceramics is introduced into a composite as the constituent on all volume or by in form of coatings. Calcium phosphate compounds - hydroxyapatite (HA) and tricalcium phosphate (TCP) were used as bioactive ceramics. HA and TCP are the basic inorganic components of the hard tissues of an organism. HA and TCP show excellent biocompatibility and are well integrated with bone tissues due to interactions at the interface and growing of new tissues into its pore structure. The inclusion of biologically active ceramics in structure of composites leads to effective osteointegration of composite material with living tissue and creation of firm biomechanical interface.

All new composite materials were *in vitro* and *in vivo* examined on biocompatibility, cytotoxicity and carcinogenicity. For these purposes, an express method of cultivation of cellular culture was used. The osteointegration of composite materials with living tissue, the process of bone tissue formation on the surface and into composite materials were investigated on small animals - rats and rabbits.

5 CONCLUSION

EB processing was used for radiation modification and manufacture of new CMs for orthopedic implants. CMs were made on a basis of reinforced polymers by various fibers and bioactive ceramics. CMs with modules of elasticity ranging from 10 to 40 GPa, bending strength 200 MPa and more, compressive strength 150 MPa and more which satisfy the strength criteria of supporting elements of joints were designed. The wear rate of crosslinked UHMWPE is more than 20 time less in comparison with unirradiated samples. EB-induced graft copolymerization of MMA on the surface of UHMWPE samples significantly increase its adhesion to bone cement.

6 ACKNOWLEDGMENTS

The work was supported by the STCU, Kyiv, project #957. The authors wishes to express gratitude to Prof. N.Dedukh, Dr. S.Malushkina, and Prof. V.Radchenko, SJPI, for conducting of *in vitro* and *in vivo* testing of new composite materials on biocompatibility.

REFERENCES

[1] G. Popov, A. Avilov, V.Deryuga, V.Rudychev, and I.Zalyubovsky. Proceedings of the 18th Particle Accelerator Conference., New York, USA, 2000, Vol. 4, p. 2549-2551.

[2] A.Avilov, V. Deryuga, S.Korenev, and G. Popov. Sixth International Conference on Electron Beam Technologies, EBT 2000, Varna, Bulgaria, p. 86-87.

[3] V.T.Lazurik, V.M. Lazurik, G. Popov , Yu. Rogov. Abstract book of the ICAP-2002 Conference, p.49, East Lansing, MI, USA. (Paper in a press).

[4] A.Lisitsky, S. Pismenesky, G.Popov and V.Rudychev. Radiation Physics and Chemistry Vol. 63, 2002, p. 591-594.

[5] W. Johnson, B.Lyons, Radiation Physics and Chemistry Vol. 46, 1995, p. 829-832.