

The Use of PEEK and PEKK in Prosthodontics

PEEK ve PEKK'in Protez Dişinde Kullanımı

ABSTRACT

It is stated that the search for new materials in today's dentistry continues in order to meet aesthetic and functional expectations. As a result of these searches, materials such as PEEK (polyetheretherketone), PEKK(polyetherketoneketone) and BioHPP(bio high performance polymer) have become widely preferred in dentistry. PEEK is a thermoplastic polymer. It offers features such as durable structure, tissue compatibility and lightness. Therefore, it is attracting interest as a metal alternative and is considered as a promising material in dental treatment applications. In addition, PEEK's biocompatibility properties enable it to be used in the biomedical field. PEEK is a material that resembles natural tooth color and has been used as a biomaterial in orthopedics for many years. PEKK is a newly developing polymeric material. PEKK biomaterials are elastic with excellent shock absorption and fracture resistance, demonstrating ultra-high performance compared to other thermoplastic composites, offering exceptional mechanical strength, chemical resistance, and high thermal stability. BioHPP is a PEEK-based bio high-performance polymer that has been shown as a dental substrate material. It can be used in different areas of dentistry due to its advantages such as excellent physical and aesthetic properties, low weight and biocompatibility. "PEEK and PEKK, which are polymer materials, can be successful alternatives aesthetically, mechanically, and biologically to dental implants, crowns, bridges, and removable denture framework materials in dentistry." However, it is emphasized that they should be used with caution due to insufficient clinical studies. Especially the fatigue stress and long-term performance of PEEK require further research. Therefore, studies based on more comprehensive and reliable clinical data on the use of these materials are needed.

Keywords: Bio HPP, PEEK, polyetheretherketone, PEKK

ÖZ

Günümüz diş hekimliğinde yeni materyal arayışının estetik ve fonksiyonel beklentileri karşılamak amacıyla devam ettiği ifade edilmektedir. Bu arayışlar sonucunda PEEK (poli-eter-eter-keton) ve Bio HPP (biyo yüksek performanslı polimer) gibi materyaller diş hekimliğinde yaygın olarak tercih edilmeye başlamıştır.

PEEK, termoplastik bir polimerdir. Dayanıklı yapısı, dokuya uyumu, hafiflik gibi özellikler sunmaktadır. Bu nedenle, metal alternatifi olarak ilgi çekmekte ve dental tedavi uygulamalarında umut verici bir materyal olarak değerlendirilmektedir. Ayrıca, PEEK'in biyouyumluluk özellikleri de biyomedikal alanda kullanılabilmesini sağlamaktadır. PEEK, doğal diş rengine benzeyen bir materyal olup, uzun yıllardır ortopedide biyomateryal olarak kullanılmaktadır.

PEKK yeni gelişen polimerik bir malzemedir. PEKK biyomateryalleri mükemmel şok emilimi ve kırılma direnci ile elastiktir. Diğer termoplastik kompozitlerle karşılaştırıldığında ultra yüksek performans sergilemekte, olağanüstü mekanik mukavemet, kimyasal direnç ve yüksek termal stabilite sunmaktadır.

BioHPP ise dental altyapı materyali olarak gösterilen bir PEEK bazlı biyo yüksek performanslı polimerdir. Mükemmel fiziksel ve estetik özelliklere sahip olması, düşük ağırlığı, biyouyumluluğu gibi avantajları nedeniyle diş hekimliğinde farklı alanlarda kullanılabilmektedir. Polimer malzemeler olan PEEK ve PEKK, diş hekimliğinde dental implantlara, kuronlara, köprülere ve hareketli bölümlü protez altyapı malzemelerine estetik, mekanik ve biyolojik açıdan başarılı alternatifler olabilir."

Ancak, klinik çalışmaların yetersiz olması nedeniyle dikkatli kullanım gerektiği vurgulanmaktadır. Özellikle PEEK'in yorulma stresi ve uzun vadeli kullanım performansı daha fazla araştırma gerektirmektedir. Bu nedenle, bu materyallerin kullanımı hakkında daha kapsamlı ve güvenilir klinik verilere dayanan çalışmalara ihtiyaç duyulmaktadır.

Anahtar kelimeler: Bio HPP, PEEK, polietereterketon, PEKK

INTRODUCTION

The search for new materials in today's dentistry to increase patient comfort and meet aesthetic expectations continues. With the advancement of technology, expectations in the properties and performance of the materials used in dentistry have increased. In addition, the search and expectation for aesthetics, which has recently increased in social life, has brought dentistry to an advanced level in the use of aesthetic materials. Materials used in dentistry must show certain basic properties. PEEK has become a widely preferred material in the field of dentistry because it offers several features such as its durable structure, tissue compatibility, light weight, modifiability and can be used with CAD/CAM systems. Since it can be used instead of metal alloys, it attracts the attention of researchers and is in their focus. ^{1,2} These physical and mechanical properties revealed in research show that PEEK is a very promising material for dental treatment applications.³

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PEEK is a semi-crystalline thermoplastic polymer belonging to the poly-aryl-ether-ketone (PAEK) family. This polymer consists of aromatic molecular chains linked together by ketone and ether functional groups. PEEK is synthesized as polyetheretherketone by a stepwise growth dialkylation reaction of bis-phenolate. Typically, PEEK synthesis takes place around 300 °C in a polar solvent and involves the reaction between 4,4'-difluorobenzophenone and hydroquinone disodium salt.^{1,4} This special polymer has a melting point around 335 °C and has a semicrystalline thermoplastic structure. It has good mechanical properties, easy processing, high hardness and good dimensional stability at high temperature. It is physically and chemically stable and resistant to aging. Furthermore, PEEK has excellent biocompatibility and can be successfully used in the biomedical field.⁴ PEEK is a synthetic polymer material that resembles the color of natural teeth and has been used as a biomaterial in orthopedics for many years. The most important property for orthopedic implant application is Young's (elastic) modulus. Another good feature of PEEK is its low Young's (elastic) modulus (3-4 GPa). This Young's modulus value is very close to human bone. 3

PEEK is a chemically inert material. It is insoluble in any solution except 98% sulfuric acid at room temperature. Thanks to its high mechanical, physical, thermal properties and dimensional stability, PEEK material is one of the rare polymers preferred as an alternative to many metallic materials in the industry. 6

PEEK can be modified by adding functionalized monomers before polymerization or by chemical treatments such as sulfonation, amination and nitration after polymerization. In addition, it is inherently radiolucent and compatible with imaging techniques such as computed tomography (CT), magnetic resonance imaging (MRI) and X-ray. ⁷

Recently, a PEEK-based bio high-performance polymer (BioHPP) has been demonstrated as a dental substrate material. Due to its excellent properties such as outstanding physical properties, superior aesthetic properties, low specific gravity, low plaque affinity and high biocompatibility, BioHPP can be used in many areas of dentistry. ⁸

PEKK is a new polymeric material with suitable properties for various applications. A metacrylate-free, high-performance thermoplastic, PEKK was first introduced by Bonner in 1962 and has been used for different industrial purposes since then. Widely used in restorative, prosthetic, and implant dentistry fields, PEKK is a promising material for cranial and orthopedic implants. It stands out with its high mechanical strength and the surface modification advantage of the second ketone group, offering a wide range of applications in biomedical fields. 9-11 PEEK and PEKK are characterized by the presence of aromatic rings and they exhibit distinctions in relation to their ether and ketone group compositions. Notable disparities exist between these two polymers. Specifically, PEKK incorporates an extra ketone group, resulting in heightened polymer polarity and rigidity, consequently elevating the melting temperatures. PEKK has 80% higher compressive strength and better fatigue properties compared to PEEK. 12-13

IMPLANT PEEK and PEKK

Bone can remodel according to Wolff's law, once the implant is loaded, the surrounding alveolar bone continuously shows functional adaptation , depending on the load applied to it. Therefore, osseointegrated implants, together with the surrounding bone, form a functional unit that is resistant to repetitive loads. This principle, called Wolff's law, indicates that bone remodeling is influenced by mechanical function. Reducing the stresses in the bone surrounding the implant prevents resorption of the bone structure around the implant by

eliminating abnormal loads and allowing normal loads to be maintained. 4

Hahnel et al. found in a study that implant abutments made of PEEK material showed equal or lower biofilm formation values than those made of ZrO. 15

However, the use of metallic materials in medical applications has some limitations. First of all, the strength and elastic modulus of metal alloys are considerably higher than human bone tissue. For example, the elastic modulus values of titanium-based alloys and stainless steel (>100 GPa) are significantly higher than human bone tissue (10-30 GPa). This large difference can lead to stress accumulation between the implant and surrounding tissues and absorption by neighboring bone tissues. This can lead to bone resorption and consequently prosthetic failure, a factor that hinders the acceptance of metal alloy implants. PEEK eliminates the disadvantages of titanium with its elastic modulus close to human bone.⁵

Schwitalla et al. compared the biomechanical behavior of three different dental implants by finite element analysis (FEA): The aim of the present finite element analysis was to show the differences in the biomechanical behavior of an Endolign dental implant and a commercial powder-filled PEEK. Titanium served as a control in this study. Type 1 consists entirely of titanium, Type 2 of powder-filled PEEK and Type 3 of Endolign. Endolign represents an implantable carbon fiber reinforced (CFR)-PEEK containing parallel oriented endless carbon fibers. According to the manufacturer, it has an elastic modulus of 150 GPa. A force of 100 N was applied vertically to the three implant materials with an angle of 30° to the implant axis. Type 2 showed a higher stress distribution and maximum deformation value, while Type 1 and Type 3 showed similar stress distributions. ¹⁶

In their in vitro study, Hang-ying Jin et al. found that the bond strength of Bio HPP used as a substructure material in implant fixed prostheses was higher than that of titanium. They stated that a good marginal fit and fracture resistance were obtained with CAD/CAM designed Bio HPP substructure and that Bio HPP can be an alternative to metal substructures.⁸

Aly Abdelrehim et al. evaluated the retention losses of CAD/CAM produced zirconia, Chrome-Cobalt (Cr-Co) and Bio HPP bar attachments and concluded that Bio HPP can be an alternative to Cr-Co and zirconia.¹⁷

BioHPP is a very remarkable material in implantology due to its excellent mechanics as well as biocompatibility. It is used not only as a substructure in removable prostheses, but also as a substructure in implant prostheses and as implant abutments. BioHPP is considered a suitable material for abutments, reducing stress to the implant.¹⁸

Implants made of PEEK material have been reported to have many superior properties compared to conventional metallic alloy and ceramic implants. PEEK and PEEK composites are radiolucent for X-rays. Furthermore, PEEK implants have an elastic modulus (3-4 GPa) similar to human bone tissues(10-30 GPa) (and favorable biocompatibility, resulting in a significant reduction of the stress seen in titanium and ceramic implants. Therefore, PEEK implants are more advantageous compared to other alternatives and are considered a preferred option in medical applications.¹⁹ When carbon fiber reinforcement is added to PEEK material, the elastic modulus value can be increased to approximately 18 GPa, which is closer to cortical bone. PEEK is colorless except for titanium coating or carbon fiber reinforcement (CFR). Thanks to this feature, it does not pose an aesthetic problem when used as an implant. In other words, PEEK implants are aesthetically advantageous due to their natural color, except in reinforced or coated forms.⁵

Due to its similar to PEKK dentin elastic modulus, sufficient strength, and wear resistance, it can be used as a dental implant material. Dental implants made of thermoplastic resins have shown acceptable results in terms of bone contact percentages. PEKK provides an alternative material to titanium implants as it does not contain metal. PEKK can be used for implant abutments, framework material for implant prosthesis, prosthetic crown materials over the implant.²⁰

In a study conducted by Yuan B. et al., a comparison was made between the surface modifications of PEKK and PEEK implants. The findings revealed that PEKK exhibited a higher presence of ketone groups, facilitated sulfonation more readily, and demonstrated superior bone-like apatite precipitation when compared to PEEK.²⁰ The researchers concluded that PEKK offers enhanced osteointegration capabilities and greater mechanical stability in comparison to PEEK. Consequently, they suggested that surface-modified PEKK holds promise as a viable option for applications in spinal and orthopedic procedures due to its favorable osteointegration properties.²¹⁻²³

USE OF PEEK and PEKK MATERIAL IN FIXED PARTIAL DENTURES

PEEK is able to resist deformations in the face of uniaxial tension and compression forces and it was reported that it can withstand to the forces of 1383 N. (Plastic deformation starts at approximately 1200 N).

Waltimo et al. analyzed the integration of PEEK material as a key element in crown and bridge prostheses because of its capacity to resist a maximum bite force of 909 N in the molar area [5]. In this field, there are three ways to transform PEEK material: Milling from blanks with (CAD/CAM) software, pressing from granules or pressing from pellets with a special vacuum pressing device. Blanks and pellets are prepressed forms from raw material PEEK granules.²⁴

Stok et al. found higher fracture strength for CAD/CAM milled FDPs of three-unit fixed dental prostheses (FDPs) made with PEEK compared to FDPs pressed from granules. Several studies have shown that a pretreatment of PEEK using sulfuric acid increases its surface energy and thus improves its bonding properties to dimethacrylate-based resin composites.²⁵

In a case report published by Andrikopoulou et al., a treatment of 14-year-old patient with cleft lip and palate and also congenital lateral incisor deficiency was presented. In the prosthetic rehabilitation of this patient, a Hawley appliance and a resin-bonded fixed prosthesis with Bio HPP substructure were compared. In the study, it was stated that the resin-bonded fixed prosthesis using Bio HPP substructure was more advantageous in terms of aesthetics. It was reported to have provided a more natural appearance in terms of color, which significantly improved the patient's smile aesthetics. In addition, the use of this fixed prosthesis enabled a more comfortable experience to the patient. In conclusion, it was emphasized that the Bio HPP-based fixed prosthesis is a more aesthetic and comfortable prosthetic solution for patients with cleft lip and palate. It is also aesthetically advantageous that it does not have a metal orthodontic wire extending to the buccal surface like the Hawley appliance.²⁶

The mandatory use of resin cement when bonding a BioHPP substructured resin-bonded fixed dental prosthesis (RBFDP) provides a bond strength of 25 Mpa, which is considered an adequate bonding value and allows minimally invasive tooth preparations without retaining elements.^{27,28}

After evaluating the studies that different surface treatments and resins have been used, PEEK may be considered as a suitable material for FDPs, especially in load bearing areas.²⁹

Hang-ying J. et al. stated that PEEK in its pure form has a low resistance to bending fatigue, thus limiting its application. Pure PEEK was initially used in prostheses on a temporary basis until another component, zirconium oxide known as BioHPP, was added for the fabrication of both abutments and superstructures in overdentures or hybrids.⁸

Zoidis et al. presented the use of PEEK material as a resin-bonded fixed provisional prosthesis in a clinical case report. ³⁰

In this study, they concluded that good quality bonding of PEEK substructure material with resin cements can extend the life of restorations with minimally invasive tooth preparations without retention elements. When thin teeth such as mandibular incisors are used as abutments, the enamel can be fully protected, resulting in high bond strength. Another advantage of the PEEK framework is its high bond strength with light-polymerized composite veneers. PEEK has a low specific gravity, which allows the production of low-weight prostheses. Thus, it provides increased patient satisfaction.² In addition, recent publications have reported that PEEK is a suitable material for double crown telescopic systems.²⁵

Merk et al. aimed to compare the retention values of double crowns according to different taper angles and fabrication differences. Primary crowns were made of ZrO2 and secondary crowns were made of PEEK material fabricated in three different ways; (i) CAD/CAM milling breCam BioHPP (bredent, Senden, Germany, LOT: 394172); (ii) PEEK pellet pressing BioHPP Pellet (bredent, Senden, Germany, LOT: 393554); (iii) PEEK granule pressing BioHPP Granulate (bredent, Senden, Germany, LOT: 379806). The taper angles of the primary crowns were 0, 1 and 2 degrees. A tensile test setup was created for retention load measurement. The primary crown of the socketed mold was fixed in a universal testing machine (Zwick 1445, Zwick, Ulm, Germany). The secondary crown was wetted with artificial saliva (Glandosane, cell pharm GmbH, No. 9235461109) and placed in a final position on the corresponding primary crown. In each of the 20 cycles, a 5 kg weight was placed on top for 20 seconds to provide a comparable initial state for each sample. The secondary crown was pulled at a speed of 50 mm/min using a hook mounted on the designed holder. It was shown that the pellet pressed group had significantly higher retention load values compared to the other groups by comparing the fabrication method within 0° taper angle. For crowns with a taper angle of 1°, the CAD/CAM fabricated secondary crowns had significantly lower retention load values than the pressed groups. However, they reported that the type of pressing had no effect on the results. They observed no effect of taper on retention values among secondary crowns pressed from PEEK pellet material.24

PEKK has been used as the base material for implant-supported complete fixed dental prostheses (ICFDP) due to its lightweight nature and ability to work well with various veneering materials. It is becoming increasingly popular for its flexible manufacturing options, which include milling and heat pressing; however, there are limited reports endorsing its practical application in clinics. ³¹⁻³³

Keilig et al.'s finite element analysis demonstrated a significant impact of uniformly distributed stress within the framework material of small bridges consisting of three and four units. Additionally, the adjacent tissues remained unaffected by strain, thus verifying the potential of the polymer PEKK as a viable alternative to metal frameworks.³⁴

USE of PEEK and PEKK in REMOVABLE PARTIAL DENTURE

Conventional removable partial dentures with chromium-cobalt frameworks are offering a predictable and inexpensive treatment for patients with partial edentulism.³⁵ However, there are some disadvantages such as metal allergies of some patients, the heavy weight of the metal substructure and its unaesthetic appearance. At this point, Bio HPP appears as an alternative material.

Prostheses and parts made of BioHPP material are much softer than prostheses made of traditional Cr-Co material, tooth enamel structure and porcelain. Porcelain scratches caused by the rigid structure of Cr-Co clasps of removable partial dentures can be eliminated thanks to the elasticity of BioHPP.

Tannous et al. reported that denture clasps made of PEEK material showed relatively lower retention forces than Co-Cr clasps.³⁶ However, it can be said that the BioHPP retentive arm designed on a tooth with an undercut of 0.5 mm has clinically sufficient retention.²⁷ The flexibility of BioHPP can reduce the distal torque and stress on the abutment teeth. Therefore, it can be assumed that BioHPP will be a suitable alternative for support teeth with reduced periodontal support when restoring cases with distal extensions.³⁰

In addition, the clasps obtained from BioHPP provide a healthy periodontium, especially when they're close to the tissue, due to the low plaque affinity of the material [27]. BioHPP also has the advantage of lower specific gravity. In one study, two different traditional removable partial dentures, one with a BioHPP lingual plate and the other one with a Cr-Co lingual bar, were compared. It was reported that the prosthesis made of BioHPP material weighed 27.5% less than the one made of Co-Cr, despite the use of a lingual plate.³⁰

PEEK has also been used successfully in patients with maxillofacial defects. Costa Palau et al. successfully closed the antral part of the obturator prosthesis with 'PEEK OPTIMA' material in patients with oral maxillary defects. This method resulted in a lighter prosthesis and did not cause any adverse effects on the tissues in contact with PEEK. It was also reported that the contact tissues responded positively and the patient's aesthetics, retention and comfort were significantly improved compared to other prostheses. These findings indicate that PEEK material has attracted attention as an effective and satisfactory treatment option for patients with maxillofacial defects.³⁷ The white color of PEEK material has a superior aesthetic appearance compared to traditional metal substructures. However, more studies and research are needed to fully evaluate the efficacy of PEEK obturator prostheses compared to traditional acrylic prostheses. More comprehensive studies in this field will more clearly reveal the advantages and effects of PEEK material and its application areas. 5,7

Lee et al. aimed to evaluate the retentive force and deformation of PEEK and PEKK Akers clasps with various designs and undercut depths in their in vitro study. The study found that all PEKK specimens exhibited brittle fracture following the bend test, whereas PEEK specimens only displayed plastic deformation.³⁸

Sun et al presented a digital workflow for applying PEKK in removal speech bulb prosthesis. $^{\rm 39}$

There are not enough clinical studies yet for the safe use of PEEK and PEKK as removable partial denture materials. There is no scientific evidence on how this material will behave in the face of fatigue stress, so this material should be used with caution, at least until clinical evidence is available. 40,41

Other Uses of PEEK and PEKK

Elashmawy et al. evaluated the bond strength and retention of these materials in an in vitro study on endocrowns produced with CAD/CAM

from different materials. The materials were; resin infiltrated ceramic (Vita Enamic), partially stabilized tetragonal zirconia (Katana), lithium disilicate ceramic (IPS e.max CAD), PEEK and BioHPP. After appropriate surface treatment, the restorations were cemented using a resin cement (Panavia F2.0) and bonded to a special attachment unit and fixed in a universal testing machine. The amount of axial load required to remove the restoration from the tooth structure was measured (n = 12, a = 0.05). The evaluations were classified as adhesive separation from the tooth structure without damage to the supporting tooth structure and cohesive fracture of the supporting tooth structure. As a result of this study, the retention values of resin infiltrated ceramic and lithium disilicate ceramic material were significantly higher than the other materials. Resin infiltrated ceramic and lithium disilicate were associated with fractured tooth sections during debonding, while Katana and PEEK specimens were separated from the remaining tooth structure. It is possible to conclude from this study that PEEK can be a good alternative to other materials when tooth structure is to be preserved.⁴²

Rajamani et al. conducted a study to evaluate the clinical performance of inlay restorations made of Bio HPP PEEK in terms of retention, marginal discoloration, color matching, marginal fit, secondary caries, surface texture, wear-anatomical form, postoperative sensitivity and fracture resistance using modified Ryge criteria by comparing them with the widely used zirconia (sintered monolithic zirconia, Zolid, Amann Girrbach AG, Koblach, Austria). 40 patients were selected and 20 of the mandibular and maxillary molars had inlay restorations made with zirconia CAD/CAM using Bio HPP PEEK and 20 with zirconia CAD/CAM. These restorations were then evaluated by two prosthodontists blinded to the study according to modified ryge criteria at 1st week, 3rd month, 6th month and 12th month. 90% of the BioHPP PEEK veneers were rated as satisfactory compared to 95% of the zirconia veneers. They found a sensitivity score of 10% for BioHPP PEEK inlays and 15% for zirconia inlays. They did not find any significant difference with other parameters in this study. BioHPP PEEK was found to be satisfactory when used as indirect aesthetic restorations, with a relatively low fracture rate over a one-year observation period compared to zirconia inlays in posterior teeth. BioHPP PEEK was said to be a suitable alternative with a high level of accuracy in terms of retention, marginal fit and aesthetics.43

PEKK is also applicable in maxillofacial rehabilitation. Oh et al. detailed the rehabilitation process of a mandibulectomy patient using a fibula free flap and implant-supported prosthesis with a PEKK framework material.⁴⁴

CONCLUSION

Thermoplastic polymers are promising materials whose use in prosthodontics is rapidly increasing. However, the use of these materials should be cautious as there are not enough clinical studies yet. Further research and clinical studies will help us better understand the advantages and effects of these materials.

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