HIGH-PERFORMANCE POLY-ARYL-ETHER-KETONE (PAEK) POLYMERS USED IN DENTISTRY

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ABSTRACT
Poly-ether-ether-ketone (PEEK) and poly-ether-ketone-ketone (PEKK) are the two best-known members of the high-performance poly-aryl-ether-ketone (PAEK) family. PEEK and PEKK are thermoplastic materials in aromatic polymer structures in which ketone and ether functional groups are bonded to each other. PAEK polymer family, which is used in the medical field, has recently started to be used in the field of dentistry. PAEK polymer family is an option for metal restorations due to its advantageous features such as showing similar mechanical properties with metal infrastructure materials traditionally used in dentistry, enabling the production of more aesthetic restorations in addition to these, being produced with CAD/CAM technology and being biocompatible. Although the usage area of PAEK polymers in dentistry is increasing day by day, many types of research are carried out on this subject as it can be an alternative to the traditional materials used in dentistry. This review aims to investigate the properties and usage areas of PAEK polymers used in dentistry.

Keywords: Polymers, Poly-ether-ether-ketone, Poly-ether-ketone-ketone.

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INTRODUCTION
Considering the esthetic expectations, the increasing interest in metal-free restorations are increasing day by day, and in parallel, the use of metal-free polymer materials in oral implantology and prosthetic applications is increasing (1). Polymer material, which has been used frequently in dentistry poly-ether-ether-ketone (PEEK) and poly-ether-ketone ketone (PEKK) materials are the two most well-known members of the high-performance poly-aryl-ether-ketone (PAEK) family (2) (Fig. 1).

PAEK polymers are linear compounds in which aromatic compounds are connected by ether and ketone bonds in a different order (3). The material-specific properties of PAEK polymer differ according to the functional ketone and ether ratio in the structure. The number of functional groups can affect the mechanical and thermal properties of the material. The higher the ratio of ketone groups to ether groups,
the higher the hardness and melting point of the polymer chain (4).

It is thought that PAEK polymers can replace metal and glass ceramics due to their good stress distribution, acceptable fracture resistance, and good shock absorption capabilities (5).

General properties of PAEK polymer:
✔ Good mechanical strength despite increasing temperatures,
✔ Good resistance to impacts,
✔ Good resistance to abrasion,
✔ Low water absorption,
✔ Good chemical resistance,
✔ Potential resistance to radiation (6).

Biocompatibility of PAEK polymer has been shown in studies and this material has been used for orthopedic and spinal implants since 1980 (3,7). PAEK polymer can be used in many areas of dentistry such as crown-bridge prosthesis, temporary implant abutment material, and denture base material (8). Unlike methacrylate-based polymer materials, PAEK polymer does not contain any residual monomers in its structure. No allergy cases have been mentioned in the literature related to PEEK (9). Due to its superior properties in comparison with traditional polymer materials, PAEK polymers are widely used in dentistry (8).

Properties of PEEK and PEKK Polymers

PEEK polymers are semi-crystallized linear thermoplastic materials that can be used instead of metal due to their good durability and corrosion resistance (10,11). The pure skin-colored PEEK polymers have a compound structure in which the ketone and ether groups are connected by aryl groups (4,12) (Fig. 2).
PEEK polymer restorations which can be produced by casting with lost wax technique or CAD/CAM technology under pressure and heat are highly resistant to high temperatures (13). The radiolucency properties make PEEK polymers compatible with imaging methods such as tomography, magnetic resonance, and X-ray (3, 14). PEEK is a chemically inert material. Although the modulus of elasticity (3-4 GPa) of the PEEK polymer is close to the human cortical bone (7-30 GPa), it is not the same (15). In addition, tensile properties are similar to enamel, dentin, and bone (16-18).

Due to the superior properties of PEEK polymer for dental use, PEKK polymer, another member of the PAEK family, has become the focus of studies for researchers (2). PEKK has a linear structure in which ketone and ether groups are interconnected like PEEK polymer, while the second ketone in PEKK polymer structure increases the hardness and melting temperature of the material (4, 19, 20) (Fig. 3). PEKK has excellent physical and mechanical properties due to its higher melting temperature and compressive strength compared to other polymer materials (21).

Table 1. Comparison of mechanical properties of PEEK and PEKK polymers with other materials (2).

|                      | PEEK     | PEKK   | Titanium | PMMA     |
|----------------------|----------|--------|----------|----------|
| Tensile Strength (MPa) | 100.69   | 115    | 240–890  | 48–62    |
| Elastic modulus (GPa)  | 3.5      | 5.1    | 103–114  | 3.8 ÷ 103|
|                         |   |     |     |     |
|-------------------------|---|-----|-----|-----|
| Flexural strength (MPa) | 163.88 | 200 | 65  | 107–117     |
| Compressive strength (MPa) | 118-169 | 246 | 130-170 | 76      |
| Melting temperature (°C) | 334-350 | 363-386 | 1650–1670 | 160    |
| Hardness                | 26–29 VHN | 252 MPa | 90 VHN | 89–95 MPa |
| Water absorption (mg/mm³) | 0.1–0.5 | 8.7 | 0.04 | 0.1–0.3 |

**Usage of PEEK and PEKK Polymers in Dentistry Implantology**

Although titanium (Ti) and its alloys have excellent mechanical properties for dental implants, electrolyte structures released from the surface of the implants over time can result in immune response (23). In addition, the modulus of elasticity of titanium is higher than bone. Due to this fundamental difference, titanium material can be failed (24,25). PEEK can be considered as an alternative dental implant material because of its close elastic modulus to the bone, resistance to abrasion and fatigue, radiolucency that does not cause artifacts in magnetic resonance (MR), and computerized tomography (CT) (25,26).

Schwitalla A. et al.,12 could not find a significant difference in bone resorption and soft tissue inflammation around metal and PEEK structures. PEEK polymer is considered an alternative to titanium in the preparation of implant abutments. Gheisarifar et al.,27 in their study evaluating the viability of human gingival fibroblasts (HGFs) and their adhesion with abutment materials after surface changes, explained that laser surface modification causes titanium and gingival fibroblast attachment on PEEK surfaces. In addition, the plasma surface treatment applied to the surface of the polymer PEEK increased the wettability of the material, improved the proliferation of HGF. Guo et al.,28 dental implant materials increase cytocompatibility of titanium, zirconia, and modified PEEK to the surface of the ultraviolet (UV) light and non-thermal plasma (NTP) processes are applied, the application of argon plasma surface cytocompatibility varies according to the cell type and the effect of the processed material specified. In addition, they have shown that UV...
light and oxygen plasma treatments can improve the attachment of fibroblast cells surface titanium, zirconia, and PEEK surfaces. PEKK polymer has also advantageous properties such as lightness, abrasion resistance, elastic modulus close to dentin, and sufficient durability (5). In oral implantology, PEKK polymer can be an alternative to titanium since it does not contain metal in its structure (12). PEKK can be used as implant abutments and biomaterial due to its superior mechanical properties. According to the results obtained in the research, the percentage of contact area with the bone of the implants produced from thermoplastic resin materials is at an acceptable level (29). The compatibility of PEKK polymer with different materials, such as combining PEKK attachments with titanium, may create long-term retention in implant prostheses (30,31,32).

**Fixed Dentures**

PEEK polymer may be more advantageous than ceramic and metal alloy due to its similar mechanical properties with enamel and dentin tissue. However esthetic properties of PEEK can not be satisfactory for most clinical cases. Owing to its grayish color and opacity, it should be covered with veneer material in clinical use. It has been indicated that modified PEEK polymer can be used in crown-bridge prostheses (33).

The techniques used for the production of prosthetic infrastructure from PEEK material are injection molding and CAD/CAM methods. In the injection molding method, polymer materials are processed at twice the speed and pressure compared to typical bench-top press machines. However, it should be noted that this method can cause unexpected mechanical and physical problems in the remelting of PEEK polymer if the infrastructure is not cooled and crystallized correctly (34). The properties of the materials produced by CAD/CAM technology, another production method of PEEK material, remain stable, and more precise infrastructure products can be made by taking advantage of the benefits of digital workflow. Compared to metal infrastructures, PEEK polymer requires less milling abrasion and can be produced faster (34,35). The latest developments in extrusion-based filament 3D printing technology increase the processability of high-performance polymers. But research on 3D-printed PEEK is rare due to processing difficulties (36).
Bauer et al.,\textsuperscript{37} showed that the fracture strength of PEEK crowns is higher compared to zirconia and ceramic crowns in their studies. Stawarczyk et al.,\textsuperscript{38} have reported 2354 N (Newton) fracture strength for fixed prosthesis produced from PEEK polymer by CAD/CAM technology. According to the previous studies, this value is on average two times higher than the chewing forces which are approximately 600 N in the posterior region (39). Sloan et al.,\textsuperscript{40} investigated the bonding strength of lithium disilicate material with PEEK and zirconia materials and as a result of their study, they found that the bonding strength between PEEK polymer and lithium disilicate material is significantly lower in terms of the bonding strength between zirconia and lithium disilicate.

After applying different surface treatments to the PEEK polymer surface, Tsuka et al.,\textsuperscript{41} investigated the strength of the shear bond with different resins, and the samples that applied laser groove treatment indicated significantly higher bonding resistance than those of the no-treatment and air abrasion treatment groups.

Similar to PEEK material, PEKK polymer structures may also be used as alternative restoration materials in fixed prostheses due to their superior mechanical properties (29,30). With the development of CAD/CAM technology, the production of modern restorations by new materials has become easier than traditional methods. Recently, PEKK material can also be used by CAD/CAM technology for prosthetic restorations. PEKK polymer can be used in fixed dentures as monolithic restoration or framework with veneering material (29,33,37,38).

Choi et al.,\textsuperscript{42} have compared Pekkton\textsuperscript{®} (high-performance polymer), Yamahachi\textsuperscript{®} (PMMA), Mazic Duro\textsuperscript{®} (nano-hybrid ceramic), Vipi Block Monocolor\textsuperscript{®} (PMMA), and Vita Enamic\textsuperscript{®} (hybrid ceramic) materials according to the amount of wear on the opposing tooth. While significant wear was observed in the PEKK polymer structure, the same polymer caused the least wear on the opposing tooth. However, PEKK and both PMMA materials are easily deformed and displaced under stress due to their low elastic modulus.

Gouveia et al.,\textsuperscript{43} investigated the effect of surface treatments and manufacturing process methods of pressed PEKK, milled PEKK, milled PEEK samples produced by different methods of PAEK polymers on the shear bond strength.
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of the composite. They reported that 110 µm aluminum oxide airborne particle abrasion significantly affected the shear bond strength of PEEK and PEKK surfaces with composite resin. It is noted that the PEKK polymer of the production process (milled or heat-pressed), the application of the same adhesion procedures does not have any effect on the shear bond strength.

**Removable Dentures**

Removable dentures with chrome-cobalt infrastructure and clasps are widely used in prosthetic applications due to their cost-effectivity. However, it has some disadvantages such as metallic taste, increased denture weight, possible allergic reaction, and unaesthetic appearance (44). Due to these disadvantages, 20% ceramic-filled modified PEEK polymer can be used in removable dentures because of its advantages such as lightweight and white color (44). Another material most commonly used in removable prostheses is polymethyl-methacrylate (PMMA). PEEK polymer is an alternative option to PMMA due to the absence of residual monomer and increased fracture strength (45).

In their study, Zoidis et al., 44 showed that PEEK material weighs 27.5% less than the chromium-cobalt infrastructure material, although a lingual plate was made instead of a lingual bar. Mayinger et al., 46 investigated the shear bond strength between polyetheretherketone (PEEK) and cold-cured polymethylmethacrylate (PMMA) materials after surface treatment indicated that the application of 0.4 MPa- 110 µm Al₂O₃ aluminum oxide can be recommended to increase the bond strength. Papathanasiou et al., 47 evaluated PEEK polymer, polyamide, acetal resin, and heat (methylmethacrylate) PMMA acrylic resin materials for color stability, gloss, and surface roughness after everyday staining different solutions. In this study, which compared the polymer materials used in removable prostheses, they reported that PEEK polymer is the most stable material in terms of surface properties and discoloration in daily staining solutions, and PEEK material is a suitable material for removable prostheses.

PEKK polymer like PEEK material has recently been used in the manufacture of substructures and clasps for removable dentures by using digital technology (48). Sun et al., 48 produced the removable bulb obturators from PEKK polymer by 3D printing technology. At the
6-month follow-up of the case, the PEKK infrastructure removable bulb obturator prosthesis showed proper retention and stability. Tannous et al.,49 in this study, evaluate the retentive force of clasps made of cobalt-chromium (Co-Cr) alloy and three different thermoplastic resin materials (PEEK, PEKK, polyoxymethylene (POM)). They analyzed this research by insertion/removal test simulating 10 years of use. Although thermoplastic retainers showed lower retention than Co-Cr retainers, they maintained retention despite the application of 15,000 joining and separation cycles. They noted that properly designed resin retainers will be sufficient for clinical use. Ding et al.,50 demonstrated the construction of conventional total prostheses with PEKK infrastructure produced by CAD/CAM method in their clinic report. They did not observe any biological or prosthetic complications during the 1-year follow-up.

CONCLUSION

In dentistry, PAEK polymers have an increasing area of use due to their superior properties. Due to their properties comparable to metal infrastructure materials, PAEK polymers have become the focus of research. From the studies conducted, we think that PAEK polymers will have an even increased use in dentistry clinical practice.

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