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Review Article

The Role of Polyetheretherketone (PEEK) Polymer in Dentistry - A Review

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Abstract

Evolution of scientific knowledge has brought forth numerous materials in Prosthetic dentistry. Poly ether ether ketone (PEEK) is one such material that finds popular use in Prosthodontics. PEEK is a semi-crystalline linear polycyclic thermoplastic which is expected to substitute many metals in the family of biomaterials. PEEK can find a place in implantology as dental implant, superstructure or implant abutment. PEEK has proven its versatility in a very short span of time and has found a space in prosthetic advancements. This article reviews the characteristics of PEEK which are suited for the present and futuristic contexts of the development of dentistry.

Keywords: PEEK Implants; Polyether Ether Ketone (PEEK); Fixed Partial Denture Framework; RPD Framework; Modified PEEK Polymer; Carbon Fiber Reinforced-Poly Ether Ether Ketone (CFR-PEEK); Obturator; Dental Implant

Abbreviations

PEEK: Polyether Ether Ketone; CFR-PEEK: Carbon Fiber Reinforced-Polyether Ether Ketone

Introduction

Many polymers are currently available, such as Polytetrafluoroethylene (PTFE), Poly methylmethacrylate (PMMA), Polylactic acid(PLA), Ultra high molecular weight polyethylene(UHMWPE), Poly glycolic acid (PGA), and only a few for bone replacements. Most of the polymers can absorb liquids, swell, leach unwanted products and the -properties could be affected by sterilization [1-3]. In 1978 English scientists developed PEEK. In the 1980s it was commercialized for industrial applications viz. the fabrication of aircrafts, blades of turbine, pistons, insulation for cables, bearings and compressor plate valves [4]. By the late 1990s, PEEK emerged as the leading thermoplastic replacement for metallic components to be used in trauma and orthopaedic treatment. In 1992 PEEK has found a place in dentistry as aesthetic abutments and later as dental implants. Later many changes have been brought in composition to modify and improve the working characteristics of implants [5].

PEEK is a semicrystalline, polycyclic, sulfonated aromatic high-temperature thermoplastic polymer with a linear structure. It belongs to the family of polyaryletherketone. This material is obtained by binding the ketone and ether functional groups between aryl rings. It is tan-coloured in its pure form. The monomer unit of ether ether ketone monomer polymerizes via step-growth dialkylation reaction of bis-phenolates to form polyetheretherketone. A standard synthesis route for PEEK is by the reaction between 4,40 -difluorobenzophenone and disodium salt of hydroquinone in a polar solvent such as diphenyl sulphone 300 8C. Modification of PEEK is also possible by the addition of functionalized monomers (pre-polymerization) or post-polymerization modifications by chemical processes such as sulphonation, amination and nitration [6]. They are produced in three viscosities - high, medium and low- with the same formula (-C6 H4 -OC6 H4 -O-C6 H4 -CO-) n (Figure 1). PEEK gets its strength from the aromatic chain of ring structure. It is highly inert and hence resistant to chemical erosion [7,8].

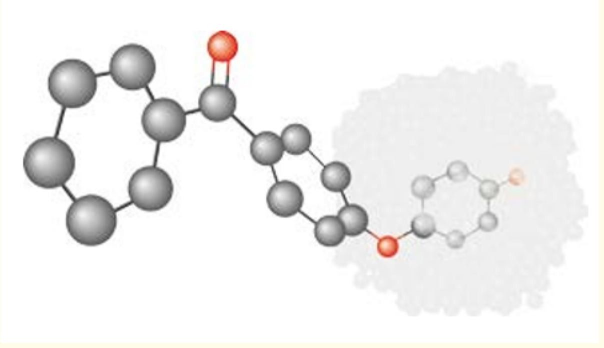

Figure 1: Chemical structure of PEEK

(Bredent BioHPP catalogue)

Advantages of peek [9]:

- Good dimensional stability.
- High mechanical properties, tough and durable,
- Melting point 340°C.
- Glass transition temperature: 143 °C
- Good frictional and wear resistance,
- Elastic modulus is similar to bone.
- High-temperature resistance.
- Metal-free hence no metal allergy and no metallic taste.
- Digitally designed to match the patient's anatomy.
- Pure material, no additives, no colouring.
- No abrasion of the antagonist.
- No veneer chipping, no framework fracture.

Physical and mechanical properties

The characteristic molecular chain configuration of PEEK allows for enhanced physical and mechanical properties in comparison to other polymers. A summary of physical and mechanical properties of PEEK is given in table 1.

Mechanical properties
E modulus - 4,000 Mpa
Flexural strength - >150 Mpa
Water absorption - 6.5g/mm^3
Water solubility - <0.3g/mm^3
Breaking load tests on three-unit FPDs
Max stress without fracturing - >1,200 N (no cycling)
Max stress without fracturing (mechanical and thermal cycling) - >1,200 N
Other properties
Melting range Approximately - 340°C
Bond strength - > 25 Mpa
Density - 1320 kg/m^3
Hardness - 110 HV

Table 1: Physical and mechanical properties for PEEK [10-12].

Solubility

The solubility of peek is 0.5w/w%, and it cannot be affected by long term water exposure, even at a temperature of up to 260°C [4]. While comparing the physical and mechanical characteristics of PEEK and other CAD/CAM polymers, PEEK exhibits less moisture absorption and solubility. However, hardness values were comparable to those of PMMA.

Elastic modulus

Modulus of elasticity of PEEK is 3.1Gpa which is similar to that of bone. This property places it in an advantageous position to be used in implant dentistry. PEEK can easily be modified by incorporating other materials like carbon fibres, thereby increasing the elastic modulus up to 18Gpa [13]. PEEK's modulus approximates that of dentin and cortical bone. It could result in the reduction of stresses that are transferred to the abutment teeth and also to the cementation interface when compared to titanium and other materials. It is a very light material with low density (1.32 g/cm^3) [14] (Table 2).

Material	Tensile strength (Mpa)	Youngs's modulus (Gpa)
PEEK	80	3-4
CRF-PEEK	120	18
Cortical bone	104-121	14
PMMA	48-75	3-5
Dentin	104	15
Enamel	47.5	40-83
Titanium	954-976	102-110

Table 2: Tensile strength and elastic moduli of PEEK, CFR-PEEK PMMA and mineralized human tissue [10-12].

Flexural strength, wear resistance and tensile strength

PEEK exhibits excellent wear resistance similar to the rate of resin materials when opposing natural teeth. The tensile properties of PEEK are identical to those of enamel and dentin, making it suitable for frame woks of restoratins [15].

Density of PEEK is 1320 kg/m^3 and thermal conductivity is 0.25 W/m K. However the mechanical properties of do not change during sterilization with steam, gamma radiation and ethylene oxide. Its Melting point is > 280°C and hence it shows resistance to deterioration during various sterilization procedures. Radiation also does not cause disintegration. It is an economical material and can easily be prepared in the mouth [3].

Mechanical properties of the PEEK are similar to those of dentin and enamel. PEEK is rated as having superiority over metal alloy and ceramic restorations. CAD-CAM milled fixed prostheses made of PEEK shows high resistance to fracture (2354N). It exhibits higher resistance to fracture than lithium disilicate ceramic (950N) and zirconia (981-1331N). During mastication teeth are cyclically load with a force of 400 N. Because of the high fracture resistance, PEEK is used for making frame works. Publications of Stawarczyk., *et al.* refers to the high fracture resistance. Fracture related load was 1383 N for a 3-unit PEEK framework without veneering [2].

Biological properties

Peek is highly indicated for allergic patients as an alternative material. Peek has low reactivity, nontoxicity, low solubility intraorally, and has one of the best biocompatibility profile [11]. PEEK implant is less stiff than Ti or Zr and is known to reduce the stress shielding effect. Because of this bone resorption is reduced and eventually cause increase in osseointegration [16].

Common forms of PEEK used in dentistry

Two commercial brands of peek are generally used in dental and medical fields. PEEK-OPTIMA is used in the USA, whereas BioHPP is used in Europe. Both the products belong to the class of modified PEEK material with enhanced properties.

Peek-optima™

PEEK-OPTIMA™ developed in 1999 by Invibio Biomaterial Solution Co. It is a poly-aromatic semicrystalline thermoplastic material having a melting temperature of 343°C, crystallization peak of 160°C and glass transition temperature of 145°C. Addition of carbon fibres improves properties such as hardness and creep resistance. PEEK-OPTIMA™ is used in dentistry for making healing screws, temporary prosthetic abutments, precision attachments and implant-supported restoration frameworks [17].

BIOHPP™

Bredent GmbH specifically developed BioHPP™ (Bio High-Performance polymer) for dental applications. This PEEK material modification includes the addition of ceramic fillers with grain size between 0.3 - 0.5 mm. It is anti-allergic in nature and has excellent polishing properties, low plaque affinity, and good wear resistance. The small size of the grain is responsible for improved polishing properties and homogeneity. It has been used for telescopic restorations, implant abutments, secondary structures associated with a bar-supported prosthesis, and three to four-unit FPDs [12].

Surface modifications

Bioactive materials are incorporated to improve the bioactivity of PEEK.

Based on the particle size of these materials, PEEK composites are classified as

1. Conventional PEEK
2. Nanosized PEEK.

PEEK can be modified by two treatments.

The first is a chemical treatment, which is rarely used, and only two options are available:

1. Wet chemistry modification.
2. Sulfonation treatment.

Second is the physical treatments:

1. Plasma modifications (such as nitrogen and oxygen plasma, ammonia/argon plasma, oxygen plasma, oxygen and argon plasma, methane and oxygen plasma, ammonia plasma, and hydrogen/argon plasma)
2. Accelerated neutral atom beam (anab).

For surface coating, materials such as titanium, gold, titanium dioxide, diamond-like carbon, tert-butoxides, and hydroxyapatite (HA) are used. Conventional PEEK composite, known as HA (hydroxyapatite), has good biocompatibility and osteoconduction. If HA content is increased, tensile modulus and microhardness improve but tensile strength and strain decrease [3].

Application of the surface coatings is done by the following techniques (Table 3).

Plasma immersion ion implantation and deposition, vacuum plasma spraying, aerosol deposition, arc ion plating, physical vapour deposition, electron beam deposition, cold spray technique, spin coating, ionic plasma deposition and radio-frequency magnetron sputtering [18].

Surface Modifications	Procedures	Materials
Surface topographical Modifications	• Acid etching	Sulfuric acid
	• Sandblasting	TiO_2, alumina (Al_2O_3)
Coating	• Plasma spraying	Hydroxyapatite (HA), titanium (Ti)
	• Spin coating	Nanosized HA crystals containing surfactants, organic solvent, an aqueous solution of $Ca(NO_3)_2$ and H_3PO_4
	• Electron-beam evaporation (EBE) • Plasma immersion ion implantation (PIII)	Ti; Silicate Titanium dioxide (TiO_2); calcium (Ca); water (H_2O); Argon (Ar)
Chemical modifications	• Sulphonation	Sulfonate groups ($-SO_3^-$)
	• Amination • Nitration	Amine functions Nitrate functions
Improving hydrophilicity	• UV irradiation • Plasma gas treatment	UV-A light, UV-C light Oxygen plasma
Incorporating with bioactive properties	• Bioactive inorganic materials	Nano-TiO_2(n-TiO_2); nano-fluorohydroxyapatite (n-FHA)

Table 3: Surface modifications of PEEK.

Medical and dental applications

PEEK emerges as an excellent alternative to metal implant components, especially in orthopaedic and traumatic applications because of the bio compatibility and bone like elastic modulus. An example is carbon fibre reinforced (CFR-PEEK) fixation plates which serve as an alternative to stainless steel bone plates. CFR-PEEK is used in cardiovascular applications, fracture fixation, femoral prosthesis in artificial hip joints, finger joint replacements, total disc replacement and interbody fusion cage in vertebral surgery, spinal and cranial applications (Figure 2a-4). Implants used in orthopedics usually make use of metals, polymers, ceramics and composites. Metals, such as Ni-Ti, Ti, Co-Cr, are used for permanent and temporary implants, but they have drawbacks such as allergies, high elastic modulus, the radiopacity of this metal causes artefacts in CT-Scans and it can cause stress on the peri-implant bone. The drawbacks of ceramics include low fracture toughness and high elastic modulus. In short, PEEK has emerged as the best possible biomaterial substitute for metallic implants and ceramics [3,4].

Figure 2a and 2b: Spinal implants of peek.

(Source: https://www.odtmag.com/contents/view_online-exclusives/2017-01-05/a-porous-peek-solution-for-spinal-implants/.)

Figure 3: Cranial implants of peek.

(Source: https://www.designnews.com/materials-assembly/peek-cranial-implant-debuts-mdm.)

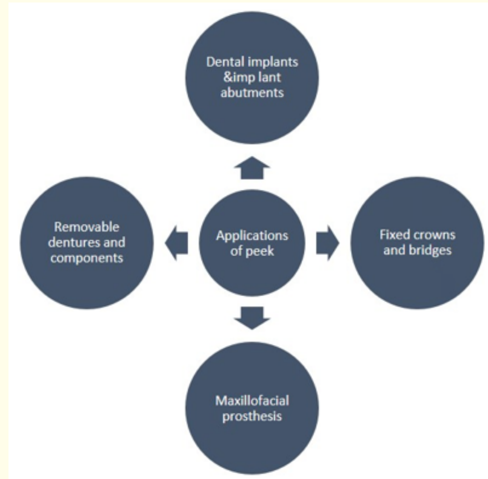

Figure 4: Major applications of PEEK in dentistry

PEEK implants

In implantology, titanium is accepted as the first choice in standard treatments due to its highly favoured mechanical properties and biocompatibility (Figure 5a and 5b). Titanium has several advantages, and there are few disadvantages too, due to the gradient difference in the elastic moduli of a titanium implant and its surrounding bone. This may cause stress at the implant-bone interface during load transfer and which might result in peri-implant bone loss. Titanium has aesthetic problems too because it cannot transmit light and hence a dark shimmer of the peri-implant soft tissue may appear in thin biotype mucosa. If the lip position is very high during smile, this can initiate aesthetic problems. PEEK is biocompatible and has an elastic modulus of 3.6 GPa, which is closer to that of bone. If required the modulus can be modified to match that of the cortical bone (18 GPa) through carbon fibre reinforcement [9]. It can be used as a substitute to titanium implants and thereby it is possible to overcome the metallic characteristics. Because of the matching modulus, PEEK can reduce the stresses in bone and prevent subsequent bone resorption [19].

Implant abutments

Abutments are made of different materials such as titanium, gold, zirconium and ceramics [7] (Figure 6). PEEK abutments are also in the use in recent times. In the case of implant screw breakage, PEEK screws are easier to be removed. However, it is demonstrated that PEEK abutments can withstand intraoral masticatory forces similar to titanium abutments. PEEK's proven soft tissue behaviour supports the excellent recovery of gingival tissue. HAF has antibacterial properties which can prevent peri-implantitis and early implant failures [20].

Figure 5a: PEEK dental implant and titanium implant

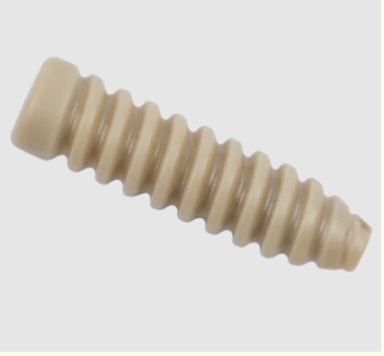

Figure 5b: PEEK Dental implant

(Source: http: windsorbeach.commedical.)

Figure 6: Implant abutment of peek.

(Source: https://www.medicalexpo.com/prod/bhi-implants/product-102429-952219.)

Semicrystalline structure of PEEK is responsible for reducing fragility and hence deformation occurs rather than breakage. In one study, on prostheses made over PEEK abutments, prostheses remained intact and abutments only deformed. The functioning prosthesis could be salvaged by a replacement of the abutment [21]. Koutouzis., *et al*. in a randomized controlled clinical trial (RCT) concluded that there is no significant difference in bone resorption and soft tissue inflammation between PEEK and titanium abutments. Additionally, the oral microbial flora was similar to titanium, zirconia or PMMA abutments [22].

Peek as removable partial denture material

PEEK is better suited for patients who have allergy to metal and who do not like the unpleasant metal display of the denture framework and retentive clasps. Besides, many of these polymers are heat resistant and hence amenable to autoclave disinfection [9].

Tannous., *et al*. have compared prostheses made of chrome-cobalt and PEEK and observed that peek had lower retentive strength [23]. In combination with high-performance polymer, PEEK could be used as an alternative to metallic partials with replacing acrylic teeth [24] (Figure 7a and 7b). PEEK removable partial prostheses with distal extension reduces torque forces and the stresses on the tooth due to its elasticity. Colour Changes are minimal in PEEK compared to other prosthesis resin materials. A comparative evaluation on surface roughness and free surface energy of polishing methods used in the clinic and laboratory to PEEK, PMMA and a composite resin and found that lower surface roughness and free surface energy were obtained in PEEK [25].

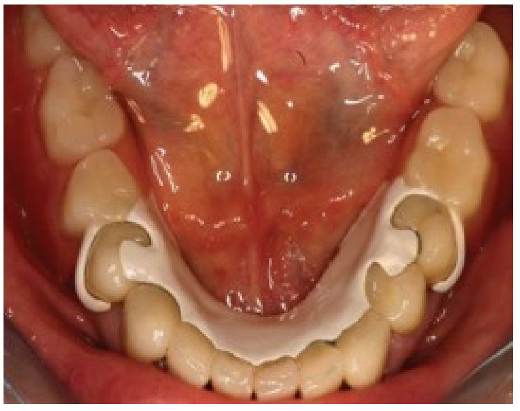

Figure 7a: RPD frame work made of PEEK

Figure 7b: PEEK clasps of RPD frame work

(Source: http://www.guident.net/articles/general/POLYETHE RETHERKETONE-PEEK-AN-INNOVATION-IN-DENTISTRY.html.)

Fixed dental prosthesis

PEEK metal-free crowns and bridges possess high biocompatibility and mechanical properties (Figure 8a and 8b). In comparison to ceramic and metallic materials, peek dental three unit bridge substructure did not weaken by *in vitro* ageing. In implant-supported prosthetic systems, crowns made of PEEK served successfully [26]. While comparing the biocompatibility profile, PEEK has higher rating than that of metal-based ceramics. However, some researchers suggested that it should be covered with veneer to ensure precision [27]. PEEK is considered as a light material and hence it may be a well suited alternative to chrome-cobalt prosthesis [20].

Figure 8 a and b: Fixed prosthesis made of PEEK. 8b: PEEK Fixed Prosthesis.

(Source: https://www.bredent.co.uk/wp-content/uploads/2017/02/BioHPP-2013.pdf.)

PEEK restorations have adequate fracture resistance required to withstand masticatory forces exerted in the anterior (300N) and posterior regions (500-600N). No damage of frameworks or de-cementations were observed in prolonged chewing simulation *in vitro* studies equivalent to 5 years intraoral use [28].

Peek cad-cam milled partial dentures

Using CAD-CAM, dental prostheses can be made chair-side. CAD-CAM designed polymethylmethacrylate (PMMA), and composite fixed dentures have superior mechanical properties compared to conventional fixed dentures [29]. PEEK can be used as an alternative to PMMA for CAD-CAM restorations. Three-unit PEEK FPD made by CAD-CAM has been shown to have a higher fracture resistance than pressed granular- or pellet-shaped PEEK prostheses (Figure 9). The fracture resistance of the CADCAM milled PEEK fixed dentures is higher than those of lithium disilicate glass-ceramic (950N), alumina (851N) [30], zirconia (981-1331N) [31]. The abrasive properties of PEEK are exceedingly good. Though the elastic moduli and hardness are low, the abrasive resistance of PEEK is competitive to metallic alloys [32]. Taking into consideration the abrasion resistance, mechanical properties and adequate bonding to composites and teeth, a PEEK fixed partial denture is expected to have a satisfactory survival rate.

Figure 9: CAD CAM milled RPD framework.

(Source: https://www.dentalcadcamshop.com/production/blocks-for-cerec-inlab/ernst-hinrichs/juvora-dental-peek.html.)

Resin-bonded and retained fdps/splints (RBR)

PEEK is used for conservative RBR single-tooth restorations. Andrikopoulou., *et al.* presented a clinical case restoring the anterior maxillary area in a patient with a cleft lip/ palate. A peek framework coated with resin was fabricated to restore a missing lateral and which simultaneously splinted the remaining anterior teeth. The authors observed that the low modulus of PEEK, with the use of composite resin coating, provided superiority over ceramic and metal-ceramic restorations because occlusal forces are significantly dampened and reduced the risk of debonding [33].

Peek as maxillofacial prosthetic material (MFP)

Restoration of maxillofacial defects with PEEK is not very common. Various alloplastic materials in conjunction with standard soft-tissue techniques have been used in the restoration of maxillofacial defects (Figure 10). PEEK exhibits an excellent combination of strength, stiffness and durability. Patients get excellent postoperative aesthetic and functional results without complications such as infections or extrusions. MFPs are usually printed. To 3D print PEEK, a 3D printer with an extruder that can reach 400°C, a chamber heated of 120°C, and a build plate that can heat to 230°C to remove the part and avoid warping. Because PEEK implants are customizable, easily workable, inert, and nonporous, they represent an ideal alloplastic material for maxillofacial reconstruction [34].

Figure 10: Obturator frame work.

(Source: http://www.quintpub.com/userhome/ijp/ijp_33_3_Tasopoulos_p333.pdf.)

PEEK orthodontic wires

Because of the acceptable colour, PEEK can be used as an aesthetic orthodontic wire (Figure 11). PEEK orthodontic wires can provide orthodontic forces similar to titanium-molybdenum (TiMo) and nickel-titanium (Ni-Ti) wires [35].

Veneered PEEK

Standard Veneering System techniques can be used to fabricate restorations from the PEEK-based dental polymer substructure. If the veneer chips, PEEK substructure can allow repair without necessitating crown or bridge replacement [36].

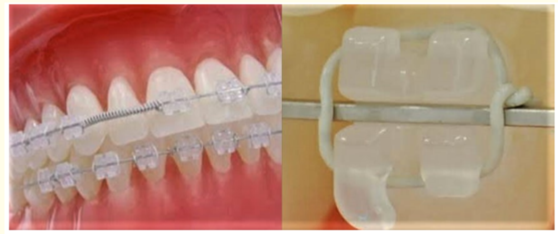

Figure 11: PEEK Orthodontic appliance.

(Source: https://www.orthomax.com.au/october-2017-product-of-the-month/.)

Bonding of PEEK to composites

One of the significant advantages of PEEK is that it can bind to light polymerised indirect composites. PEEK also requires holding elements and retentive abrasions similar to metal and ceramic resin-bonded prostheses [24]. The application of opaque material increases resistance to shear forces. Cleaning and roughening followed by processing with acetone, phosphate-based methacrylate linings or tribochemicals ensures good bonding between PEEK and composites. PEEK exhibit extreme resistance to most chemical substances. Rocha., *et al*. reported that sulfuric acid or a mixture of sulfuric acid and hydrogen peroxide could be used in roughening the PEEK surface. With sand blasting on the PEEK, the surface area and wettability can be effectively increased [37]. Stawarczyk., *et al*. reported that the use of Visio.link or Signum PEEK bonding significantly increased the bond between composite resins and PEEK [38].

Colour and radiolucency

PEEK dental polymer allows clinical diagnostics by the imaging techniques such as X-ray, MRI and CT due to its radiolucent nature. It provides treatment through PEEK substructure without need for substructure removal and replacement [9].

Conclusion

PEEK is emerging as a prosthodontic material which might replace many conventional materials. Due to its favorable chemical, mechanical and physical properties it is used in producing fixed and removable prostheses. In a relatively short span of time, peek became the material of choice for metal free restorations in medical as well as dental applications. Due to the high elastic modulus close to that of bone and dentin, there is an increasing use of the material in implantology. Due to the superior mechanical and biological properties of PEEK, it can be considered that in the future, prostheses made from polymer will have a place in routine applications and PEEK material will be used in dental post and core systems and the field of endodontics. However, more research has to be undertaken to validate clinical evidence.

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