REVIEW ARTICLE

Dental biomaterials and a novel composite of Zirconia and Poly Ether Ether Ketone [PEEK] for dental implants

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Article Code: IDJSR 0126

Quick Response Code

Abstract

Restorative materials [filling, denture and implant materials] are designed to replicate the shape and function of natural teeth. Development in materials science, biotechnology, nanotechnology, robotics and biomechanics has dramatically improved the way we look at the replacement of components of human teeth. Restorative biomaterials are the foundation for the replacement of hard tissue and it is unique because of the complexity of the oral cavity, which includes microbial presence, high forces, ever changing pH and a warm and cold fluid environment. Success of a restorative biomaterial depends on its physical characteristics like mechanical properties, thermal properties, electrical properties, electrochemical properties, color, optical properties, and biological characteristics like biocompatibility along with local tissue physiology and systemic comorbidities of the recipient. In this literature review we comprehensively analyze the ideal properties required for a successful dental implant material, limitations in present implant material and novel approach to manufacture a stress shielding free dental implant.

Keywords: Dental implants**,** Stress shielding**,** Restorative materials**,** Prosthodontics**,** Functionally graded implants

Introduction

A major part of today's dental practice deals with repairing and/or replacing missing tooth structure(s). The material which used to repair or replace the lost or missing part of teeth either partially or completely is called as dental restorative biomaterial. Classification of hard tissue replacement procedures are shown in figure1.

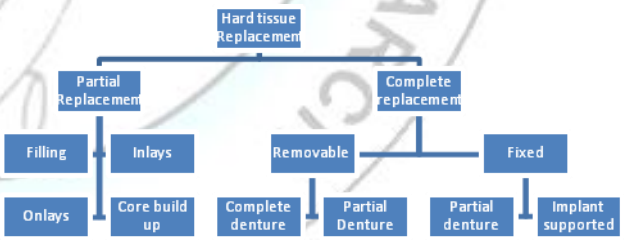

Figure 1 Classification of Hard tissue replacement treatment procedures.

Dental implants have a centuries-long history; indeed there is evidence that prehistoric peoples sought this technology. As dentistry progressed in the past century, experimental implant designs focused on materials and techniques that might serve as quality anchorages for conventional dental prostheses[1]. By the mid-20th century, a number of sophisticated techniques had been developed, including subperiosteal, transosteal and blade

implants[2]. Highest degree of interplay between biological and physical properties of a material is needed in case of replacing entire tooth or multiple teeth using dental implant. Many times the biomaterial fails clinically because of fracture or deformation. The reasons for such failure are either due to failure of compliance by the patient or inability of the biomaterial to match the physical and the biological requirements[2]. Factors like detailed understanding of the biological environment, exposure to various functional and para-functional forces, condition of the tissues receiving the material and medical co-morbidities should be always considered while developing and selecting a biomaterial.[1]

In recent decades predictable dental implants were introduced and have revolutionized dentistry. However, none of these were able to meet the all ideal requirements of the implant material. In this comprehensive review we will discuss in detail the successful requirements of a dental implant biomaterial, current limitations and novel approach to overcome the some of the limitations faced by the most of the present dental implants.

The requirements of successful implant biomaterial include: biologic compatibility, mechanical compatibility, morphologic compatibility, imaging and esthetic compatibility[1-6].

Biologic Compatibility

Like color, biocompatibility is not a property of just a material, but rather a property of how a material interacts with its environment. A material's color depends on the character of the light source, how the light interacts with the material, and how the observer interprets the reflected light.[2] In this sense; the material's color depends on its environment. Similarly, biocompatibility of a material depends not only on the nature of the material but also on its environment[2] All intraorally placed parts are in continuous interaction with saliva [an aqueous solution of about 0.1N chlorides with varying amounts of sodium, potassium, calcium, phosphate, carbon dioxide, sulphur compounds and mucin]. The pH 5.5 to 7.5, temperature fluctuation of ±36.5°C and exposure to a variety of foods and drinks are added challenges, exclusive to oral environment. Loads may be up to 1000N [average masticatory force 150 N- 250 N] [2,3]. With such hostile conditions, the implant biomaterial should be corrosion resistance. It should not show any immune response, mutagenicity, carcinogenicity or teratogenicity. Moreover, it should exhibit satisfactory bio adhesion and no cytotoxicity. On the other hand this should also be compatible with various pre-existing or potential medical conditions like osteoporosis, diabetes mellitus, xerostomia, immunodeficiency conditions[4,6].

Mechanical compatibility

There should be smooth transfer of stress. Many times the biomaterial fails clinically because of fracture or deformation. So the stress plays a major role in making a biomaterial successful for its application as dental implants. The combination of forces and their corresponding displacement are unique to each patient. These factors should be considered in developing new implant biomaterial. Tensile, compressive and shear are the various stresses and their corresponding deformations should be considered in designing dental restorative material. The material should be mechanically compatible to mechanical properties of receiving tissue in order to minimize the interfacial discrete stress. The mechanical properties like formability, adhesion, tensile strength, compressive strength, ductility, fatigue resistance, wear resistance, young's modulus, toughness and the physical properties like density, thermal conductivity, electrical conductivity, optical property, thermal expansion are considered for any material to be used as dental implants[3-8].

Morphological Compatibility

Surface morphology plays an important role in biological interactions of the implant material to promote growth. If a particle size is smaller than 10 micron the surface will be more toxic to fibroblastic cells and have an adverse influence on cells due to their physical presence independent of any chemical toxic effects[4]. If the pore is larger than 500 micron the surface zone does not maintain sufficient structural integrity because it is too coarse[4]. Of all the cellular response, cellular adhesion is the most important response necessary for developing structural and functional integrity at the bone and implant interface[5]. It alters the entire response to biomaterials. Surface roughness in the range 10nm to 10 micron influences the interfacial biology[6,7]. As it is the same order as the size of the cells and large biomolecules. Micro roughness at this level includes material defects, such as grain boundaries, dislocation steps and kinks and vacancies that are active sites for adsorption and therefore influence the bonding of biomolecules to the implant surface. Micro rough surfaces promote significantly better bone apposition than smooth surfaces, resulting in a higher percentage of bone in contact with the implant. It may influence the mechanical properties of interface, stress distribution and bone remodeling[7,8]

Imaging Compatibility

Once placed, the dental implant should be radiologically distinguishable from its neighboring

tissues as this will aid in evaluation of the implant and the nearby tissue in future. On the other hand, MRI provides essential and potential lifesaving information, so the dental implant biomaterial should be Ferro-magnetically compatible with imaging systems[2].

Esthetic Compatibility

With modernization of dentistry, today's market is not only looking for functional and spatial replacement for teeth, but also for substitutes that are visually as natural as possible. Though, dental implants are inside the bone, their optical properties have significance, owing to the translucent cortical plates and thin gingiva that cannot camouflage the color of the implant material. Also, under ideal circumstances implanted part should not be visible, any exposure of the implant should not be drastically unpleasing to cause discomfort to the patient. Hence, the implant biomaterial should be esthetically pleasing if it is visible and should be esthetically compatible with the adjacent tooth and tissue [2,4].

Limitations of currently used biomaterials for dental implants

Currently titanium and titanium alloys are the material most often used in implant manufacturing and have become gold standard[1]. Though it is proven as biocompatible, accumulation of titanium in the inner organs and lymph nodes has been reported[9-10]. Galvanic side effects after contact with saliva have also been reported[9]. Although allergic reactions to titanium are rare, cellular sensitization has been demonstrated[10]. Despite numerous modification to fabrication and design of titanium implant and abutments there is still the disadvantage of its unnatural dark grayish color which often is visible through the peri-implant mucosa, therefore impairing esthetic outcomes in the presence of a thin mucosal biotype[9]. The long term success of dental implant depends mainly on minimizing the amount of marginal bone loss after several years of functional loading. Even though the improvements of surface treatments and design modification provided somewhat improved results concerning marginal bone loss, still the problem exists. This is mainly because of the incapability of the implant biomaterial to meet the mechanical property of the host bone tissue. The elastic modulus of titanium and zirconia are 110 Gpa and 210 Gpa respectively which are 5-14 times greater than that of compact bone [15 Gpa] [11,12]. Because of this stiffness, implants do not adequately strain the bone which can result in disuse atrophy and bone resorption. This phenomenon is referred as stress shielding and is an important cause of long term failure of dental implants. Moreover the problems associated with the present, coated metallic implants consist of stress shielding of the surrounding bone and poor survival of coatings over time, resulting in severe biocompatibility issues[10-16]. The long term success of implants requires not only osseous integration but also the establishment of a mucosal barrier around the implant to generate a sufficient seal between the oral cavity and bone margin. This is compromised with titanium dental implants. One more problem with titanium implants is fracture of implant parts due to stress transfer pattern. As a result of this force and stiffness of the implant the marginal bone loss is also a problem in long term. The comparison of mechanical properties of implant material and bone is shown in figure-2.

Materials	Young's Modulus [GpA]	Poisson's Ratio	Density[kg/m^3]
Cortical bone	14	0.3	1700
Cancellous bone	3	0.3	270
Titanium	110	0.35	4500
Hydroxyapatite	40	0.27	3219
Zirconia	200	0.31	6000

Figure 2 Materials and bone properties [13]

In addition; titanium implants are known to cause image distortions in MRI scans, in other words these are not MRI compatibility, in case patient needs an MRI in future, the implant has to be removed and thereby causing heavy loss to the patient in means of financial as well as function[10]. To summarize the challenges faced by the current implant material and the need to look for new implant biomaterial are as follows[10-16]

1. Esthetic incompatibility with titanium and its alloys.
2. Stress shielding causes marginal bone loss
3. Galvanic side-effects with titanium implants.
4. Risks of immunogenicity.
5. MRI incompatibility
6. Fracture of implant components in long term use.
7. Soft tissue incompatibility with titanium implants as a result incidence of peri-implantitis is high.

Zirconia and PEEK composite as novel implant biomaterial

A single composition with a uniform structure cannot satisfy all the requirements mainly the challenges as said above. To improve the acceptance and long term success of dental implants, the concept of functionally graded material [FGM] is a favorable approach[13]. FGM is a heterogeneous composite material including a number of constituents that exhibit a

compositional gradient from one surface of the material to the other subsequently, resulting in a material with continuously varying properties in the thickness direction. Therefore FGM is useful as the composition of tissue shows a continuous change from one composition to another. For example the suitable design of porous bone with a porosity gradient from a dense, stiff external structure [the cortical bone] to a porous internal one [the cancellous bone] and with an adequate degree of interconnectivity exhibits that functional gradation is applied by biologic adaptation. So in our novel implant biomaterial we intend to develop a material that has sufficient mechanical strength to bear the occlusal force, whereas the part inside the jaw bone must have stress relaxation and adequate bone-implant contact so that the new bone attaches directly to it. The primary advantage of zirconia and PEEK composite implant biomaterial include

1. Improvement of biocompatibility.
2. Diminution of the stress shielding effect on the surrounding bones that regularly occurs.
3. Improvement of biomechanical requirement.
4. Esthetic compatibility.
5. Precluding the marginal bone loss and peri-implantitis by reducing the micro gap between implant and soft tissue interface.
6. Added advantages like no galvanic side-effects, lack of immunogenicity and MRI compatibility.

Because of its less inflammatory response, better stabilization of soft tissue contact, lower plaque retention capacity, higher affinity to osteoblasts and esthetic tooth color, 3 mol% yttrium oxide tetragonal stabilized zirconia is a viable alternative of titanium implants. The zirconia implants has high bending strength, resistance to scratching, eliminates micro gap and micro motion on crestal interface of bone and soft tissue[10,15,16]. It is image compatible [MRI] [10]. Though zirconia seems to satisfy six out of seven challenges mentioned before, the main challenge stress shielding will be a major issue as the elastic modulus is 14 times higher than the cortical bone. In order to reduce the elastic modulus we need a material which can be compatible with zirconia and elastic modulus close to cortical bone. The literature search suggest us the Poly ether ether ketone [PEEK] has the above property which can help zirconia to neutralize the stress shielding property[12,16]

Rationale for choosing Zirconia

Zirconia is a bioinert and nonresorbable metal oxide that offers mechanical properties that are similar to titanium[9-10]. The inflammatory reaction and bone resorption provoked by zirconia particles are less than those influenced by titanium particles. It is a polymorphic crystal that can be found in three crystallographic forms Monoclinic, Tetragonal and cubic. [17]

The attraction of stabilizing doping agents like CaO,MgO, CeO, Y2O3 to pure zirconia allows the production of multiphase material known as partially stabilized zirconia[PSZ]. PSZ mono structure consists at room temperature of a cubic zirconia matrix with minor tetragonal and monoclinic zirconia precipitates. Zirconia stabilized with yttrium oxide has best properties suitable for implant applications. When a stress occurs on yttrium stabilized zirconia surface, cracking energy creates a T-M transition. This crystalline modification is followed by an expansion that seals the crack. It has better mechanical properties than other combinations of Zirconia. To summarize; Zirconia has following advantages[9-10]:

1. High biocompatibility and osseointegration.
2. Great flexural strength
3. Sufficient hardness
4. High fracture resistance
5. Low bacterial adhesion than titanium
6. Minimal reaction with adjacent living tissue
7. Very low thermal and electrical conductivity
8. Chemical inertness
9. Minimal biodegradation
10. Ability to transmit light
11. No allergic abilities

However, following are the limitations of Zirconia:

1. High modulus of elasticity
2. Inability to withstand tensile stress
3. Tedious sintering process

Figure 3 Mechanical properties of ceramics & PEEK used in biomedical application [2]

Property	α - Al_2O_3	ZrO_2 [Y-TZP]	ZrO_2 [Mg-PSZ]	Dense hydroxy apatite [HA]
Bending strength [MPa]	595	1000	800	20-80
Compressive strength[MPa]	4250	2000	1850	100-900
Young's modulus[GPa]	400	150	208	70-120
Hardness [HV]	2400	1200	1120	500-800

Property	PEEK	PEEK 30% short fibres
Young's modulus[GPa]	3.6	13
Tensile strength[MPa]	92	210

Rationale for choosing PEEK

Poly ether ether ketone [PEEK] polymer is a tough, semicrystalline and poorly soluble material with high melting temperature[16]. Its crystallinity contributes to its excellent chemical resistance, mechanical properties and high service temperature. PEEK is a polymer from group polyaryl ether ketone. It is a high temperature thermoplastic polymer consisting of an aromatic backbone molecular chain interconnected by ketone and ether functional groups[12,16]. The poly ether ether ketone is of great interest as an alternative to titanium because of its biocompatibility and low elastic modulus. Study revealed that bone contact area for PEEK is 51.55% which is comparable to titanium[16]. Because of fiber reinforced PEEK has greater strength on a per mass basis than many metals with a low elastic modulus it can reduce stress shielding when compared traditional metal implants. Other advantage of PEEK as a biomaterial includes its excellent biocompatibility, outstanding bio stability, and resistance to high energy radiation such as gamma rays/x rays, good dimensional stability, natural beige color and reduced magnetic resonance imaging artifacts[12,16] Since the fatigue resistance is not as great as showed in literature, it can't be used alone as dental implants as of now. Whereas dental implants with PEEK coating reduce stress shielding effects[12,16]

Manufacturing the Zirconia and PEEK composite Dental implant

As discussed, Zirconia and PEEK are two materials with different chemical and physical properties. Combining these constituent materials into a single composite has potential to yield better material with superior characteristics. Based on Finite element analysis, the percentage of required PEEK composition is determined based on how close the elastic modulus of Zirconia combined with PEEK is achieved compared to elastic modulus of alveolar bone and corresponding decrease in stress shielding. The other mechanical and physical properties are also taken into consideration before proceeding to manufacturing stage. We consider two methods to manufacture our novel implant biomaterial

1. Spark plasma sintering.
2. Selective laser sintering.

Spark Plasma sintering:

Spark plasma sintering[SPS] or field assisted sintering technique[FAST] or pulsed electric current sintering[PECS] is efficient for any powder material application especially for nanocrystalline structure. It enables sintering of not just all forms of conventional powdered metals, but most form of ceramics, polymer, composites and porous materials. It is capable of sintering similar and functionally graded materials, seamless bonding and material surface treatment[20].

SPS operational temperature [200-2400* c] classified as low temperature sintering technology. The relatively low temperature combined with fast processing time ensures tight contact over grain growth and microstructure. The Dc pulse input used is 20 V and 1500 amps. The sintering pressure ranges from 5 to 50 KN. The sintering is done under ambient air, vacuum/inert gas [argon gas].Overall duration of the process is 5 to 20 minutes. The advantages of SPS are fast and uniform sintering, low grain growth, compaction and sintering in one process, binders are not necessary, better purification, easy operation and different material may be processed. The main disadvantage is that only simple symmetrical shape is possible[20,21].

Once zirconia and PEEK are combined after the sintering, the blocks are subjected to milling to get the desired shape of the implant using the virtual library. Thus customized patient based implants, are possible by sending the images [MRI /CT images] to the milling structure similar to crown fabrication [iTERO]; and the implants are milled to the desired size. The challenge we may face is the melting temperature of PEEK, as SPS operating temperature may reach 1000's of C momentarily, how much polymer is lost in function is not yet known. It has to be studied. The second method we would like to consider is selective laser sintering.

Selective laser sintering [SLS]:

It is additive rapid manufacturing process by using a laser to selectively sinter [heat and fuse] a powdered material. SLS uses high pulsed carbon dioxide laser to fuse small particle of plastic, metal, ceramic, glass powder into a mass that has desired 3-D shape. It enables the direct manufacturing of products with complex generation[21]. Laser selectively fuses powdered material by scanning cross section generated from a 3-D digital [from CAD file, in our case it is patient CT image] on the surface of a powder bed. After each cross section is scanned the powder bed is lowered by one layer thickness a new layer of material is applied on top and the process is repeated until the part is

completed. Unlike other additive manufacturing process like sterolithiography [SLA] and fused deposition modeling [FDM] SLS do not require support structure. This is due to the fact that the part being constructed is surrounded by unsintered powder at all times. This allows for the construction of previously impossible generations. The main challenge with this technique will be not feasible for large scale production. But the main advantage here will be combining the materials and milling to desired shape will be done in single step. Thus implants can be designed similar to cortical bone in case SLS proved to be better manufacturing process in the feasible study to mimic the Osseo incorporation that means both on growth and ingrowth[22].

Summary and Conclusion

Attempts to replace hard tissue of teeth with implanted materials have been observed in ancient human remains. This has been documented in the dental literature since 19th century. Dental implants vary in material dimensions, geometries, surface properties and interface geometry. At present there are more than 2000 different dental implants are available in the market. Certain manufacturers alone offer more than 100 different implants in varying shapes and materials[6]. Even though so many implants are available still the quest of ideal implant biomaterial is not yet met. The most common failure mechanism seen with present implant system is alveolar crest resorption. A tangible number of implants do not survive for long term function[4]. This is because none of the present implant biomaterial is both physically and biologically compatible with the alveolar bone. Many biocompatible materials are not considered due to their lack of strength to withstand the masticatory forces. In order to continue the function and survive both ultimate tensile strength and modulus of elasticity must be considered[5]. Unless bone experience at least 50 micro strain on a routine basis it will begin to resorb[6]. The main goals of all dental implants are rapid return to its primary function [i.e. mastication], stronger, safer Osseo integration and long term fixation of implants to bone. To achieve these goals, the design of the implant must fulfill certain biomechanical and biomaterials characteristics including in vitro and in vivo performances on implants, mechanical compatibility to test smooth transfer of the stress between the placed implants and receiving hard and interfacial tissues and the response of latter[2,5,6,10,13]. Functionally graded materials shows promising results and this can be successfully applied to dental implants[13]. The present and future dental implant biomaterial research should target towards the compatibility, decreasing the stress shielding and optimal bone loading . The proposed zirconia and PEEK composite implant design could aid in improving the long term success of dental implants by minimizing the stress shielding and close mechanical compatibility to adjacent biological tissues.

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