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Review

Applications of polyetheretherketone (PEEK) in oral implantology and prosthodontics

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ARTICLE INFO

Article history:
Received 2 June 2015
Received in revised form
15 September 2015
Accepted 8 October 2015

Keywords:
PEEK
Implants
Prosthodontics
Polymers
Bioactivity

ABSTRACT

Purpose: Polyetheretherketone (PEEK) is a polymer that has many potential uses in dentistry. The aim of this review was to summarize the outcome of research conducted on the material for dental applications. In addition, future prospects of PEEK in the field of clinical dentistry have been highlighted.

Study selection: An electronic search was carried out *via* the PubMed (Medline) database using keywords 'polyetheretherketone', 'dental' and 'dentistry' in combination. Original research papers published in English language in last fifteen year were considered. The studies relevant to our review were critically analyzed and summarized.

Results: PEEK has been explored for a number of applications for clinical dentistry. For example, PEEK dental implants have exhibited lesser stress shielding compared to titanium dental implants due to closer match of mechanical properties of PEEK and bone. PEEK is a promising material for a number of removable and fixed prosthesis. Furthermore, recent studies have focused improving the bioactivity of PEEK implants at the nanoscale.

Conclusion: Considering mechanical and physical properties similar to bone, PEEK can be used in many areas of dentistry. Improving the bioactivity of PEEK dental implants without compromising their mechanical properties is a major challenge. Further modifications and improving the material properties may increase its applications in clinical dentistry.

Contents

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http://dx.doi.org/10.1016/j.jpor.2015.10.001
1883-1958/

1. Introduction

Polyetheretherketone (PEEK) is a synthetic, tooth colored polymeric material that has been used as a biomaterial in orthopedics for many years [1–3]. The monomer unit of etheretherketone monomer (Fig. 1) polymerizes *via* step-growth dialkylation reaction of bis-phenolates to form polyetheretherketone. A common synthesis route for PEEK is the reaction between 4,4′-difluorobenzophenone and the disodium salt of hydroquinone in a polar solvent such as diphenyl sulphone at 300 °C. It is a semicrystalline material having a melting point around 335 °C. PEEK can modified either by the addition of functionalized monomers (pre-polymerization) or post-polymerization modifications by chemical processes such as sulphonation, amination and nitration [4].

The major beneficial property for orthopedics implant application remains its lower Young's (elastic) modulus (3–4 GPa) being close to human bone [5]. PEEK can be modified easily by incorporation of other materials. For example; incorporation of carbon fibers can increase the elastic modulus up to 18 GPa [5]. The titanium and its alloys have elastic modulus significantly higher than bone and resulting in severe stress-shielding and failure [6]. The modulus of carbon-reinforced PEEK is also comparable to those of cortical bone and dentin [7,8] so the polymer could exhibit lesser stress shielding when compared to titanium which used as an implant material (Table 1). Moreover, tensile properties of PEEK are also analogous to those of bone, enamel and dentin [9–12], making it a suitable restorative material as far as the mechanical properties are concerned.

In contrast to titanium, PEEK has very limited inherent osteoconductive properties [17]. Hence, a considerable amount of research has been conducted to improve the bioactivity of PEEK implants [18–22]. There are a number of methods that have been proposed to improve the bioactivity of PEEK including coating PEEK with synthetic osteoconductive hydroxyl apatite [18,23], increasing its surface roughness and chemical modifications [24] and incorporating bioactive particles [25]. PEEK has white color and excellent mechanical properties, hence it has been proposed for other prosthodontic applications such as fixed prostheses [26] and removable prostheses [27]. The effects of surface modification of PEEK have been investigated for bonding with different luting agents [26,28] and extracted teeth [29]. The potential of PEEK for various dental applications has been shown in Fig. 2. Moreover, PEEK can also be used an esthetic orthodontic wire. Compared to other polymers, such as polyether sulfone (PES) and polyvinylidene difluoride (PVDF), PEEK orthodontic wires are able to deliver higher orthodontic forces but at a cross-section of that similar to metallic wires such as cobalt–chromium (Co–Cr), titanium–molybdenum (Ti–Mo) and nickel–titanium (Ni–Ti) [30]. Due to these unique physical and mechanical properties, PEEK is a promising material for dental applications. The aim of this review is to summarize the outcome of research conducted on the material for prosthodontic applications. In addition, future prospects of PEEK in the field of clinical dentistry have been highlighted.

2. PEEK as an implant material

According to Wolff's Law, the bone remodels according to the load that has been applied to it. Stress shielding is the reduction in volume of the bone around an implant due to the shielding of normal loads by the implant. Finite-element analysis (FEA) of carbon-fiber reinforced PEEK (CFR-PEEK) implants suggested that they could induce lesser stress shielding than titanium [6]. However, since PEEK dental implants have not been used widely clinically, it is unknown if there is a difference between the bone resorption around PEEK and titanium implants in human subjects. Moreover, a more recent FEA study by Sarot et al. suggests there is no difference between the stress distribution around PEEK and titanium dental implants [31]. Indeed, more clinical trials are vital to conclude whether or not PEEK implants produce lesser stress-shielding than titanium implants.

Unmodified PEEK is inherently hydrophobic in nature, with a water-contact angle of 80–90° and bioinert [32,33]. Indeed, studies have shown that there is no significant effect of unmodified PEEK on the proliferation rate of cells *in vitro* [34]. On the contrary, some studies have observed an increased protein turnover in cells in contact with conventional- and CFR-PEEK [35]. Animal studies have suggested that PEEK can survive for up to 3 years while inducing non-remarkable localized inflammation [33]. Nevertheless, quite a few studies suggested that there is no significant difference between the osseointegration of PEEK and conventional implant materials such as zirconia and titanium [36,37]. Conversely, recent proteomic studies have indicated that PEEK inhibits mRNA processing that may lead to a decreased cellular proliferation rate on the surface and cytotoxic effects may be produced in the long-term [38]. Nonetheless, the same proteomic studies have found no difference between the bioinertness of PEEK, zirconia and titanium [38]. Although unmodified PEEK, is considered as a biointert material however, there has been no conclusive evidence of osseoconductive effects of PEEK *in vivo* and *in vitro*. Hence, in its unmodified form, the long term survival rate of PEEK implants is questionable.

In order to improve the mechanical and biological properties, a number of modifications have been attempted in PEEK materials. However, PEEK dental implants have not been extensively used clinically and there is insufficient data to deduce their long-term efficacy in human subjects.

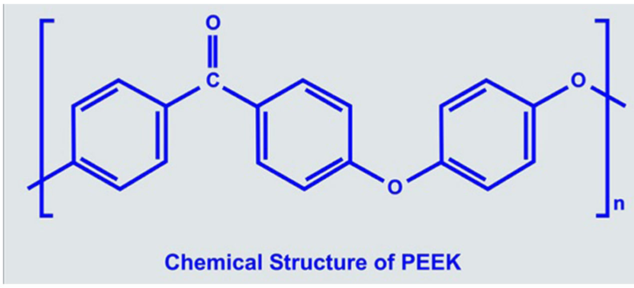

Fig. 1 – Chemical structure of monomer unit of polyetheretherketone (PEEK).

Table 1 – The tensile strength and elastic moduli of PEEK, CFR-PEEK, PMMA and mineralized human tissues.

Material	Tensile strength (MPa)	Young's modulus (GPa)	References
PEEK	80	3–4	[11]
CFR-PEEK	120	18	[11]
Cortical bone	104–121	14	[9,13]
PMMA	48–76	3–5	[14,15]
Dentin	104	15	[8,10]
Enamel	47.5	40–83	[7,8,12]
Titanium	954–976	102–110	[16]

PEEK, polyetheretherketone; CFR-PEEK, carbon-reinforced polyetheretherketone; PMMA, polymethylemethacrylate.

2.1. *Nano-structured PEEK surfaces*

The beneficial role of nanomaterials is well known for dental applications [25,39]. In recent years, PEEK has also been modified at the nano-level in order to improve its bioactivity and osseoconductive properties [40]. Conventionally, PEEK has been coated using bioactive materials such as osseoconductive calcium hydroxyapatite (HAp) or titanium by means of plasma-spraying [23,41]. In this process, particles are sprayed onto the surface of an implant through a plasma torch. The plasma melts the particles to deposit on the implant surface and producing a rough surface layer. Although spraying of a bioactive layer may be suitable for larger implants, the coating produced is not suitable for the relatively smaller dental implants. This is because the highly rough ($R_a \sim 7\ \mu m$) and very thick apatite layer [23] that may get delaminated leading to implant failures [42]. Another disadvantage of using plasma-spray to coat PEEK with HAp are the high temperatures involved in the process. High temperatures could damage PEEK structure due to its relatively low melting temperature (*ca.* 340 °C). Furthermore, the low bond strength (2.8 MPa) of plasma-sprayed HAp coatings on CFR-PEEK has been suggested to result from the evaporation of carbon fibers from the surface of the implant due to the high temperatures during the coating process [43].

There has been a lot of focus on nanoscale coating of PEEK with bioactive apatite [19] and production of bioactive PEEK nanocomposites [22]. Osteogenic implant coatings are used to modify the surface properties of dental implants. Bioactive surface coatings can improve the interaction with bony tissues and results in better osseointegration of implant materials [44]. Spin-coating is another method for coating a thin layer of nanoscale calcium hydroxyapatite on PEEK surface [18–20]. In this process apatite dissolved in organic solvents is slowly dropped onto the surface of an implant rotating at high speeds [19]. Upon heat-treatment a thin layer of HAp is formed on the implants. Animal studies have shown that spin-coated PEEK implants have higher bone-implant contact (BIC) when compared to uncoated PEEK. However, no significant differences in removal torque could be observed [19,20]. Alternatively, nanoscale surface modifications of PEEK can be produced using plasma-gas etching [45]. In this process, low-pressure gases are used to introduce nano-level surface roughness and functional group on the surface of PEEK implants and inducing more hydrophilicity for a better material–tissue interaction [46]. *In vitro* evaluation of gas-plasma modified PEEK implants has shown promotion of proliferation and differentiation of human mesenchymal cells seeded on the implant [45]. Conversely, PEEK modified by low-pressure oxygen plasma implanted into the bones of rabbits has not shown significantly higher BIC than that around unmodified PEEK [24].

Recently, Nakahara et al. have investigated the implanted CFR-PEEK hip stems in sheep. CFR-PEEK hip stems were plasma-sprayed (17 nm-thick coating) using TiO_2 and hydroxyapatite *via* plasma spraying and dipping in α-Tricalcium phosphate (α-TCP). They have reported excellent biocompatibility and mechanical properties for hip implant applications without the release ot any metallic ions. In addition, cementless fixation was attained even for load-bearing applications while using HA-coated CFR/PEEK implants [47,48]. These finding have suggested a strong potential of coated PEEK materials for dental implant applications. However, no clinical trials investigating coated PEEK dental implants in humans have been conducted so far and required to assess their biocompatibility prior to clinical application.

In order to improve biological and physical properties of PEEK, a variety of nano-modification have been attempted (Fig. 3). Electron-beam (e-beam) deposition involves decomposing and depositing a very thin, nano-rough layer of a material on a substrate by exposing the material to a beam of electrons [49]. Coating PEEK with titanium using this method has shown to increase the hydrophilicity leading to enhanced cellular proliferation [50]. An anodized nano-porous layer of e-beam coated titanium can carry immobilized bone morphogenic protein-2 (BMP-2) [50]. BMP-2 is a growth factor that has been shown to increase the bone deposition in implant sites [51,52]. A PEEK implant coated with a titanium/BMP-2 coating could be an attractive aspect and a great potential for PEEK oral implantology applications. However, e-beam coated implants have not been tested *in vivo* so their clinical prospects are still not very clear. A substrate placed in plasma of particles connected to a high voltage can get coated by a thin layer of the particles of that material. This process is known as plasma immersion ion implantation (PIII) [53]. Although, PEEK coated with TiO_2 using PIII has shown partial activity against *Staphylococcus aureus* and *Eschrechia coli*, its antimicrobial effects against periodontal pathogens is yet to be determined [54]. Similarly in case of apatite-coated PEEK implants, no human trials investigating the use of e-beam coated PEEK

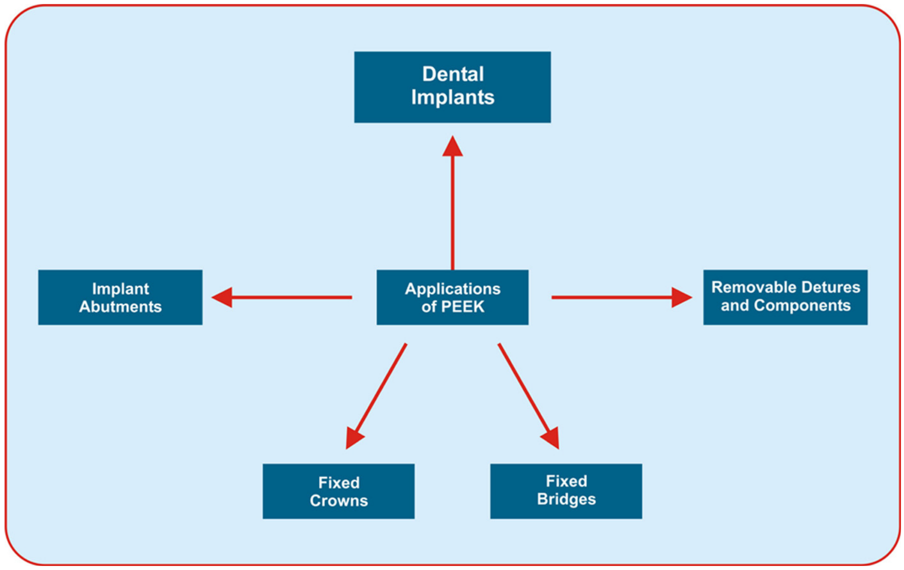

Fig. 2 – Major applications of polyetheretherketone (PEEK) in dentistry.

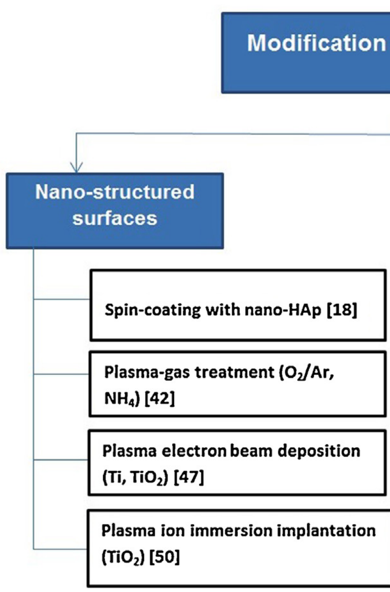

Fig. 3 – Nano-modification of polyetheretherketone (PEEK) to increase its bioactivity.

implants have been reported. Therefore, these implants cannot be employed into clinical applications until sufficient data validating their safety and longevity has been recorded in literature.

Nano-structured PEEK surfaces produced by etching with sulfuric acid (sulfonation) and rinsing with distilled water have been observed to induce an accelerated osseointegration compared to the unmodified PEEK *in vitro* and *in vivo* [55]. A combined effect of production of a highly nano-porous etched surface and enhanced hydrophilicity due to the presence of sulfuric acid groups (SO_3H) could explain the improved biocompatibility of sulfonated PEEK [55–57]. However, it has also been seen that there is a decreased initial bone formation when sulfonated PEEK is implanted *in vivo* which could be explained by the presence of residual sulfuric acid on the surface. This effect can be minimized by rinsing the implants with acetone to remove the residual sulfuric acid [55]. More recent experiments have focused on using strong alkalis to introduce functional groups (OH groups) on PEEK surface which can induce formation of a biomimetic apatite layer when immersed in simulated biomimetic fluid (SBF) [58]. However, conventional biomimetic coatings can take up to 48 h to be produced. Nonetheless, microwave-assisted biomimetic coating can produce an apatite layer on PEEK in as quickly as 4 min [59]. Still, no studies have attempted to investigate the bond-strength of this apatite layer. Since debonding of bioactive coatings can be a cause of implant failures, studies need to evaluate the quality of the coating before biomimetically coated PEEK can be deemed suitable for clinical usage.

2.2. *Bioactive PEEK nano-composites*

In order to increase the bioactivity, bioactive inorganic particles have been incorporated to PEEK using melt-blending and compression molding techniques [60]. However, incorporating bioactive HAp particles in the size range of 2–4 μm has a negative impact on the mechanical properties of PEEK [60]. This can be overcome using nano-sized particles instead of larger particles [22,25]. Implants made of PEEK nano-composites have a number of advantages such as increased bioactivity better mechanical properties [22,25]. Incorporating nano-sized particles like those of hydroxyfluorapatite has been suggested to impart anti-microbial properties against *Streptococcus mutans*, a common oral pathogen, in addition to improving osseointegration *in vivo* [25]. Furthermore, animal studies have exhibited that nano-TiO_2/PEEK implants have a higher bioactivity compared to pure PEEK [22,61]. Dental hard tissues are anisotropic in nature and their mechanical properties vary from one point to the other with in the same tissue [62,63]. The PEEK nano-composites can enable researchers to synthesize biomaterials with variable combinations of mechanical properties required for any particular application. For example, besides being used as implants, these bioactive nano-composites could be used as indirect intracoronal or extracoronal restorations. These restorations can have an additional advantage of being anti-bacterial as reported by Wang et al. [25]. However, more studies are needed in order to ascertain the usage and manipulation of the composites before these composites can be used as restorative materials.

2.3. *PEEK implant abutments*

Considering adequate biocompatibility, implant healing abutments can be constructed using PEEK [64,65]. A randomized, controlled clinical trial (RCT) conducted by Koutouzis et al. suggested that there is no significant difference in the bone resorption and soft tissue inflammation around PEEK and titanium abutments [65]. Furthermore, the oral microbial flora attachment to PEEK abutments is comparable to those made of titanium, zirconia and polymethylmethacrylate [64]. A close match of elastic moduli of bone and PEEK surface reduces the stress shielding effects and encourage bone remodeling. Hence, PEEK could prove to be a viable alternative to titanium in constructing implant abutments.

3. PEEK as a removable prosthesis material

Dentures can be constructed by using PEEK computer-aided design and computer-aided manufacture systems [2]. Tannous et al. [66] has suggested that denture clasps made of PEEK have lower retentive forces compared to cobalt–chromium (Co–Cr) clasps [66]. However, since the study was conducted on metal crowns *in vitro*, it is not known how effective the esthetic PEEK clasps would be in retaining dentures in the clinical setting. Another application of PEEK is the construction of a removable obturator [27]. Nevertheless, more studies are needed to evaluate the efficacy of PEEK obturators compared to conventional acrylic prostheses. To date, no clinical studies or systematic reviews focusing on the use of PEEK dentures have been published. However, owing to the superior mechanical and biological properties of PEEK, it will not be surprising if dentures constructed from the polymer are routinely constructed in near future.

Table 2 – Tensile bond strength of PEEK to dental tissues using various surface conditioning and adhesive systems.

Surface conditioning	Adhesive system	Tensile bond strength (MPa)	Reference
Air abrasion	Visio.link	2.12 ± 0.78	[29]
	Signum Bond	2.97 ± 0.92	
	Ambarino P60	1.94 ± 0.87	
Sulfuric acid	Visio.link	2.06 ± 0.80	[29]
	Signum Bond	1.88 ± 0.95	
	Ambarino P60	2.18 ± 0.99	
Piranha acid	Visio.link	2.44 ± 1.07	[29]
	Signum Bond	2.01 ± 0.98	
	Ambarino P60	0.34 ± 0.33	

PEEK, polyetheretherketone.

4. PEEK crowns

A variety of procedures have been suggested to condition the surface of PEEK in order to facilitate its bonding with resin composite crowns. Even though air abrasion with and without silica coating creates a more wettable surface [67], etching with sulphuric acid creates a rough and chemically altered surface which enables it to bond more effectively with hydrophobic resin composites (shear bond strength: 19.0 ± 3.4 MPa) [26]. It has been observed that etching with sulfuric acid for 60–90 s can exhibit shear bond strength to resin composite cements as high as 15.3 ± 7.2 MPa after being stored in water for 28 days at 37 °C [68]. Etching with piranha acid and using a bonding agent have been shown to produce tensile bond strength to composite resin as high as 23.4 ± 9.9 MPa in aged PEEK specimens [69]. No significant differences were observed in the tensile bond strength of PEEK crowns and dentin abutments (Table 2) using air abrasion and sulfuring acid etching techniques [29].

These studies suggest that PEEK can be used under resin-composite as a coping material. Because the mechanical properties of PEEK are similar to those of dentin and enamel, PEEK could have an advantage over alloy and ceramic restorations.

5. PEEK CAD-CAM milled fixed partial dentures

Using CAD-CAM to manufacture restorations makes it possible to produce dental prostheses chair-side [70]. CAD-CAM designed composites and polymethylmethacrylate (PMMA) fixed dentures have superior mechanical properties compared to conventional fixed dentures [71,72]. PEEK is another material that can be used an alternative to PMMA for

CAD-CAM restorations. Three-unit PEEK fixed partial denture manufactured *via* CAD-CAM has been suggested to have a higher fracture resistance than pressed granular- or pellet-shaped PEEK dentures [73]. The fracture resistance of the CAD-CAM milled PEEK fixed dentures is much higher than those of lithium disilicate glass-ceramic (950N), alumina (851N) [74], zirconia (981-1331N) [75].

The abrasive properties of PEEK are excellent. Despite of significantly low elastic moduli and hardness, abrasive resistance of PEEK is competitive with metallic alloys [76]. However, no clinical studies have attempted to compare the abrasion produced by PEEK crowns on teeth to that produced by other materials such as alloys and ceramics. Hence, it is still unknown if PEEK crowns can function efficiently in harmony with dentin and enamel. Considering good abrasion resistance, mechanical attributes and aforementioned adequate bonding to composites and teeth, a PEEK fixed partial denture would be expected to have a satisfactory survival rate.

6. Conclusion

Because of its mechanical and physical properties being similar to bone and dentin, PEEK can be used for a number of applications in dentistry including dental implants. Increasing the bioactivity of PEEK dental implants without affecting their mechanical properties is a major challenge. PEEK is also an attractive material for producing CAD-CAM fixed and removable prosthesis owing to its superior mechanical properties compared to materials such as acrylic. Further research and clinical trials are required to explore this material and possible modifications for further dental applications.

Conflict of interest

No conflicts of interest.

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