

Advancement in PEEK Properties for Dental Implant Applications: An Overview

Ayushi Pandey¹, Dr. Vinay Pratap Singh²

¹Mechanical Engineering Department, HBTU Kanpur, 208002

²Assistant Professor, Mechanical Engineering Department, HBTU Kanpur, 208002

Abstract- Dental implants are used as a prosthetic treatment for treating edentulism. There are several factors that can impact the survival of a dental implant but the crucial one and the most determining factors is osseointegration that results for the performance of a dental implant. The objective is to make the osseointegrated dental implants act almost similar to the natural teeth for which different materials are extensively studied that are having bioactive properties or surfaces of materials are modified so that it could be a viable alternative to the already existing conventional materials, these modifications are somewhat done either by synthesizing or reinforcing the bioactive materials, hence improving the longevity of implants. The aim of this document is to deliver the background and the research performed on the different materials in the field of dentistry. Moreover, the future possibility of high-performance thermoplastic polymer Polyether ether ketone (PEEK) and GFR-PEEK/CFR-PEEK in “clinical dentistry” is emphasized.

Key Words: Dental implants, bioactive materials, PEEK.

1. INTRODUCTION

Dental implants enhances the quality of life for the patients having tooth loss because of any situation[1]. Since Brånemark conceptualized osseointegration and the probability of artificial dental replacement, a restorative approach came into existence[2,13]. Since 1969, the application of dental implants for oral and maxillofacial reformation promptly expanded as per the requisition of patients[2]. The occlusal forces basically induces the stresses and strains inside the dental implant and affects the jawbone surrounding the implant[2]. It came to be a challenging task when the bone losses were too severe for the human body and in such case the osteogenic, osteoinductive and osteoconductive property-based materials are preferred[14]. Bioactive materials activate a biological response from the body resulting in the direct chemical bond between the implant and host tissues at the interface[17]. Thus, bioactive materials play a vital role in implant[17].

Titanium (Ti) and its alloy Ti-6Al-4V[1,3,5] are the conventionally used bio-friendly material but they have setbacks of its own like hypersensitivity, non-aesthetic, as well as the radiopacity of Ti and its alloys moderately releases aluminum and vanadium ions that eventually curtails the applications of metals there were many patients who also reported the allergy due to titanium [14] and out of all this the major reason because of which mechanical stress is not properly distributed between the implant and jawbone is the modulus of elasticity of titanium(Ti) that is 110 GPa[3,5] more than that of bone which is 13.8- 14 GPa[3,5] causes the medical phenomenon of bone resorption by shielding the alveolar bone from occlusal stresses for sustaining bone volume called as stress shielding[1]. Therefore alternatives are studied and considered so as to overcome these drawbacks. In which the first alternative were the ceramic-based dental implants , zirconia[1] that acquires the recommended mechanical strength, low plaque affinity, good resistance to corrosion in biological fluids, and in addition to all this it was aesthetically fulfilling the demand of consumer but the modulus of elasticity is 210 GPa[3,5] which acts as a restraint for further usage of this material. Keeping these limitations in check the synthetic polymers were the next to be examined because of their adaptability and

Presently, the polymers such as PLA, PTFE, UHMWPE, PMMA and PGA were taken into the consideration. Out of which some were weak others were too flexible and cannot withstand the amount of strength as per the specifications. During composite polymerization, the monomer chains initiate a cross-linking method and creates a stress at the tooth-restoration interfaces[6,4]. This stress is affected by the elastic modulus and volumetric polymerization shrinkage[6]. As stated, control of the curing speed leads to more flowability of the composite during polymerization and reduces the amount of polymerization stress[6]. The only known method to lessen shrinkage is to lessen the number of methacrylates or use polymerization chemistry[6]. The maximum rate of polymerization shrinkage takes place in the course of the phase transition from a viscous into a viscoelastic state and then in the elastic phase[6]. Altogether, polymerization shrinkage decreases by a slight increase of light intensity with the soft-start photoactivation method[6].

2. PEEK as an alternative material for Dental Implants

In 1978, PEEK was developed as a synthetic polymer, with the monomer unit of etheretherketone (Fig.1) that polymerizes through a mechanism of step-growth dialkylation of bis-phenolates [10]. The chemical structure of PEEK is an amalgamation of aryl rings having ketone and ether groups, belonging to the family of polyaryletherketone polymer[7]. Two ways to synthesis PEEK are - varying percentages of 4, 4'-difluorobenzophenone with electrophilic component that is 3, 5-difluoro benzophenone or 2,4-difluoro- benzophenone in nucleophilic aromatic substitution polycondensation reactions with hydroquinone in a polar solvent that is diphenyl sulphone at 300°C[8,9]. PEEK is also a semi-crystalline with a melting point close to 335°C[10]. The glass transition temperature of amorphous PEEK is 145° C, and the melting temperature of unblended polymer is 343°C[3,8].

Polyetheretherketone (PEEK) is almost like a tooth-colour, polycyclic, aromatic, thermoplastic organic polymer with complementary mechanical and chemical properties for biomedical usage [10]. PEEK, a biocompatible polymer, has also been used in fields related to tissue fixation and rehabilitation [11]. Its medical practice started in the 1980s and in the 1990s it was widely used as a substitute for metal implants in orthopaedics such as spinal surgery, cardiovascular application, fracture fixation, joint replacement, maxillofacial surgery, and femoral prostheses where it acted as an alternative to stainless steel bone plate[11].

And this is all because of its superior mechanical characteristics and biocompatibility that is widely used as a provisional abutment[3]. Implant's long-term sustainability is generally determined by soft tissue management which is complex and difficult to accomplish therefore the provisional prosthesis placed before the final one is done to allow the soft tissues to develop and heal more rapidly[3]. Regarding its mechanical properties, PEEK is radiolucent material, non-toxic, stable even at very high temperatures of more than 300°C and with no mutagenic effects[3,9,11]. It has outstanding abrasion and wear resistance and small coefficient of friction[1,3]. In medical, the main objective is to optimize the power-to-weight ratio by using high-performance materials available as per the research [8]. PEEK can be modified either by pre-polymerization with the reinforcing materials (such as glass and carbon fibers) or by post-polymerization through chemical processes of sulphonation, amination, and nitration[9,10].

PEEK Implants can improvise the soft tissue stability[19]. Moreover, these implants are lucid to X-rays, which is a very beneficial factor in the analysis of treatment advancement by computed tomography or nuclear magnetic resonance in the postoperative healing phase[19].

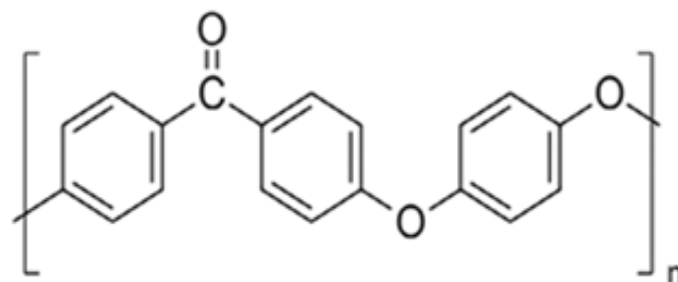


Fig .1. Chemical Structure polyetheretherketone (PEEK)[10]

3. Pre-polymerized Modification in PEEK

The major advantage of using PEEK as an implant application remains its lower modulus of elasticity (3-4GPa) close to human bone(14GPa) and dentin(15 GPa), hence PEEK modulus can be improvised by reinforcing it with glass/carbon fibers(Table 1) so as to achieve up to 12- 18 GPa[8,10]. Different reinforced PEEK composites have been prepared so as to elevate the properties of Pure PEEK material , such as nano-TiO₂/PEEK (PEEK combined with nano-particles of titanium oxide) , short carbon fiber-reinforced/continuous fibre-reinforced PEEK(CFR-PEEK) and glass fiber-reinforced PEEK (GFR-PEEK) with the elastic modulus of 18GPa for CFR-PEEK and 12GPa for GFR-PEEK, etc[10,11].

In dentistry, CFR-PEEK is highly operated in the palatal section of maxillary obturator prostheses in patients that are particularly having immense oral-nasal defects[12]. The toughness and high fatigue resistance of CFR-PEEK can also

result in the minimization of the implant fracture[12]. n-TiO₂/PEEK, has been exhibited to enhance the bioactivity of PEEK and build on osteoblast attachment[11].

Finite-element analysis (FEA) of short/continuous carbon-fiber reinforced PEEK (CFR-PEEK) for dental implants are suggested so that they could promote lesser stress shielding than titanium and its alloy that were used conventionally[10]. But the clinical trials of , PEEK dental implants is not widely performed so it is still not verified if there is any difference between the bone resorption around PEEK or titanium implants[3]. Certainly, more clinical trials are vital to deduce this very fact in detail [3].

CFR-PEEK is more preferred due to its compatibility, adaptability with modern imaging techniques[30]. According to the energy dissipation theory, the load exerted on an implant with small deformation implies for the energy conservation characteristic of rigid implants. Sarot et. al[28] also reported the stress distribution of 30% CFR PEEK and Ti using a finite element method (FEM), the results was based on the presumption of an endless carbon fiber (considered as a stronger version of CFR-PEEK) dental implant which eventually decreases stress peaks at the bone-implant attachment due to reduction in the elastic deformation[28]. But in one of the report presented by, Schwitalla et.al[20] in which they compared Powder-filled PEEK and 60% parallel-oriented endless carbon fiber CFR-PEEK with an elastic modulus of 150 GPa and after this concluded that due to higher stress concentrations, the endless carbon fibre CFR-PEEK implant could not be advised and in addition to this CFR-PEEK is black due to the carbon fibers, thus making it more unfavorable, aesthetically ,so there are varying data's which could not reveal the exact status of PEEK composites[20,28].

Table -1: The tensile strength and elastic moduli of different materials

MATERIAL	Tensile Strength (MPa)	Young's Modulus (GPa)	References
PEEK	80	3-4	Sandler, 2002 [22]
Cortical Bone	104-121	14	Rho, 1993 ;Martin, 1989; [23,35]
CFR-PEEK	120	18	Sandler, 2002 [22]
PMMA (Polymethylmethacrylate)	48-76	3-5	Zafar, 2014;Vallittu, 1998; [32,33]
Titanium	954-976	102-110	Lee, 2012 [21]
Dentin	104	15-30	Chun, 2014; Rees, 1993 [29,31]
Enamel	47.5	40-83	Staines, 1981; Cavalli,2004; Rees, 1993; [36,29,30]
GFR-PEEK	147-154	12	Lee, 2012 [21]
Zirconia	77-85	210	Lee, 2012 [21]

4. Post-Polymerized Modification / Surface Modification of PEEK

Pure PEEK is naturally hydrophobic, with a water-contact angle of 80–90° and high hydrophobicity, that shows superior bioinert property, but inadequate ingrowth in the surrounding tissue[19]. Additionally, PEEK is disinfected by ethylene oxide, gamma radiation or steam under pressure[21]. Recently, PEEK is also modified at the nano-level in order to enhance its bioactivity[10]. Traditionally, PEEK are coated by plasma spraying of bioactive materials such as calcium hydroxyapatite-HAp or titanium particles[10]. The plasma melts the bioactive materials to covert the implant surface and produce a irregular surface layer[11]. Although spraying the bioactive material may be apt for larger implants, but the coating produced does not proves to be useful for smaller dental implants[10,16,18]. This is because the formation of uneven surface and thick hydroxyapatite layer on the dental implant that gets delaminated is certainly a major causes of the implant failure[16].One more drawback is of high temperature that could weaken the PEEK structure because of its remarkably low melting temperature of 340°C[10]. PEEK can also be altered by multiple plasma modifications such as methane and oxygen plasma, hydrogen/argon plasma, ammonia/argon plasma and nitrogen and oxygen plasma [16]. Surface coatings can be applied using the following techniques such as physical vapour deposition, aerosol deposition,

plasma immersion ion implantation, cold spray technique, electron beam deposition, ionic plasma deposition, radio-frequency, vacuum plasma spraying, and spin coating[11,16].

TiO₂, HAF, and Hap (nano-particles) are combined with PEEK through melt-blending so as to produce bioactive nanocomposites and increasing surface roughness too [10,24]. chemical modifications are done by the fusion with bioactive properties that are examined experimentally first (sulphonation, amination and nitration) (Table 2)[10,17]. Moreover, modified PEEK shows superior tensile properties than unblended PEEK[10,11]. It has been suggested that the mixing of Nanoparticles of hydroxyfluorapatite (n-FHA), could suppress bacterial adhesion and reducing the threat of peri-implantitis[11]. Therefore, n-FHA have good potential to be procured in dental implant applications[3].

The heat treatment methods can also elevate the degree of crystallinity and pacify the residual stress and shrinkage distortion, therefore in a way increasing the mechanical functioning of PEEK parts[16]. Hence, the PEEK composite could be customized by carbon fibers to almost replicate the property of human cortical bone[10].

Table 2: Surface Modification of PEEK [3]

Surface Modification	Processes	Material	References
Coating	Plasma spraying	Titanium (Ti);Hydroxyapatite(HA-p)	Rust-Dawicki 1995; Ha, 1994 Suska, 2014; [26,25,27]
Surface conversion	Sandblasting	aluminium oxide (Al ₂ O ₃) , TiO ₂	Xu, 2015;Suska, 2014; [25,37]
Chemical Alteration	Sulphonation	Sulfonate groups (-SO ₃ -)	Yee, 2013 [38]
Integrating with bioactive properties	Bioactive inorganic materials	Nano-TiO ₂ (n-TiO ₂);nano-fluorohydroxyapatite(n-FHA)	Wang, 2014 ;Wu, 2012; [18,39]
Upgrading Hydrophilicity	Plasma gas treatment	Oxygen plasma	Waser-Althaus, 2014; Poulsson, 2014 Xu, 2015[40,39,34]

5. CONCLUSIONS

The review attempted to probe the different practices that are performed to improvise the bioactivity of PEEK dental implants and optimize the direct attachment or connection of osseous tissue to an alloplastic material without intervening connective tissue. In medical terms, the effective implant should hold out against the forces of mastication. Therefore, future studies are advised for better clarity, depicting the different materials and their impacts and variations it has on the firmness of the implants when they are exposed to occlusal and masticatory forces.

REFERENCES

1. PEEK dental implants: a review of the literature Andreas Schwitalla 1, Wolf-Dieter <https://doi.org/10.1563/AAID-JOI-D-11-00002>
2. Application of Finite Element Analysis in Dentistry https://www.academia.edu/29356527/Application_of_Finite_Element_Analysis_in_Dentistry.
3. PEEK with Reinforced Materials and Modifications for Dental Implant Applications <https://doi.org/10.3390/dj5040035>
4. Composite resin polymerization and relevant parameters, S.R.Schricker <https://doi.org/10.1016/B978-0-08-100383-1.00009-6>
5. On the Future Design of Bio-Inspired Polyetheretherketone Dental Implants <https://doi.org/10.1002/mabi.201900239>.DOI:10.1002/mabi.201900239
6. Polymerization Shrinkage, Shrinkage Stress, and Degree of Conversion in Bulk-Fill Resin Composites After Different Photo-Activation Methods , Sara Majidinia, Hossein Bagheri, Shadi Ramezani, Mohammad Jafari, Negin Vatanparast, Fatemeh Namdar 10.4103/denthyp.denthyp_41_19
7. Surface Modifications of (PolyEtherEther Ketone) via Polymerization Methods—Current Status and Future Prospects. <https://doi.org/10.3390/ma13040999>

8. Developments of PEEK (Polyetheretherketone) as a biomedical material: A focused review Shivam Verma Nitin Sharma Saurabh Kango Sumit Sharma <https://doi.org/10.1016/j.eurpolymj.2021.110295>
9. Synthesis, characterization and study of the thermal properties of new polyarylene ethers P.A Staniland, C.J.WildeF, A.Bottino, G.Di Pasquale A.Pollicino, A.Recca
10. Applications of polyetheretherketone (PEEK) in oral implantology and prosthodontics Shariq Najeeb, Muhammad S Zafar, Zohaib Khurshid, FahadSiddiqui <https://doi.org/10.1016/j.jpor.2015.10.001>
11. Polyetheretherketone (PEEK) as a medical and dental material. A literature review Doi: 10.18103/mra.v5i4.120
12. Bone grafts in dentistry doi: 10.4103/0975-7406.113312
13. Branemark PI, Hansson BO, Adell R, et al. Osseointegrated implants in the treatment of the edentulous jaw. Experience from a 10-year period. *Scand J Plast Reconstruct Surg Suppl.* 1977; 16:1–132.
14. Carbon Fiber Reinforced PEEK Composites based on 3D-Printing Technology for Orthopaedic and Dental Applications, Xingting Han 1, Dong Yang 2, Chuncheng Yang DOI: 10.3390/jcm8020240
15. Bioactivity and Osseointegration of PEEK Are Inferior to Those of Titanium: A Systematic Review Shariq Najeeb 1, Zohaib Khurshid Bds 2, Doi: 10.1563/aaid-joi-D-16-00072
16. THE CURRENT STATE OF PEEK IMPLANT OSSEOINTEGRATION AND FUTURE PERSPECTIVES: A REVIEW *European Cells and Materials* Vol. 40 2020 (pages 1-20) DOI: 10.22203/eCM.v040a01 ISSN 1473-2262
17. Bioactive Materials for Tissue Engineering Scaffolds Larry L Hench, Julian R Jones https://doi.org/10.1142/9781860949647_0001
18. Wu X, Liu X, Wei J, Ma J, Deng F, Wei S. Nano-TiO₂/PEEK bioactive composite as a bone substitute material: in vitro and in vivo studies. *Nanomedicine* 2012; 7:1215-1225.
19. Surface Modifications of Poly (Ether Ether Ketone) via Polymerization Methods—Current Status and Future Prospects Monika Flejszar doi: 10.3390/ma13040999
20. Finite element analysis of the biomechanical effects of PEEK dental implants on the peri-implant bone. Schwitalla AD, Abou-Emara M, Spintig T, Lackmann J, Müller WDJ *Biomech.* 2015 Jan 2; 48(1):1-7.
21. Stress shielding and fatigue limits of poly-ether-ether-ketone dental implants. Lee WT, Koak JY, Lim YJ, Kim SK, Kwon HB, Kim MJ *J Biomed Mater Res B Appl Biomater.* 2012 May; 100(4):1044-52.
22. Sandler J., Werner P., Shaffer M.S., Demchuk V., Altstädt V., Windle A.H. Carbon-nanofibre-reinforced poly(etheretherketone) composites. *Compos. Part A Appl. Sci. Manuf.* 2002; 33:1033–1039. Doi: 10.1016/S1359-835X(02)00084-2.
23. The relative effects of collagen fiber orientation, porosity, density, and mineralization on bone strength. Martin RB, Ishida J *J Biotech.* 1989; 22(5):419-26.
24. Najeeb S, Khurshid Z, Matinlinna JP, Siddiqui F, Nassan MZ, Baroudi K. Nano modified peek dental implants: bioactive composites and surface modification—a review. *Int J Dent* 2015. Article ID 38Pub ahead of print].
25. Suska F, Omar O, Emanuelsson L, Taylor M, Gruner P, Kinbrum A, et al. Enhancement of CRF-PEEK osseointegration by plasma-sprayed hydroxyapatite: a rabbit model. *J Biomater Appl* 2014; 29:234–42.
26. Cook SD, Rust-Dawicki AM. Preliminary evaluation of titanium-coated PEEK dental implants. *J Oral Implantology* 1995; 21:176–81.
27. Ha S, Mayer J, Koch B, Wintermantel E. Plasma-sprayed hydroxyapatite coating on carbon fibre reinforced thermoplastic composite materials. *J Mater Sci Mater Med* 1994;5:481–4
28. Evaluation of the stress distribution in CFR-PEEK dental implants by the three-dimensional finite element
29. Rees J., Jacobsen P. The elastic moduli of enamel and dentine. *Clin. Mater.* 1993; 14:35–39. Doi: 10.1016/0267-6605(93)90045-9.
30. Cavalli V., Giannini M., Carvalho R.M. Effect of carbamide peroxide bleaching agents on tensile strength of human enamel. *Dent. Mater.* 2004;20:733739.doi:10.1016/j.dental.2003.10.007.
31. Chun K.J., Choi H.H., Lee J.Y. Comparison of mechanical property and role between enamel and dentin in the human teeth. *J. Dent. Biomech.* 2014; 5:1–7. Doi: 10.1177/1758736014520809.
32. Vallittu P. Some aspects of the tensile strength of unidirectional glass fibre-polymethyl methacrylate composite used in dentures. *J. Oral Rehabilitation.* 1998; 25:100–105. doi: 10.1046/j.1365-2842.1998.00235.x
33. Zafar M.S., Ahmed N. Nano indentation and surface roughness profilometry of poly methyl methacrylate denture base materials. *Technol. Health Care.* 2014; 22:573–581.
34. Poulsson A.H., Eglin D., Zeiter S., Camenisch K., Sprecher C., Agarwal Y., Nehrbass D., Willson J., Richards R.G. Osseointegration of machined, injection moulded and oxygen plasma modified PEEK implants in a sheep model. *Biomaterials.* 2014; 35:3717–3728. Doi: 10.1016/j.biomaterials.2013.12.056.
35. Rho J.Y., Ashman R.B., Turner C.H. Young's modulus of trabecular and cortical bone material: Ultrasonic and micro tensile measurements. *J. Biomech.* 1993; 26:111–119. Doi: 10.1016/0021-9290(93)90042-D.
36. Staines M., Robinson W., Hood J. Spherical indentation of tooth enamel. *J. Mater. Sci.* 1981; 16:2551–2556. Doi: 10.1007/BF01113595.

37. Xu A., Liu X., Gao X., Deng F., Deng Y., Wei S. Enhancement of osteogenesis on micro/nano-topographical carbon fiber-reinforced polyetheretherketone-nanohydroxyapatite bio composite. *Mater. Sci. Eng. C.* 2015; 48:592–598. Doi: 10.1016/j.msec.2014.12.061.
38. Yee R.S.L., Zhang K., Ladewig B.P. The effects of sulfonated poly (ether ether ketone) ion exchange preparation conditions on membrane properties. *Membranes.* 2013; 3:182–195. Doi: 10.3390/membranes3030182.
39. Wang L., He S., Wu X., Liang S., Mu Z., Wei J., Deng F., Deng Y., Wei S. Polyetheretherketone/nano-fluorohydroxyapatite composite with antimicrobial activity and osseointegration properties. *Biomaterials.* 2014; 35:6758–6775. Doi: 10.1016/j.biomaterials.2014.04.085.
40. Waser-Althaus J., Salamon A., Waser M., Padeste C., Kreutzer M., Piele U., Müller B., Peters K. Differentiation of human mesenchymal stem cells on plasma-treated polyetheretherketone. *J. Mater. Sci. Mater. Med.* 2014; 25:515–525. Doi: 10.1007/s10856-013-5072-5.