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Evaluation of some properties of polyetheretherketone composites used for biomedical applications

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Abstract. Polyetheretherketone is considered to be a prime candidate with the potential to replace biomedical metallic materials as an orthopedic and dental implant on account of its elastic modulus similar to that of human cortical bone. This study presents the effect of polyetheretherketone specimens incorporated with different nano titanium dioxide and nano hydroxyapatite loading up to (1.5 wt%) have been prepared through a series of processing stages involving melt compounding, granulating and hot pressing. Following analysis of mechanical and chemical interactions by flexural, surface roughness and fourier transform infrared spectroscopy respectively. The results showed that the nano titanium dioxide and nano hydroxyapatite particles were uniformly disperse into polyetheretherketone, so the flexural modulus, flexural strength and surface roughness of polyetheretherketone biocomposites obviously increased with the addition of nano powder. On the other hand, break strain decreased with the rise of the total nano titanium dioxide and nano hydroxyapatite content. Furthermore, the best properties obtained when reinforced with nano hydroxyapatite.

Keywords: Polyetheretherketone, Hydroxyapatite, Titanium Dioxide, Polymer composites, dental implants.

1. Introduction
A dental subgingival implant is a fixture, surgically placed into the alveolar bone, which functions as an artificial root that can stabilize and support a fixed or removable prosthesis [1-2]. The implant material, usually titanium and its alloys [3], zirconia [4], or, as a potential future material, fiber reinforced composite (FRC) [5]. Over the last several decades, commercially pure grade 2 or 4 titanium and its alloys have been the material of choice for endosseous implants [6]. However, titanium has been shown to exhibit a variety of problems. Because of the high modulus of elasticity of the titanium alloys, dental implants made from the material can cause stress-shielding [7] which may lead to periodontal bone loss [8-9]. Polyether-ether-ketone commonly referred to as PEEK was first introduced in the late 1990s as a high performance thermoplastic polymer for replacing metal implant components. The material was initially used in orthopedics for the development of “isoelastic” hip stems and fracture fixation plates, with stiffness comparable to bone [10]. By April 1998, PEEK was commercially offered as a substrate for an implant material [11]. Poly-ether-ether-ketone (PEEK), a unique high performance semi-crystalline polymer, is one of the most potential thermoplastics for medicine, automotive and aerospace applications, with the advantage of good impact performance,
Chemical inertness, heat resistance and biocompatibility [12-16]. Hydroxyapatite (HAp) is an interesting biomaterial with potential orthopedic, dental, and maxillofacial applications due to its excellent biocompatibility, bioactivity, and osteoconductivity [17-18]. Some structural features of HA are presented in Figure 1 and Table I. This structure consists of Ca$^{2+}$ ions surrounded by PO$_4^{3-}$ ions and OH$^-$ with a Ca/P ratio of 1.6 [19-20].

![Figure 1. Hydroxyapatite hexagonal crystal structure [20].](image1)

### Table 1. Hydroxyapatite crystallographic data [19].

| Mineral | apatite |
|---------|---------|
| General group formula | A$_5$(BO$_4$)$_3$X$^-$ |
| Where A=Ca, Sr, Ba, Fe, Pb, Cd and rare earth; BO$_4$=PO$_4^{3-}$, VO$_4^{3-}$, SiO$_4^{4-}$, AsO$_4^{3-}$, CO$_3^{2-}$; X=OH$^-$, Cl$^-$, F$^-$, CO$_3^{2-}$ | |
| Formula | Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ |
| Crystale structure | Hexagonal |
| Symmetry group | P6$_3$/m |
| Class | 6/m |
| Lattice parameters | a=b=9.432 Å, c=6.881 Å; α=β=90°, γ=120° |
| Ca/P ratio | 1.2-1.6667 |

Titanium dioxide (TiO$_2$) material has been demonstrated with good antimicrobial activity [21-24], biocompatibility, bioactivity [25-28] hydrophilicity [29], and corrosion resistance [30]. Titanium dioxide occurs as two important polymorphs, the stable rutile and metastable anatase. Figure (2) shows the geometrical structures of the unit cells of anatase and rutile TiO$_2$. The unit cells contain four Ti atoms and eight O atoms for anatase TiO$_2$ and two Ti atoms and four O atoms for rutile TiO$_2$, respectively [31].

![Figure 2. Unit cells of anatase TiO$_2$ (a) and rutile TiO$_2$ (b). Large light-blue and small red spheres are Ti$^{4+}$ and O$^{2-}$ ions, respectively [31].](image2)
The basic properties of anatase and rutile are shown in Table 2:

| Property               | Anatase     | Rutile     |
|-----------------------|-------------|------------|
| Crystal structure     | Tetragonal  | Tetragonal |
| Lattice parameters    | a = 0.3785  | a = 0.4594 |
|                       | c = 0.9514  | c = 0.29589 |
| Density (kgm$^{-3}$)  | 3894        | 4250       |
| Hardness (Mohs)       | 5.5-6       | 6-6.5      |
| Bulk modulus (GPa)    | 183         | 206        |

Tang et al. investigated cyclic load on the PEEK/HA composite with different content of HAp showed the HAp/PEEK composite is a promising fatigue-resistant material for biomedical applications [33]. Wong et al. illustrated the bending modulus of strontium-containing hydroxyapatite/polyether ketone (Sr-HA/PEEK) increased with increasing the volume fraction of Sr-HA. The elastic modulus of 25 vol% and 30 vol% Sr-HA reinforcement showed 113% and 136% increase, respectively, in comparison with pure PEEK. The bending strengths of 25 vol% and 30 vol% Sr-HA reinforcement showed 25% and 29% decrease, respectively, in comparison with pure PEEK [34]. Kim et al. incorporated 30CaO-70SiO$_2$ (CS) microspheres into PEEK to obtain a bioactive bone-repairing material with mechanical properties similar to those of the natural bone. It was observed the formation of hydroxyapatite on the surfaces of all CS-PEEK composites after immersion into simulated body fluid (SBF), indicating a potentially bond to the natural bone. Additionally, the bending stiffness and strength increased in 38% and in 6%, respectively, with the addition of 20 vol% CS particles. It was not observed a significantly decrease of the mechanical properties of the composites after immersion in SBF [35].

Wang et al. incorporated nano-FHA into PEEK in order to enhance its antibacterial property and osseointegration of implant materials. Mechanical tests revealed that nano-FHA acts as reinforcement filler in PEEK considering that both E and tensile strength increased in 210% and 67%, respectively, with the incorporation of 40 wt% nano-FHA into PEEK. Furthermore, microbiological assays indicated that the composite possesses an antibacterial activity. The in vivo assays showed high bioactivity, osseointegration and bone-implant contact [36].

The main aim of this study was to fabrication of poly(ether ether ketone) (PEEK) composite containing nanohydroxyapatite and nano titanium dioxide at different weight fraction (0, 0.5, 1, 1.5)% for two types of reinforcement and assess the some mechanical properties and chemical analysis was used.

2. Materials and Methods

2.1. Sample Preparation

PEEK(551G) granule, Nano hydroxyapatite and Nano titanium dioxide were purchased from (Jilin Joinature Polymer Co., Ltd, china), (N & R Industries, Inc, China) and (Hangzhou Union Biotechnology Co., Ltd, china) respectively with purity 99.5%, 99% and > 99.8% respectively. The two nano particles have 20nm particle size. The biopolymer composites containing (0, 0.5, 1, 1.5) wt% for two types of nano powder were fabricated via a series of processes melt compounding, granulating and hot pressing process. PEEK granule were dried in an oven 80 °C for 1 h prior to compounding and hot pressing. In brief, nano powder were dispersed in ethanol alcohol using ultrasonic mixer to obtain a homogeneous mixture and then mixing with PEEK granule for 20 min. After well dispersed, the mixture was dried in a oven at 90 °C for 24 h to remove the excess ethanol alcohol.

In the compounding process, Compounding was carried out in an internal mixer (AHAAKE BUCHLER PRODUCT, HBISYSTEM 90, USA) at temperature of 360 °C and mixing speed at 90 rpm. The press was done by using hot press type (TOYOSEIKI, Japan). Temperature in hot press was adjusted at 360°C when reaching this temperature the pressure was applied for (15) min and its value equal (15MPa). The mould was then removed from hydraulic press and put in cooling system cooled with water jet (5 L/min) at temperature room temperature. The mould was opened, and then the composite sheet was removed and cutting the specimens by CNC machine for each test.
2.2. Characterization

The flexural property of synthesized composite [width (b)~13 mm, thickness (d)~4 mm and length~160 mm] was measured by three-point bending using Universal testing machine (SANTAM, Type STM-50, Iran) followed by ASTM D790-03[37]. The support span was 128 mm with the cross head velocity at 5 mmmin⁻¹. The flexural strength, flexural modulus and flexural stain at break of composites were calculated by using the given equations [38]:

\[
\text{Flexural Strength} = \frac{3FL}{2bd^2} \tag{1}
\]

\[
\text{Flexural Modulus} = \frac{L^3M}{4bd^3} \tag{2}
\]

\[
\text{Flexural Strain} \% = \frac{6Dd}{L^2} \tag{3}
\]

Where, \(F\) is the maximum flexural load, \(L\) is the support span mm, \(b\) = width of the sample, \(d\) = thickness of the sample, \(D\) maximum deflection of samples and \(m\) = slope of the linear portion of the flexural load-deflection curve, respectively.

The measurement of roughness surface was done by fixing the sample on the machine (TR200, type TA620 stand and column, Time group Inc.), and applying the needle of the device perpendicular to the sample and taking the reading on different places on the surface of sample. The prepared samples were characterized by attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy followed by ASTM E1252 [39] using (BRUKER-type I11316, Germany) FTIR spectrophotometer for 32 scans over the range of 700–4000 cm⁻¹ at a resolution of 4.0 cm⁻¹. For these analyses the samples were mixed crystals with KBr (potassium bromide).

3. Results and Discussion

3.1. Flexural Test

Figure (3) shows that the variation in flexural strength of the composite specimen increases with an increasing percentage of two type of reinforcement (from 0 to 1.5%) as they resist the deformation of the composite material. The flexural strengths of the sample were found to be about 7% higher than that of pure polyetheretherketone. The plastic region of sample depends on ductility of the PEEK matrix and interparticle distance of reinforcements. At higher % reinforcing, the interparticle distance increases make matrix hard to undergo yielding, increasing the flexure strength [40]. The highest flexural strength reached a value of 163.431 MPa for (PEEK+1.5%HAp) and showed good bend properties. While about 162.321 MPa for sample reinforced with 1.5%TiO2. Also the same trend was observed for flexural modulus in figure (4) were improved for all composites when adding nano particles. The highest flexural modulus of was obtained for the 1.5% composite reinforced because of excellent particle dispersion and distribution. On the other hand, while total reinforcement raises from 0 wt% to 1.5 wt% the flexural break strain % results of HAp/PEEK and TiO2/PEEK separately decreased as seen in figure (5). Such a results reveals that the existence of ceramic powder in biocomposites could importantly delay the plasticity to brittleness transmission of the polymer composites which rise with increase particle reinforcement [41].

![Figure 3. Results of flexural strength for polymer composites with two types of reinforcement.](image-url)
3.2. Surface Roughness
Figure (6) shows the effect of nano particles on surface roughness of nanocomposites, this figure indicate the reinforcing leads to a clear increase in surface roughness. From this figure it can be noticed that the maximum surface roughness was obtained when using HAp as reinforcement material. The increased in surface roughness was reached to (1.253μm) for (1.5%HAp+PEEK) while reached to (1.0163 μm) for (1.5%TiO2) compared with value of (0.478 μm) for neat PEEK.

3.3. FTIR Analysis
Figure (7) is the IR spectrum of HAp. In this figure, IR characterization curve for HAp the absorption peak at 3443.41cm⁻¹ is corresponding to the contracting vibration peak of O-H in H2O; the absorption peaks at 1036.90cm⁻¹ are corresponding to the key band of PO₄³⁻; the absorption peak at 790.89cm⁻¹ is corresponding to the key band of PO₄³⁻; the absorption peaks at 568.10 cm⁻¹ and 603.51cm⁻¹ belong to the bending vibration absorption peak of PO₄³⁻.

The spectrum of TiO₂ show in figure (8) exhibits an intense and wide band centered at ~3426.99 cm⁻¹ attributed to the O–H stretching, as well as peaks at 1654.66 and 1043.50 cm⁻¹ arising from the bending vibration of coordinated H₂O and Ti–OH [42]. The peak at ~566.42cm⁻¹ is related to the Ti–O–Ti stretching, and that at 1465.75 cm⁻¹ has been assigned to TiO₂ lattice vibrations [43].

FTIR spectra Figure (9) revealed bands attributed to the PEEK main chain in it, the stretching vibration peak for C=O is at 1648.10 cm⁻¹; the aromatic ring framework vibration peak is at 1593.49 cm⁻¹ and 1485.73 cm⁻¹; asymmetric stretching vibration peak for R-O-R is at 1217.06cm⁻¹; symmetric stretching vibration peak for R-CO-R is at 925.29cm⁻¹; bending vibration absorption peaks for C-H out of the benzene ring plane is at 835.27cm⁻¹ and 765.07cm⁻¹, meanwhile, at 836.92cm⁻¹ is the
characteristic peak of aromatic ring para-position substitution [44]. It can be again deduced that the chemical structure of PEEK substrate is not observably altered by the addition of nanoparticles bio composite samples as can be seen in figures (10 &11). Also it was clear that no new peaks and manifestly peaks shift were observed.

**Figure 7.** FTIR analysis for HAp powder.

**Figure 8.** FTIR analysis for TiO$_2$ powder.

**Figure 9.** FTIR analysis for pure PEEK.
4. Conclusions

In this paper, the flexural behavior, surface roughness and FTIR analysis of nHAp/PEEK and nTiO$_2$/PEEK composites were investigated through, three-point flexural tests, surface roughness test and FTIR analysis it was found that:

1. The flexural behavior of polymer composite improved by the increase weight fraction of powder but the higher values obtained at (1.5wt%) for two types of powders. While the flexure break strain% showed opposite behavior.
2. The surface roughness of polymer samples increased with increase weight fraction of powder but the higher values obtained at (1.5wt%) for two types of powders.

3. The best properties obtained when reinforced with (nHA) than reinforced with (nTiO₂).

4. The chemical structure of PEEK substrate is not observably altered by the addition of nanoparticles bio composite samples.

5. The above results suggest that 1.5% HA +PEEK has clinical potential as an effective material for dental applications.

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