2 Biomaterials Used in Orthopedics

Dominique G. Poitout

The great advances in orthopedic surgery over the past few decades and the fact that it constantly out-performs itself are the result of a policy of rigor in various areas.

Rigor in the training of the surgeons in this discipline, which demands a long period of training in specialist departments.

Rigor in performing operating techniques as a result of which hazardous improvisation is excluded.

Rigor in the choice of materials, the use of which has opened up the way to progress but the quality of which determines the results.

Precision and reliability are therefore the key words of the orthopedic surgeon who is preparing and executing an osteotomy in the same way as an engineer approaches the bridges and road surfaces for the arch of a bridge. He needs a good knowledge of the laws of physics and of the rules of mechanics, but he also has to be able to apply this knowledge to living matter.

I also believe it to be important to stress that orthopedists are clinicians and care for patients and that, if clinical practices develop in a direction which is not in line with their wishes, even though the theory and the calculations are accurate, we should not try to understand how this should work but why it does not work. Indeed, there are so many parameters involved in human clinical medicine that it is often difficult, when trying to describe a movement or define the stresses on a particular material, to take all the normal physiological parameters into account.

D.G. Poitout, MD
Faculté de Médecine Nord, Sce Chirurgie Orthopédique et Traumatologie, Aix-Marseille Université, Centre Hospitalier et Universitaire Marseille North, Chemin des Bourrely, 13015 Marseille, France
e-mail: Dominique.POITOUT@ap-hm.fr

Behavior of Biomaterials in Situ

Although the functional aspects of implanted materials can be anticipated fairly reliably, it is very often difficult to anticipate how well they will be tolerated clinically. For materials of any kind there are two aspects which have to be taken into account. They are:

on the one hand the *adhesion* between a biomaterial and the part of the human body with which it will be in contact,
on the other, the *aging* of the product implanted.

Adhesion involves all the problems of using cements and adhesives, the role of which is to transmit and distribute the stresses over the largest area of contact possible. This adhesion problem is far from being resolved satisfactorily from the practical point of view and there is still plenty of scope for the researchers to investigate. Should

D.G. Poitout (ed.), *Biomechanics and Biomaterials in Orthopedics*,
DOI 10.1007/978-1-84882-664-9_2

a prosthesis be cemented, screwed, or introduced with force, hoping that its irregular surface will allow the bone to grow again and for the prosthesis to be fixed into the bone? More and more surgeons are currently abandoning these latter methods because of the frequency of painful failed fixations requiring surgery to be repeated (6–8 % on average after 12 months). Cement has its drawbacks but according to the current state of knowledge seems to be the best compromise for fixing material into bone.

Aging. As soon as it has been implanted in the body, the biomaterial finds itself in an environment which is more aggressive than sea water, not least on account of its higher temperature and its sodium chloride content. Furthermore, there are also the variations in pH which may lead to a rapid breakdown of plastics and may accelerate_metal corrosion.

I would like to dwell on this problem of metal corrosion for a few moments. Some metallic materials are very resistant to generalized corrosion. This is the case for Vitallium, stainless steels, or alloys based on titanium, but they are still vulnerable to corrosion if pitted, the risk of which increases with contact friction which leads to breaks in the protective passive layer. It is also necessary to take into account the simultaneous action of the corrosive environment on the prostheses and the mechanical stresses to which they are subjected. This results in the risk of corrosion under stress, and corrosion due to fatigue which can lead to the appearance of weak points with the risk of breakage. Another well-known case of corrosion is galvanic corrosion caused by placing two different metals in contact with each other in a conducting liquid which then behave like an electric battery.

When there is corrosion, metal ions pass into the body. Therefore, some studies have shown that for austenitic stainless steel osteosynthesis plates, 9.1 mg of the alloy passed into the body 2 years after having been implanted. That is to say that there is a release of iron, nickel, and chromium in an equal proportion to that of the composition of the alloy. For example, in an individual who had had intramedullary pinning of the tibia, after 18 years he was found to have a nickel concentration in his serum, urine, hair, and nails which was up to 18 times the normal concentration, almost the same level as is found in workers in the nickel industry.

More generally, the implantation of foreign material, and particularly a metallic material, always has consequences for the surrounding biological environment. It was even possible to demonstrate a transformation of the proteins left in contact with nickel, in particular by electron transfer at the metal–electrolyte interface.

The problems listed above therefore require the practitioner to know the mechanical and chemical properties of the materials to be implanted without, of course, forgetting the sterilization conditions which can alter certain materials (such as gamma rays on plastics, ethylene dioxide absorbed by certain materials then released producing toxic reactions).

If the surgeon cannot check all the properties of the material he uses by appropriate tests, he has to rely on the manufacturer's literature to make his choice. But if he knows the properties that he can expect for a given application, the dialog will be more to the point.

That is the current direction in the area of French orthopedics.

Biomaterials Used in Orthopedics

As it would be excessive to give an exhaustive list of all the biomaterials used in orthopedics, we will only take a few examples from each of the five main classes of orthopedic biomaterials;

metals and metal alloys,
ceramics and ceramo-metallic materials,
bone replacement materials and allografts
carbon materials and composites, polymers.

Metal Alloys and Metals

First, where steels are concerned, the introduction of alloys leads to a spectacular improvement in oxidation. Molybdenum plays an essential role in resistance to corrosion caused by pitting.

Chromium also plays an essential role from the point of view of corrosion. Indeed, exposed to the air or to an oxidizing environment, chromium allows a very thin, invisible film of chromium oxide to form – this is called the passivation phenomenon. A minimum chromium content of 12 % is necessary to give steel its stainless properties.

Other elements can be added; this is true for nickel which, when in a proportion of 10–14 %, makes it possible to obtain an improvement in mechanical performance without leading to brittleness.

Steel with a high carbon content is therefore suitable for temporary surgical implants (osteosynthesis plates, intramedullary nails) because of its malleability and its stainless properties. But its poor prolonged resistance to corrosion means that it has to be removed after a few years.

Alloys based on cobalt–chromium are shaped by microfusion or casting, which is less good mechanically, and only very rarely has it been possible to make forgeable alloys, owing to considerable additions of molybdenum, tungsten, and nickel.

Although these materials have a resistance to corrosion and a breaking load which is better than stainless steel, their elastic limit is very close to the breaking load, which prevents any possibility of permanent deformation. And, as their resistance to fatigue is low, a significant breakage rate has been seen for femoral implants.

Their modulus of elasticity is high, at around 200,000 MPa, which poses the same problems as when using stainless steels (the modulus of elasticity of a bone being less than 20,000 MPAI). Due to their great hardness, alloys based on chromium and cobalt are the best compromise to date for making prosthetic femoral heads.

Titanium alloys have high resistance to all forms of corrosion and have good mechanical properties. Their modulus of elasticity is low, 110,000 MPa, which is half that of other alloys such as stainless steels. They have excellent biocompatibility, a high breaking load, and an elastic limit close to that of the breaking load, which eliminates any problems of permanent deformation in the case of high stresses, but also limits their use as a material in osteosynthesis. Owing to the passivation phenomenon, titanium covers itself spontaneously with a protective film of titanium oxide which renders it remarkably resistant to corrosion. This can be increased even further by the chemical process of anodization. There is one negative element that should be emphasized which is that titanium alloys have poor friction properties in that it is not possible to use them as prosthetic femoral heads or in the axis of a hinged prosthesis. Current trials, aiming to improve the friction characteristics by laying down deposits of titanium nitride or carbide, have not been very successful because these deposits are irregular and thin so that the layers abrade after a few thousand cycles.

Hydrogen or nitrogen ion inclusion techniques are still at the experimental stage.

Finally, the alloy most frequently used currently is an alloy containing a combination of aluminum and vanadium; Ti_6AP_4V, which has properties clearly superior to those of nickel–chromium–cobalt alloys. This is certainly the best solution today for all diaphyseal implants, particularly femoral hip implant which is subjected to high mechanical stresses.

Other metallic biomaterials could, in future, be useful in orthopedics; more specifically zirconium, tantalem, and nobium, all three of which display excellent biotolerance. However, progress still has to be made with alloys before they can rival titanium alloys.

Ceramics and Ceramic–Metal Compounds

Ever since man discovered that fire can modify the properties of clay (hydrated aluminum silicate), ceramics have never stopped developing. New ceramics have been developed and these materials take various forms:

oxides: aluminum oxide (Al_2O_3), zirconium oxide (ZrO_2),
carbides: silicon carbide (SiC),
nitrides, bromides, and fluorides.

The science of ceramics has also meant that new textures can be created such as ceramic composites with various fibers combining metals and ceramics, which are called ceramic–metals or even cermets. There are also controlled crystallization glasses called vitroceramics.

The New Ceramics

Sintered oxides are either pure oxides such as alumina or mixtures of oxides. When high-purity alumina is used in the medical field, the specification is extremely precise. Alumina is a hydrophilic material (unlike polyethylene which is hydrophobic), it is very hard, slightly less so than diamond (which is, moreover, used to grind and polish it), and its modulus of elasticity is 380,088 MPa, which is practically twice that of the metal alloys. Its resistance to flexion, however, is low, which limits the indications in which it can be used as an osteosynthesis rod or plate. When alumina was first used as a prosthetic hip compound, there were many failures of the femoral head when used with an acetabulum also made of alumina.

The two pieces machined for each other:

tended to jam if the slightest particle of wear debris came between them.

produced very little wear debris, certainly, but as these were crystals they led to synovial reactions comparable to microcrystalline arthritis.

prevented any isolated change in one of the pieces of the prosthesis if only one became damaged.

The existence of a high modulus of elasticity, far higher than that of methyl methacrylate and that of cortical bone, led to problems when sealing an alumina acetabulum with methyl methacrylate because unsealing occurred more frequently and usually occurred between the cement and the acetabulum and not between the bone and cement, as is normally the case. On the other hand, if the alumina acetabulum is directly screwed into the bone, the quality of the fixation is exceptional and the mobility of the implant normal because of the almost inevitable appearance of a film of fibrous tissue between the implant and the bone. The use of alumina currently, therefore, seems to be restricted to femoral heads and sliding surfaces in contact with polyethylene.

Zirconia (ZrO_2) also has excellent mechanical properties, in particular flexion, together with satisfactory resistance to wear and friction, but in some cases it breaks! We hope that zirconias stabilized by yttrium oxide (Y_2O_3) and by alumina ($R_{12}O_3$) will be used routinely as friction components in total prostheses of the hip.

Carbides and Nitrides: These new materials include silicon carbide, which appears to have greater resistance to flexion than alumina as well as a higher modulus of elasticity, but its coefficient of friction is lower than that of alumina.

Ceramic–Ceramic and Ceramic–Metal Compounds

Fiber composites are a compromise between a deformable solid (for example, carbon fibers or alumina fibers) and a matrix which resists deformation (such as alumina or silicon carbide). To date, the first experiments with mixtures of aluminum oxide and iron have not produced useful results for improving the properties of the material. On the other hand, other combinations with molybdenum and its carbide, with tungsten and its carbide, or with titanium combined with zirconium oxide, seem to improve the resilience and toughness of the material considerably.

Glass and Vitroceramics

The mechanical strength of some glasses can be greatly improved by being transformed into vitroceramics. Direct anchoring, as for conventional ceramics, can, together with glasses and the vitroceramics, be performed by mechanical or chemical processes. In the case of vitroceramics anchored mechanically the dimensions of the interconnections between the pores are sufficiently large to allow colonization by bone tissue. Unfortunately, the mechanical properties of these vitroceramics are relatively poor. Resistance to breakage on flexion remains around 20 MPa, which is far too low for use in internal prostheses.

It seems that glasses and vitroceramics anchored chemically give better results. These materials initially have better mechanical strength than those of porous materials and are better than those of bone, but these criteria do not last. On the other hand, adhesion only seems to occur if the implant is immediately placed into intimate contact with the bone tissue, which is not always easy to do in practice, because, as in the case of bio-inert materials, a fibrous capsule forms which isolates the material from the bone.

Natural, Biological, or Synthetic Bone Replacement Materials

Bone loss can be remedied today either by natural autologous or homologous bone grafts or with ceramic-like materials. This is particularly true for madreporic coral or synthetic coral which consist of calcium phosphates and fluoroapatites and are comparable to the vitroceramics we have been discussing.

Natural calcium carbonates are skeletons of madreporic corals with their organic part removed. They consist of virtually pure aragonite ($CaCO_3$). Used experimentally to replace bone substance losses or to fill cavities, it seems that the tendency is for the fragment of natural calcium carbonate to be resorbed, then for the carbonated skeleton to be replaced centripetally and gradually by bone. The structure of coral skeleton makes it possible to re-establish the intra-medullary circulation and its resorption releases calcium ions reused by the body for the precipitation of phosphocalcium apatite. However, the mechanical properties of the corals, which have a strength under flexion of the order of 3 MPa, and under compression of 16 MPa, are much inferior to those of bone and the clinical applications are comparable to bone autografts and allografts.

Materials Obtained by Synthesis

With comparable porosity, the mechanical properties of synthetic materials are generally superior to those of natural materials. Only the compressive strength of tricalcium phosphate, which is between 7 and 21 MPa, is of the order of magnitude of that of coral. As for the latter, there are ultimately extremely few clinical applications.

Allografts

Bone is a living tissue consisting of cells as well as of a prosthetic structure on which calcium and phosphorus have been precipitated. The introduction into the body of a bone graft of any kind will lead to the progressive destruction of its cells without modifying the supporting protein lattice. Indeed, although the cells are antigenically specific to any particular individual (various HLR groups), the collagen which forms the architecture of the bone is the same throughout the human race and will not give rise to rejection phenomena. Whether we use an autograft or an allograft, the clinical development of this tissue is approximately comparable and the cells will die. The protein structure on which the phosphocalcium raster is fixed will no longer exist and the bone cells of the host will recolonize the bone which serves as a mold. After several years, new bone will be reformed from the cells of the host.

As massive samples cannot be taken from the same person without running the risk of causing problems at the donor site, we turned to preservation by cryopreservation of the bone homografts in bone banks. In order for it to be preserved "indefinitely", it is necessary for the bone to be stored in very cold conditions below −80 °C. For these technical reasons, we chose to store the cryopreserved bone – preserved in 10 % DMSO in liquid nitrogen at −196 °C; which, subject to certain precautions, gives the most reliable results. Cryopreserved bone makes it possible to reconstruct a bone segment which had to be resected due to the existence of a bone tumor at that site and also to reconstruct the locomotor architecture after a considerable loss of bone substance due to trauma.

Massive osteocartilaginous fragments are used ever more frequently to reconstruct articular surfaces which have been damaged or removed as part of the excision of a tumor. Smaller, spongy fragments can also be used in addition to osteosynthesis to fill a bone cavity or to complete the fixation of an arthroplasty. The results we are obtaining currently are wholly encouraging and in many cases have made it possible to avoid amputation or the use of massive prostheses, the long-term mechanical future of which is not guaranteed. Between 1978 and 2000, the Marseilles Bone Bank has supplied 1744 massive bone parts used for grafts.

Carbon Compounds

Since 1967, numerous procedures have been used to create biomedical carbon but so far none have given absolute biological stability. It cannot, therefore, yet be considered for use routinely in human biology, in spite of the very many suggestions which have been made (osteosynthesis plates, nails, joint prostheses) and in spite of its unrivalled endurance to fatigue (easily able to exceed ten million cycles). The natural communicating porosity of its structure allows colonization into the mass of the prosthesis by the surrounding biological tissues, and the structural flexibility of the composites harmonize with the elasticity of the host bone. The fact that they cannot be deformed means that they cannot be used as osteosynthesis plates and as the carbon fibers cannot tolerate lengthening, even to a very small extent, nor can they be bent to more than 30 ° without breaking. They cannot be used as a prosthetic ligament because fixing this ligament into bone is very difficult.

Finally, the many particles from wear found in the ganglions, and even in the spleen, mean that we have to be careful when using these composites. Owing to the hardness of the surfaces obtained by the ceramization treatment, it may be possible to consider using carbon as an articular surface, placing polyethylene in between the opposing surfaces.

Polymers

Numerous products have been suggested but, of course, they cannot all be considered.

As far as their common properties are concerned, it is important to stress the fact that they age physically and chemically.

The following will be discussed:

1. Silicones, which are chemically inert, have good biotolerance and a high hydrophobic capacity. They are used in plastic surgery or in orthopedics in the form of elastomer rubbers for joint prostheses of the fingers, for example.
2. Polyacrylics, and more specifically, methyl polymethacrylate, are well known in the area of orthopedics as they are used as a cement for fixing prostheses. The time that cements take to grip varies considerably depending on the type of used; also the polymerization reaction, which is very exothermic. If none of the heat were to be dissipated to the exterior while polymerizing, the mass of cement could reach more than 70 °C. It is thought that the maximum temperature should generally be no more than 40–50 °C in vitro, which is relatively close to the coagulation point for proteins (56 °C) and that of bone collagen (70 °C). It would therefore be desirable to find a new, weakly exothermic cement, which sets relatively slowly, but this is not yet available.

Currently, the cement penetrates the interstices of the bone more effectively and leads to even more secure anchorage if it is more fluid or less viscous. It is therefore preferable to use a cement with a viscosity of less than 100 Newton/s/m^2 after mixing.

Similarly, the porosity is a decisive factor in the mechanical behavior of the cement. For a particular cement, the size of the pores does not depend on the maximum temperature, but on the mixing and usage conditions. On the other hand, the number of bubbles per unit volume, for any particular cement, depends on the maximum polymerization temperature.

Finally, all acrylic cements show volume changes between the beginning of the mixing and the end of hardening. Currently, it appears that cement starts by contracting approximately 2.5–6.5 microns per 2 mm thickness. As far as the mechanical properties of cement are concerned, the Young’s modulus is low (of the order of 3000 MPa) and traction strength and compressive strength are approximately a quarter of the strength of normal bone. It is therefore important to emphasize the preparation of the cement, the frequency of the movements, and the role of the additives. In this area, the addition of powders only very slightly changes their mechanical properties. On the other hand, when a liquid, such as an antibiotic, is to be added, this leads to serious weak points appearing and causes fractures to start which will only spread under stress. Finally, irradiation does not cause any significant changes in the mechanical behavior of the cement.

3. Saturated polyesters, which are condensation polymers, are essentially represented by polyethylene terephthalate. This polymer has good resistance to chemical agents, good tolerance in solid form and good mechanical properties. However, its behavior in a humid environment is poor, with a sharp reduction of its mechanical properties. It is used in orthopedics in the form of plaited threads to make prosthetic ligaments (Dacron or Rodergon, for example). The poor elastic elongation properties (1.25 Y approximately) seem to be a very worrying factor for how this prosthesis behaves over time because the relative physiological elongation of the cruciate ligaments of the knee, for example, is 26–25 Y.
4. Polyolefins. In this group it is UHMW (Ultra-high-molecular-weight) polyethylene which is used for making friction components for prostheses of the hip, knee, and elbow because of its mechanical properties. A great deal of research is currently being carried out to improve its properties, and in particular its resistance to creep with, for example, the incorporation of carbon fibers. Polyethylene reticulated by ionizing radiation with grafting of polytetrafluoroethylene should also improve the resistance to wear and creep. The use of a metal backing for prosthetic cupulae also seems to limit the extent of creep. Polypropylene can be used for ligament use but here, too, its elastic elongation risks breaks in or detachment of the implant.

To conclude, how do these biomaterials behave in use? It should be borne in mind that the main reasons why these materials fail are due to an as yet inadequate understanding of the properties of the materials used. Detachment is due to a breakdown in the cements and requires research to be carried out into their properties together with research into the mechanics of the transfer of loads between the implant and the bone. The extent of wear on the polyethylene parts will mean that the properties of these products will have to be changed, while amending the design of the parts. The introduction of ceramics to reduce the extent of wear has not managed to stop it, and until these materials are made less brittle, there will still be the risk of accidents.

There is still insufficient experience with carbon composite materials and only rigorously controlled experiments will enable us to say whether the hoped for advantages of these new materials are accompanied by serious disadvantages linked to a possible fragmentation of the fibers.

Finally, in the case of metal alloys, an analysis of the behavior of the parts in use shows that the resistance to fatigue corrosion should be studied in experimental conditions to enable easier comparison of the advantages and disadvantages of the various alloys proposed.

Care should be taken not to reach too hasty a conclusion as to the risks of certain techniques and, perhaps even more importantly, the wholly beneficial effect of the new techniques where it is not possible to be entirely sure of the scientific objectivity of the measures. In practical terms, all the phenomena involved in the behavior of implantable materials start at the surface of the implants. It is therefore by studying the surfaces and their changes by physicochemical or mechanical treatment that advances can be made in the current techniques for manufacturing surgical implants. Reconstruction of joint cartilage with collagen, osteocartilaginous allografts, or artificial substances will allow enormous advances to be made in the treatment of arthroses, the number of cases of which rise as life expectancy increases.

Finally, many materials used today will probably be abandoned in the years to come. On the other hand, new products will appear which will be based on the arthroplasties of the year 2000. Today we are probably only aware of one third of the materials we will be using in 20 years time.