

## DENTAL IMPLANT MATERIAL (POLYETHERETHERKETONE, TITANIUM AND ITS ALLOYS, ZIRCONIA)

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### ABSTRACT

The goal of this article is to inform the reader of three distinct types of biomedical materials applied in the production of dental implants, focusing on characteristics and categorizations of biomaterials based on: titanium (Ti + its alloys), commercially manufactured synthetic polymers (polyetheretherketone) and ceramic materials (zirconium dioxide). Considering the development and construction of implants, specific material requirements are named (mechanical properties), corrosion resistance, compatibility, morphology, etc.

Each of these materials represents a specific group of biomedical materials and has a number of advantages. However, in relation to the differences in their nature (metal, plastic, ceramic base), it is necessary to approach the choice of material for dental implants with respect to the specific implant design and the patient's health limitations.

**Keywords:** dental implants, PEEK, Zirconia, Titanium

### INTRODUCTION

The medical field of dentistry, or stomatology, and maxillofacial surgery has a close relationship with materials and the technology of their production. The replacement of missing hard and soft tissues in the oral cavity is primarily dependent on the prosthetic materials from which crowns, dentures and fillings are made. The emphasis in selection is on the following: biological tolerance, aesthetics, mechanical/physical properties, and durability under multiple circumstances in oral conditions (variable conditions). Materials of dental implants should have a direct contact with the bone → a phenomenon known as osseointegration (the process during which the implant is integrated into the human bone and thus becomes its rigid component and part). In order to improve the osseointegration, a variety of modifications in the implant surface have been investigated, such as surface treatments and coatings (Hubáľková, & Krňoulová, 2009; Riznič, 2020; Zafar, & Khurshid, 2020). During the last decades, significant progress has been made in basic and applied research on

dental restorative materials. Prosthetic dentistry uses a large variety of materials of organic and inorganic origin - metals and their alloys, ceramic materials, and plastics (graphical representation below, breakdown by: *Dental Implants: Materials, Coatings, Surface Modifications and Interfaces with Oral Tissues*).

### PEEK (POLYETHERETHERKETONE)

The introduction of Ti dental implants, despite their considerable advantages, can be associated with various risks such as: allergies, occasional metal hypersensitivity. As an alternative, polyetheretherketone (chemical nomenclature, abbreviated: PEEK) is introduced. PEEK is a semi-crystalline engineering thermoplastic used since 1980 (invented in 1978) in industry as a substitute for metals and alloys. It is also possible to encounter the designation biocompatible polymer. The term biocompatible refers to a material intended for medical purposes, physiologically harmless, meeting prescribed standards (Ensinger, 2022; Mishra, & Chowdhary, 2022). The chemical structure of PEEK is shown in Fig. 1.

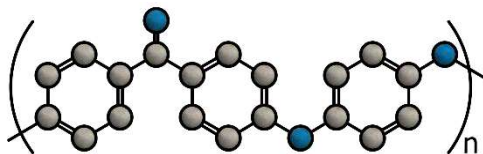


Figure 1. Chemical structure of PEEK

PEEK belongs to the group of PEAK polymers (for example: PEK - Polyetherketone, PEKEKK - Polyetherketonetherketoneketone, etc.) containing low-flexible ketogroups and benzene cores, which ensures the rigidity of the chains; on the other hand, ether linkage reduces the rigidity of the chains (its number, order, ratio of oxygen and CO bonds of benzene cores affects the mechanical and thermal properties of individual PEAK polymers) (Horák, et al., 2010). PEEK, as the most important representative of this group, has a density of  $1.32 \text{ g.cm}^{-3}$  (DIN EN ISO 1183-1) but

insolubility, as polymers possess hydrophobic surfaces with low surface energy reducing the cellular adhesion (Geetha, Prabhu, & Nivas Sundar, 2020). This is often neutralized by surface modification, coating or blending with bioactive particles. Melting temperature is about  $334 \text{ }^\circ\text{C}$  (crystallization peak:  $343 \text{ }^\circ\text{C}$  and glass transition temperature:  $145 \text{ }^\circ\text{C}$ ) (Panayotov, Orti, Cuisinier, & Yachouh, 2016). Tensile strength ultimate is in the interval 90-100 MPa, tensile modulus is equal to 4000 MPa (DIN EN ISO 527). The tensile modulus can be increased several times by applying suitable fibres (carbon reinforcing fibres in PEEK matrix:  $E = 18 \text{ GPa}$ , glass reinforcing fibres in PEEK matrix:  $E = 12 \text{ GPa}$ ) (Lee, et al., 2012; Najeeb, et al., 2015) - comparison of the tensile modulus of selected materials - Fig. 2. Study (Schwitalla, Spintig, Kallage, & Müller, 2015) compares the flexural behaviour of PEEK materials for dental application. The results of the publication show that by adding carbon fibers to the base polymer matrix the flexural strength and flexural modulus values can be increased (see Table). Other PEEK material properties:

- sensitive to the notch effect (compared to Polymethyl methacrylate, however, PEEK shows a higher resistance to notch concentration) (Muhsin, Hatton, Johnson, Sereno, & Wood, 2019). Notched Izod fracture toughness min for PEEK is  $4 \text{ KJ.m}^{-2}$ . Based on the available data, it can be argued that the toughness of the material increases with increasing molecular weight. On the contrary: an increase in crystallinity decreases toughness values. Similarly, polymer aging has a similar effect on toughness (Kemish, & Hay, 1985; Kurtz, 2019);
- good resistance to fatigue (study Ferguson, Visser, & Polikeit, 2006: "In practice, the total non-recoverable deformation of PEEK-OPTIMA would be negligible, with maximum 0.1% strain after 2000 hours at a stress level of 10 MPa, vanishingly small, compared to the time-dependent

*changes which could be expected in the surrounding bone due to remodelling effects.”);*

- good abrasion resistance (pin-on-disk test method, weight loss of PEEK material 0.004 g, weight loss of PEEK composite material + 30% glass reinforcement → 0.001 g, under the conditions determined in the study by Hanumantharaju, Shivananda, Hadimani, Kumar, & Jagadish, 2000);
- high resistance to organic/inorganic reagents;
- resistance to the effect of ionizing radiation (compared to Ultra High Molecular Weight PE, PEEK is highly resistant to the effect of ionizing radiation) (Ferguson, et al., 2006);
- exhibits long-term stability in aqueous environments (data shown that PEEK will not be affected by a repeated exposure to steam, in relation to the fact that PEEK implants must be sterilized) (Godara, Raabe, & Green, 2007);
- biocompatibility (results based on long-term contact with cell cultures as well as animal tests have confirmed that PEEK and composites with PEEK are bioinert and biocompatible in their

bulk form. Bioactivity - bonding to bone, can be improved by adding hydroxyapatite - HA) (Kurtz, 2019; Medical PEEK Lexicon, 2022);

- bacterial adhesion to PEEK: attachment - adhesion of bacteria to the surface of PEEK (or any biomaterial in general) presents a difficult, complex issue. Changes in the chemical, physical and topographical properties of biomaterials result in changes in bacterial adhesion to the surface (and subsequent biofilm formation/growth) (Renner, & Weibel, 2011). Similarly, the mode of testing (in vivo, in vitro) plays an important role in the relationship of bacterial colonization onto the observed surface area. There are initial investigations hinting at the application of antimicrobial coating-agents produced to reduce the adhesion of the underlying biomaterial (however, there are a number of unanswered questions related to the issue with regards to effective functioning in the variable implant environment) (Kurtz, 2019; Lynch, & Robertson, 2008).

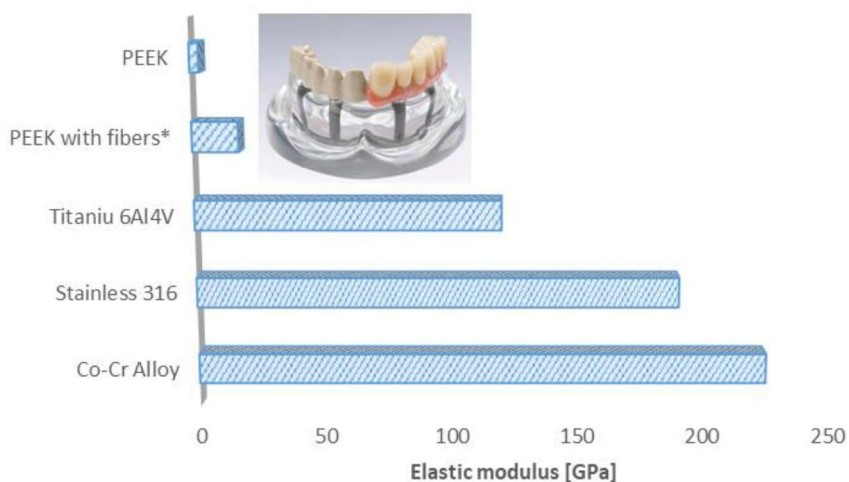


Figure 2. Elastic modulus of different kind of materials (manufacturer of PEEK: *Invibio*, Ltd.) \*PEEK with carbon reinforced fibres + PEEK prosthetic framework (Horák, et al., 2010; Jarman-Smith, 2017)

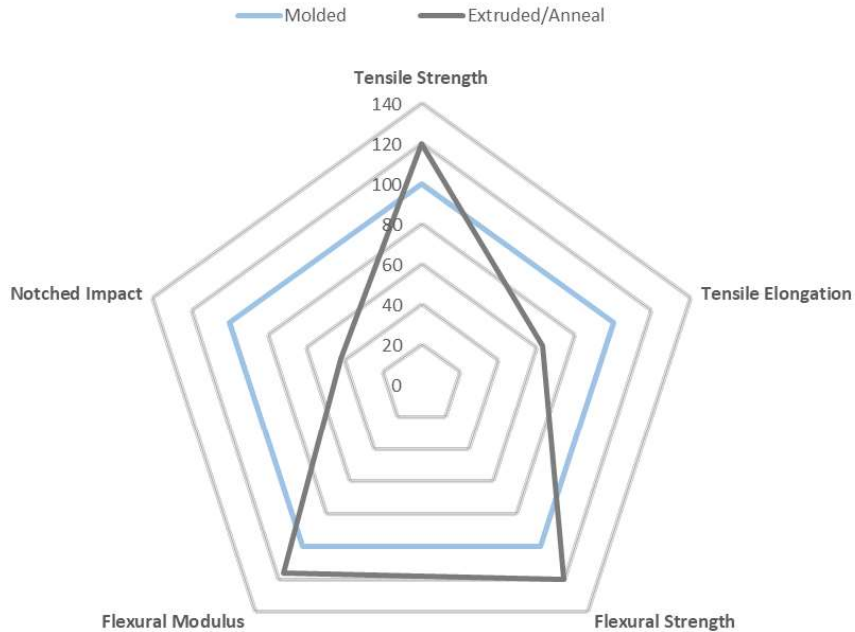


Figure 3. Differences between properties of injected-molded and machined PEEK (Kurtz, 2019)

Table1. Bending modulus and bending strength of PEEK without / with fibers (Schwitalla, et al., 2015)

Sample (without / with fibers)	Bending modulus [GPa]	Bending strength [MPa]
PEEK-OPTIMA LT1 ( <i>Invibio</i> Ltd.) without fibers	2.73±0.26	182.91±19.31
PEEK-OPTIMA LT1CA30 ( <i>Invibio</i> Ltd.) 30 % multi-directional chopped carbon fibers	4.09±0.8	188.53±34.45
PEEK-OPTIMA Ultra Reinforced ( <i>Invibio</i> Ltd.) more than 50 % uni-directional continuous carbon fibers	47.27±10.3	1009.63±107.33

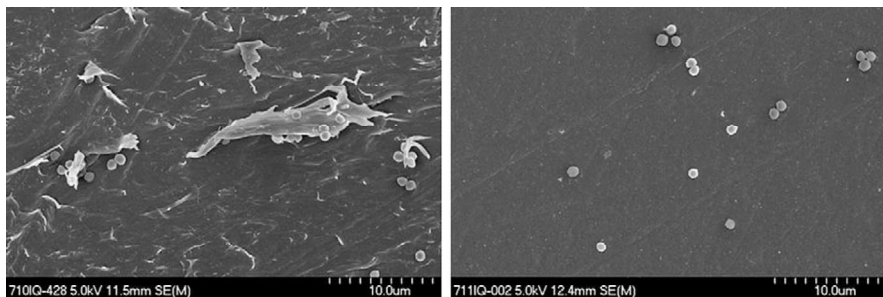


Figure 4. SEM images of PEEK surface: production by machining and injection molding (adherent-bacteria *S. aureus*) (Kurtz, 2019)

Applications of PEEK: PEEK for bone replacement, PEEK for spine surgery-spinal cages, PEEK for orthopedic surgery, PEEK

for dental implants, PEEK for cardiac surgery (pump, heart valves).

## TITANIUM AND ITS ALLOYS

Titanium is highly resistant to corrosion (it forms a stable, insoluble oxide layer on the surface with an ability to recover when damaged - the so-called passivation layer with a thickness of about 2-10 nm), a non-toxic excellent biocompatibility material (due to its low level of electrical conductivity, high corrosion resistance and thermodynamically stable state at physiological pH values). Commercially, titanium and its alloys were first applied in dental (and conventional) prosthodontics in 1977. These metals (and alloys) can be used for: dental crowns, dental bridges, root inlays, and composite restoration designs (Anusavice, Shen, & Rawls, 2012; Hubálková, & Krňoulová, 2009; Vavříčková, Dostálová, & Vahalová, 2008).

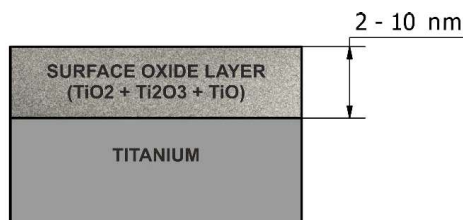


Figure 5. Schematic illustration of native oxide layer on Ti (Pisarek, Roguska, Marcon, & Andrzejczuk, 2012)

Titanium has a high melting point - about 1668 °C, high rate of oxidation (above 900 °C), density 4.5 g.cm<sup>-3</sup> (for comparison: nickel-chrome: 8 g.cm<sup>-3</sup> / gold alloys 15 g.cm<sup>-3</sup>), modulus of elasticity 100 GPa, yield strength is in the interval 170-480 MPa, hardness (according to Vickers) in the interval 126-263, elongation 24-15 %. Based on the concentration of impurities, pure titanium can be divided into four groups (grade 1 to grade 4, according to ASTM F-67) with different physical properties (the reason for the ranges of values in the properties above).

Pure titanium exists in two allotropic modifications (the presence of impurities affects the crystallization temperature and phase transformations - see Fig. 6):

- at temperatures up to 883 °C, its atoms form a hexagonal lattice (referred to as the  $\alpha$  phase),
- above 883 °C, recrystallization occurs (phase  $\beta$ ), the atoms forming a cubic area-centred lattice (Dierk-Raabe, 2022).

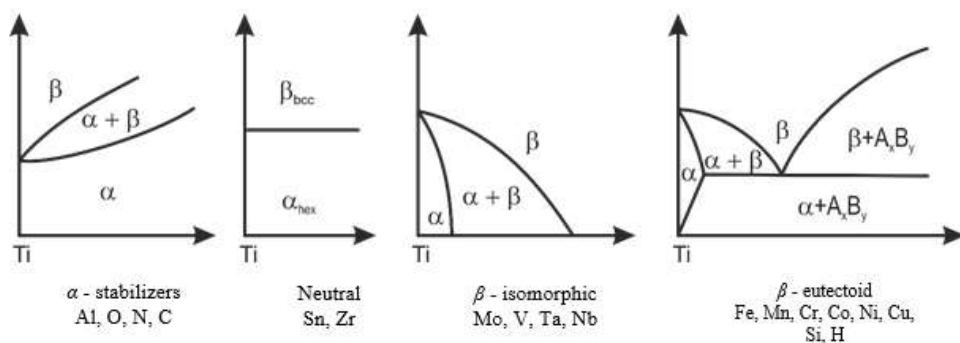


Figure 6. The effect of the presence of elements on the phase transformation (Dierk-Raabe, 2022)

The current trend in the development of dental implants is towards shorter healing times, which is ensured by chemical modification of the inert Ti surface (to increase its bioactivity and reduce the risk

of infection). The main methods of surface modification of implants include the following: modification with fluoride ions, hydrophilization of the original inactive/hydrophobic surface and coating

with a layer of porous titanium dioxide. The intraosseous part of the implant (the part inserted into the bone) can be modified in the following ways:

- Abrasive blasting/sandblasting (suitable for high-quality dense bones): the surface of the Ti implant is roughened by abrasive particles (e.g.  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ , sand particles) carried by compressed air or liquid through the nozzle. The resulting surface topography depends on the properties/sizes/shapes of the abrasive particles used,
- Coating with hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  (suitable for low

density bones)/ glass ceramics/ peptides, a typical example of coating is plasma spraying of the surface,

- Chemical etching: removal of the Ti passivation layer of the implant (application of  $\text{HNO}_3 + \text{HF}$  or  $\text{HCl} + \text{H}_2\text{SO}_4$ ),
- Anodization: by increasing the surface layer of titanium dioxide → increasing the area required for cell adhesion (Hrazdira, 1990; Elias, Fernandes, Galiza, dos Santos Monteiro, & de Almeida, 2019; Schupbach, Glauser, & Bauer, 2019; Antala, 2021).

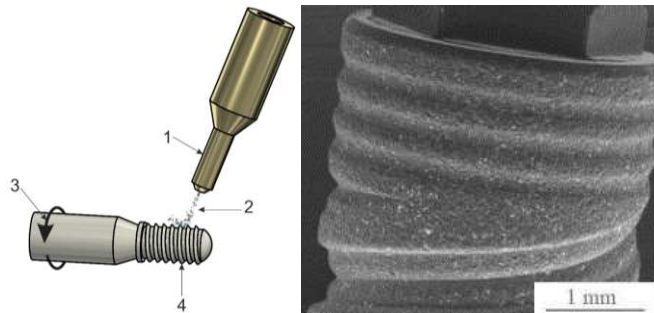


Figure 7. Left side: Illustration of the abrasive blasting process 1 - nozzle, 2 - abrasive particles, 3 - implant holder, 4 - dental implant (Elias, et al., 2019), right side: dental implant (Schupbach, et al., 2019)

The most widely used titanium alloy in dentistry is Ti-6Al-4V (which is an  $\alpha$ - $\beta$  alloy), the aluminium in the alloy stabilises the  $\alpha$  phase and vanadium the  $\beta$  phase. By heat treatment of the alloy, it is possible to modify the strength. The strength value is higher compared to pure Ti, but there is a risk of gradual release of Al/V into the body (vanadium is highly toxic both in elemental state and in oxide form; aluminium has

been reported to cause potential neurological disorders) (Liu, & Shin, 2019).

In contrast, niobium does not cause toxic reactions in the body. Replacing vanadium with niobium in the original Ti-6Al-4V alloy yields the → Ti-6Al-7Nb alloy. Both of the described Ti alloys are acceptable for biomedical applications. The mechanical properties of the two alloys are similar (Fig. 8) and their corrosion resistance is akin to that of pure titanium 7.



<u>Ti-6Al-7Nb</u>	<u>Ti-6Al-4V</u>
Elastic modulus [GPa] = 105	Elastic modulus [GPa] = 117
Yield strength [MPa] = 795	Yield strength [MPa] = 560
Hardness (Vickers) = 330	Hardness (Vickers) = 320
Elongation [%] = 10	Elongation [%] = 10-15

Figure 8. Properties of two  $\alpha$ - $\beta$  Ti-based alloys for dental prostheses (for comparison) (Anusavice, et al., 2012; Constantinescu, 2019)

## ZIRCONIA

Atoms of ceramic materials are bonded by covalent/ionic bonds or a combination of the two (the type of bond affects the resulting properties). The properties of ceramics intended for dental applications depend on: the amount of individual components used, the melting temperature, the production technology and the indication. Ceramics are resistant in several ways: they do not react with liquids, gases, alkalis (acids), they are stable, corrosion-resistant, wear-resistant and temperature-resistant (apart from conditions of a so-called thermal shock, where they crack when suddenly heated/cooled), with high hardness and strength. It lacks the properties typical of metals: ductility (ability to deform plastically) / toughness (absorption of energy on breaking). Its mechanical properties depend on the specific type of ceramic material, e.g.: Zirconia-based ceramics ( $ZrO_2$ ) have flexural strengths reaching the flexural strength of steel, but fracture toughness values are lower compared to steel. The chemical stability of  $ZrO_2$  (ZIRCONIA) is comparable to  $Al_2O_3$  (ALUMINUM), the modulus of elasticity of  $ZrO_2$  reaches half the value of the modulus of elasticity of  $Al_2O_3$  (in abrasion resistance it is possible

to reach 5 times the value compared to  $Al_2O_3$ ), the material is bioinert (the cytotoxicity of zirconia ceramics is less than the cytotoxicity of Lithium disilicate). In dentistry, ceramics formed by combining oxygen with metals, semi-metals (metalloids) are used for producing ceramic restorations: all-ceramic or metal-ceramic crowns and bridges, inlays, onlays, veneers and implants, or teeth produced as removable restorations/implants. Zirconium dioxide is an alternative substitute for  $Al_2O_3$  (for crowns and implant abutments) (Anusavice, et al., 2012; Ptáček, 2002; Hubálková, & Krňoulová, 2009; Özkurt, & Kazazoğlu, 2010; Zhang, & Kelly, 2017; Vavříčková, Dostálová, & Ulrichová, 2011).

Types of zircon ceramics (Kovalský, et al., 2022; Zhang, & Lawn, 2018):

- 1<sup>st</sup> generation: contains 0.25% (w/w) alumina + a three-molecule concentration (3 mol%) of yttria oxide, resulting in the yttrium-stabilized tetragonal polycrystalline zirconia 3Y-TZP (achieves a flexural strength in the range of 0.8 to 1 GPa, grain size 0.2-0.5  $\mu m$ ). First generation zirconia ceramics are transparent (opaque), for this reason they are used only in applications with

zero aesthetic requirements. Based on the ISO standard it is (ISO 6872:2015) in the fifth class of ceramics,

- 2<sup>nd</sup> generation: change of composition - in relation to modification of translucency (to increase it) → reduced alumina content, change of production technology, increased sintering temperature, minimized formation of porosity. In relation to the colour of the material when light hits it (characteristic pearlescence),

second generation zirconia is usable monolithically - in most cases only in the lateral section,

- 3<sup>rd</sup> generation (in two available variants): addition of 5 mol% yttria stabilized tetragonal zirconia polycrystal (5Y-TZP) - the aesthetic, least resistant variant of zirconia / compromise designed 4Y-TZP (addition of 4 mol% yttria stabilized tetragonal zirconia polycrystal).

Table 2. Selected manufacturers of ceramic materials (Schwitall, et al., 2015)

Selected manufacturers	Oxide ceramics (ZrO <sub>2</sub> )
	LAVA™ ZrO <sub>2</sub> (3M ESPE, Nemecko)
	Procera® ZrO <sub>2</sub> (Nobel Biocare™, Švédsko)
	Zirkon-Zahn 3Y-TZP (Upcera Dental, Čína)
	ZERAMEX® ZrO <sub>2</sub> (Dentalpoint AG, švajčiarsko)
	BoneTrust® balance ZrO <sub>2</sub> (Dentmia Medikl Sağlık, Turecko)

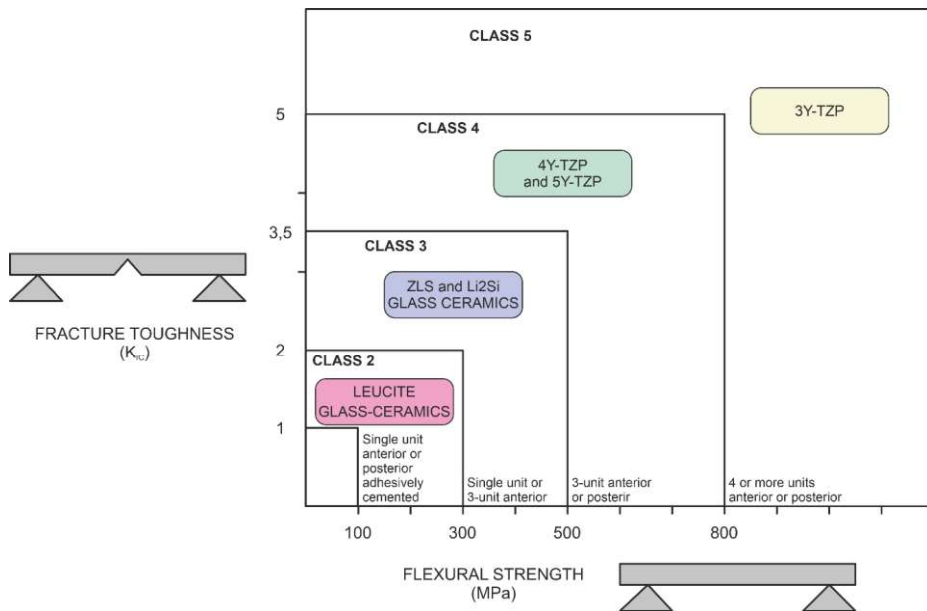


Figure 9. An overview ceramics classification according to ISO 6872:2015



## CONCLUSIONS

When choosing a dental implant material, emphasis should be placed on mechanical resistance, physical properties, biocompatibility, bioactivity, and biomechanics. Each of the materials described meets the demanding requirements for this group of biomaterials. Titanium is the most commonly used "tooth replacement" material, but its disadvantage is its exposure to various risks, such as allergies and occasional metal hypersensitivity. Suitable alternatives appear to be the plastics group - polyaryletherketones - namely PEEK (including reinforced composite materials) and zirconia ceramic materials.

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