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Strength of Polyether Ether Ketone Composite as a Major Connector Material for Removable Partial Dentures

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Abstract

AIM: Polyetheretherketone (PEEK) composite was tested mechanically as a maxillary removable partial denture (RPD) framework material instead of cast cobalt chromium (Co-Cr) alloy.

METHODS: Partial edentulous upper jaw cast was scanned using structured-light 3D scanner, palatal strap (PS) designs for RPD were designed by a designing dental laboratory software. Computer-aided design/computer-aided manufacturing machine fabricated PSs patterns using their designs' stereolithography software files. PSs were made from PEEK reinforced by ceramic fillers using thermal injection press technique and Co-Cr alloy using centrifugal casting, each material group was subdivided into two subgroups according to the storage conditions (stored and non-stored subgroups), storage took place in deionized water for about 180 days at 37.5°C ± 2°C. All specimens were subjected to fracture resistance test using universal testing machine then maximum compression load (MCL) result values were subjected to statistical analysis (independent-sample *t*-test and one-way between-groups analysis of variance). PEEK composite specimens were scanned by field emission microscope (FEM) and energy dispersive spectroscopy. Storage water of PEEK composite was analyzed using atomic absorption spectroscopy (AAS).

RESULTS: In either stored or non-stored subgroups of PEEK composite straps, they showed significant lower mean MCL values than corresponding alloy subgroups (p = 0.0001). FEM scanning showed fillers agglomerations in nonstored PEEK composite and their nearly absence from stored PEEK composite specimens. AAS detected Aluminum Al element in PEEK composite storage water.

CONCLUSION: Mechanically, thermally injected ceramic reinforced PEEK composite could not replace cast Co-Cr alloy as PSs material for maxillary RPD. Biocompatibility concerns raised in this study due to suspected Al leaching and ceramic fillers dissolution from PEEK composite matrix.

Introduction

The increasing number of partially dentate people requires replacement of their missing teeth by dentures. Although current treatment choices include fixed partial dentures and implants, removable partial dentures (RPDs) still have advantages in many clinical situations and can still be widely used in clinical practice. The indications for the treatment using RPDs are wide. RPDs can be indicated to overcome financial limitations, as provisional prostheses, to facilitate hygiene access, and to overcome biomechanical issues associated with dental implants. However, a need exists to advance both material and fabrication technology due to the unwanted health complications associated with the present conventional RPDs [1].

Cobalt-chromium (Co-Cr) alloys belong to base-metal alloys and are used widely in the orthopedic field and dentistry. In dentistry, Co-Cr alloys are used as metallic frameworks for RPDs and also as metallic substructures for porcelain-fused-to-metal restorations and implant frameworks. The interest in using Co-Cr alloys in dentistry is due to their low cost and satisfactory physical and mechanical properties [2].

The type of the leached element and its quantity has an influence on the corrosion characteristics of the metal alloy. Many metals such as Cr and Co are toxic, even at low levels of exposure. Although Co is an essential element, Co at higher concentrations is toxic and carcinogenic. The studies point out that inhalation or ingestion of hexavalent Cr can have systemic effects that are distant from the site of exposure. Hexavalent Cr is isostructural with sulfate and phosphate at physiological pH, it can spread through the body and even reach to the brain. Cr (VI) is a toxic and strong oxidizing agent which crosses cell membrane. Cr(VI) compounds are considered human carcinogens by the International Agency for Research on Cancer [3], [4], [5].

Once Co and Cr are artificially implanted in the human body through the use of medical devices, metal ions and wear particles release from Co-Cr alloys can cause toxicity or adverse health effects. Co–Cr alloys could thus cause harmful effects in the human body [5].

Since the 1950s, polyamide resin (nylon) has been used to make RPDs in the United States that do not contain any metal components. Recently, several thermoplastic resins have been approved and introduced to the market for use as denture bases. The use of RPDs made either from thermoplastic resin alone or a combination of thermoplastic resin and metal is now rapidly gaining popularity among patients and dentists [6].

English scientists in 1978 developed poly-ether-ether-ketone (PEEK), a semi-crystalline linear polycyclic aromatic thermoplastic polymer. PEEK became an important alternative choice for metal implant elements, especially in orthopedic and traumatic applications as well as spinal implants [7].

Zoidis *et al*. [8] described using PEEK modified by 20% ceramic fillers (BioHPP) in combination with acrylic resin as an alternative framework material, for a distal extension RPD prostheses in a clinical case report.

The present study was conducted to investigate the mechanical strength of PEEK polymer reinforced by ceramic fillers (granular BioHPP® - Bredent/Germany) when used as a maxillary RPD framework with and without water storage, in comparison to cast Co-Cr alloy, as well as investigating the tested polymer specimens microstructure.

Materials and Methods

Materials

Materials used in this study are listed in Table 1, with their brand name, chemical composition, and manufacturer.

Table 1: Materials used in this study with their brand names and manufacturers

Materials	Brand/chemical name	Manufacturer
Polyether ether ketone reinforced by ceramic fillers (PEEK/ceramic F)	BioHPP® Granules	Bredent GmbH and Co.KG
Cobalt Chromium casting alloy	Wironit®	Bego inc.
CAD/CAM milling wax blanks	breCAM.wax	Bredent GmbH and Co.KG
Ethyl alcohol	Ethyl alcohol (absolute and 70%)	El-Gomhouria For Trading Chemicals and Medical appliances/Egypt
Purified de-ionized water	Purified de-ionized water	Pharmapack Pharmaceutical Industries/Egypt

PEEK: Poly-Ether-Ether-Ketone, CAD: computer aided design, CAM: computer aided manufacturing.

Designing of specimens

The study stone cast for the upper partial edentulous jaw (bilateral missing of second premolar, first, and second molar) was scanned using structured-light 3D scanner (SHERA eco-scan 7 - SHERA Werkstoff-Technologie GmbH and Co. KG/Germany), the resulted image was used by designer device software (Dental wings 3 series - Dental Wings Inc. Montréal [Québec]/ Canada) to design palatal strap (PS) major connector for the upper RPD, the design stored in the form of (stereolithography CAD software file format) files, which were used by computer-aided design/computer-aided manufacturing (CAD/CAM) machine (SHERA eco-mill 5x - SHERA Werkstoff-Technologie GmbH & Co. KG/ Germany) to fabricate PS specimens.

Two designs were drawn by dental wings series series using the scanned image of the stone cast, one for the PEEK composite (granular BioHPP®) straps, the other for the cast Co-Cr alloy straps. Both designs were the same regarding the anteroposterior dimensions and the dimensions between the two edentulous spaces, the anteroposterior dimensions in both designs were not <8 mm to ensure sufficient rigidity [9]. The only difference between both designs was the thickness of the straps, the design thickness for PEEK composite PS (granular BioHPP®) was higher than that for Co-Cr alloy straps. Hence, the design thickness of Co-Cr alloy straps was 0.7 mm and that of PEEK composite straps was 1.4 mm.

Preparation of specimens

PEEK composite PS

In case of ceramic fillers reinforced PEEK composite PSs CAD/CAM machine (SHERA eco-mill 5x) milled wax patterns for PS from wax blocks (breCAM.wax/ Bredent - GmbH), then these wax patterns were burnt out during fabrication of reinforced PEEK composite PSs by thermal mould injection technique. The used PEEK composite was PEEK polymer reinforced by ceramic fillers (granular BioHPP® Bredent - GmbH) and was injected using Thermopress 400 device Bredent-GmbH (Figure 1). Thermopress 400 device was adjusted on program 20 using temperature of 400°C.

Figure 1: Finished granular BioHPP® palatal strap

Cast Co-Cr alloy PS (CPS1)

CAD/CAM machine (SHERA eco-mill 5x) milled acrylic patterns of PS for casting of CPS, using

CAD/CAM polymethylmethacrylate acrylic blocks (PMMA breCAM.multiCOM -Bredent-GmbH and DD PMMA cast Dental direkt-GmbH), then these patterns were burnt out during conventional casting of CPS using centrifugal casting machine, the used metal alloy was Wironit®/Bego.inc (Figure 2).

Figure 2: Cast cobalt chromium alloy palatal strap

Grouping

A total of 12 specimens were fabricated (12 PS) and were equally divided according to the tested material groups (PEEK composite (granular BioHPP®) - cast Co-Cr alloy (Wironit®), each of the two main groups was further subdivided equally into two subgroups (depending on presence or absence of water storage), with total of four subgroups with following code letters: Non-stored BioHPP PS (BPS1), stored BPS2, non-stored CPS1, and stored CPS2. Each subgroup included three specimens.

Storage conditions

Storage was carried out by immersion in deionized water using glass flasks (Simax™ - Kavalier/Czech Republic), straps and glass flasks were disinfected using ethyl alcohol and rinsed by deionized water before storage, storing was carried out in incubator (BioTECH BTC/Egypt) adjusted at temperature of 37°C for about 180 days. Straps were visually inspected by naked eye before storage to check the absence of any residues or investment material remnants, all deionized water packs were all from the same manufacturer and with the same batch number (Pharmapack purified water – Pharmapack pharmaceutical industries-Egypt), each PS was stored separately in a tightly closed glass flask and immersed in about 50 ml deionized water.

Testing procedures

Due to the possibility of infection or presence of any degradation chemicals in storage water, safety precautions were taken during exposure of technicians and researchers to storage water according to the OSHA and NIOSH occupational health safety guidelines.

Fracture resistance test

All subgroups specimens (stored and non-stored) were subjected to fracture resistance test under compression, using universal testing machine (Instron model 3345 series/England – operated by Bluehill software version 3.3), all specimens were subjected to loading with their fitting surface side facing loading applicator rod with rounded end of 5 mm in diameter, mounted in the upper jaw (Figure 3), using crosshead speed of 5 mm/min [10], [11], [12]. Stored specimens were tested after removal from storage water, washing by running water and complete drying.

Figure 3: BioHPP® palatal strap during fracture resistance test using universal testing machine

For the sake of testing procedure accuracy, all PSs were marked on their fitting surface side using a marker pen, on the same area using same palatal anatomical landmark as a reference point. It was done to determine the area of load application to assure that all specimens were loaded at the same area (i.e., standardization of loading point) [12]. Stored specimens were marked after storage, to avoid storage water contamination.

In the fracture resistance test, most of PEEK composite PS did not show complete fracture, but showed deformation till complete extension on the testing table of the universal testing machine (Figure 4), in this case, the test was stopped when the rod applicator forced the strap to touch the testing table completely

Figure 4: BioHPP® palatal strap showed complete extension deformation after performing fracture resistance test

by complete extension, to avoid getting false results about the compression load value, and the maximum compression load (MCL) till the beginning of complete extension was recorded with the maximum extension length; therefore, the term “maximum compression load” MCL was used in this study instead of “maximum fracture load.”

Field emission microscope (FEM) scanning and energy dispersive spectroscopy (EDAX) analysis

Deformed PEEK composite (granular BioHPP®) straps were scanned using FEM (Quanta FEG 250), scanning was performed after fracture resistance mechanical testing, one specimen from each PEEK composite subgroup (BPS1 and BPS2) was scanned.

For microstructure analysis, flat smooth piece of BioHPP was cut from injected BioHPP sprue after thermal pressing, for EDAX scanning and microstructure study by FEM, the cut specimen was wiped with alcohol before EDAX scanning.

Flat smooth piece was needed as in EDAX analysis, the sample needs to be polished into a flat surface, decreasing height differences at the interfaces and removing the geometric effects that arise from the irregularities of specimen surface [13].

Atomic absorption spectroscopy (AAS)

According to the EDAX analysis of BioHPP, titanium Ti and aluminum Al elements were found to be involved in the BioHPP microstructure, so atomic absorption spectroscopy (AAS) was used for Al and Ti detection in a representative sample from BioHPP straps storage water.

As-received fresh-water samples taken directly from deionized water packages were screened for Al and Ti elements as baseline reference readings. Water packages were all from the same manufacturer and with the same batch number.

Atomic absorption spectrometer (ZEEnit 700P/ Germany) was used with the instrumental conditions adjusted according to the manufacturer’s suggestions. Nitrous oxide acetylene was used for Al and Ti detection.

Statistical analysis

After performing a pilot study with three specimens for each subgroup, the sample size was calculated by G*Power version 3.1.9.2 for sample size analysis at α = 0.05 and 90% power and effect size equal to 3.263893 which yields a sample size of three samples per subgroup.

Statistical analysis was computed using SPSS (Statistical Package for the Social Sciences, IBM SPSS Statistics for mac, version 24 software, Armonk, NY: IBM Corp., USA).

Data of mechanical testing results were presented as means and standard deviation. Data were checked for normality using Kolmogorov–Smirnov test and Shapiro–test and were found to be normally distributed.

Statistical analysis was carried out using independent-sample *t*-test to explore the effect of water storage on MCL for PS of both materials (PEEK composite (BioHPP®) and cast Co-Cr alloy (Wironit®).

A one-way between-groups analysis of variance (ANOVA) was conducted to explore the effect of different materials for PS on MCL with and without water storage.

Results

Statistical analysis of mechanical testing results

The effect of water storage

As independent-sample t-test was carried out to explore the effect of water storage on MCL for BioHPP® and CPS, for BioHPP and Co Cr alloy PSs, there was no statistically significant difference between water storage and no water storage subgroups in mean MCL value, with p value for BioHPP ($p = 0.554$) and for Co-Cr alloy ($p = 0.101$) (Table 2).

Table 2: Effect of water storage on means of maximum compression load for the two tested straps materials

Type of palatal strap	Water storage	Mean maximum compression load (*n*)	SD	SEM	*p*
BIOHPP Palatal Strap	No water storage	97.6667^{a,*}	13.6504	7.88106	0.554
	6 months of water storage	108.4^{a}	25.36691	14.64559	
CO-CR alloy palatal strap	No water storage	440.7^{a}	48.32898	27.90275	0.101
	6 months of water storage	575.5667^{a}	98.79131	57.03719	

*Different letters indicate significant difference between stored and nonstored subgroups within the same level of the palatal strap material. SD: Standard deviation, SEM: Standard error of mean.

The effect of material type

A one-way between-groups ANOVA was conducted to explore the effect of PS material type on MCL. In either no water storage or water storage subgroups, there was a statistically significant difference at $p < 0.001$ level ($p = 0.0001$), CPS showed a statistically significant higher “mean MCL” in stored and non-stored subgroups (Table 3).

FEM and EDAX results

FEM and EDAX of BioHPP specimen for microstructure study

FEM backscattered electron detector scanning image of the surface of BioHPP specimen specified for microstructure study showed PEEK matrix (darker background) reinforced by ceramic fillers (white points) (Figure 5), which agrees with the description of BioHPP® microstructure under scanning electron microscope stated in the brochure of the product published by the manufacturer company (Bredent-Germany).

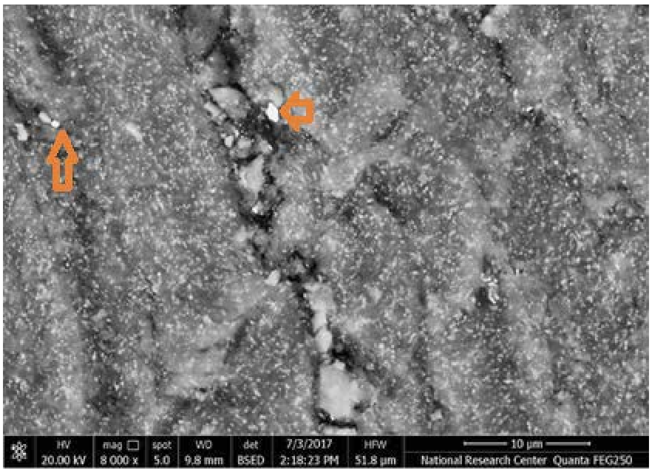

Figure 5: 8000X micrograph of field emission microscope scanning image of BioHPP surface specified for EDAX analysis, suspected ceramic fillers clusters or agglomerations (orange arrows)

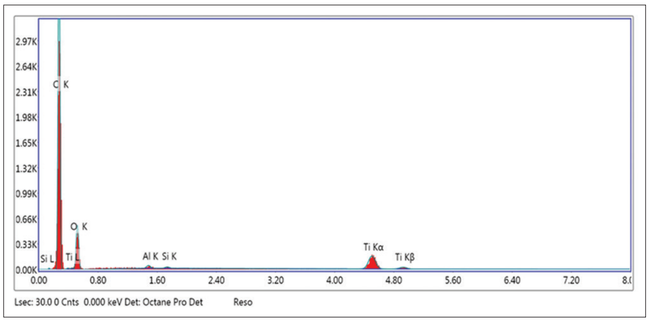

Figure 6: EDAX of a dark spot in the micrograph of the BioHPP® field emission microscope scanning in Figure 5

As shown in Figure 5, there are also some large white spots which most probably represent ceramic fillers agglomerations.

EDAX analysis of a dark area spot of the BioHPP FEM scanning image in Figure 5 is shown in Figure 6 and the distribution of elements revealed by scanning is illustrated in Table 4.

Furthermore, EDAX analysis was made for one of the white spots which appeared in BioHPP scanning image in Figure 5 and was suspected to be ceramic fillers agglomeration (Figure 7 and Table 5), which revealed higher weight percentage of oxygen, aluminum, silicon, and titanium, with the lower weight percentage of carbon in comparison to EDAX of the dark area spot, also scanning revealed presence of sulfur and iron elements in this white spot (Table 5).

FEM for non-stored BioHPP straps

FEM scanning was made for one of the deformed non-stored BPS1 after mechanical testing. As the straps of this subgroup did not fracture after the mechanical test, and only showed permanent deformation the scanning was done for the site of the load application on the fitting surface of the strap.

Table 4: Elements composition in energy dispersive spectroscopy analysis of a dark spot in the micrograph of the BioHPP® field emission microscope scanning in [Figure 5]

Element	Weight %	Atomic %	Net Int.	Error %
C K	68.78	76.46	452.7	4.99
O K	26.55	22.16	77.57	11.75
AlK	0.26	0.13	6.82	20.1
SiK	0.12	0.06	3.62	31.94
TiK	4.3	1.2	64.33	5.05

It is evident in the image linear and branching defects, the large white spots (orange arrows) which are suspected to be ceramic fillers agglomerations are observed to be concentrated in these linear and branching defects (Figure 8).

Table 3: The effect of palatal strap material type on the maximum compression load means (analysis of variance test)

Water storage	Type of strap material	Mean maximum compression load (*n*)	SD	SE	95% CI for mean		*p*
					Lower bound	Upper bound	
No water storage	BIOHPP palatal strap	97.6667^{a,*}	13.6504	7.88106	63.7572	131.5761	0.0001
	CO-CR alloy palatal strap	440.7^{b}	48.32898	27.90275	320.6442	560.7558	
6 months of water storage	BIOHPP palatal strap	108.4^{a}	25.36691	14.64559	45.3851	171.4149	0.0001
	CO-CR alloy palatal strap	575.5667^{b}	98.79131	57.03719	330.1554	820.9779	

*Different letters indicate significant difference between palatal straps within the same level of storage conditions. CI: Confidence interval, SD: Standard deviation, SE: Standard error.

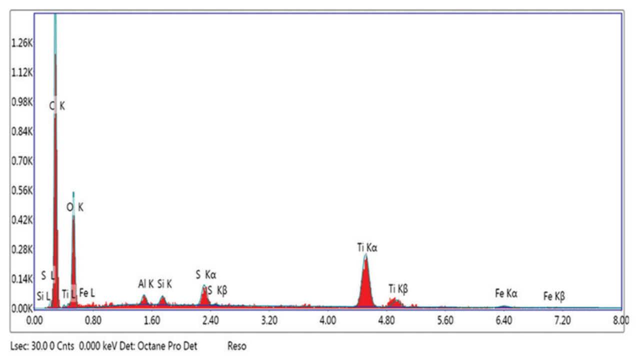

Figure 7: EDAX analysis of a white spot appeared in the micrograph of BioHPP® surface field emission microscope scanning image shown in Figure 5

Table 5: Elements composition in energy dispersive spectroscopy analysis of a white spot appeared in the micrograph of BioHPP® surface field emission microscope scanning image shown in [Figure 5]

Element	Weight %	Atomic %	Net Int.	Error %
C K	53.92	65.14	181.71	7.37
O K	33.91	30.76	74.99	11.7
AlK	0.59	0.32	10.38	14.53
SiK	0.47	0.24	9.75	15.57
S K	1.35	0.61	26.35	10.63
TiK	9.13	2.77	96.1	4.24
FeK	0.62	0.16	3.55	45.35

FEM for stored BioHPP straps

Another FEM scanning image was made for the load application site on the fitting surface of one deformed (not fractured) BioHPP strap after water storage (BPS2) and after mechanical testing (Figure 9), it demonstrated many linear and branching defects. However, the white spots which are suspected to be ceramic fillers agglomerations are not observed in the scanning image.

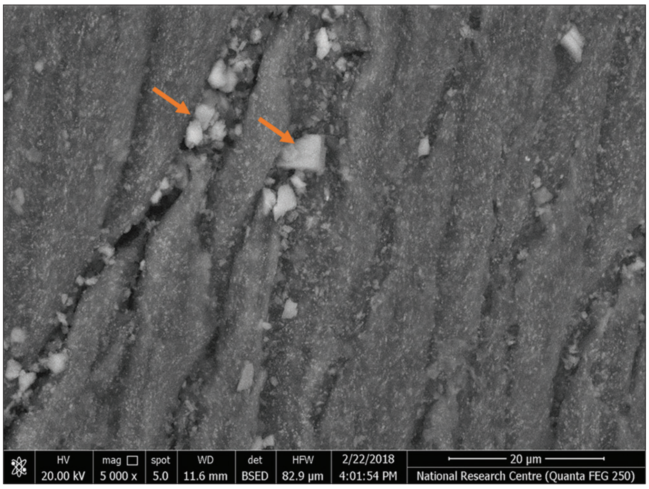

Figure 8: 5000X micrograph of field emission microscope BSED scanning image of load application site of deformed non-stored BioHPP strap (BPS1) after mechanical testing, large white spots suspected to be ceramic fillers clusters/agglomerations (orange arrows) with different dimensions

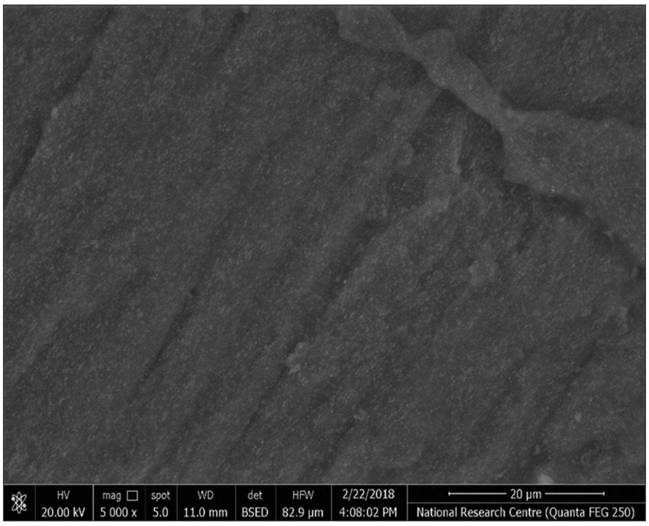

Figure 9: 5000X micrograph of field emission microscope BSED scanning image of loading application site of deformed stored BioHPP strap (BPS2) after mechanical testing

Results of AAS

Results of AAS of BPS storage water and AAS of control as-received freshwater samples taken directly from deionized water packages are shown in Table 6.

Discussion

Co-Cr alloys are base metal alloys used widely for making framework of removable dental prostheses [14], but one of the most important concerns related to Co-Cr casting alloy is its biological safety, which is related to its corrosion in the oral cavity, as systemic and local toxicity, allergy, and carcinogenicity all result from elements and ions leached from alloys into the oral cavity during corrosion [15].

Table 6: Results of atomic absorption spectroscopy atomic absorption spectroscopy

Tested liquid	Al[a]	Ti[b]
BioHPP storage water	10.62 ppm	Nil
As-received freshwater sample from deionized water package	Nil	Nil

[a]Detection limit: 0.030177 ppm, [b]Detection limit: 2.0196 ppm.

Polyaryletherketones consists of PEEK and polyetherketoneketones (PEKK) and it was recently introduced in dentistry. Recently, PEEK and PEKK were introduced to the dental market as high-performance biomaterials and claimed to be chemically inert [16].

A thermoplastic high-performance polymer material was tested in this study, which was mould-injected PEEK polymer reinforced by ceramic fillers (granular BioHPP®) regarding its mechanical strength, to be used as a suitable alternative for cast Co-Cr alloy (Wironit®), in fabrication of major connectors for maxillary teeth-bounded RPDs.

BioHPP® is a high-performance polymer, and according to the manufacturer's information, it is based on PEEK polymer reinforced by special ceramic fillers (with the grain size of 0.3 to 0.5 μm) and was introduced for manufacturing the superstructure prosthesis on dental implants by Bredent-GmbH company. BioHPP is considered a semi-crystalline and pigmented thermoplastic polymer, with a base material of PEEK which contains about 20% ceramic fillers [17].

CAD/CAM technology was used in the designing and preparation patterns of specimens, to assure standardization of specimens' dimensions between the two tested material groups.

Most BPSs in this study did not fracture after fracture resistance test but showed permanent deformation instead, only one stored strap belonged to (BPS2) fractured completely. Water storage had no statistically significant effect on the mean MCL value of BioHPP straps (Table 2). However, mean MCL values in both subgroups (BPS1 and BPS2) were significantly lower than the corresponding values of Co-Cr subgroups (CPS1 and CPS2) (Table 3). They were also lower than the expected average maximum bite force at first molar area for patients wearing upper and lower RPD, which is in the range of 130–150 N [18]. According to the previous results, BioHPP straps could suffer permanent deformation during mastication and could not provide sufficient strength to resist biting forces during mastication in comparison to cast Co-Cr alloy straps.

EDAX showed the presence of aluminum, titanium, and silicon elements, and their weight percentage increased in the scanning of a white spot appeared in the FEM scanning image of BioHPP® specimen when compared to a dark area scanning (Figures 5-7). These white spots represent ceramic fillers or ceramic fillers clustering. By reviewing different published literature about different trials for reinforcing PEEK polymers by ceramic fillers, it is highly expected that Al,Ti, and Si elements could be related to ceramic fillers composition [19], [20], [21], [22], [23], which may be silica (SiO_2), titanium dioxide (TiO_2), alumina (Al_2O_3) fillers, or combination of the previous.

Furthermore, presence of silicon element could be related to the composition of silane coupling agent, used to treat fillers surface, to improve the wettability and adhesion between fillers and polymer matrix. Silanes are one of the most popular coupling agents for filler surface treatment [24], [25], [26]. BioHPP® is a white pigmented PEEK composite, so titanium dioxide could be used by the manufacturer for white pigmentation of BioHPP and that could be another explanation for the presence of titanium element in the EDAX analysis [27].

In this study, fillers agglomerations or clusters were observed in FEM scanning of BioHPP specimen specified for EDAX analysis and in FEM scanning micrograph of non-stored BioHPP strap (BPS1) (Figures 5 and 8). Nearly, absence of fillers clusters was observed in FEM scanning micrograph of stored BioHPP strap (BPS2) (Figure 9), which is considered an evidence for leaching of fillers clusters from BioHPP matrix due to storage in water of human body temperature (37°C).

Presence of ceramic filler agglomerations or clusters in PEEK composite (BioHPP) specimens without water storage could be related to some factors. First, it could be related to using thermal injection mould technique for preparing PEEK composite (BioHPP) specimens, which is not included in the recommendations by the manufacturer company of BioHPP (Bredent-Germany), as the manufacturer recommends another manufacturing technique for BioHPP, using vacuum pressing machine (2 press system/Bredent. GmbH), but unfortunately the available large ring sizes of "2 press system" were not available in Egypt at the time of BioHPP specimens fabrication (2016/2017), and as processing of removable denture frameworks needs large size flasks or rings some laboratories in Egypt depended on thermal injection moulding by Thermopress 400 device Bredent-GmbH to overcome this problem.

Absence or inefficient coupling or adhesion between fillers and PEEK polymer matrix could be another factor for observing ceramic filler agglomerations or clusters in non-stored PEEK composite (BioHPP) specimens, as concluded in another study conducted to investigate the effect of silane modified fillers for reinforcing polymers. It was found that the unmodified silica fillers exhibited a high tendency to form agglomerates, while the modification of silica surface with silane induced dispersion of silica agglomerate structures [24].

Joseph *et al*. stated that as the filler loading in the polymer increases, and at high filler loadings, if fiber/matrix adhesion is poor, the fillers get agglomerated rather than forming a continuous network. In this case, the mechanical property improvement gained from fillers addition would be lower [28].

Overloading of PEEK polymer with ceramic fillers could be another reason for formation of ceramic fillers agglomerates or clusters in granular BioHPP®. Kuo *et al*. stated in their study about reinforcing PEEK polymers by nanosized SiO_2 and Al_2O_3 particulates that ultimate tensile strength showed a maximum peak at about SiO_2 or Al_2O_3 content of 5.0–7.5 weight%, but with a greater amount of nanoparticles, the strength started to decrease due to local particles clustering. This was explained by Kuo *et al*. that the greater viscosity of the PEEK/nanoparticles mixture at higher nanoparticles concentration during the hot press processing, which caused agglomerates of fillers which, in turn, decreased the reinforcing effects of fillers [19].

Agglomerations of dispersed filler particles resulted in decreased mechanical strength due to the lower strength of the agglomerates themselves [29]. This could explain the presence of ceramic fillers clusters or agglomerates in the defects of deformed BioHPP straps (BPS1) (Figure 8), which might be caused by the detachment of clusters or agglomerates from polymer matrix forming large voids and cracks. It can be concluded in this study that in dry conditions, ceramic fillers clusters or agglomerates are considered weak points, decreasing the strengthening effect of ceramic fillers in case of thermal mould injected granular BioHPP®.

After water storage, leaching of fillers agglomerates or clusters was observed due to nearly absence of fillers clustering from FEM scanning micrograph of deformed BioHPP strap after water storage (BPS2) (Figure 9). The final confirmation of degradation or leaching of ceramic fillers from BioHPP in this study came after AAS of BioHPP storage water. It showed Al concentration of about 10.6 ppm in storage water and Nil concentration of Al in fresh sample of deionized water. The detection of Al element in BioHPP storage water could be related to leaching of ceramic fillers agglomerates/clusters as confirmed by FEM scanning image of stored BioHPP (BPS2) strap, or due to ceramic fillers corrosion [30], or both of the previous explanations, and both explanations could expose the patients to real health hazards.

Inhalation or oral exposure of aluminum could carry risks to patient as: Irritation, mutagenicity, reproductive toxicity, neurological toxicity, and metabolic disorders, depending on the dose of exposure, the type of aluminum compound and its bioavailability, route of administration, and other factors which were analyzed by a wide review made by Krewski *et al*. [31] about possible health hazards of aluminum for human beings.

Conclusions

Within the limitations of this study, it could be concluded that:

1. Thermal mould injection of granular BioHPP® instead of using vacuum pressing machine recommended by the manufacturer company (2 press system/Bredent. GmbH) would produce PEEK composite which does not have the enough mechanical strength to be used as maxillary RPD framework
2. Leaching of ceramic fillers agglomerates or clusters from thermal mould injected granular BioHPP® matrix into saliva in the oral cavity during service is highly suspected, which could expose the patient to the risks of ingestion or inhalation of ceramic fillers
3. Aluminum element leaching from thermal mould injected granular BioHPP® was detected, which also could expose patients to hazards of aluminum ingestion or inhalation.

Recommendations

1. The future research studies are needed for further evaluation of other types of BioHPP® PEEK composites as CAD/CAM or pellet form BioHPP, as they may show different degradation and mechanical properties different from that of granular BioHPP
2. More future research studies are needed for further evaluation of mechanical and biodegradation properties of granular BioHPP, which is manufactured by the vacuum pressing machine recommended by the manufacturer company (2 press system/Bredent. GmbH), as the change in the pressing technique or machine could have an impact on material's properties
3. More biodegradation studies are needed to evaluate the amount and rate of leaching of ceramic fillers and aluminum from BioHPP, to determine and evaluate the expected health hazards from intraoral use.

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