

ORIGINAL ARTICLE

SILORANE INCORPORATED WITH HYDROXYAPATITE AND FLUOROAPATITE –TO INVENT A NEW BIOACTIVE RESTORATIVE MATERIAL

Shoaib Khan¹, Madiha Pirvani², Saad Bin Irfan³, Saima Akram⁴, Mariam Qidwai⁵, Mohammad Asif Nathani⁵

¹Department of Science of Dental Materials, Ziauddin College of Dentistry, ²Department of Science of Dental Materials, Dow International Dental College, Dow University of Health Science, ³Department of Operative Dentistry, Ziauddin College of Dentistry, ⁴Department of Oral Pathology, Ziauddin College of Dentistry, ⁵Department of Science of Dental Materials, Altamash Institute of Dental Medicine, Karachi, Pakistan.

ABSTRACT

Background: There were a number of restorative materials, which were fulfilling the requirements of a dental restorative material partially or somewhat completely with some limitations. 3M ESPE recently introduced a new dental restorative material, Filtek™ Silorane, which was claimed to fulfil the main objective completely, which was even confirmed by the recent studies. In order to make the best available dental restorative material an ideal restorative material it has to be bioactive. This study has been planned for the invention of a Silorane based bioactive material. It was proposed to incorporate the known bioactive materials (Hydroxyapatite and Fluoroapatite) in Silorane and analyze its chemical characterization. The main objective of a restorative dental material is to restore the function and aesthetics of the dental patient.

Methods: Hydroxyapatite and Fluoroapatite were synthesized and incorporated in Silorane by 5, 10, 40, 50 and 60% weight ratio. The resultant samples were chemically analyzed by FTIR and Raman Spectroscopy.

Results: The incorporation of synthesized Hydroxyapatite and Fluoroapatite into Silorane resulted in the innovation of a new bioactive restorative material. The resultant FTIR and Raman spectra shows that the Silorane incorporated by 40, 50 and 60% hydroxyapatite and fluoroapatite were altering the chemical structure of Silorane while spectrum of the samples with 5 and 10% of hydroxyapatite and fluoroapatite shows the apatites presence without changing the chemical structure of Silorane.

Conclusion: A novel bioactive restorative material was invented by the incorporation of synthesized nano-Hydroxyapatite and Fluoroapatite into Filtek™ Silorane. The chemical characterization showed that bond was formed between the apatites and siloxane functional groups which results in the best available dental restorative material.

Keywords: Silorane; Hydroxyapatite; Fluoroapatite; FTIR Spectroscopy; Raman Spectroscopy.

Corresponding Author:

Dr. Shoaib Khan

Ziauddin University, College of Dentistry
4/B Shahrah-e-Ghalib, Clifton, Karachi, Pakistan.
Email: shoaib.khan@zu.edu.pk
doi.org/10.36283/PJMD8-4/005

INTRODUCTION

Silorane is named after the functional groups present in the material, Oxirane and Siloxane, has been introduced to the dentistry recently. Siloxane is a recognised hydrophobic material, which enhances the long-term intra oral physical strength of the material. Oxirane based resin also known as epoxy based monomer contain an oxygen ring molecule¹. The polymerisation shrinkage of Oxiranes, which polymerises by a cationic ring opening

mechanism, is low when compared with Methacrylates, which polymerises via a free radical mechanism. Several studies proved that Silorane have less than 1% polymerization shrinkage which is also claimed by the manufacturer. In order to sum up, except being a bioactive material, it fulfils all the properties of being an ideal restorative material²⁻⁶.

Despite manufacturer's claim and previous studies, which shows, that Silorane have better marginal seal than composites^{7,8} some studies also claim that

dental composites have better marginal seal than Silorane⁹. Therefore, to invent a bioactive Silorane based material, it is proposed to incorporate the hydroxyapatite and fluoroapatite in Silorane and to perform chemical characterization. Well-known bioactive materials with excellent biocompatibility are Hydroxyapatite (HA) and Fluoroapatite (FA), which contain apatites, which is similar to the apatites found in human teeth and bones in crystal structures¹⁰. To prevent the micro-leakage and other related disadvantages result due to the polymerization shrinkage of recently used dental restorative materials, incorporation of HA and FA have been done in several dental restorative materials to obtain the required bioactivity and bonding properties at the tissue-material interface. Hydroxyapatite and fluoroapatite are certified osteoconductive material, which binds to enamel and dentine chemically.

The unique property of a bioactive material is the formation of the apatite interfacial layer. It is impossible for a material to fulfil the desired chemical and mechanical properties, for dental applications. Therefore, the focus of biomaterial scientists is to develop a restorative material with desirable properties¹¹⁻¹⁷. The biocompatibility and osteo-integration of dental implants is also improved by Hydroxyapatite coatings¹⁸. Mostly inert materials are being used nowadays clinically. There have been several studies to develop an ideal restorative material with similar bioactive and bonding properties as of apatites. It is believed that the mechanical and bond strength of the material will be modified by apatites present in the dental restorative material which will integrate with the dental structure, if Hydroxyapatite and Fluoroapatite is incorporated in the material^{19,20}. Enhanced mechanical properties and bond strength have been reported by incorporating hydroxyapatite and fluoroapatite in glass ionomer cement and dental composites^{11,12,17,21,22}. This study's objective was to incorporate the Silorane with Hydroxyapatite / Fluoroapatite and characterize the obtained material chemically using FTIR and Raman Spectroscopy.

METHODS

Initially it was proposed to add 40, 50 and 60% of hydroxyapatite and fluoroapatite in Silorane based dental restorative material. But large amount of hydroxyapatite and fluorapatite was observed in the resultant spectrums of Silorane. Therefore, addition of 5 and 10% of HA and FA in Silorane was suggested. The samples were then examined for chemical characterization under Fourier Transform Infra-Red and Raman Spectroscopy. The resultant

spectrums obtained from FTIR and Raman Spectroscopy were used to determine the results. Hydroxyapatite and Fluoroapatite were obtained by the method discussed by Rehman et al. and Khan et al^{19, 23}. Silorane FTIR and Raman Spectrum were compared with the spectrums of Khan et al²⁴. After dissolving the Silorane in tetrahydrofuran (THF), 5, 10, 40, 50 and 60% of Hydroxyapatite and Fluoroapatite was added in Silorane by weight. THF dissolved the Silorane completely; required ratios by weight of resultant hydroxyapatite and fluoroapatite particles were then incorporated in the dissolved solution of Silorane. Evaporation of THF was achieved by leaving the material overnight in the multiple Petri dishes of different concentrations of hydroxyapatite and fluoroapatite. Resultant material is then examined by FTIR and Raman Spectroscopy for chemical characterization.

RESULTS

Silorane was incorporated by Hydroxyapatite in the proportion of 5, 10, 40, 50 and 60% by weight. The figure shows FTIR spectrum of hydroxyapatite incorporated in Silorane with defined percentages. The presence of hydroxyapatite is clearly visible in the structure of Silorane (Figure 1) spectrum. Broader higher intensity CH₃ bands can also be seen in the sample. OH bands were also seen in all the samples.

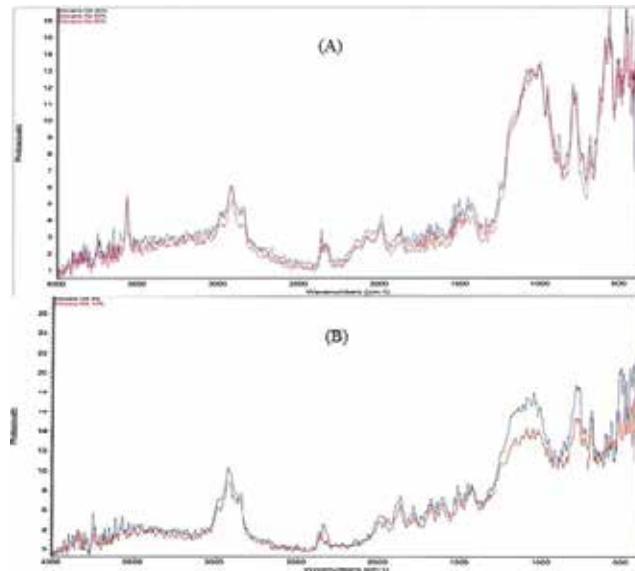


Figure 1: FTIR spectrum of Silorane incorporated with Hydroxyapatite by 5, 10, (B) 40, 50 and 60 % (A) wt. ratio.

In Figure 2 O-Si-O bands can be seen at around 1200 cm⁻¹ and a lower intensity peak of phosphate group of hydroxyapatite was observed at 963 cm⁻¹.

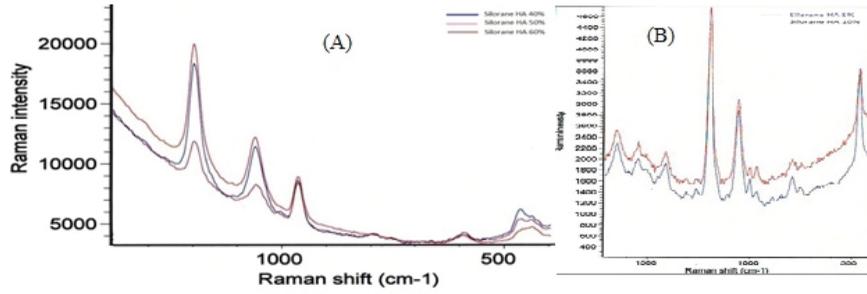


Figure 2: Raman Spectrum of Hydroxyapatite incorporated Silorane with 5, 10, (B) 40, 50 and 60% (A).

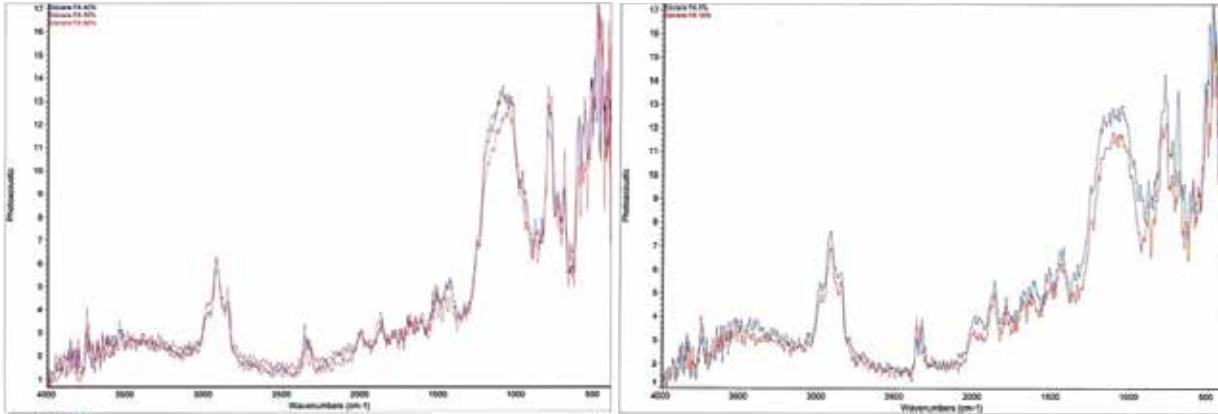


Figure 3: FTIR Spectrum of Silorane incorporated by Fluoroapatite 5, 10, (B) 40, 50 and 60% (A) by wt.

The FTIR spectrum of Silorane incorporated by Fluoroapatite with 5, 10, 40, 50 and 60% is shown in Figure 3. Hydroxyapatite OH peak was not present, but the

well-defined CH₃ peak at 2915 cm⁻¹ can be seen in the spectrum. The phosphate and O-Si-O peak can be seen in the similar zones of around 1000 – 1200 cm⁻¹.

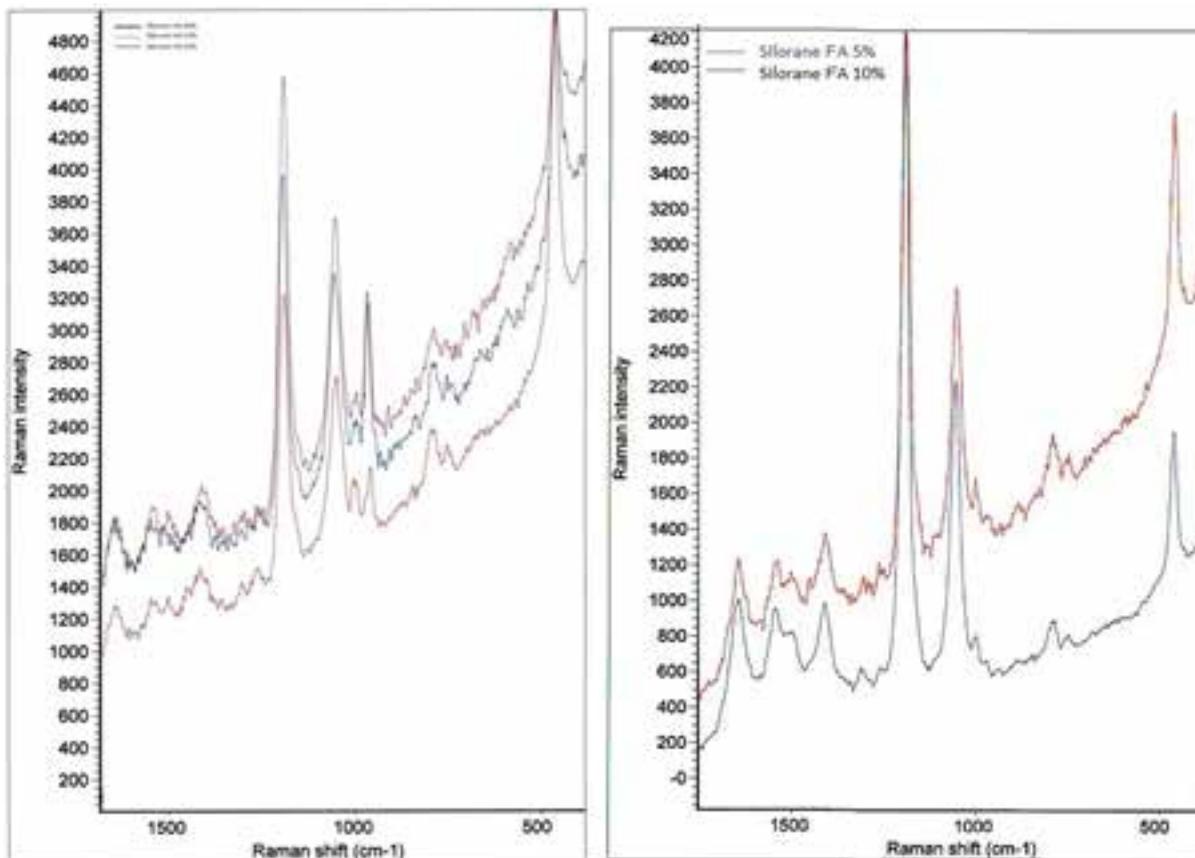


Figure 4: Raman Spectrum of Silorane incorporated with Fluoroapatite. 5, 10, (B) 40, 50 and 60% (A) by wt.

The Raman spectrum of Fluoroapatite incorporated in Silorane by 5, 10, 40, 50 and 60% by wt is shown in Figure 4. The O-Si-O stretching peaks can be seen

around 1200 and 466 cm^{-1} . Low intensity phosphate bands can be observed at the peak of 963 cm^{-1} .

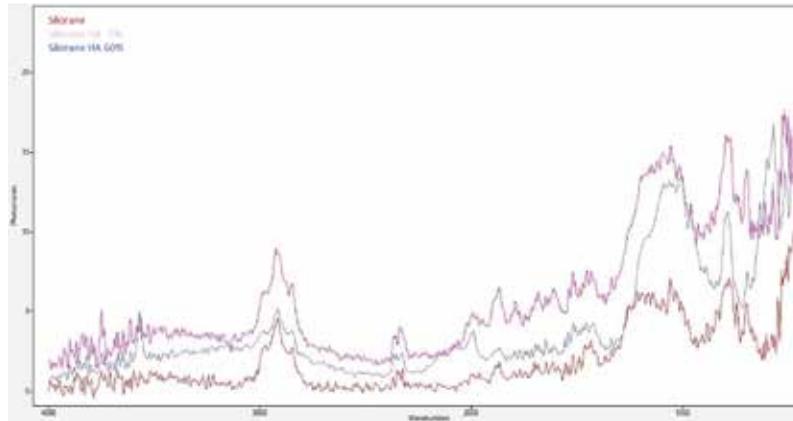


Figure 5: FTIR Spectrum of Hydroxyapatite incorporated in Silorane by 5 and 60%.

The FTIR spectrum of Silorane and Silorane added with 5 and 60% hydroxyapatite was compared. Even though the unique chemical structure of Silorane was maintained with the traces of Hydroxyapatite in the sample with 5% hydroxyapatite.

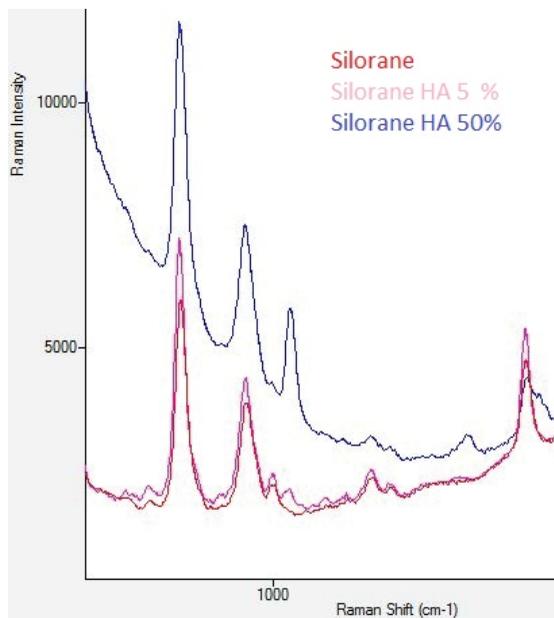


Figure 6: Raman Spectrum of Hydroxyapatite incorporated in Silorane by 5 and 50 %.

Raman Spectrum in Figure 6 also presents the same observation the chemical structure of silorane is altered by adding 40, 50 and 60% hydroxyapatite resulting in excess amount of hydroxyapatite shown in the spectrum. On the other hand, 5 and 10% of hydroxyapatite did not alter the existing structure of silorane with traces of apatite.

DISCUSSION

Dissimilar quantity of Hydroxyapatite and Fluoroapatite particles were mixed in the solution which was formed by dissolving Silorane in THF. Initially it was suggested to add 40, 50 and 60% of HA and FA in Silorane and the obtained samples were then chemically analysed by FTIR and Raman Spectroscopy. FTIR and Raman spectrum indicated increased content of hydroxyapatite and Fluoroapatite, which was altering the chemical structure of Silorane. It was, therefore, recommended to add 5 and 10% of HA and FA in Silorane. This theory can be described as commercial grade Silorane was used which is offered by the manufacturer in solid paste form and is ready to use for dental professionals, hydroxyapatite and fluoroapatite were added in 40, 50 and 60% as a filler content resulting in disturbing the filler content of supplied material Silorane. Even the FTIR and Raman Spectra displayed increased content of hydroxyapatite and fluoroapatite. For this reason a minimal quantity of HA and FA was suggested to be incorporated i.e., 5 and 10% and the resultant material is characterized chemically by FTIR and Raman Spectroscopy.

FTIR and Raman spectrum of Silorane incorporated by 40, 50 and 60% of Hydroxyapatite is displayed in Figure 1 and 2. Hydroxyapatite can be seen in both the spectrums which is incorporated in Silorane. Bands of Silorane and Phosphate group of HA were observed in the similar spectral zone as described by Khan et al²⁴. The FTIR spectrum shows clear existence of hydroxyl group. The bands in the region of 2915 cm^{-1} indicates the SiOCH_3 group but appear slightly distorted. In the region of 550 – 1200 cm^{-1} Phosphate and O-Si-O bands can be seen. The Raman spectrum shows a prominent peak of O-Si-O at around 1200 cm^{-1} and the region at 963 cm^{-1}

shows a phosphate peak^{25,26}. Similar chemical properties were seen in the Raman and FTIR spectrums of Silorane incorporated with 40, 50 and 60% hydroxyapatite, with a little variation in intensities. To invent a bioactive restorative material was the main objective of the experiment. The Silorane material should be bioactive after the incorporation of hydroxyapatite and should also be able to maintain same chemical, physical and mechanical properties.

By adding the hydroxyapatite in Silorane we increased the filler contents up to 60% which may result in increased bioactivity but may compromise the mechanical and physical properties because the filler was already present in the material. This is the reason it has been suggested to incorporate 5 and 10% hydroxyapatite in Silorane, and the resultant material is characterized by Raman and FTIR to check chemical properties. The resultant spectra show sharp peak of SiOCH_3 at 2915 cm^{-1} and incorporation of hydroxyapatite in Silorane with hydroxyl peak of low intensity. The FTIR spectrum of Silorane and Silorane added with 5 and 60% hydroxyapatite was compared in Figure 5. The spectrum noticeably displays the illustration of 60% hydroxyapatite incorporated in Silorane with indicates traces of hydroxyapatite altering the O-Si-O structure in 2915 and around $1000 - 1100 \text{ cm}^{-1}$ region.

Similar results were obtained when Fluoroapatite was incorporated in Silorane when compared with hydroxyapatite incorporated Silorane. Figure 3 and 4 displays the FTIR and Raman spectrum of fluoroapatite added in Silorane by 5, 10, 40, 50 and 60% respectively. Increase in filler content resulted in modified Chemical structure of Silorane when 40, 50 and 60% fluoroapatite was added. The spectrum of 5 and 10% of fluoroapatite did not alter the existing structure of silorane and shows traces of apatite. The concentration of fluoride in the filler matrix may increase by the addition of fluoroapatite to Silorane because the material already contained fluoride ions.

No study was available previously for the reference of this study as Silorane is introduced in the market very recently. The synthesized hydroxyapatite and fluoroapatite is then analyzed by FTIR and Raman Spectroscopy for chemical characterization. The spectrums of HA and FA were confirmed with the previous studies. Silorane was incorporated by Hydroxyapatite and fluoroapatite as a filler material, bioactive nature of a material can be increased by the addition of additional bioactive material however the physical chemical and mechanical properties of the material may be altered, particularly altering the mechanical properties. The filler content of the material was altered when Hydroxyapatite and fluoroapatite used in 40, 50 and 60% by

weight, by changing the chemical structure of the Silorane. Better results were obtained when Hydroxyapatite was incorporated in 5 and 10% instead of 40, 50 and 60%. Apatites presence was confirmed without changing the Silorane structure chemically in the samples with 5 and 10% of hydroxyapatite and fluoroapatite.

This study contributes in the invention of a novel bioactive restorative material. Silorane was incorporated by HA and FA successfully followed by chemical characterization. There is a need to perform several other experiments on Silorane incorporated by apatites to observe the physical, mechanical and biological properties of the material. As the obtained material showed some bioactivity and remaining properties were not condensed, the invention can be taken as a breakthrough in the field of restorative dentistry. And it would be an added advantage if the mechanical, physical and bonding properties improve after the incorporation of apatites.

CONCLUSION

A novel bioactive restorative material was invented by the incorporation of synthesized nano-HA and FA into Filtek™ Silorane. FTIR and Raman spectroscopic techniques were used to analyse the chemical structural which showed that bond was formed between the apatites (OH, Ca and PO) and siloxane (Si - O - Si) functional groups.

ACKNOWLEDGEMENTS

The authors would like to thank to the School of Engineering and Materials, Queen Mary University of London, United Kingdom, for all the help during the experiment. We would also like to thank Prof. Dr. Saeeda Baig for all the help in the write-up.

CONFLICT OF INTEREST

There was no conflict of interest among the authors.

AUTHORS CONTRIBUTION

This work was carried out in collaboration among all the authors.

REFERENCES

1. Maghaireh GA, Taha NA, Alzraikat H. The Silorane-based Resin Composites: A Review. *Oper Dent.* 2017;42(1):E24-e34.
2. Navarra CO, Cadenaro M, Armstrong SR, Jessop J, Antonioli F, Sergo V, et al. Degree of conversion of Filtek Silorane Adhesive System and Clearfil SE Bond within the hybrid and adhesive layer: an in situ Raman analysis. *Dent Mater.* 2009;25(9):1178-85.

3. Weinmann W, Thalacker C, Guggenberger R. Siloranes in dental composites. *Dent Mater.* 2005;21(1):68-74.
4. 3M-ESPE. Filtek Silorane - Low Shrink Posterior Restorative. 3M Health Care Limited; 2007.
5. Sharafeddin F, Moradian M, Motamedi M. Evaluation of shear bond strength of methacrylate- and silorane-based composite resin bonded to resin-modified glass-ionomer containing micro- and nano-hydroxyapatite. *J Dent (Shiraz, Iran).* 2016;17(2):142-8.
6. Koliniotou-Koumpia E, Kouros P, Dionysopoulos D, Zafiriadis L. Bonding strength of silorane-based composite to Er-YAG laser prepared dentin. *Lasers Med Sci.* 2015;30(2):509-16.
7. Joseph A, Santhosh L, Hegde J, Panchajanya S, George R. Microleakage evaluation of Silorane-based composite and methacrylate-based composite in class II box preparations using two different layering techniques: an in vitro study. *Indian J Dent Res.* 2013;24(1):148.
8. Krifka S, Federlin M, Hiller KA, Schmalz G. Microleakage of silorane- and methacrylate-based class V composite restorations. *Clin Oral Investig.* 2012;16(4):1117-24.
9. Kermanshah H, Yasini E, Hoseinifar R. Effect of cyclic loading on microleakage of silorane based composite compared with low shrinkage methacrylate-based composites. *Dent Res J.* 2016;13(3):264-71.
10. Combes C, Cazalbou S, Rey C. Apatite biominerals. *Min.* 2016;6(2):34.
11. Rehman IU, Khan AS, Ahmed Z, Edirisinghe MJ, Wong FSL. Preparation and characterization of a novel bioactive restorative composite based on covalently coupled polyurethane-nanohydroxyapatite fibres. *Acta Biomaterialia.* 2008;4(5):1275-87.
12. Lucas ME, Arita K, Nishino M. Toughness, bonding and fluoride-release properties of hydroxyapatite-added glass ionomer cement. *Biomater.* 2003;24(21):3787-94.
13. Wong LH, Tio B, Miao X. Functionally graded tricalcium phosphate/fluoroapatite composites. *Mater Sci Eng.* 2002;20(1-2):111-5.
14. Seredin PV, Goloshchapov DL, Prutskij T, Ippolitov YA. Fabrication and characterisation of composites materials similar optically and in composition to native dental tissues. *Results Phys.* 2017;7:1086-94.
15. Habibah TU, Salisbury HG. Hydroxyapatite dental material. StatPearls. Treasure Island (FL): StatPearls Publishing LLC.; 2018.
16. Dahiya MS, Tomer VK, Duhan S. Bioactive glass/-glass ceramics for dental applications. In: Asiri AM, Inamuddin, Mohammad A, editors. *Applications of nanocomposite materials in dentistry*: Woodhead Publishing; 2019. p. 1-25.
17. Mazumder S, Nayak AK, Ara TJ, Hasnain MS. Hydroxyapatite composites for dentistry. In: Asiri AM, Inamuddin, Mohammad A, editors. *Applications of nanocomposite materials in dentistry*: Woodhead Publishing; 2019. p. 123-43.
18. Nasar A. Hydroxyapatite and its coatings in dental implants. In: Asiri AM, Inamuddin, Mohammad A, editors. *Applications of nanocomposite materials in Dentistry*: Woodhead Publishing; 2019. p. 145-60.
19. Rehman I, Moshaverinia A, Ansari S, Moshaverinia M, Roohpour N, Darr JA. Effects of incorporation of hydroxyapatite and fluoroapatite nanobioceramics into conventional glass ionomer cements (GIC). *Acta Biomaterialia.* 2008;4(2):432-40.
20. Vaidya A, Pathak K. Mechanical stability of dental materials. In: Asiri AM, Inamuddin, Mohammad A, editors. *Applications of nanocomposite materials in dentistry*: Woodhead Publishing; 2019. p. 285-305.
21. Zakir M, Al Kheraif AA, Asif M, Wong FS, Rehman IU. A comparison of the mechanical properties of a modified silorane based dental composite with those of commercially available composite material. *Dent Mater.* 2013;29(4):e53-9.
22. Hamama HH. Recent advances in posterior resin composite restorations. In: Asiri AM, Inamuddin, Mohammad A, editors. *Applications of nanocomposite materials in dentistry*: Woodhead Publishing; 2019. p. 319-36.
23. Khan S, Privani M, Humayoun S, Anjum O, Akram S, Nathani MA. Synthesis of nano - Hydroxyapatite and nano – Fluoroapatite particles by Sol-Gel method. *PakJMedDent.* 2019;8(2): 40-44.
24. Khan S, Privani M, Nathani MA. Chemical Characterization of Silorane by FTIR and Raman Spectroscopy. *Pak J Med Dent.* 2015;04(03):17-9.
25. Gnyba M, Keranen M, Kozanecki M, Bogdanowicz R, Kosmowski BB, Wroczynski P. Raman investigation of sol-gel-derived hybrid polymers for optoelectronics. *Opto-Electro Rev.* 2002;10(2):137-43.
26. Navarra C. Raman Analysis of dentin-adhesion interface: University of Trieste; 2008.