IOSR Journal of Dental and Medical Sciences (IOSR-JDMS)
e-ISSN: 2279-0853, p-ISSN: 2279-0861.Volume 22, Issue 5 Ser.6 (May. 2023), PP 33-37
www.iosrjournals.org

Role Of The Polyamide And Polyetheretherketone (PEEK) Material As An Alternative Of Denture Base In Terms Of Water Sorption And Water Solubility

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Abstract
Background: *Polyamide termoplastic material (nylon) is one of the non metallic material that is frequently used as the removable partial denture base due to its flexibility, aesthetic, comfort and higher flexural and impact strength. However, high water sorption has been recognised as a problem that effects dimensional and colour stability, causes surface roughness after a few weeks of wear and the induction candida growth. Recently, polyetheretherketone (PEEK) has been introduced as a denture base material due to its low elasticity modulus close to the bone, low water sorption and water solubility. The purpose of this literature review is to know the role of polyetheretherketone (PEEK) material as an alternative of denture base in terms of water sorption and water solubility.*
Discussion: *The long service of denture depends on chemical properties associate with low water sorption and water solubility. Water sorption and water solubility depend on type of material, polymer chain chemical structure, homogeneity of material and method of fabrication. PEEK has low water sorption and solubility due to its homogenous small particle size (0,3-0,5μm) and hydrophobic nature because of the nonpolar polycylcic aromatic chemical structure.*
Conclusion: *PEEK is a bioinert material with low water sorption and water solubility as it produces low dimensional changes, good colour stability and low reaction to oral soft tissue.*
Key Word: *Polyamide nylon, Polyetheretherketone, Water sorption, Water solubility*

Date of Submission: 08-05-2023 Date of Acceptance: 18-05-2023

I. Introduction

A wide variety of dental materials have been developed to meet patients' needs, including the base material for removable partial dentures (1). Accuracy of denture base depends on the selection of denture base material and fabrication method that can produce good dimensional stability. The requirements for an ideal denture base are accuracy of adaptation to the tissue, with minimal volume change, dense, nonirritating surface, lightweight in the mouth, sufficient strength (resistance to fracture or distortion), easily kept clean, esthetic acceptability, potential for future relining and low initial cost (2). According to the International Organization for Standardization (ISO) 1567, denture base is classified as heat processed polymer (RAPP), autopolymerized polymer, thermoplastic blank or powder, light active materials and microwave cured materials (3).

PMMA has been extensively used as a denture base material because of its desirable properties such as simple laboratory processing, satisfactory aesthetics and durability, repairable and acceptable cost. Despite these characteristics, PMMA has some drawbacks like polimerization shrinkage, residual monomer, dimensional instability, water sorption and solubility, effect of metal clasp on esthetic, candida infection and potential of allergic reaction. Considering the drawbacks of conventional heat-polymerized PMMA, an injection molding technique like thermoplastic resin material resulted in alternative to acrylic resin as denture base.(4,5)

Thermoplastic resin have been used for decades in dentistry. This material are made of linear or less branched chains, that means may be repeatedly softened by heating and hardened by cooling without undergoing a chemical change. These materials may be considered as being composed of bundles of chainlike molecules (called polymers) of many different lengths and molecular weights. Thermoplastic materials can be broadly classified as polyamide nylon, polyester, polycarbonate, polyoxymethylene (acetal resin), polymethyl methacrylate and polyetheretherketone (PEEK) (6). Polyamide nylon is one of the type of thermoplastic resin materials that have been used frequently due to its high flexural and impact strength, flexibility, aesthetic and comfort used in denture base. However,

due to certain disadvantage of nylon polyamides such as high water sorption, it can cause dimensional instability, tendency of base color to deteriorate, effect on mechanical properties, development of surface roughness after a few weeks' wear and candida infection (4,7,8).

Water sorption and solubility causes dimensional instability, subjecting the material to internal stresses that may result in crack formation which cause fractures of the denture (decrease strength of the material). Because water interacts with the polymer chains, it may lead to effective plasticization of the structure, solvation or reversible rupture of weak inter-chain bonds, and irreversible disruption of the polymer matrix. Water molecules spread between the macromolecules of the material, forcing them apart that affects dimensional behavior and denture stability; therefore, water sorption and solubility of these materials should be as low as possible. Water sorption of a denture base resin may cause discoloration, halitosis which alters patient satisfaction. In other words, a higher water sorption rate tends to affect the material properties and consequently reduce the service life of a denture within the oral cavity; therefore, it is preferred to use materials with minimum possible water sorption rates (8).

Recently, the usage of others material such as polyeheretherketone (PEEK) is one among the metal free restorations that has many potential uses in dentistry. Due to its excellent mechanical and aesthetics properties, PEEK is gaining importance in oral implantology and prosthodontics used as framework for removable prosthesis. However, a promising polymer-based framework has recently been introduced that consists of a modified polyetheretherketone polymer (BioHPP) frame combined with acrylic resin denture teeth and a conventional acrylic resin denture base (10). BioHPP (High performance polymer) is a high tech thermoplastic polymer based on Polyetheretherketone (PEEK) that contains 20% ceramic microparticles fillers with a particle size about 0,3-0,5 microns (11). Polyetheretherketone (PEEK) has good colour stability due to high polishability in a lack of plaque retention, low water sorption and solubility in oral cavity compare with other denture base materials (12). In the study of Demrici F (2021), the solubility values of the PEEK group in distilled water were found to be similar to the heat cure acrylic group with lower solubility and water sorption values of PEEK group were found compared to other denture base materials (13).

Poyamide nylon

Nylon is a generic name used for certain types of thermoplastic polymers belonging to the class known as polyamides. The use of nylon as a denture base material has been described in the literatures in the 1950s. Nylon polyamide is semicrystalline heterochain polymers that are produced by the condensation reactions between a diamine NH2-(CH2)6- NH2 and a dibasic acid, CO2H-(CH2)4-COOH. These groups are polar and can form intra- and inter-chain hydrogen bonds that caused nylon material will absorb some water (14). The weakness of thermoplastic nylon is amide (-NH2) and chromophores (C = O) groups, which easily absorb water and stain, thus susceptible to discoloration and the surface becomes rough. The higher the concentration of amide groups, the greater the absorption of water and discoloration (15). The chemical structure of a polyamide nylon is showed below (8).

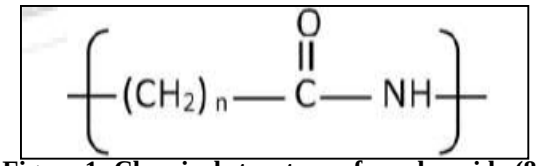

Figure 1: Chemical structure of a polyamide (8)

Nylon is hygroscopic, its moisture content varies slowly with the surrounding conditions. On immersion in water, the material swells or there is a linear expansion. The flexibility of nylon varies greatly depending on the type of moulding powder used, temperature of injection and pressure of injection. Flexibility can be advantageous in conditions when the buccal undercut on the maxillary tuberosity are present together with reduced width of the buccal vestibule and in gingival recession (10).

Polyetheretherketone (PEEK)

The development of thermoplastic high-performance polymers (HPP) has led to an increasing interest in dentistry due to their excellent properties, which has made them suitable for many applications in the field of restorative and prosthetic dentistry. The polyaryletherketone (PAEK) family shows ultra-high mechanical performances and chemical resistance among all the thermoplastic polymers. These materials were introduced to substitute well-known metallic alloys and ceramics for achieving different fixed restorations and removable prostheses. The term PAEK covers a number of closely related high-performance thermoplastics, like polyetheretherketone (PEEK), polyetherketoneketone (PEKK) and aryl ketone polymer (AKP). Polyetheretherketone (PEEK) is a linear, aromatic, semi-crystalline thermoplastic, developed from bisphenol salts

and aromatic dihalides via nucleophilic substitution. The structures of PEEK and PEKK both have aromatic rings, which differ in terms of the ratio of ether and the keton group (16).

PEEK material was first developed by British scientists in 1978 and in the 1980s was used in the aircraft and turbine industries due to its resistance to high temperatures and hydrolysis. Then the use of PEEK is growing until it is used in the field of medicine and extends to the field of dentistry. PEEK is an aromatic polycyclic linear semicrystalline thermoplastic polymer.This material is obtained from the combination of ketone and ether functional groups between the aryl rings. The molecules in PEEK polymer are linear bonds of 100 monomer units with an average molecular weight of 80,000-120,000 g/mol. The PEEK molecule is relatively rigid due to the presence of an aromatic ring (benzene) bonding structure which gives PEEK its very high mechanical strength. PEEK material can be produced by injection molding method or using CAD-CAM (11,12). The chemical structure of PEEK material can be seen in Figure 2.

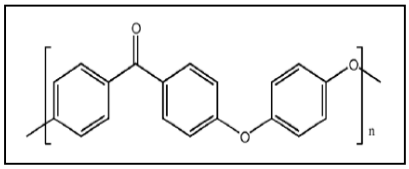

Figure 2. Chemical structure of polyetheretherketone (PEEK)(11,12)

PEEK has several advantages such as resistance to hydrolysis, good mechanical properties, resistance to high temperatures (335.8°C), non-toxic and carcinogenic, bioinert (low water absorption and good color stabilization), lighter than nylon (1.32g / cm3), less irritating and allergic reactions, low plaque afinitiy and bone-like modulus of elasticity and is therefore better from a biomechanical point of view, and it absorbs destructive fracture energy and functional stresses, reducing the forces transferred to the abutment teeth. Meanwhile, some of the shortcomings of PEEK are in terms of aesthetics when compared to nylon. In the field of dentistry, PEEK can be used in implants, the manufacture of fixed dentures, orthodontic braces and removable partial dentures. PEEK is suitable for use in the manufacture of removable partial dentures because it replaces metal materials so that it is suitable for metal allergy patients, free from metallic taste, easy to polish, lightweight and has minimal plaque retention. PEEK also provides benefits to the health of the abutment teeth, especially in free-toed cases because the elasticity of the PEEK material can reduce torque and stress on the abutment teeth. In addition, PEEK has good color stabilization due to low surface roughness, water sorption and solubility of the material into the oral cavity compared to other materials (11,13,16). Modified PEEK material consists of ceramic filler with a grain size of 0.3 to 0.5 µm and due to this very small grain size, constant homogeneity can be produced. This homogeneity is an important prerequisite for these outstanding material properties and forms the basis for consistent quality. The fine granularity of the filler is the basis for the extremely good polishing properties that emerge later. The deposit of plaque is prevented and the degree of discolouration is reduced due to the fact that the surfaces are polished to a high shine (11). Discoloration in PEEK is also reduced by the low surface-free energy and bioinert properties that unreactive to any chemical, thermal, and post-irradiation changes except strong acids such as sulfuric acid (17,18). According to Zoidis P (2015), in his follow-up he founded that there is no breakage of denture framework, good clasp retention, and color stability of modified PEEK material (Bio-HPP PEEK) (19). Liebermann A et al (2016) reported that PEEK material can be recommended for long-term restorations because of low water absorption and solubility properties (18).

Water Sorption

Water sorption can cause two conditions: first, changes in dimensions that affect weight and volume where the increasing of water sorption will affect the changes in dimensions; second, water sorption acts as plasticizer and reduces the mechanical properties of the material. Mechanism of water sorption is simple because the water molecules penetrate into the cavities between the hydrophilic polymer bonds which will promote the bond to separate and reduce secondary bonding forces (Van der Waals forces) between bonds. This will have an impact on the physical and mechanical properties of the materials used (20). Polyamide materials have high water sorption due to several factors such as hygroscopic properties, polarity of the polyamide molecules which form hydrogen bonds from water molecules that breaks the bonds between polyamide molecules that affect the dimensional stability, hydrophilicity of amide bonds that form the main chain of polyamide resin, the polymer chain bonds are linear so they are unable to resist water sorption and the water molecule size is < 0.28 nm which is smaller than the distance between the polymer chains in the polymer matrix.(21,22)

According to the specifications of ISO (International Standards Organization) No 1567 , water sorption of denture base is <32 g/mm3 and water solubility is <1.6 g/mm3. In PEEK materials, water sorption is around 6.5 g/mm3 and water solubility is around <0.3 g/mm3 (12).

The formula of water sorption is described as below(23)

Water sorption (mg/mm^3)= $\frac{\text{m2-m3}}{\text{V}}$

m2 = mass after immersion (mg)
m3 = reconditioned mass (mg)
v = volume (mm^3)

Water Solubility

Solubility describes about the mass of diluted polymer in material. The dissolved material in the resin denture base is an unreacted monomer, plasticizers and initiator. These monomers can cause reactions in soft tissues so that low water solubility of denture materials is needed. The formula for calculating the solubility of the material (water solubility) is as follows: (23)

Water solubility *(mg/mm^3)*= $\frac{\text{m1-m3}}{\text{V}}$

m1 = conditioned mass (mg)
m3 = reconditioned mass (mg)
v = volume (mm^3)

Zoidis P (2019) stated that due to its insolubility in water and low reactivity with other materials, modified PEEK (Bio-HPP) could be suitable for patients allergic to Cr-Co, or sensitive to the metallic taste of conventional Cr-Co frameworks (19).

II. Dicussion

Water sorption and solubility of the material are one of the chemical properties that must be considered in denture base materials (10). Water sorption can trigger discoloration, halitosis and changes in the dimensions of the denture base so that internal stress occurs and causes cracks or failure of the denture material. Water sorption also can affect the material properties thereby affecting the long term effect of dentures. In addition, because of the direct contact of denture base with the oral mucosa, the use of biocompatible materials is also needed to prevent hypersensitivity reactions or toxic release from denture materials. Polyamide is one of the thermoplastic materials that has a high water sorption compared to other thermoplastic materials where the results of the study of Nguyen LG (2017) showed that water soprtion and solubility of polyamide materials continuously absorb liquid after soaking for 8 weeks but are still within acceptable limits specified by ISO (6). The same thing was also shown by the study of Jang DE et al (2014) which compared the water absorption of three materials (PMMA, thermoplastic polyamide, thermoplastic acrylic). It was found that after immersion for 8 weeks, thermoplastic polyamide had the highest water immersion value (8). Research of Hemmati MA (2015) regarding the comparison of water sorption and flexural strength of polyamide thermoplastic materials with PMMA showed that PMMA has high water sorption (19.11±0.90 g/mm3) compared to thermoplastic polyamide materials (14.74±1.36µ). g/mm3). This can be attributed to the technique of making thermoplastic polyamides using injection molding which shows good fitting, good adaptation to the network, smaller shrinkage after the polymerization process, accuracy and better dimensional stabilization than compression molding techniques (7).

According to Zoidis P (2015) that BioHPP PEEK is a material that has recently been used in dentistry because it has stain resistance and good color stabilisation. In addition, BioHPP PEEK is also suitable for patients with history of metal allergies because of the inability of this material to dissolve in water and low reaction to other materials (19). According to Tekin S et al (2018), PEEK is a bioinert material that is resistant to chemicals and can only solube by strong acids such as sulfuric acid (12). In addition, according to Skirbutis G (2017),PEEK is also a material with low water sorption and solubility (24).

III.Conclusion

The water sorption and solubility of denture base depend on the type of materials. Water sorption can cause two things, namely dimensional changes that affect weight and volume and act as a plasticizer and reduce the mechanical properties of the material. While the solubility of the dissolved material in the resin denture base is an unreacted monomer that can cause a reaction in the soft tissue so that a denture material with low solubility is needed. Polyamide thermoplastic material is one of the denture base materials that has the highest water sorption compared to other thermoplastic materials. However, this water sorption is lower than PMMA thermoset materials due to differences in manufacturing techniques. Modified PEEK is a material that can be an alternative in replacing denture bases due to its hydrophobic nature and homogenous small particle ceramic size (0,3-0,5µm) that effect on water diffusion for low water sorption (6.5µg/mm^3) and water solubility (<0.3 g/mm^3), which is lower than

other thermoplastic materials and complies with the specified standards by ISO (water sorption <32 g/mm^3 and water solubility <1.6 g/mm^3).

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