A Review on Orthopaedic Biomaterials: Properties, Advances, and Future Directions

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Abstract

Orthopaedic biomaterials play a pivotal role in advancing fracture fixation, joint replacement, and dynamic stabilization within orthopaedic applications. Primarily composed of metals, these biomaterials exhibit outstanding properties including high strength, ductility, fracture toughness, hardness, corrosion resistance, durability, and biocompatibility. Despite their versatility, the landscape of orthopaedic implant materials remains dominated by a limited range of metals, ceramics, composites and polymers. However, the durability of these implants is challenged by biological reactions and material degradation caused by wear and electrochemical corrosion. This article examines the developments that have taken place with respect to the biomaterials and their applications as implants in orthopaedic surgery. This encompasses history, types and properties of metals, polymers, ceramics, composite biomaterials, and processes of fabricating them. The characteristics like biocompatibility, mechanical properties, fluid stability, and the ability to induce osseointegration and the relevance of such materials for implants in orthopaedic surgery is also discussed in this article. Special attention is given to the development of novel bioactive metallic materials and their means of improving wear resistance and biocompatibility by changing the surface and applying coats. The scope of the review further covers advanced technologies including smart bio-materials, 3D/4D printing, use of nanotechnology, and prosthetics. Further, the review article discusses the current status and future trends concerning materials for orthopaedic surgery in greater detail.

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Introduction

In today's rapidly evolving world, orthopaedic concerns are increasing due to accidents, advancing age, and congenital factors. To address orthopaedic fractures and other bone issues effectively, the use of orthopaedic implants and prosthetics are essential. Substance that has been engineered to interact with biological systems for medical purposes, whether therapeutic (e.g., implants, drug delivery systems) or diagnostic (e.g., biosensors) referred as Biomaterials. These materials are typically designed to be compatible with living tissues and can be derived from natural sources, synthetic polymers, metals, ceramics, or composites thereof [1]. As per the evolution there are 3 generations of biomaterials. The First-Generation Biomaterials (1950s-1980s) focused on inertness that did not interact extensively with biological systems. The Second-Generation Biomaterials (1980s-early2000s) focused on improving bioactivity and enhancing interactions with biological tissues. Lastly, the Third Generation Biomaterials (early 2000s-present) emphasizes advanced functionality, tissue regeneration and customization for specific medical applications [1,2]. The selection of biomaterials is based on the specific needs of medical treatments, like orthopaedic implants, dental work, or tissue engineering, to ensure safety, effectiveness, and compatibility [3].

Compatibility of orthopaedic implants with the human body is crucial for successful application in healing, correcting deformities, and restoring lost functions. While advancements in biomaterials and prosthetics have been made, challenges remain in diagnosing infections, and dealing with implant toxicity, corrosion, and wear-and-tear. The development of novel biomaterials and prosthetic devices, with the introduction of nanotechnology, is essential for advancing orthopaedic care, improving patient outcomes, and meeting the evolving healthcare needs of diverse patient populations.

This review offers an overview of diverse medical biomaterials, emphasizing the promising role of metal materials in orthopaedic implants. Methods to enhance the surface biocompatibility of metal materials, such as surface treatments and coating techniques, were reviewed. The discussion also addressed the current limitations of these approaches and outlined future research directions aimed at enhancing their overall effectiveness.

Properties of biomaterials

1. Biocompatibility: By definition, biocompatibility refers to the ability of biomaterials to meet their intended function in a certain clinical setting, particularly within the body of a patient, without inflicting any adverse effects [1]. This ensures that there is maximum success in treatment while protecting the patients as much as possible. Biocompatibility is, therefore, an imperative aspect for the faster placement of new, innovative devices to the healthcare market. The skin irritation and cytotoxicity were the first two testing protocols for material toxicity and skin irritability according to the American Standards and Test Methods International (ASTM) during late 1980s. These standards were later revised by the International Organization for Standards (ISO) [4]. Biocompatibility evaluation involves assessments such as: genotoxicity, cytotoxicity, irritation or intracutaneous reactivity and testing for implantation and hemocompatibility [5,6].

2. Mechanical properties: The mechanical characteristics of biomaterials are the contributing factors to their performance and appropriateness for particular biomedical applications. It includes Young's modulus, ultimate tensile strength, yield strength, ductility, fatigue resistance, corrosion resistance, and fracture toughness [1]. Corrosion resistance is the most crucial property owing to the extreme differences between the body environment and the atmosphere. Metals that withstand oxidation in air might be seen succumbing to internal corrosion within the human body due to body fluids which contain ions that facilitate corrosion. Thus, it is important to look for ways to reduce ion release from metals and at the same time protecting the metals for long lasting periods [6,7].

3. Tribological behaviour: Tribology is a field that examines surface interactions between hard materials in the context of relative motion, emphasizing friction, wear and lubrication [8]. Although rigid material, including brittle ceramic materials can endure external mechanical forces, they are unsuitable for joint implants due to their inefficiency under stress impacts. Therefore, metals and rigid plastics are used instead because of the advantageous properties they possess over time. Presently, regular materials for arthroplasties include blends such as Ceramic-on-UHMWPE, Metallic-on-UHMWPE, Ceramic-on-Ceramic, CoCrMo-on-CoCrMo and Al_2O_3-on-CoCrMo [1,9]. Inadequate friction characteristics can result in excessive wear to the surfaces of an implant causing metal debris shedding into the adjacent tissues. This can provoke unwanted reactions in the tissues and markedly shorten the lifespan of the implant [10].

4. Osseointegration: Osseointegration is a phenomenon where the living bone tissue grows on the implant surface forming a direct structural and functional interaction. It guarantees the stability, functionality, and longevity of the endoprosthesis, especially of orthopaedic and dental implants [11]. Surface is a key factor contributing to the process of osseointegration as it is clearly understood in the review by Geraldo Roberto Martins Matos [12] and Wennerberg [13]. They explained how the surface designs of dental implants affect their integration with the bone, with particular focus on the role of textures and finishes in the implants' performance.

Classification

Biomaterials comprise a varied range of materials [14]. We have categorized biomaterials based on the primary materials they are composed of, as shown in the Figure 1.

1. Metallic Biomaterials

Surgical implants rely heavily on metals and metallic alloys, because of their superior strength, resistance to fracture, interatomic bonding and ease of engineering processes. They are commonly used in orthopaedics, dentistry, peripheral cardiovascular devices, and neurovascular implants. Due to their good electrical conductivity, they are also used in cardiac pacemaker devices for neuromuscular stimulation. Prosthetic devices can be made from a range of metallic biomaterials as per requirements and properties [1,15,16].

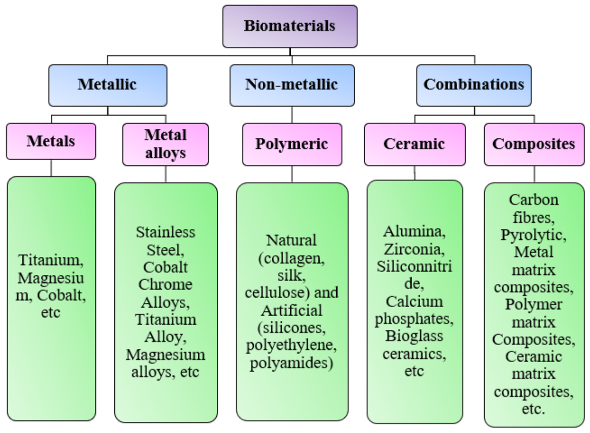

Figure 1: Classification of different types of biomaterials.

316L Stainless Steel: 316L stainless steel (SS) is widely used for the fabrication of implants due to its resistance to corrosion, ease of processing, good mechanical properties, and biocompatibility [14,17]. Due to lesser carbon content than the 316 standards, it reduces the chances of inter-granular corrosion after welding. Despite having many qualities of good biomaterial this stainless steel is prone to corrosion, especially due to chloride ions in blood. The elastic modulus of this SS ranges approximately from 200 to 210 GPa, while that of natural bones ranges from 3 to 20 GPa. Due to this significant difference, it leads to joint separation over a period of time [1,15,18].

Cobalt Chrome: Cobalt Chrome (CoCr) alloys are known for their excellent mechanical properties, corrosion resistance and biocompatibility. They often contain additional metals like nickel, molybdenum, to enhance the overall properties. These alloys are often cast because of their work-hardening tendencies above room temperature, which makes them ideal for hip implant components and dentures. However, these materials can leach toxic ions into the biological environment, potentially causing cancerous growths and other unwanted effects. The elastic modulus of these alloys' ranges up to 220-230 GPa. Due to the significant difference in the elastic modulus between bones and implants, stress shielding occurs, leading to bone atrophy. Altering the surface of cobalt-chromium alloys by direct laser interference patterning has been proved to be as biocompatible as commonplace stent materials. This leads to the possibility of using it for fast endothelialisation while preventing thrombosis in the cardiovascular system [1,17,19].

Titanium and titanium alloys: Since 1960s, titanium and its alloys have been utilized in biomedical fields, from dentistry, cardiovascular, orthopaedics, prosthetics, craniofacial surgeries to reconstructive joint procedures. Titanium and its alloys are valued for their non-reactive nature, biocompatibility, as well as stiffness, and performance reliability over time. Nitinol, a nickel-titanium alloy, enjoys thermal memory, shape recovery properties, and excellent absorption qualities. However, over time it releases nickel ions, which increases toxicity within the biological environment. The β-Titanium alloys have also been developed, which cause minimal stress shielding due to their lower modulus of elasticity as compared to its other states. However, at high temperatures they lose their structure and properties [1,20].

Magnesium and magnesium alloys: It is the most likely candidate material for bone implants and biomedical applications because of its antitoxic nature. Its Young's modulus is also comparable to that of bones, helping to reduce stress shielding effect. They have high cell compatibility with macrophages thus enhancing tissue healing and efficiency of implants performance. Their implants dissolve in physiological environment and are eventually replaced by bones tissues eliminating the need of secondary surgery procedures [21]. Magnesium, being a soft metal, suffers from low corrosion resistance and low mechanical integrity. The excessive bodily corrosion of magnesium and its alloys when implanted in the human body risks inciting pathological reactions discouraging the alloy due to excess loss of mechanical strength and failure of the implants. Surface treatment is a common method to enhance the bioactivity of magnesium alloys and control their degradation rate [22,23].

2. Polymeric biomaterials

Polymeric biomaterials can be natural or synthetic, offers tuneable physical, chemical and biological properties, making them suitable for a variety of medical applications. They exist as bulk materials, coatings and pharmaceutical nanoparticles in drug delivery systems. Natural polymers such as horn, hair and cellulose have been used in medicine for ages, especially in suturing. Some of the major polymeric biomaterials with significance in orthopaedics include polymethyl methacrylate (PMMA), polyether ether ketone (PEEK), polylactide (PLLA) and ultra-high molecular weight polyethylene (UHMWPE). PMMA bone cements are widely used for various purposes such as denture implants, prosthetic bone, skull bone replacements, eye tags and kidney treatment membranes etc. UHMWPE is found in the acetabular components of total hip replacement systems, in the knee joint prosthesis systems, and in polypropylene mesh used for finger joints replacements, intravenous cannulas, and non-absorbable sutures [24]. Besides the dental and orthopaedic implants, silicone and other polymeric biocompatible materials are also used extensively in plastic surgeries [25,26].

3. Ceramics

Ceramic biomaterials are compounds made from metals, non-metals, metal oxides, nitrides, sulphides and carbides. They have high mechanical strength, better corrosion resistance, electrical insulation and chemical stability. There are three categories of ceramic biomaterials based on their interactions with physiological environment: bioinert, bioactive, and bioresorbable [27]. Bioinert ceramics like $A1_2O_3$ (alumina), ZrO_2 (zirconia), Si_3N_4 (silicon nitride) are chemically inert, causing minimal tissue reaction making them safe for use in articular components. They have high wear and compressive strength. The first highly pure alumina, Biolox® was obtained from chemically purified and grounded corundum powders by Erhard Doerre in the beginning of 1974 [28]. Bioactive ceramics such as cellulose and bioactive glasses bond well with bone but are often used as coatings on metal implants due to their inferior mechanical properties. Bioresorbable ceramics include calcium sulphate, calcium phosphates, and porous hydroxyapatite etc. They dissolve in the body and are gradually substituted with new tissue over time. Such materials do not promote inflammation and are effective in treating the bone fracture. Due to similarities between, bioactive and biodegradable ceramics, they are often researched simultaneously [27,29].

Table 1: Comparison of different types of biomaterials.

	Metals and alloys	Polymers	Composites	Ceramics
Type	Cobalt and its alloys, Stainless steel, magnesium and its alloy, titanium and its alloys etc.	Natural (collagen, silk, cellulose) and Artificial (silicones, polyethylene, polyamides)	Metal matrix composite, Ceramic matrix composite and polymer matrix composite	Bioactive, bioresorbable and bioinert
Benefit-s	High tensile strength, thermally and electrically conductive	Radiolucenc-y, high corrosion resistance, flexibility and adaptability	Customizability and enhanced properties according to the requirement	Excellent hardness, corrosion resistance, non-biodegradable and non-conductive
Issues	Less corrosion resistance, insufficient bio tolerance, material fatigue over time	Low wear resistance, tensile strength and mechanical strength	Complex processing	Brittle, low wear resistance, high stress shielding and less osseointegr-ation
Uses	Joint replacemen-t, spinal implants and bone fixation	Bone fixation, regeneration, and Cartilage, ligament and tendon repairs	Long bone (femur, tibia) fixation and artificial ligaments	Total hip replacement, total knee replacement, spinal implants and dental implants
e.g.	Ti-6Al-4V, Ti6Al7Nb, CoCrMo, 316L, 316LVM Stainless Steel etc.	PMMA, PLA, PVA, PCL, PEEK PVA–PVP co-polymers, UHMWPE etc.	Glass fiber composite, carbon fiber-reinforced polymers (CFRPs), bioactive ceramic composites etc.	Alumina (Al_2O_3), zirconia (ZrO_2), silicon nitride (Si_3N_4) and bioactive glasses etc.

4. Composites

Composites are the materials made up of two or more different constituents: the matrix and the dispersed phase. The matrix is normally ductile, weaker and ultimately surrounds the dispersed phase providing support to it. Together, these combinations climb the overall property of the material. The performance of composites relies on the shape, size and orientation of dispersed phase within the matrix. They offer great variety of mechanical and biological properties, effectively optimizing design and minimizing their impact on surrounding tissue [30]. They are considered beneficial due to their ability to vary elastic properties in order to provide better mechanical integration with bones or tissues but still possess high strength and endurance. For example, a more dynamic insulation system is provided through the use of carbon fibre reinforced epoxy plates. They are thinner and can be used where the support of broken bones is required to hasten their healing without introducing bulky interfaces. Composite biomaterials can be of the following variety of types: Ceramic Matrix Composite, Metal Matrix Composite, Polymer Matrix Composite and the materials known as advanced composites [14].

Methods of Preparation

Table 2: Comparison of methods for preparing biomedical materials.

Methods	Advantages	Limitations	Ref.
Electrodeposit-ion	Cost-effective, protective, less reactive and biocompatible layers formation	Some materials can't be easily deposited and hard control over size	[23]
Solvent Casting with Particulate Leaching	Good control over porosity and cost-effective used in bone and cartilage tissue engineering	Requires optimization, potential toxicity from solvents and gives limited mechanical properties.	[31-33]
Electrospinning	Produces fine, uniform fibers that mimic ECM, high surface area	Scalability issues, complex setup	[33, 34]
3D Bioprinting	Enables complex tissue structures, personalized applications	Maintaining cell viability and functionality	[33,35]
Phase Separation	Good for creating porous structures	Difficult to control pore uniformity	[33,36]
Melt Processing	Suitable for high-strength applications, good for thermoplastics	Limited to thermoplastics, high processing temperatures	[32,33]
Gas Foaming	Environment friendly, suitable for porous structures used in drug delivery and tissue engineering.	Challenges in maintaining pore uniformity	[32,33]
Sol-Gel Process	Produces bioactive ceramic materials, good for coatings	Time-consuming, potential shrinkage during drying	[31]

In order to prepare biomaterials materials, several advanced engineering techniques are employed. These techniques are directed toward achieving certain properties, such as biocompatibility, mechanical strength, or porosity. These techniques can be utilized in designing scaffolds, implants, and drug delivery systems. List of methods employed for preparing biomedical materials are shown in table 2.

Methods of improving biomaterials

Improving biomaterial properties is very crucial for successful integration and functionality in medical applications. Two significant methods to enhance their properties are coating methods and surface treatments.

1) Coating method: Coating methods involve applying a layer of material onto the surface of a biomaterial to improve its properties. Various types of coatings can be employed, including:

a. Biopolymer coating and bioceramic coating: Biopolymers, such as chitosan, alginate, hyaluronic acid, and bioceramics, such as calcium phosphate like dicalcium phosphate dihydrate (DCPD), hydroxyapatite (HA) and fluorinated hydroxyapatite (FHA) are often used for coating biomaterials. This is due to their origin and favourable interactions with biological tissues. These coatings can facilitate cell adhesion, proliferation, and differentiation, thereby improving the overall biocompatibility of the underlying material [37]. For example, chitosan promotes osteoblast adhesion and proliferation, making it a suitable candidate for orthopaedic applications. Calcium phosphate coatings like DCPD helps in bone regeneration, HA and FHA are used to improve resistance to decay, improve biocompatibility and promote osteointegration [38].

b. Hydrogel Coating: Hydrogels are hydrophilic polymer networks that can absorb significant amounts of water. Their coatings can enhance the biocompatibility by providing a softer, more flexible surface that mimics the extracellular matrix (ECM). This mimicry can improve cellular interactions, reduce inflammation, and promote tissue integration [39]. Hydrogels have been particularly effective in promoting cellular behaviour and facilitating drug delivery in various biomedical applications [40].

c. Antibacterial Coating: To reduce the risk of infection associated with implanted biomaterials, antibacterial coatings can be applied. These coatings often incorporate antibacterial agents, such as silver nanoparticles, which release ions that inhibit bacterial growth. This method not only improves biocompatibility but also enhances the longevity and functionality of the implant [41]. Antibacterial coatings have been shown to effectively reduce microbial colonization on surfaces, thus minimizing the chances of implant-related infections [42].

d. Bioactive Glass Coating: Bioactive glasses are a class of biomaterials that can bond with bone and stimulate healing. Coating metallic implants with bioactive glass can enhance their integration with surrounding tissues and promote osteogenesis, making them suitable for orthopaedic applications [3,43]. These coatings can also release ions that stimulate biological responses, improving overall biocompatibility.

2) Surface Treatment: Surface treatment improves the biomaterial by altering the physical and chemical properties at the nano/microscale level. These treatments can affect surface roughness, charge, and chemical composition leading to enhanced biological responses [44]. Some common surface treatment methods include:

a. Plasma-immersion ion implantation: When high voltage is applied to gas, they get ionized producing plasma. These ions are directed to the target substrate. The substrate is provided with high voltage bias attracting positively charged ions from plasma toward itself. The high energy ions cause them to penetrate into the surface of the substrate and hence the surface is modified. This process enhances surface wettability, improves surface roughness, and introduces functional groups that promote cell adhesion and growth. The treated surfaces can interact better with proteins and cells, leading to improved biocompatibility [45].

b. Chemical Modification: Chemical treatments involve altering the surface chemistry of biomaterials by applying various chemicals to introduce specific functional groups. For instance, salinization can be used to create surfaces with amino or carboxyl groups, enhancing protein adsorption and cell attachment. This method is particularly effective for improving the performance of implants in contact with biological fluids [46].

c. Surface Roughening: Creating micro- or nanoscale roughness on the surface of biomaterials can significantly enhance cell adhesion and proliferation. Techniques such as sandblasting, etching, or using laser treatments can create a roughened surface that mimics the natural topography of bone, leading to better osseointegration in orthopaedic and dental implants [12].

d. Biomimetic Approaches: This method aims at developing biomaterials that closely mimic/resemble the structure and functions of biological systems. Mimicking the natural extracellular matrix (ECM) can lead to improve cell attachment, proliferation, and biocompatibility. Techniques such as electrospinning and 3D printing can create fibrous structures resembling the ECM protein, promoting better cellular interactions and tissue integration. Additionally, modifying surfaces to present specific bioactive molecules can guide cellular behaviour, improving healing and integration [44].

Complexities of Biomaterial Implants

I. Due to difference in elastic modulus of biomaterials and bones, stress shielding becomes the major issue related to biomaterials.

II. The loading phase in biomaterials involving cycles of bending, twisting and shearing stresses, presents challenges in fatigue resistance, material degradation, and performance under multi-axial loading conditions.

II. With time many biomaterials start to release ions into the body that are harmful for the organs as well as for blood circulation. Inflammation from surgery or traumatism can usually cause ion deposits, thus making the situation surrounding the implants more severe.

IV. Over time, some of the biomaterials need to be replaced due to the decay or degrade of their properties.

V. The internal body fractures of implants usually become compromised due to the ions deposited from inflammation associated with surgical or injury procedures.

Future Aspects of Biomedical Materials

With the advancements in biomedical materials, several future trends are apparent.

I. Smart Biomaterials: These biomaterials are able to react to external stimuli such as temperature, pH or mechanical stress without harming the internal environment, allowing for customized solutions in medication practices like shape memory polymers. These polymers can change their shapes inside a body using body temperature. The week, self-expanding borne stents and scaffold for tissue regeneration were made from these polymers. Such characteristics of shape memory polymers make them a relevant innovation for future biomedical material design [44,47].

II. Bioprinting and 4D Bioprinting: In spite of the fact that 3D bioprinting has gone a long way into tissue engineering, 4D bioprinting is a relatively new technology that incorporates the time dimension. Thus, the materials that are printed can transform in shape or perform different functions after a period of time. One recent example is 4D bioprinting of aortic valve models that can open and close in response to blood flow [48,49]. This technique can be very beneficial for the advancement of biomaterials.

III. Nanotechnology and nanocoating's: The mechanical strength, wear and tear resistance, corrosion resistance etc. of orthopaedic biomaterials can be increased with the incorporation of nanotechnologies in the biomaterials. For example, HA nanocoating's are done to improve the osseointegration of biomaterials [50,51,52].

IV. Personalized and Patient-Specific Biomaterials: The progress in 3D printing technology and computational modelling has made it possible to create tailored biomaterials for specific patient anatomy. 3D printed implants can be designed for a complicated case of bone reconstruction using the patients CT or MRI scans and other information. Customized biomaterials allow for better adjustment and working efficiency of the device in the patient's body, and consequently minimizing the chances of rejection risk of the implant and its complications. Additionally, utilizing genetic and molecular information in biomaterial design further increases their compatibility with human tissue [53,54].

Conclusion

I. There has been a continuous evolution in the betterment of biomaterials. Metallic biomaterials are still playing their authentic role in orthopaedic implants due to their mechanical stability. Furthermore polymeric, composite, ceramic biomaterials are also being utilised for their biocompatibility, osseointegration and corrosion resistance properties respectively.

II. Surface treatments and coating methods aimed to enhance implant functionality are being utilised for improving biomaterial properties as well as for their customize use. These treatments help to promote better integration with biological tissues, reduce infection risks, and increase the durability of implants.

III. With the advancements in biomedical materials, several future trends are apparent. These consist of the emergence of functional biomaterials or smart biomaterials, better development of bioprinting, and the use of nanotechnology across drug delivery systems and tissue engineering. It is also anticipated that customized and green materials will be integral in enhancing medical technologies of the future.

As ongoing research advances, orthopaedic implants will become increasingly safe, versatile, and tailored to meet the specific needs of patients, offering substantial improvements in both patient care and quality of life.

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