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Novel innovations in dental implant biomaterials science: Zirconia and PEEK polymers

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Abstract
Recent drive towards metal-free tooth coloured aesthetic dental implants had led researchers to search for potential substitutes of the "gold standard" dental implant material titanium, and consequently, zirconia and PEEK polymers have been introduced in this regard. Both these materials are aesthetically pleasing, highly biocompatible and have the potential to osseointegrate *in vivo*. However, routine clinical use of these dental implant materials is still faced with some challenges. Nevertheless, current research works are very much focussed on overcoming their limitations and optimizing their properties. The present article provides an insight into the structural and compositional properties of these materials, their limitations and clinical use, biomechanical perspectives and the scope of future research works and developments.

Keywords: Bioinert, Stress shielding, Transformation toughening, Low Temperature degradation, Bio HPP, CFR-PEEK

Introduction

Amongst all other dental implant materials available, titanium and its alloys stand distinguished owing to the several desirable properties they possess; that enable them to score over other biomaterials. This in light of favourable long term clinical survival rates reported in literatures has made titanium the "gold standard" material for the manufacturing of endosseous dental implants. However, one of the principal disadvantages of titanium is its dark greyish colour, which is often visible through peri-implant mucosa, therefore impairing aesthetic outcomes in the presence of thin gingival biotypes [1], particularly in the anterior segments of maxillary dentition [2]. Another problem relates to the allergenic potential of titanium. Allergies to titanium in medical literatures have been reported [3] but whether the findings of these studies can be extrapolated to the oral cavity and dental implants is debatable [4]. However, a review article concluded that titanium could induce hypersensitivity in susceptible individuals and might play a critical role in causing implant failure in such patients [5]. The modulus of elasticity value of titanium is significantly higher compared to human bone that can lead to a stress shielding effect which ultimately results in peri-implant bone atrophy and aseptic loosening of implants. These limitations of titanium coupled with increasing demands of the patients for metal-free dental implants led researchers to search for substitutes of titanium and consequently Zirconia and PEEK implants have recently been introduced in the dental implant industry.

Ceramics have a long history of usage in dental implant industry as bio-inert or bioactive coatings but their inherent brittleness and low fracture toughness limited their usage as implant bulk material. However, the recent drive towards ceramic dental implants have been attributed to the introduction of high strength toughened ceramics, particularly the yttrium – stabilized tetragonal zirconia polycrystals (Y-TZP). These materials in addition to good mechanical properties exhibit excellent biocompatibility, superior esthetics and low plaque affinity [1]. The first zirconia dental implant system was introduced in 1987 under the trade name Sigma implant (Sandhausen, Intermed, Lausanne, Switzerland). Since then, other systems like CeraRoot system (Oral Iceberg, Barcelona, Spain), Re-Implant system (Re-Implant, Hagen, Germany) and Z-systems (Z-systems, Konstanz, Germany) have also been made commercially available. Due to material limitations, these implant systems manufactured are one piece implant systems but recently two-piece zirconia implant systems like SDS® and Zeramex® are also emerging with promising results.

Polymers used in dentistry are in general bio-tolerant materials that exhibit poor adhesion to hard and soft tissues. Initially, they got popularity in dental implant industry mainly as inserts for dampening force transfers such as those used in IMZ (Interpore, Inc) and Flexi-root (Interdent Corp.) systems. However, the popularity remained short-lived due to poor mechanical properties of these materials which resulted in inadequate long term performance and high time and cost associated with the maintenance of such devices. Recently, two significant developments have restored the interest in polymers as dental implant materials and this time even as implant bulk material. One of them have been the addition of a new polymeric material - PEEK(polyether ether ketone) to the list and the other being the art of combining polymers and other categories of synthetic biomaterials either as composites or as surface coatings to improve mechanical properties and tissue attachments. PEEK polymers have been in orthopaedic field for several decades and found their way into dentistry in the last decade of 20th century first as aesthetic restorative material and later as implant fixture material. In addition to its superior mechanical properties compared to other polymeric materials, what distinguishes PEEK from other polymers is that quite unlike other polymers which are bio-tolerant materials and exhibit fibro-Osseo integration, PEEK polymers exhibit bio-inert behaviour and has the capability to Osseo integrate *in vivo* [6]. Nevertheless, the BIC percentages are found to be lesser than Titanium and Zirconia dental implants. Current researches are focused upon increasing their limited bioactive and Osseo integrative potentials through surface coating technologies.

Structural properties and their implications

Pure unalloyed zirconia is chemically Zirconium dioxide (ZrO_2) and at ambient pressure exhibits three different crystallographic forms depending upon temperatures – up to 1170 degree C the structure is monoclinic, between1170 degree C to 2370 degree C it assumes a tetragonal crystal form and from 2370 degree C up to the melting point it exhibits a cubic structure. Alloying pure zirconia with stabilizing oxides, such as CaO, MgO, Y2O3 or CeO_2, allow the retention of metastable tetragonal structure at room temperature [7]. The most common stabilizer used for dental applications is Yttria (Y_2O_3) and the addition of 3-5 mol% of Y_2O_3 results in stabilized core ceramic referred to as yttrium-stabilized tetragonal zirconia polycrystals [8].Surface flaws in the form of cracks or fissures, incorporated during industrial manufacturing or dental procedures, fails to propagate as applied load causes stress concentration at the crack tip leading to conversion of tetragonal phase to monoclinic phase accompanied by 3-5% volume increase. The volumetric expansion induces compressive stress and put crack into compression, closing the tip and retarding its growth, thereby enhancing the fracture toughness of the material. This phenomenon is referred to as transformation toughening and accounts for the high fracture toughness of yttrium-stabilized tetragonal zirconia polycrystals (Y-TZP) [9].

A related but undesirable phenomenon has also been linked with the tetragonal to monoclinic phase conversion of zirconia known as Low Temperature Degradation (LTD) or Aging of zirconia. LTD is a low temperature negative phenomenon which occurs as a result of slow surface transformation of the metastable tetragonal crystals to the stable monoclinic structure in the presence of water or water vapour by stress corrosion mechanism [7]. This conversion ultimately results in a cascade of events as the transformation of one grain results in local volume expansion and causes stress to neighbouring grains. Due to the stress the neighbouring grains also transform into the monoclinic phase. The sudden volume expansion leads to swelling of the surface and uplifting of the grains creating micro-gaps along the grain boundaries through which water molecules penetrate into deeper layers and the cycle continues culminating in micro- and macro-cracking of Zirconia [10, 11]. Though some *in vitro* and *in vivo* studies [12, 13] have shown that aging does not affect the clinically related mechanical properties of zirconia even if some *t-m* phase transformation has occurred, as this degradation process is extremely slow, however, a notable feature of this phenomenon is that it occurs at an accelerated rate in the temperature range of 200-300 degree C [7]. The clinical relevance of this came to light when dramatic failures of several hundred hip prosthesis in 2001 were linked to this accelerated aging procedure. Steam sterilization in the autoclave had caused the degradation in certain batches of Prozyr® zirconia ball heads which led to dramatic failures [14]. Thus, the importance of accurate processing techniques in avoiding accelerated aging as compared to normal aging process in Zirconia implants came to be very well recognized. LTD depends on several processing factors like porosity, residual stress, grain size, stabilizer content and sintering temperature [7]. Variability in these factors can bring about variability in LTD resistance of Zirconia implants.

Polyetheretherketone (PEEK) is a semi-crystalline aromatic high temperature thermoplastic material belonging to the family of polyaryletherketone (PAEK) and has the basic formula (- C_6H_4—O-C_6H_4—O- C_6H_4—O-) n. The chain of aromatic ring structure gives PEEK good mechanical strength, high inertness and resistance to chemical erosion. Furthermore, its properties can be altered to suit the biological demand by addition of others materials such as carbon fibres (carbon fibre reinforced/ CFR-PEEK) and ceramic micro-particles fillers (Bio-HPP).). For example, the modulus of elasticity of PEEK is about 3.6 GPa [15], by reinforcing it with carbon fibres (CFR-PEEK), the modulus value can be increased up to 18 GPa to match that of cortical bone[16]. Similarly, BioHPP (High Performance polymer) contains about 20% ceramic filler particles with grain size 0.3µm to 0.5µm dispersed in PEEK polymer matrix [17]. Due to the very small grain size of the ceramic particles, constant homogeneity can be produced which accounts for the excellent mechanical properties of these materials.

From the biomechanical point of view, PEEK materials can be considered superior to other implant biomaterials due their young's modulus value being in closest proximity to bone than any other material. They flex iso-elastically with bone which may result in homogeneous distribution of load, minimal stress shielding effect and prevention of stress concentration. Their close proximity to natural teeth colour imparts good aesthetic properties and make them suitable for use in anterior segments of jaw. Besides, Kistler *et al* [18] in their research works have shown that Bio HPP is extremely resistant to abrasion and has excellent colour stability and anti-discoloration properties. Their low solubility in water and low reactivity to other materials makes them particularly suitable for use in patients with allergies [19]. PEEK materials are also amenable to CAD-CAM technology [20]. PEEK dental implants are radiolucent in nature and their radiolucency can of considerable benefit to patients who has to undergo MRI scan as it will result in fewer artifacts during imaging.

Surface modification methods

Non-modified surface of zirconia implant is bio-inert with osteoconductive potential that can allow apposition of bone on to its surface when in contact with it [21]. In an in- vitro study, it was found that zirconia grains can serve as a nucleation site for calcium based minerals such as hydroxyapatite and cauliflower-like growth of calcium phosphate minerals can be seen to spread over the whole surface of zirconia[22]. Results of several studies have demonstrated that surface modifications of zirconia implants can bring its Osseo integration potential at par with titanium implants [23, 24, 25]. However, surface modifications of zirconia implants is more challenging compared to titanium implants due to it high hardness value, sensitivity to surface cracks and LTD phenomenon. Nevertheless, common methods employed for surface modifications of zirconia dental implants include sandblasting, acid etching, a combination of sandblasting and acid etching and laser treatment. The ICE surface of Ceraroot® Dental Implant System (Oral Iceberg, Barcelona, Spain) is acid etched. The ZLA surface of Straumann® PURE Ceramic implant (Straumann AG, Basel, Switzeland), the ZERAFIL™ surface of Zeramex® ceramic implants (Dentalpoint AG, Spreintenbach, Switzerland) and the SDS® implant surfaces are sand blasted and acid etched while the SLM surface of Z-systems® ceramic implant (Z-systems, Konstanz, Germany) is laser modified.

Non-modified PEEK is a bio-inert material [26] like zirconia but quite unlike zirconia, PEEK is devoid of any osteoconductive potential. Also, PEEK is hydrophobic in nature with water contact angle of 80-90 degree C [27]. Hence, surface modifications of PEEK are geared towards enhancing their bioactivity, hydrophilicity, surface free energy and roughness values. Melt blending of PEEK with bioactive nano-fillers such as nano-particle titanium dioxide ($nTiO_2$) and nano-particle fluorohydroxyapatite (nHAF) to produce bio-active PEEK composites has been described by Wan *et al* [28] and Wu *et al* [29]. Such PEEK composite such as PEEK-$nTiO_2$ and PEEK-nHAF exhibit superior mechanical properties and enhanced bio-activity. Attempts have also been made towards nano-modifications of the PEEK surface with little or no effect on the core. Some of these nano-modification methods include spin coating of PEEK implants with nano-hydroxyapatite (n HAP), plasma immersion ion-implantation (PIII), electron beam deposition and gas plasma nano-etching [20]. Among these, a significant advantage of gas plasma nano-etching technology is that besides incorporating nano-level roughness on the implant surface, it also render the surface extremely hydrophilic with water contact angle approaching 10 degree [30]. Besides, since there is no coating involved in plasma-etched implants, there is no risk of delamination of these coatings. However, it has been observed that the induced effects of gas plasma etching on the surface properties of PEEK implants is temporary and diminishes over time[30]. A study showed that treating PEEK with pulsed Nd: YAG laser before gas plasma etching can prolong the effects [31].

Sterilization methods

Due to susceptibility to LTD, quite unlike titanium implants, steam sterilization is not a very popular method of sterilizing zirconia implants. Zirconia dental implant manufacturing companies these days rely on alternate sterilization methods such as plasma or chemical sterilization which are gentler to the material to avoid any compromise of the bulk material properties. Z-system ceramic implants (Z-systems, Konstanz, Germany) are plasma sterilized, Coralroot® Dental Implant System (Oral Iceberg, Barcelona, Spain) and Straumann® PURE Ceramic implant (Straumann AG, Basel, Switzeland) are sterilized in ethylene dioxide. Zirconia changes in beta, gamma or other high energy radiation its color from white to black, gray, purple or pink so zirconia dental implants are excluded from gamma sterilization [32].

PEEK materials can withstand high temperature and are amenable to steam sterilization [33]. They are also resistant to radiation and chemical attack and can be sterilized by gamma radiation and ethylene oxide without structural damage [33, 34].

Discussion

Despite significant improvements in their properties being made, zirconia still remains a brittle ceramic material with vulnerability to surface flaws and manufacturing errors. Material flaws usually assume the form of pores or micro cracks of sub millimetre scale [35]. Such flaws in the presence of high bending movements of biomechanical overload can initiate crack propagation and result in early implant failure [36].Therefore special considerations, clinical expertise and strict quality control during manufacturing is necessary to improve clinical outcomes with zirconia implants. The use of reduced diameter (3.25 mm) zirconia implants should be avoided [36]. Slight over-preparation of the osteotomy site is recommended to avoid the need for hand torqueing and, thus, the possible unfavourable bending forces on the implants [37], especially in dense bone. As occlusal load induced bending moments increase with bone loss, any rapid marginal bone loss should be investigated for possible mechanical complications, including fixture fracture [38].

Majority of the zirconia dental implants currently available in the market are one-piece system. This has its own potential disadvantages. Firstly, it leaves no scope for use of angled abutments in case the surgical placement of implant fails to meet the prosthodontic requirements. Secondary, there is absence of conventional submerged healing phase with these single –piece implants. The implants are immediately exposed to forces from tongue and mastication [39] and this becomes critical in case the implant placement fails to meet the primary stability criteria. Thirdly, cementation remains the only option to connect prosthesis to these single piece implants. Technical and biological complications are found to be more frequent if the restorations are cemented rather than screw retained [40]. And lastly, single piece implants often necessities the need to adjust the shape and size of the abutments through grinding which severely affects the fracture strength of Zirconia [41].

Until now, only few short term clinical reports are available with zirconia dental implants which provide satisfactory results. Controlled clinical trials with follow up of 5 years or longer are necessary to properly evaluate the clinical performance of zirconia implant and to recommend them for routine clinical use [1]. On the basis of short term studies available, following inferences can be drawn:

i. Osseo integration levels and soft tissue response for Zirconia implants may be comparable or even superior to those of titanium implants[23-25,42]
ii. They were found to have low, well distributed and similar stress distribution when compared to titanium implants [43].
iii. Coated or surface modified zirconia implants showed higher removal torque value than machined zirconia implants [44, 45].

Thus, we see that zirconia despite being an aesthetic implant material with excellent biocompatibility, good mechanical properties and Osseo integration potential, suffers from certain limitations such as high elastic modulus value (210 GPa), high manufacturing cost, high vulnerability to surface flaws and LTD. Consequently, PEEK polymers have been added as an additional substitute to esthetic implant material list. One of the greatest possible advantages of PEEK over zirconia and other implant materials is the closest resemblance of its mechanical properties to bone which may significantly reduce the stress shielding effect and increase the clinical longevity of implants. However, a 3-dimensional finite element comparative study performed between titanium implant and CFR-PEEK with 30% carbon fibers (achieving an elastic modulus value of 17.4 similar to cortical bone) demonstrated otherwise [46]. The CFR-PEEK implants presented higher stress concentration in the cervical area and at the cortical bone than titanium implants and so the investigators concluded that the CFR-PEEK does not present any advantage over titanium implants in terms of load distribution.

CFR-PEEK is a versatile foundation material whose bulk properties can be altered to match the desired need by varying the percentage addition of carbon fibers. For e.g. CFR-PEEK can have the whole range of elastic modulus values from 18 to 150 GPa depending upon the percentage of carbon fibers addition [47]. However, a notable disadvantage of CFR-PEEK is its black color due to presence of carbon fibers and it does not meet the criteria of aesthetic implant material. Hence, tooth colored PEEK composites such as PEEK-nTiO_2 and PEEK-nHAF have been recommended for this purpose.

One of the greatest limitation of PEEK is their bio-inertness. Surface treatments or hybridization (PEEK composites) can serve to solve this problem by imparting them bio-active character. Recent researches are also focussed on improving the bioactivity of PEEK implants at Nano-scale levels. However *in vivo* studies are very limited in this regard and more animal studies are needed before these implants can be deemed suitable as human dental implants.

Conclusion

In spite of the promises they offer, these newer generation zirconia and PEEK dental implants cannot be recommended for routine clinical use in absence of sufficient number of in-vivo studies and long term clinical trials. More number of clinical investigations particularly in the form of long term longitudinal as well as comparative studies are required to comprehensively evaluate the clinical performance of these implants. Several research works are also needed to overcome their material limitations and optimize their properties. Nevertheless, the fact must be told that these materials do hold great potentials to attend to the metal-free and aesthetic restorative demands of the patient and may be even replace the 'gold standard' titanium as dental implant material in future.

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