EGYPTIAN
DENTAL JOURNAL
www.eda-egypt.org

Vol. 68, 1731:1739, April, 2022

Print ISSN 0070-9484 • Online ISSN 2090-2360

Fixed Prosthodontics and Dental Materials

Submit Date : 2022-02-27 • Accept Date : 2022-03-26 • Available online: 2022-03-30 • DOI : 10.21608/edj.2022.123175.1993

EFFECT OF NANOPARTICLES ON SURFACE ROUGHNESS OF DIGITALLY AND CONVENTIONALLY CONSTRUCTED RPD FRAMEWORK

Enas Darwish* *and* Mai Helmy*

ABSTRACT

Aim: This study aims to compare the effect of adding Silica -oxide nanoparticles on surface roughness of removable partial denture framework constructed digitally with Poly(ether-ether-ketone) PEEK versus computer-aided designed -computer manufactured (CAD/CAM)

Methodology: A total of 80 Mandibular Kennedy class III modification 1 partially edentulous cast were constructed as a model to simulate the oral cavity and partial denture was fabricated, PEEK is being introduced more commonly in the construction of the partial dentures, this study aimed to evaluate the effect of adding Silica -oxide nanoparticles on surface roughness of denture base constructed with Poly(ether-ether-ketone) PEEK. Partial dentures were prepared for experimentation of surface microroughness into two main groups 40 in each group. Group I: conventional fabrication of RPD framework using PEEK material which was subdivided into two Group IA: acted as a control, no fillers were used in this group, and Group IB: Ten weight percentage (10 wt. %) of hydrophobic nano-SiO2 incorporated with the PEEK. Then, Group II: CAD/CAM milled frameworks (Digital constructed using ExoCad software also, Subdivided into two groups Group IIA acted as a control, no fillers were used in this group, and Group IIB: Ten weight percentage (10 wt. %) of hydrophobic nano-SiO2 incorporated with the PEEK. Then, a digital profilometer was used to determine the surface roughness of the specimens. Surface hardness was conducted by The Rockwell hardness test machine used in this study. ANOVA and Tukey tests were used for the statistical analysis ($p < 0.05$).

Results: Group II (digital fabricated RPD with CAD/CAM milled frameworks) showed Statistically significantly lower surface roughness than Group I: conventional fabrication of RPD framework using PEEK material. On the Other hand, there was a statistically significant difference in Sud division groups as the groups which incorporated with silica nanoparticles were showed statistically significant higher in surface roughness than the controlled groups which constructed with PEEK materials without any additives in both major groups either constructed with conventional manner of RPD or constructed with (CAD/CAM) digital manner.

* Associate Professor, Prosthodontic Department, Faculty of Dentistry, Cairo University

Conclusion: the results showed a significant difference in the surface roughness and contact angle between groups (group I and group II), where surface roughness of pure peek framework either constructed conventionally or digitally showed statistically lower than that incorporated with sio2 nanoparticles. On the other hand, a digitally constructed framework showed a statistically lower surface roughness than that constructed conventionally.

KEYWORDS: Kennedy class III, CAD/CAM, Surface roughness, Silica -oxide nanoparticles.

INTRODUCTION

Polymethylmethacrylate (PMMA) is considered the most used material for the fabrication of dentures. However, PMMA has acceptable not only functional, physical, and mechanical properties but also has a suitable appearance and inexpensive equipment needed for its fabrication. But the PMMA dentures are susceptible to fracture during use or when dropped onto hard surfaces. These fractures are due to either flexural fatigue or impact which is generally associated with material properties /or framework design integrity also, PMMA although heat cured resin, but had a minimal amount of residual monomer that allowed the saliva to penetrate between the polymer chains and results in increased the surface roughness. [1-4]

PEEK (Polyetheretherketone is a semi-crystalline thermoplastic biomaterial) could be considered as an innovative material to replace PMMA. It is one of the Polyaryletherketones (PAEKs) polymer group family, which is characterized by ultra-high molecular weight polyethylene (UHMWPE)

Poly(ether-ether-ketone) (PEEK), on the other hand, is one of the best choices to resolve stress shielding issues due to its outstanding biocompatibility and biomechanical properties. Recently, some researchers had described the impact of incorporating nanoparticles into denture resin to improve its mechanical properties. [5-9]

The SiO2 nanoparticles are mostly used to reinforce the polymethyl methacrylate PMMA. also, Many studies were reported that added nano-SiO2 (0.25, 0.5, and 0.75%) to the PMMA repair resin and found that the highest increase in flexural strength is observed with 0.25%compared with the higher concentrations. [10-11]

Therefore, lower concentrations of nano-SiO2 into PMMA to assess mechanical properties have been recommended for further investigations.

However, research into SiO2 nanofillers as PEEK reinforcement in the dental field is minimal. SiO2 is characterized by its small particle size, large surface area and it has excellent biocompatibility as well as optical, thermal, and mechanical properties. The surface of silica is usually hydrophilic has three chemical groups isolated hydroxy, hydrogen-bonded hydroxy, and siloxane groups. This hydrophilic surface of bare SiO2 can be reduced hydrophobic such as dimethyldichlorosilane, polydimethylsiloxane and hexamethyldisilane by reacting its surface hydroxyl groups with organofunctional groups, Compression molding has been used to successfully fabricate PEEK composites reinforced with SiO2 nanofillers for industrial processes. Moreover, several researchers reported that the tensile bond strength was improved when increasing the SiO2 content in PEEK.[12-14]

As a result, further research is required to fully understand the influence of nanofiller particle form, structure, particle size, total volume, and coating in PEEK for dental applications.

Surface roughness of dental materials plays a major role in bacterial plaque accumulation and adherence, bacterial adhesion is increased on rough surfaces because of increased surface area, therefore materials with low surface roughness are essential for reduced bio adhesion. [15-17]

The objective of this in-vitro study was to compare the surface roughness of conventionally constructed class III partial denture framework to that constructed digitally using EXOCAD software, (with and without si02 nanoparticles incorporation).

METHODOLOGY

Total Eighty frameworks were constructed, and divided equally into two main groups, Group I, received Forty conventionally fabricated PEEK frameworks with Subgroups, Group IA and Group IB as Group IA: acted as the control group, the framework was fabricated with no fillers, and Group IB: the framework was fabricated with Ten weight percentage (10 wt. %) of hydrophobic nano-SiO2 incorporated with the PEEK., Group II, received Forty CAD/CAM milled frameworks. with Subgroups, Group IIA and Group IIB as Group IIA: acted as the control group, the framework was fabricated with no fillers, and Group IIB: the framework was fabricated with Ten weight percentages (10 wt.%) of hydrophobic nano-SiO2 incorporated with the PEEK.

For the four groups, an experimental model of the Mandibular edentulous case (Kennedy class III Modification 1) was fabricated and ready to be used as a master model to simulate the oral cavity. Primary surveying of the experimental model was done to ensure and located the presence of desirable undercut to select the suitable clasp assembly using a NEY surveyor. Guiding planes were prepared on the distal surface of the first left premolar and right canine bilaterally and also, were prepared on the mesial surfaces of the right and left the second molar using a stone, then, Rest seats were prepared in the near zone of the edentulous span bilaterally and a cingulum rest was prepared on the canine using size two round bur.

Preparation of PEEK/SiO2 Nanocomposites

Semi-crystalline PEEK fine powder (VICTREX® PEEK polymers, Victrex Technology Centre, Lancashire FY5 4QD, UK.) with an average particle size of 50 microns for compression molding was used as the polymer matrix.

The hydrophobic nano-SiO2 particles (NanoTech Egypt Co., Giza, Egypt) were used as filler materials. Before mixing, PEEK powder was dried overnight in a vacuum oven at 120 C to allow sufficient humidity elimination. Then, mixed with nano-SiO2 particles.

Then, mixed in a planetary ball mill (Emax, Retsch GmbH, Haan, Germany) at 25C and 400rpm for 2 h.

The PEEK/SiO2 nanocomposites were fabricated using a compression molding process. The as-milled dried powder was filled in a tool steel die with a 10 mm diameter. The powder was compressed at room temperature under a pressure of 35 MPa for 2 min. After cold compaction, the powder was heated to 410 c, while applying a low cavity pressure of about 2 MPa. Once the system reached the set temperature, it was held at constant temperature and pressure for 10 min to establish homogeneity within the melt. Following this, the system was permitted to cool down at room temperature under a pressure of 20 MPa.

Finally, the samples were taken out after the mold was opened.

In this study, the PEEK/SiO2 nanocomposite with 10 wt% hydrophobic nano-SiO2 particles, was used in the two groups

Divided equally between the two groups

Group I: Conventional fabrication of RPD framework

The wax pattern was applied as regular on the prepared experimental casts with applied Aker clasps on the molars and premolars and an RPI clasp was applied on the canine to engage the buccal undercuts (Distobuccal undercuts on the molars, mesiobuccally undercut on the premolar, and finally the mid buccal undercut on the canine) and the lingual bar was used as a major connector

Spring and investing of wax patterns were done. Then, the PEEK material was preheated at 400 C for 20 minutes by using the injection molding unit (Thermoflex 400) then Heated softened PEEK was injected into the mold by pressure 950mega pascal and velocity 6 bars in 240 seconds. After curing, the framework was deflated then; The sprues were separated and the pressed RPD frameworks were finished and polished according to manufacturer instructions and tried to seat on the experimental casts to check its seating and accuracy

Group IA: The framework was injected by the PEEK only

Group IB: the framework was injected using the prepared PEEK with 10% silica dioxide nanoparticles

Group II: (CAD/CAM milled frameworks (Digital constructed using ExoCad software)

The experimental mandibular is partially edentulous cast was then fixed on the scanner table and scanned using an extraoral 3D scanner*** to obtain the STL file.

The STL File was inserted into the EXOCAD software and allowed digitally surveying of the virtual experimental cast to identify areas of desirable undercut present on the teeth and soft tissue. **(Fig.1)**

The width and thickness of any part of every component were selected at these points. Rests on each abutment, minor connectors, finish lines were selected and placed according to principles of RPD design in a bounded saddle. **(Fig.2)**

The whole virtual framework design was checked from all surfaces after finishing and smoothening.

STL file of the virtual framework was used to print the resin pattern* using 3D printer then, The virtual 3D framework (STL) file was sent to the milling machine* to begin the milling process of PEEK discs*** in this step Group II was subdivided into groups.

Group IIA: were the Framework was fabricated from pure PEEK material using milling machine** (CAD/CAM technology).and Group IIB: Ten weight percentages (10 wt. %) of hydrophobic nano-SiO2 incorporated with the PEEK. Using high energy ball milling technique to disperse nano-SiO2 particles into the PEEK matrix in order to improve the

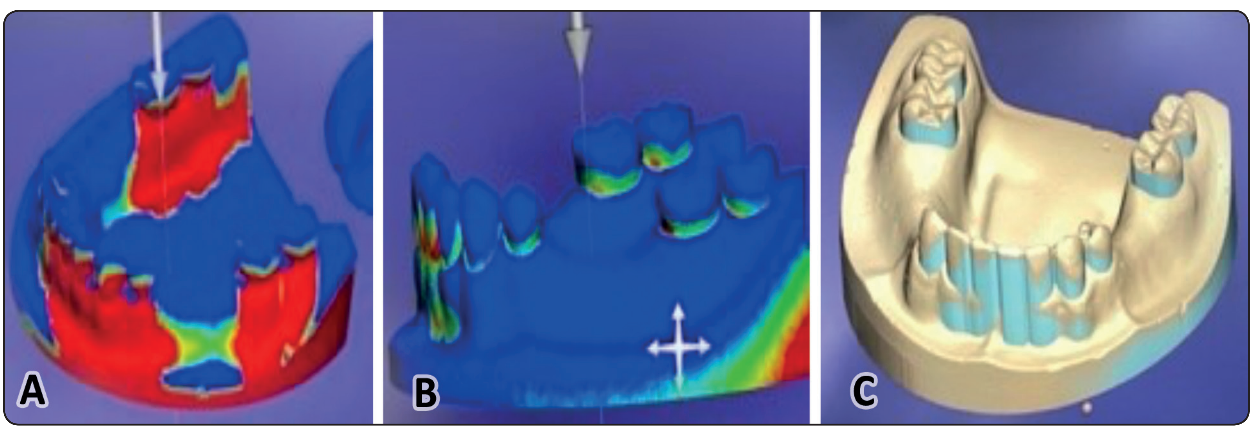

Fig. (1): **A.** change the cast tilt to detect the undercuts and adjust the path of insertion, **B:** adjust the suitable tilt and create dimpling on the abutments, **C:** create the modified cast on EXOCAD then, the design of the prospected framework was digitally standardized including; lingual bar major connector, Aker clasps on the molar and premolar abutment teeth, and RPI was applied on the canine In the form of a spine of points.

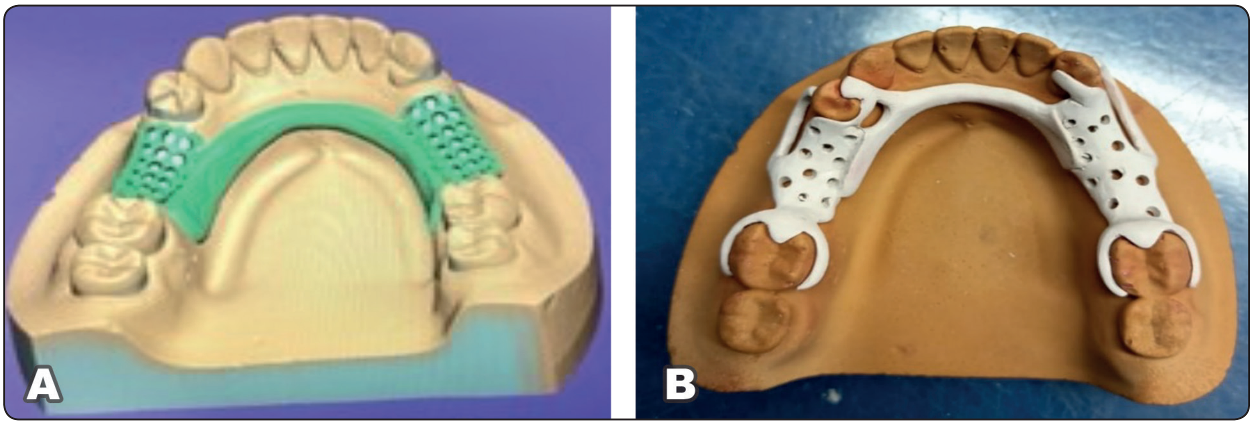

Fig. (2) **A:** select the lingual bar and denture base meshwork with thickness 1.5mm-2mm which is suitable for the fabrication of PEEK framework **B:** finished CAD/CAM PEEK framework.

mechanical properties by reducing the particle size of pure PEEK from a millimeter to a micrometer scale (~5 μm). then, silicon mold was performed for the standard peek disc in order to produce the same size Peek incorporated by 10% wt. nano-SiO2 particles disc and the performed PEEK with SiO2 particles disc was applied to the milling machine.

For all groups, the surface roughness and water contact angle were measured before and after the finishing of the framework

After milling, the sprues were removed by using a grinder (LD15C LD/ZR [Lithium Disilicate/Zirconia] Grinder Green Coarse Wheel Ceramic; Brasseler USADental Instrumentation), and the RPD framework surface was finished with a laboratory carbide Bur (HM261PX-023-HP) fine with a tapered round end, 2.3mm, and polished with a goat-hair brush and composite resin polishing paste (Luminescence; Premier) for 60 seconds.

I. Surface Roughness measurement

The surface roughness was measured (Ro) by using a contact profilometer (Surf test SV-3100; Mitutoyo Corp) after milling (baseline) and after the polishing procedures were completed.

The same surfaces were measured before and after polishing. The accuracy of the profilometer was examined periodically by using a calibration block. The tracing length was 13.3 mm, the number of points measured per specimen was 13 300, and the stylus speed was 1 mm/sec.

The surface roughness and contact angle before polishing (baseline) and after polishing for each framework were compared.

II. Contact Angle Measurement

The variation of contact angle was compared between different types of PEEK framework and PEEK/SiO2 nanocomposites which were loaded by10 wt.% of the hydrophobic nano-SiO2 under the two major groups were the RPD frameworks constructed digitally and conventionally.

All resulting data were collected, tabulated, and statistically analyzed through an ANOVA test. The level of significance will be set at $P<0.05$

RESULTS

Data were presented as the mean, standard deviation in 1 table & 2 graphs. Statistical analysis was performed with SPSS 16 ® (Statistical Package for Scientific Studies), Graph pad prism & windows excel.

Exploration of the given data was performed using the Shapiro-Wilk test and Kolmogorov-Smirnov test for normality which revealed that the significant level (P-value) was insignificant as P-value > 0.05 which indicated that alternative hypothesis was rejected, and the concluded data originated from a normal distribution (parametric data) resembling normal Bell curve.

Comparison between all groups regarding surface roughness and contact angle was performed by using the One Way ANOVA test which revealed a significant difference between them as P < 0.05 in both baselines (before finishing and polishing) & after finishing and polishing.

One Way ANOVA test followed by Tukey`s Post Hoc test which revealed a significant difference in means with different superscript letters as P < 0.05 (G IB: Conventional fabricated PEEK with nanoparticles silica oxide framework was statistically significantly the highest, followed by G IA: Conventional fabricated pure PEEK framework .then, followed by G IIB: Digital CAD/CAM fabricated PEEK with nanoparticles silica oxide framework and finally G IIA Digital CAD/CAM fabricated pure PEEK framework that was significantly the lowest), as presented in table (1) and figure (1,2).

Moreover, Comparison between before and after was performed by using Paired t-test regarding surface roughness & contact angle and revealed that after finishing & polishing was significantly higher than before as P < 0.05 in all groups as presented in table (1) and figure (1,2)

TABLE (1): Mean ± standard deviation of surface roughness and contact angle in G IA (Conventional PEEK without silica), G IB (Conventional PEEK with silica), G IIA (Digital PEEK without silica) & G IIB (Digital PEEK with silica) before and after finishing and polishing:

		G I (Conventional PEEK)				**G II (Digital PEEK)**				**P-value**
		G IA (Without silica)		G IB (With silica)		G IIA (Without silica)		G IIB (With silica)		
		M	SD	M	SD	M	SD	M	SD	
Surface roughness	Before	1.09 [a]	0.12	1.28 [b]	0.13	0.52 [c]	0.178	0.78 [d]	0.11	<0.0001**
	After	1.32 [a]	0.22	1.53 [b]	0.23	0.61 [c]	0.122	0.89 [d]	0.15	<0.0001**
	P value	0.0002**		0.0001**		0.02*		0.01*		
Contact angle	Before	90.12 [a]	1.33	100.5 [b]	1.78	60.59 [c]	0.52	94.92 [d]	1.1	<0.0001**
	After	93.72 [a]	1.53	122.4 [b]	2.16	78.25 [c]	0.52	98.52 [d]	1.75	<0.0001**
	P value	< 0.0001 **		< 0.0001**		< 0.0001**		< 0.0001*		

M: mean ***SD: standard deviation*** **** Significant difference as P < 0.05.***

Means with the same superscript letters were insignificantly different as P >0.05

Means with different superscript letters were significantly different as P< 0.05

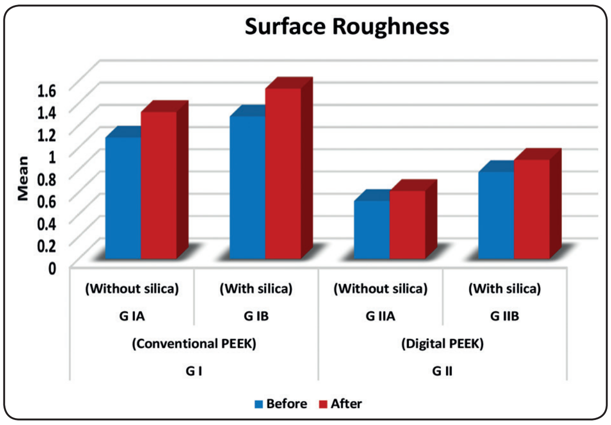

Fig. (1): Bar chart representing surface roughness of all groups before & after finishing & polishing.

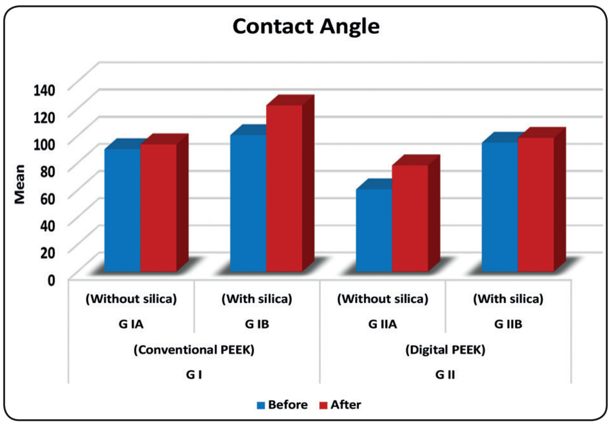

Fig. (2): Bar chart representing contact angle of all groups before & after finishing & polishing.

DISCUSSION

In this study, evaluation of mechanical properties was done for different structures of removable partial denture, where, Group I was constructed conventionally (injection) with pure PEEK, the other one with PEEK incorporated with nanoparticles (Sio2), and group II was constructed digitally (using CAD/CAM milling system).

the CAD /CAM digital system was improved the dental laboratory procedures by saving them time and effort by reducing the number of casts as diagnostic cast, master cast, modified master cast then refractory cast that performed routinely during casting of the framework. Besides that, all laboratory procedures can be standardized by computerized technology which would minimize the human variations during the fabrication of any prosthesis. [18-21]

Furthermore, The conventional (press method) construction steps require extensive human interference and materials manipulation that may additionally offer processing shrinkage and/or expansion. This may lead to increased processing errors and inaccuracies which may explain the increase of surface roughness as it also needs more and more mechanical finishing when compared to the CAD/CAM system.[22]

Many studies mentioned that the CAD/CAM fabricated materials show a reduced risk of porosities and therefore higher and more solid mechanical and physical properties. Also, many studies stated that modified PEEK with the addition of nanoparticles silica exhibits perfect desirable mechanical properties needed for partial denture frameworks such as its lightweight for improved patient comfort, improve hardness, and metal-free (no metal taste) although that may increase the surface roughness of the finished prosthesis.[23-27]

In addition, there is no definite study that shows differences in mechanical and physical properties of either milled or pressed frameworks. In this study, it was clear that the CAD/CAM method of fabrication is the better way than the conventional pressed as there was a statistically significant increase in surface roughness of the prosthesis was conventionally fabricated than those constructed with CAD/CAM system

Several studies were reported that the increase in contact angle value can be compared with the increase in surface roughness of the PEEK surface. And In case of PEEK loaded with hydrophobic nano-SiO_2, the addition of 10 wt% of the hydrophobic nano-SiO_2 increases the contact angle value by 30% compared to the pure PEEK that was coincide with this study results as the contact angle increase with increasing the surface roughness. [28-31]

Also, It has been revealed that the contact angle increases with the increase in the roughness of the surface .and it has been observed that contact angle increases with an increase in hydrophilic nano-SiO2 content in the nanocomposites. These results show that the addition of the nano-SiO2 particles can alter the hydrophobic character of the pure PEEK matrix, and the contact angle can be changed markedly via changing the content of the additive. [32-33]

CONCLUSION:

Based on the findings of this in vitro study, the following conclusions were drawn:

1. The surface roughness and hence the contact angle of pure peek framework constructed conventionally, were statistically higher than that constructed digitally.
2. Adding of sio2 nanoparticles to peek, showing an increase in the surface roughness.
3. Polishing increased the surface roughness values of a PEEK.
4. Regardless of the state of the surface being polished or not, all roughness values before and after polishing were above the clinical acceptability threshold.

REFERENCES

1. Fitton JS, Davis EH, Hoelett JA, Pearson GJ: A method of improving the bonding between artificial teeth and PMM. J Dent. 1994;13:102-108.
2. Ferracane JL.: Hygroscopic and hydrolytic effects in dental polymer networks.Dent Mater. 2006;22:211-22
3. Maji P, Choudhary RB, Majhi M. :Structural, optical and dielectric properties of ZrO2 reinforced polymeric nanocomposite films of polymethylmethacrylate (PMMA). Optik. 2016;127(11):4848-53.
4. Komagamine Y, Kanazawa M, Sasaki Y, Sato Y, Minakuchi S.: Prognoses of new complete dentures from the patient's denture assessment of existing dentures. Clinical oral investigations. 2017;21(5):1495-501
5. Ramakrishna S, Mayer J, Wintermantel E, Leong KW.: Biomedical applications of polymer-composite materials: a review. Compos Sci Technol. 2001;61(9):1189–122.
6. Ergun G, Sahin Z, Ataol AS.: The effects of adding various ratios of zirconium oxide nanoparticles to poly (methyl methacrylate) on physical and mechanical properties. Journal of oral science. 2018;60(2):304-15.
7. Bangera MK, Kotian R, Ravishankar N.: Effect of titanium dioxide nanoparticle reinforcement on flexural strength of denture base resin: A systematic review and meta-analysis. Japanese Dental Science Review. 2020;56(1):68-76.
8. Fischer, N.G.; Münchow, E.A.; Tamerler, C.; Bottino, M.C.; Aparicio, C.: Harnessing biomolecules for bioinspired dental biomaterials. J. Mater. Chem. B .2020; (8) 8713–874.
9. Komabayashi, T.; Colmenar, D.; Cvach, N.; Bhat, A.; Primus, C.; Imai, Y.: Comprehensive review of current endodontic sealers. Dent. Mater. J. 2020 ;39:703–720.
10. Gad MM, Abualsaud R, Al-Thobity AM, et al.: Effect of SiO2 nanoparticles addition on the flexural strength of repaired acrylic denture base. Eur J Dent 2020;14(1):19–23.
11. Abushowmi TH, AlZaher ZA, Almaskin DF, et al.: Comparative effect of glass fiber and nano-filler addition on denture repair strength. J Prosthodont 2020;29(3):261–268 .
12. Basgul, C.; Yu, T.; MacDonald, D.W.; Siskey, R.; Marcolongo, M.; Kurtz, S.M.: Structure-property relationships for 3D-printed PEEK intervertebral lumbar cages produced using fused filament fabrication. J. Mater. Res. 2018, (33):2040–2051.
13. Wang, Y.; Shen, J.; Yan, M.; Tian, X.: Polyether ether ketone and its composite powder prepared by thermally induced phase separation for high-temperature selective laser sintering. Mater. Des. 2021;(201) :109510.
14. Akhtar, F.H.; Abdulhamid, M.A.; Vovusha, H.; Ng, K.C.; Schwingenschlögl, U.; Szekely, G.:Defining sulfonation limits of poly (ether-ether-ketone) for energy-efficient dehumidification. J. Mater. Chem. 2021; (9):17740–17748.
15. Gashti, M.P.; Moradian, S.; Rashidi, A.; Yazdanshenas, M.-E.: Dispersibility of hydrophilic and hydrophobic nano-silica particles in polyethylene terephthalate films: Evaluation of morphology and thermal properties. Polym. Polym. Compos. 2015, 23, 285–296.

16. Parvinzadeh, M.; Moradian, S.; Rashidi, A.; Yazdanshenas, M.E.: Surface characterization of polyethylene terephthalate/silica nanocomposites. Appl. Surf. Sci. 2010, 256, 2792–2802.

17. Schmidlin, P.R.; Stawarczyk, B.; Wieland, M.; Attin, T.; Hämmerle, C.H.; Fischer, J.: Effect of different surface pre-treatments and luting materials on shear bond strength to PEEK. Dent. Mater. 2010, 26, 553–559.

18. Emad A, Din E, El A.: Assessment of CAD-CAM zirconium Framework Restoring Kennedy Class I Removable Partial Denture. 2013;(2008).

19. Bilgin MS, Erdem A, Dilber E, Ersoy I.: Comparison of fracture resistance between cast, CAD/CAM milling, and direct metal laser sintering metal post systems. J Prosthodont Res. 2016;60(1):23-28.

20. Yang L, Cheng X, Dai N, Zhu S, Yan G, Gao Y.: Computer-aided design and manufacture of the removable partial denture framework. Sheng Wu Yi Xue Gong Cheng Xue Za Zhi. 2010;27(1):170-3.

21. Harb IE, Abdel-Khalek EA, Hegazy SA.: CAD/CAM Constructed Poly(etheretherketone) (PEEK) Framework of Kennedy Class I Removable Partial Denture: A Clinical Report. J Prosthodont. 2019 Feb;28(2):e595-e598.

22. Papathanasiou, I., Kamposiora, P., Papavasiliou, G. et al. : The use of PEEK in digital prosthodontics: A narrative review. BMC Oral Health .2020;20, 217 .

23. Heimer S, Schmidlin PR, Roos M, Stawarczyk B.: Surface properties of polyetheretherketone after different laboratory and chairside polishing protocols. J Prosthet Dent 2017;117:419-25.

24. Mei L, Busscher HJ, van der Mei HC, Ren Y.: Influence of surface roughness on streptococcal adhesion forces to composite resins. Dent Mater 2011;27: 770-8.

25. Quirynen M, Marechal M, Busscher HJ, Weerkamp AH, Darius PL, van Steenberghe D.: The influence of surface free energy and surface roughness on early plaque formation. An in vivo study in man. J Clin Periodontol 1990;17:138-44.

26. Kawai K, Urano M, Ebisu S.: Effect of surface roughness of porcelain on adhesion of bacteria and their synthesizing glucans. J Prosthet Dent 2000;83: 664-7.

27. Alp G, Johnston WM, Yilmaz B.: Optical properties and surface roughness of prepolymerized poly(methyl methacrylate) denture base materials. J Prosthet Dent 2019;121:347-52.

28. Mekuria, T.D.; Chunhong, Z.; Yingnan, L.; Fouad, D.E.D.; Lv, K.; Yang, M.; Zhou, Y.: Surface modification of nano-silica by diisocyanates and their application in polyimide matrix for enhanced mechanical, thermal and water proof properties. Mater. Chem. Phys. 2019;(225) 358–364.

29. Bose, S.; Robertson, S.F.; Bandyopadhyay, A.: Surface modification of biomaterials and biomedical devices using additive manufacturing. Acta Biomater. 2018;(66) 6–22.

30. Tian, Q.; Zhang, C.; Tang, Y.; Liu, Y.; Niu, L.; Ding, T.; Li, X.; Zhang, Z.: Preparation of hexamethyl disilazane-surface functionalized nano-silica by controlling surface chemistry and its "agglomeration-collapse" behavior in solution polymerized styrene butadiene rubber/butadiene rubber composites. Compos. Sci. Technol. 2021; 201, 108482.

31. Monich, P.R.; Berti, F.V.; Porto, L.M.; Henriques, B.; de Oliveira, A.P.N.; Fredel, M.C. Souza, J.C.: Physicochemical and biological assessment of PEEK composites embedding natural amorphous silica fibers for biomedical applications. Mater. Sci. Eng. C; 2017 (79)354–362.

32. Hedayati, M.; Salehi, M.; Bagheri, R.; Panjepour, M.; Maghzian, A.: Ball milling preparation and characterization of poly (ether ether ketone)/surface modified silica nanocomposite. Powder Technol. 2011;(207): 296–303.

33. Basgul, C.; Yu, T.; MacDonald, D.W.; Siskey, R.; Marcolongo, M.; Kurtz, S.M.: Structure-property relationships for 3D-printed PEEK intervertebral lumbar cages produced using fused filament fabrication. J. Mater. Res. 2018;(33): 2040–2051.