COMPOSITE MATERIALS FORMATION FOR ORTHOPAEDIC IMPLANTS

A.M. Avilov, V.A. Deryuga, G.F. Popov, N.G. Popova, V.G. Rudychev, A.L. Shkilev
Kharkov National University, P.O. Box 60, 61052, Kharkov, Ukraine;
E-mail: popov@univer.kharkov.ua

One of most up-to-date problems of orthopaedy is the development of new materials for replacement of osseous tissue and cartilage defects. Electron beam (EB) processing of polymer composites with bioactive ceramics has been used for manufacture of artificial materials for orthopaedic implants. Experimental approaches and problems of EB processing of composites based on ultra-high-molecular weight polyethylene (UHMWPE) are discussed.

PACS*:* 29.17.+w

1. INTRODUCTION

Now there are 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 decreasing of a service life of the product and increasing of number of surgical operations.

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 based on UHMWPE for construction elements of orthopedic implants.

There are several competitive radiation-chemical processes, which realize simultaneously in the polymer composite under electron irradiation. Such processes are the crosslinking of macromolecules and creation of spatial structure in polymeric matrix of composite, the radiation grafting of macromolecules to material of filler, the destruction of macromolecules, the appearance of long-lived free radicals, etc. Every of these processes modifies selectively the different physical, mechanical, and operation characteristics of irradiated composites. The formation of conditions for preferential realization of specific radiation-chemical processes permits purposefully regulating the composite characteristics.

This work presents investigation results of influence of EB regimes irradiation, surrounding environment, post-radiation treatments of UHMWPE on variation of physical, mechanical, and operation characteristics of the finished product of UHMW-PE.

2. EB PROCESSING OF UHMWPE

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 conventional UHMWPE and of UHMWPE reinforced by carbon, glass fiber, cord, and textile.

The EB irradiation of UHMWPE samples was carried out by pulsed electron accelerator with energy range from 4 to 7 MeV, beam power up to 5 kW, in the absorbed dose rate from 100 to 1200 Gy/s, and absorbed dose within the range from 1 to 300 kGy [1]. EB processing of UHMWPE was performed in vacuum, in medium of the air or an inert gas. The absorbed dose distribution of electron beam into irradiated samples was measured by dosimetric film. An equalization of electron depth dose distribution into one - and double-sided irradiated compounds was conducted with help of simulation tools ModeRTL [2]. To provide the dose distribution with enhanced uniformity ~ 5 to 10% special semitransparent filters for beam electrons were designed and made [3].

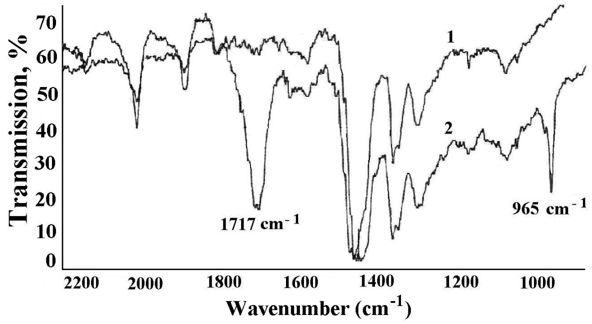
Under electron beam irradiation of UHMWPE basically two competitive radiation-chemical processes influence on properties of the finished product of UHMWPE: crosslinking and generation of long-term free radicals in bulk of UHMWPE. The radiation-induced crosslinking creates a 3-D network (gel phase) in the structure of UHMWPE that lead to significant changing its properties.

The free radicals interact with oxygen, which diffuses into the composite volume from the surrounding air. This process causes the scission of macromolecules of UHMWPE and the decrease its molecular weight. As a result, the wear of composite is increased. The wear products cause the inflammatory reactions and lysis of osseous tissue in the bone-joint boundary.

To minimize free radicals, we have investigated the process of artificial ageing of UHMWPE-based composites treated by pulsed electron beams. As result, an EB treatment of hot samples in the temperature range 100…160 ^{0}C with subsequent annealing leads to minimum value free radicals at end product.

Crosslink density was determined by placing irradiated samples in hot xylene and measuring of gel phase as well as by the use of Fourier Transform Infrared Spectroscopy (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 2020 cm^{-1}. The control of concentration of free radicals in the irradiated samples in the course of artificial aging was performed by the value of the oxidation index (OI). OI was determined as the ratio of carbonyl peak area at 1717 cm^{-1} to the radiation stable peak area at 1370 cm^{-1}.

Typical infrared absorption spectrums for UHMW-PE specimen with thickness of 200 μm which was EB-irradiated in an air (Curve 2) (absorbed dose 100 kGy) and for unirradiated specimen (Curve1) are



shown in Fig.1.

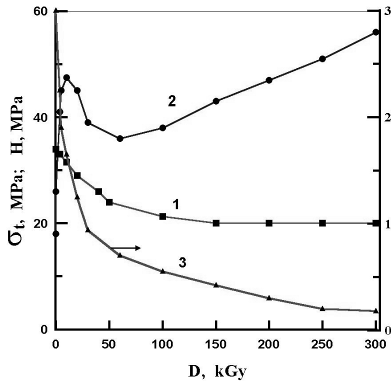
Fig.1. Infrared absorption spectrum for UHMWPE irradiated by EB in an air (2) and unirradiated (1)

The following physical, mechanical and operation characteristics for conventional and crosslinked UHMWPE were tested versus absorbed EB dose and dose rate: elastic modulus, ultimate tensile strength (σ), elongation at break (**ε**), micro-hardness (H), and wear rate. Elastic modulus, ultimate tensile strength and elongation at rupture were measured on tensile-testing machines and by acoustic methods.

Two different type of hip joint simulators were used for *in vitro* investigation of the wear rate for the crosslinked UHMWPE specimens. The first one a pin-on-disk hip simulator was used as the test device for the accelerated wear rate examining. The dependence of the wear rate of the composite on the sliding distance was investigated. The investigations were carried out as for dry friction, as in the presence of a lubricant i.e., distilled water, physiological solution or bovine serum. The measurements of wear of the composite were performed by gravimetric method after every 1000 m of the sliding distance.

The second one a friction couple type of hip simulator was used for long-term examination of the wear rate for UHMWPE specimens. A friction couple consisting of a spherical insert of UHMWPE based composite with counterface of a highly polished sphere of stainless steel with diameter 32 mm was immersed in physiological solution or bovine serum as lubricants. Insert imitates acetabulum, and a polished sphere of stainless steel imitates the head and the neck of the hip joint. Wear rate of the inserts was examined at their cyclic loading up to 100 kg in the range of $5 \cdot 10^5 \ldots 3 \cdot 10^6$ cycles by gravimetric technique.

The influence of absorbed dose on variation of physical, mechanical and operation characteristics of UHMWPE irradiated by pulsed EB with electron energy 6 MeV are shown in Fig.2 and 3. Heated to temperature 120 ^{0}C the UHMWPE specimens were irradiated in argon environment. After irradiation the specimens were annealed at temperature 140 ^{0}C under vacuum for 4 hours. Characteristics testing of radiation-modified



UHMWPE specimens was performed at temperature 25 ^{0}C.

Fig.2. Effect of an absorbed dose on the ultimate tensile strength (1), micro-hardness (2), and elongation (3) of UHMWPE

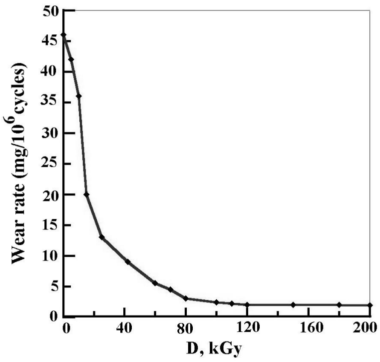


Fig.3. Effect of an absorbed dose on the gravimetric wear rate of UHMWPE

As a result of investigations it was shown, that the minimum of oxidation index into irradiated UHMWPE specimens is observed at a maximal dose rate and respectively at minimal irradiation time. For example, irradiation of UHMWPE wit EB in air results in increasing of the dose rate from 100 Gy/s to 1.2 kGy/s leading to decreasing of the oxidation index and, respectively, of the number of free radicals in 6 times. The minimum gravimetric wear rate of about 2 mg/(million cycles) and minimum of free radicals was observed in the crosslinked UHMWPE, which was irradiated by the electron dose higher than 90 kGy at specimen temperature of 120 to 150^{0}C in vacuum or in inert gas with subsequent thermal annealing.

3. GRAFTING OF MMA ON UHMWPE

In restorative surgery of joints many artificial implants are fixed to living bone by bone cement. The basis of composition of bone cement is polymethylmethacrylate (PMMA) or other acrylic polymers. Implants from UHMWPE have weak adhesion to bone cement. For increasing adhesion of UHMWPE to bone cement, the investigation of radiation grafting of MMA monomer on surface of UHMWPE 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 under heating due to free radicals. These ones are generated in the course of decomposition of peroxides and hydroperoxides appearing under irradiation. To prevent homopolymerization of MMA monomer, saline $Fe_2SO_4 \cdot 7\ H_2O$ was added in the MMA solution.

The values of degree of the MMA radiation grafting at a surface of UHMWPE samples were obtained experimentally in the range from 1 to 50 mg/cm^2. EB treatment of UHMWPE samples was conducted within the range of absorbed dose from 1 to 40 kGy. Free radicals were extracted from UHMWPE plates after radiation grafting by artificial aging of heated samples in oxygenous environment.

UHMWPE and PMMA samples were connected together by bone cement "PALACOS R", GmbH Germany containing 90% of PMMA. The tensile bonding strength between bone cement and UHMWPE samples with radiation-induced grafted MMA increased up to 80 times in comparison with the samples without radiation grafting.

Realizations of the principal possibility of a crosslinking of a thin UHMWPE layer and a graft copolymerization of MMA on the bearing surface of UHMWPE specimens by an irradiation of the thin surface layer with a thickness ~15…40 μm by low energy electrons were shown experimentally. Electrons with the energy in the range 150-200 keV were generated by the X-ray pulsed apparatus MIRA-2D with the electron tube IMAE-150E. Electron beam current parameters were the following: pulse duration of 15 ns, pulse repetition rate of 10 Hz, number of electrons per pulse of about 5.10^{12}. Such an irradiation mode avoids modification of physical and mechanical properties of the bulk material and essentially reduces a time of post-irradiation treatment of UHMWPE specimens.

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 bioceramics is introduced into a composite as the constituent over all volume or in the form of coatings. Calcium phosphate compounds - hydroxyapatite (HA) and tricalcium phosphate (TCP) were used as bioceramics. 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 bioceramics into the structure of composites leads to effective osteointegration of composite material with living bone and creation of firm biomechanical interface.

All new composite materials were 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 at the surface and into composite materials were investigated on rats and rabbits.

4. CONCLUSION

EB processing was used for radiation modification and manufacture of artificial materials based on UHMWPE for construction elements of orthopaedic implants. It was shown that a formation of conditions for preferential realization of specific radiation-chemical processes under EB processing of UHMWPE based composites permits programmable to regulate their physical, mechanical, and operation characteristics. *In vitro* examination using the hip joint simulator of wear rate of UHMWPE was carried out. The minimum gravimetric wear rate about 2 mg/(million cycles) and minimum of free radicals was observed in the crosslinked UHMWPE, which was irradiated by the electron dose higher than 90 kGy. EB-induced grafting of MMA at the surface of UHMWPE samples significantly increase its adhesion to bone cement.

5. ACKNOWLEDGMENTS

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

REFERENCES

1. A. Avilov, V. Deryuga, S. Korenev, G. Popov: *Abstract book of EBT'00 Conf.*, Varna, Bulgaria, 2000, p. 86-87.
2. V.T. Lazurik, V.M. Lazurik, G. Popov, Yu. Rogov // *Proceed. of EBT'03 Conf.* Varna, Bulgaria, 2003, p.616-622.
3. A. Lisitsky, S. Pismenesky, G. Popov, V. Rudychev // *Radiation Physics and Chemistry*. 2002, Issue 3-6, v. 63, p. 591-594.

РАЗРАБОТКА КОМПОЗИЦИОННЫХ МАТЕРИАЛОВ ДЛЯ ОРТОПЕДИЧЕСКИХ ИМПЛАНТАТОВ

О.М. Авилов, В.О. Дерюга, Г.Ф. Попов, Н.Г. Попова, В.Г. Рудычев, А.Л. Шкилев

Одной из актуальных задач в ортопедии является поиск и разработка новых материалов для замены костной ткани и хряща. Обработка полимерных композиционных материалов с биоактивной керамикой электронными пучками использовалась для изготовления искусственных материалов для ортопедических имплантатов. Обсуждаются экспериментальные достижения и проблемы радиационной технологии обработки композитов на основе сверхвысокомолекулярного полиэтилена.

РОЗРОБКА КОМПОЗИЦІЙНИХ МАТЕРІАЛІВ ДЛЯ ОРТОПЕДИЧНИХ ІМПЛАНТАТІВ

О.М. Авілов, В.О. Дерюга, Г.Ф. Попов, Н.Г. Попова, В.Г. Рудичев, А.Л. Шкілев

Однією з актуальних задач в ортопедії є пошук і розробка нових штучних матеріалів для заміщення кісткової тканини і хряща. Обробка полімерних композиційних матеріалів з біоактивною керамікою електронними пучками використовувалась для виготовлення штучних матеріалів ортопедичного призначення. Приводяться експериментальні досягнення і проблеми радіаційної технології отримання композитів на основі надвисокомолекулярного поліетилену.