Biomaterials.
The Behavior of Stainless Steel as a Biomaterial

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ABSTRACT
The biomaterials belong to the broad range of biocompatible chemical substances (sometimes even an element), which can be used for a period of time to treat or replace a tissue, organ or function of the human body. These materials bring many advantages in the diagnosis, prevention and medical therapy, reducing downtime for patients, restoring their biological functions, improving hospital management. The market in Romania sells a wide range of biomaterials for dental, cardiovascular medicine, renal, etc. Scientific research contributes to the discovery of new biomaterials or testing known biomaterials, for finding new applications. The paper exemplifies this contribution by presenting the testing of passive stainless steel behaviour in albumin solution using technique of cyclic voltammetry. It was shown that passivation contribute to increased stability of stainless steel implants to corrosive body fluids.

KEYWORDS: *biological environment, biomaterials, corrosion, cyclic voltammetry, stainless steel*

JEL Classification: I12, L61, Q55

Introduction

A biomaterial can be "any substance or combination of substances having natural or synthetic origin, which can be used on a clearly defined period as a whole or a part of a system that treats, heals or replaces a tissue or organ function of living body", or materials designed "to work under biological compulsion" (Choubey, 2005).

Biomaterials have a broad spectrum of properties and can be transformed into medical devices that can correspond to functional parameters strictly imposed. The medical techniques involving the use of biomaterials compatible with the human body, as well as methods of intervention and clinical investigations, have become extremely sophisticated. Devices made of biomaterials are used not only to restore the natural biological state, but also for more rapid restoration of tissues or human functions, reducing the downtime for patients. It is estimated that approximately 10% of the medical activities require the use of biomaterials for diagnosis, prevention or therapy (Choubey, 2005; Popescu, 2007).

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Diverse applications of biomaterials include bioreabsorbed implants, articular prostheses, artificial organs, modeling of dialysis therapy, cardiovascular modeling, hospital management and monitoring to ensure the health of the population **(**Ratner, 2004).

The biomaterials engineering has developed rapidly and diversified its products under widely recognized quality standards. At the European level it has started in the research institute JRC-Ispra, Italy, a program funded by the European Commission for investigation the current test methods of biomaterials and to study alternative methods in order to develop a coherent and modern system of standards, imposed for both manufacturers and users.

1. Classes of Biomaterials

The current biomaterials, presenting a great variety, are classified according to several criteria. After their interaction with biological environment, they are classified into bioinert, bioabsorbent or bioactive materials. By their origin, biomaterials can be natural, synthetic or artificial. From composition point of view, the category of biomaterials includes polymers (in forms of massive blocks, fibers, films, gels), ceramic materials, composite materials and metallic materials (metals or alloys). In the followings, a brief overview of these classes will be presented according various criteria:

a) According to interaction with the biological environment

Bioinert materials, such as titanium, tantalum, alumina, polyethylene or other polymers, have a very low chemical interaction with adjacent tissues. The tissue can adhere to their surface either by growing itself into the irregularities of inert biomaterials (osteointegration, osteogenesis), or using a special adhesive (e.g. acrylate). Note that adhesive procedure is not the ideal way of fixing the orthopedic and dental implants during the long term treatment. Polymeric implants are considered to be safe and effective for a time period ranging from several months to several years. However, the biological response is still inevitable, but is offset by the design of implants.

Bioabsorbent materials such as tricalcium phosphate, polyglycolic-polylactic copolymeric acid, and even some porous metallic materials, are designed to be easily absorbed by the body and replaced the adjacent tissues (bone or skin). Such materials are used for the transport of drugs or for implantable biodegradable structures (surgical thread etc.).

Vitreous materials, ceramics, glass-ceramics combinations and hydroxyapatite are included in the category of bioactive materials; these materials contain silicon dioxide (SiO_2), sodium oxide (Na_2O), calcium oxide (CaO), phosphorus oxide (P_2O_5) etc., compounds that contribute to the formation in time of chemical bonds with the tissue. Basically, there is an ion exchange reaction between the bioactive material and human body fluids. The biomaterial particles may diffuse in the liquid and vice versa, resulting a biologically active layer of calcium phosphate, which is equivalent to chemical and crystallographic structure of bone. Bioactive materials are recommended to be used for joining bones in case of fractures; however, they are not used for articular implants, where is a high degree of friction between materials in contact.

b) Criterion on nature of biomaterial

Natural biomaterials are used in medicine long time ago. In the medicine today organs, or parts of organs, of animals (pig, especially) or even human bones are used for transplants in marrow, bones, skin, blood, etc.

It is put more emphasis on replacing natural materials used in human and veterinary medicine with synthetic of artificial biomaterials. The artificial biomaterials contain at least one natural component in order to enhance the biocompatibility of the material in question and to hasten the healing process. A natural component of artificial biomaterial may be a protein (collagen, fibronectin, elastin), a polysaccharide belonging to glycosaminoglycan class (chondroitin sulfate, heparin, heparan sulfate, hyaluronic acid) or a peptide sequence having the role in cell recognition or adhesion process. These components are mostly macromolecules of the extracellular matrix of tissues that are in contact with biomaterials involved in the healing process.

c) Criterion of composition

Metals are some of the biomaterials used for orthopedic implants due to their wear resistance, high hardness and ductility. The most metallic materials used to achieve implants are stainless steels, cobalt-chromium-molybdenum alloys, titanium and titanium alloys. Titanium based materials are mainly used to achieve orthopedic implants because of similar mechanical properties with bone tissue.

The main disadvantages of these materials are their high rigidity in comparison with host tissue as well as the tendency to modify their physico-mechanical properties in the case of the investigation with computer tomography and magnetic resonance (Tutunaru, 2007). Degradation of metals and alloys in the human body is a combination of effects due to corrosion and mechanical activities. The resulted metal ions may cause allergenic, carcinogenic and cytotoxic. The cytotoxic effect of metal components of alloys decreases in the series: Cr, Co,V, Fe, Mn, Cu, Ni, Mo (Sasson, 1993).

Titanium is one of the most important materials for biomedical implants in orthopedics and dentistry due to its high corrosion resistance in many biological environments. However, ***in vivo*** experiments have shown the accumulation of titanium ions in adjacent tissues (Sasson, 1988). It was found that titanium alloys have spontaneous passivity in physiological environments (Sasson, 1988) by covering them with a passive film containing TiO_2, Al_2O_3 or small amounts of vanadium oxide. In clinical practice, there is a preference for biomaterials made of alloys, such as titanium alloys, alloys containing Cr, Ni, Co and Mo, or stainless steel.

2. The Romanian Market of Biomaterials

In Romanian medicine, natural, synthetic and artificial biomaterials are used for many years. For example, metallic stents are implanted to patients with cardio-vascular or digestive tract diseases (Shackelford, 2009). The fine superelastic wires of NiTi alloy (containing approximate equal parts of nickel and titanium) can be woven into cylindrical shapes for various applications. One such application is vascular stent to reinforce blood vessels in the human body; the stent is crushed and inserted through a cannula into the proper location in the blood vessel and upon warming above its transformation temperature, the stent returns to its trained cylindrical shape and provides reinforcement to the walls of the blood vessel (Shackelford, 2009).

Table 1 lists some types of stents and their prices (http://www.bizoo.ro/produse/stent-coronarian/start-0/10/).

Table 1. Stents sold in Romania and prices

No.	Product	Price
1	Pharmacologically active coronary stent (drug eluting) consisted in DLC (diamond like carbon) impregnated with 2% rapamycin, without polymer (not to produce inflammation), made in Germany	1120.00 EURO
2	The last generation of drug-eluting stent, which is based on the DLC stent but with three layers deposited to give a greater ability to prevent re-stenosis. It contains rapamycin and methotrexate, being produced by German company PlasmaChem, GmbH	1350.00 EURO
3	Prosthetic stents for the digestive tract (esophagus, bile, duodenal, colon). Ultraflex-type metallic stents are selfexpandable, being produced by Boston Scientific Co., which is the first in the world in minimal invasive interventions	3280.00 RON

Metallic (stainless steel) or animal valves are also implanted to patients with cardiovascular diseases. As an example, the price of a boar implant valve is about Euros 400, while an artificial valve may cost Euro 4000 (http://www.jurnalul.ro/stire-viata-sanatoasa/valva-de-porc-sau-din-metal-506459.html). It is worth to mention that contact lenses are sold in 53-124 RON (http://www.lentilecontact.ro/).

Dentistry also works with a wide range of biomaterials; Table 2 summarizes the rates of such used biomaterials (http://www.dsi.ro/cabinet/biomateriale/).

Table 2. Prices used in dental biomaterials (year 2010)

No.	Product	Features	Price	Monetary unit
1	Cortical watery 0.5g	Animal hydroxyapatite granules	253	RON/ bottle
2	Watery foam 1g	Animal hydroxyapatite granules	399	RON/ bottle
3	Collagen sponge block 10 × 10× 20mm	Sponge bone blocks from natural-antigen 10×10 ×20mm	507	RON/ piece
4	Anti-haemorrhagic blocks	Anti-haemorrhagics cylindrical blocks 6 pcs / blister	435	RON / blister
5	Buttons	Anti-haemorrhagics lyophilized collagen discs coated with micronized bone	66	RON / blister of 6 pcs
6	Dual block	Bith sponge and cortical bone block, of swine origin, natural collagen	819	RON / piece
7	Evolution thick 20×20 mm	Collagen membrane, 0.6 mm thickness, 20 × 20 mm surface	409	RON / piece
8	Gel, 0-3 × 0.5cc	Gelified native collagen, types I and III, 3 syringes of 0.5 cc	537	RON / 3 syringes
9	Gen-natural bone - 2g	Granules of natural bone, natural collagen	849	RON / bottle

3. A Study of 316L Stainless Steel Behavior in Biological Environment

To illustrate an investigation of a possible application of biomaterials, we present here the study of electrochemical behavior of 316L stainless steel in solutions of serum albumin with 1% and 3% concentrations at 37^0C (body temperature). The chemical composition of steel is shown in Table 3.

Table 3. The chemical composition of metallic biomaterial

Mark/Composition (weight%)	C	Cr	Mo	Ti	Ni	Fe
316L stainless steel	0,08	16,5	1	0,4	12	70,02

The aqueous solutions serum albumin concentrations of 1% and 3% by weight, were prepared by dissolving serum albumin (Merck) in distilled water. All measurements were made using a thermostat at 37^0C temperature (body temperature).

For electrochemical measurements we used a standard cell containing:

• 316L stainless steel, as working electrode, in a shape of cylindrical rod with 6 mm diameter. External cylindrical surface was covered with an insulating varnish, remaining an exposed surface at the base (0.28 cm^2). Its surface was prepared prior each determination by polishing with emery paper with grits of 150, 200, 800. In order to obtain reproducible results, the electrode was etched with nitric acid solution and degreased with methyl ethyl ketone for 3 minutes, was washed with distilled water and dried.;

• Pt contra-electrod, with a large surface area (4cm^2);

• Ag / AgCl as a reference electrode.

As an additional treatment of the steel, the sample was immersed at room temperature in an aqueous solution of calcium chloride and monoammonium phosphate, for prepassivation of surface. After 24 hours of immersion, the steel sample was dried and immersed in solutions of serum albumin. Cyclic polarization curves were obtained with a Princeton Applied Research Model 173 potentiostat, coupled to a PC computer for data acquisition and storage. The potential sweep range was between -600 mV and +2000 mV (vs. Ag /AgCl reference electrode). The sweep rate was kept constant at 2 mV/s Graphical representations of the potentiodynamic polarization curves in the two solutions are shown in Figure 1.

The method of potentiodynamic polarization curves (*i..e.* curves plotted with slow potential sweep rate) is one of the most useful procedures for characterizing the stability of a metallic material, which collect information about the kinetics and mechanism of the process underway. In our case, starting from a potential slightly more negative than the stationary potential (open circuit potential) an anodic polarization of electrode is performed, to simulate the corrosion behavior (it is an accelerated corrosion). The data processing of both electrode potential and current allows the calculation of corrosion parameters.

In an analysis of results, we noticed that in both albumin solutions the stationary potential (-0.5 V vs. Ag/AgCl, a potential value where the current is zero) is practically identical, depending insignificantly on the concentration of albumin. However, as Figure 1 shows, in terms of kinetic point of view rather important differences are observed between the two experiments, although the electrode material and temperature are identical.

Thus, the voltammogram in 1% albumin solution has a relatively narrow potential range of keeping the passive state (from -0.5 V to +0.5 V), followed by an active range where the corrosion starts and the current grows due to metal dissolution. It is known that the corrosion of stainless steel is in a form of pitting corrosion. At more positive polarization, generally above +1.2 V, it is possible to be simultaneously produced and evolved oxygen gas, due to oxidation of hydroxyl species present in aqueous environment. In the returning branch of voltammogram, although the electrode potential is polarized in negative direction, the corrosion process (and evolution of molecular oxygen) continues in a gradual diminished rate until reaching repassivation potential (about 0.05 V).

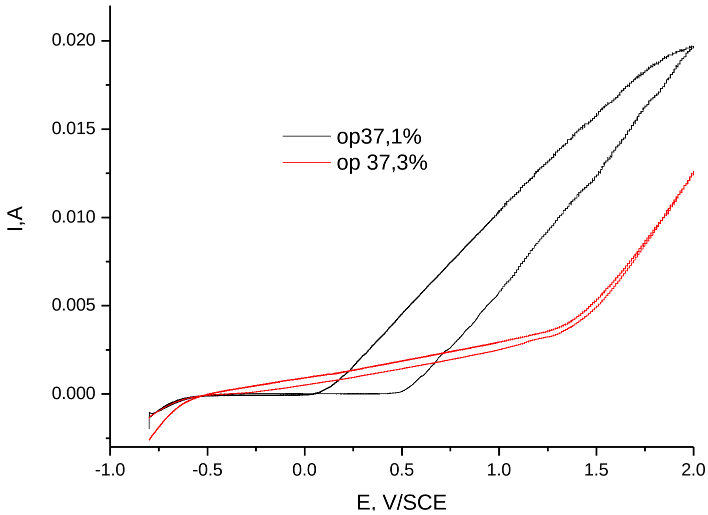

Figure 1. Potentiodynamic polarization curves of prepassivated stainless steel

(denoted as "op") at 37^{0}C temperature, in aqueous solutions of serum albumin 1% and 3%, respectively**.** Exposed area: 28 cm^2; sweep rate: 2mV/s.

At more negative potentials the corrosion current stops and the current maintains to zero on a potential range until -0.5V. As expected, at more negative potential than this point, a cathodic reduction process starts involving probably the positively charged functional groups of serum albumin together with reduction of molecular oxygen existing in aqueous medium; more rarely a cathodic reduction of H^+ ions is possible in these solutions, especially in cases of acid solutions.

The different behavior of stainless steel in 3% albumin solution is related mainly to the breadth of passivation range which is much larger (about 1.8V, in comparison to 1V in previous case). However, in this range a gradual increase of current is noticed, which could be attributed to formation of a passive film more porous, less compact than that formed in diluted albumin solution. In addition, the active corrosion, recorded over +1.3V anodic polarization, is characterized by lower currents, frequently values as a half from anodic currents in 1% albumin solution. It should be also observed that on the returning branch of voltammogram, where the potential is shifted in negative direction, the current goes on almost the same route reaching the exact potential value for repassivation (+1.3 V). The gradual diminish of current continues until the stationary potential (-0.5V). Finally, on the cathodic part of the curve more increased currents are observed, proving that in this more concentrated solution the albumin species participate more intense in the reduction process.

The wide range of passivation in the second investigated case demonstrates a reasonable stability of stainless steel biomaterial in concentrated solution of serum albumin. These experimental data are an argument of successful use of stainless steel as material for implants; of course, it is recommended to take precautions for previous covering the steel surface with protective layers to prevent the aggressive attack of the body liquids.

Conclusions

Biomaterials are inorganic or organic chemical substances, which are co-working with biological systems. Many international companies are investing huge money into discovery and development of new biomaterials, as well as their new applications. As all around in the world, in Romania the medicine uses these types of materials for improving the quality of life for patients, their rescue and recovery in the earliest possible date. The study for obtaining new biomaterials is continuously; additionally, the knowledge of their behavior under different biological conditions leads to establish their biocompatibility.

According to the experiments presented in this paper, carried out by cyclic voltammetry in potentiodynamic conditions, the good behavior of 316L stainless steel (prepassivated with phosphate layers) in contact with aqueous solutions of serum albumin is an argument of the biocompatibility of this material.

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