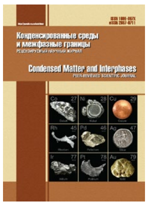

ISSN 1606-867X (Print)
ISSN 2687-0711 (Online)

Condensed Matter and Interphases
Kondensirovannye Sredy i Mezhfaznye Granitsy
https://journals.vsu.ru/kcmf/

Original articles

Research article
https://doi.org/10.17308/kcmf.2022.24/9858

Engineering of biomimetic composite dental materials based on nanocrystalline hydroxyapatite and light-curing adhesive

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Abstract

With the use of light-curing Bis-GMA (Bis-phenol-A glycidylmethacrylate) adhesive and nanocrystalline carbonate-substituted calcium hydroxyapatite (nano-cHAp), corresponding by an aggregate set of characteristics to the apatite of human enamel and dentin obtained from the biogenic source of calcium – egg’s shell of birds biomimetic Bis-GMA/nano-cHAp adhesives were synthesized.

Introduction and distribution of nano-cHAp filler in the adhesive matrix as well as its interaction with molecular groups of the latter one resulted in the change of chemical bonds that was evidenced by the data of Fourier transform infrared (FTIR) spectroscopy. In summary, for the specified nanofiller concentration increased values of Vicker hardnesses (VH) and degree of conversion were attained simultaneously while light curing of Bis-GMA/nano-cHAp adhesive.

This result would provide a considerable influence on the following application of the developed biomimetic adhesives and clinical successes of teeth restoration with the use of these composites.

Keywords: Biomimetic strategies; Nanodentology; Calcium hydroxyapatite; Adhesives

Funding: This work was supported by the grant of Russian Science Foundation, grant number 21-15-00026.

The access to scientific equipment and methodology was provided under support of the Ministry of Science and Higher Education of Russia, Agreement N 075-15-2021-1351.

Data availability*:* The data that support the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgments: The part of this research was undertaken with The Infrared Microspectroscopy (IRM) beamline at the Australian Synchrotron.

For citation: Seredin P. V., Goloshchapov D. L., AlZubaidi Asaad A. H, Kashkarov V. M., Buylov N. S., Ippolitov Yu. A., Vongsvivut J. Engineering of biomimetic composite dental materials based on nanocrystalline hydroxyapatite and light-curing adhesive. *Condensed Matter and Interphases*. 2022;24(3): 356–361. https://doi.org/10.17308/kcmf.2022.24/9858

Для цитирования: Середин П. В., Голощапов Д. Л., Альзубайди Асаад А. Х, Кашкаров В. М., Буйлов Н. С., Ипполитов Ю. А., Вонгсвивут Дж. Разработка биомиметических композитных стоматологических материалов на основе нанокристаллического гидроксиапатита и светоотверждаемого адгезива. *Конденсированные среды и межфазные границы*. 2022;24(3): 356–361. https://doi.org/10.17308/kcmf.2022.24/9858

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1. Introduction

Numerous innovations with the application of biomimetic strategies and nanotechnologies (nanodentology) provided a considerable impetus in the area of engineering of the new class related with a new class of modern adhesion restoration materials [1]. It was repeatedly shown that the enhancement of trophic, mechanical (hardness and strength), physicochemical and performance properties of adhesive polymer matrix can be attained due to the introduction of various inorganic micro- and nanofillers into its composition [2, 3]. One of the applied fillers for dental materials and bonds is calcium hydroxyapatite (HAp). High efficiency in the use of this compound is due to the similarity of its physicochemical characteristics with the inorganic component of the bone and dental tissue of a human. However, the problem of the admissible content of nanocrystalline filler in the polymer matrix of an adhesive still remains a challenge.

Therefore, the main task of our work was the determination of the proper adaptive composition and molecular properties of biomimetic adhesive based on Bis-GMA (bis-phenol -A glycidylmethacrylate), filled with nanocrystalline carbonate-substituted hydroxyapatite (nano-cHAp), providing a high degree of polymerization and mechanical hardness.

2. Methods of production and studying of the samples

To obtain the samples of biomimetic samples in our work we used bisphenol-A-glycidyl methacrylate (Bis-GMA, Polysciences, Warrington, PA, USA, code 03344)-based commercial adhesive [11,25]. Nanocrystalline carbonate-substituted calcium hydroxyapatite (nano-cHaP) corresponding to the aggregate number of features in the human enamel and dentin [4–6] was applied as a filler for light-curing Bis-GMA aadhesive. Samples of nano-cHAp were obtained using the wet chemistry method. The raw calcium hydroxide was obtained by thermal annealing from the hen's eggshells [4].

Mixing of nano-cHAp component and adhesive was performed with the use of ultrasound homogenizer QSonica Q55 (Qsonica LLC, CT, USA) for 30 s.

To solve the problems stated in the work and connected with the determination of the adaptive composition and molecular properties of biomimetic nano-filled adhesives the following samples were obtained with different content of the raw components (see Table 1).

Table 1. Composition of the synthesized biomimetic adhesives samples

Samples	Bis-GMA, ml	nano-cHAp, g
A	250	0.2
B	250	0.16
C	250	0.12
D	250	0.08
E	250	0.04
F	250	0.01

The obtained samples were investigated with the use of Fourier transform infrared (FTIR) spectroscopy technique, including the application of Synchrotron FTIR microspectroscopy at the Infrared Microspectroscopy beamline (Australian Synchrotron, Victoria, Australia). Microhardness of the synthesized biomimetic adhesive samples after their photopolymerization was determined using Vicker's technique and employing optical microscope-hardness testing instrument.

3. Results and their discussion

Measuring of microhardness in the samples of biomimetic Bis-GMA/nano-cHAp adhesives was performed by Vicker's technique.

Microhardness number (HV) in this case is determined from the following expression:

$$H_{\mu} = \frac{2P\sin(\theta/2)}{d^2}, \quad (1)$$

where P – is the applied loading, d —is the size of indentation diagonal; θ = 136° — angle at the top of the diamond square Vickers tip.

From the analysis of data in Table 1 one can see that microhardness of biomimetic Bis-GMA/nano-cHAp adhesive begins at the addition of nanocrystalline hydroxyapatite and it attains maximum at the content of ~0.16 g nano-cHAp in 250 ml of Bis-GMA adhesive. After that a decay of microhardness value is observed. Non-linear behavior of the dependence of microhardness values on nano-cHAp content is due to the changes that occur in molecular composition of the samples [7–10].

It is well known that a degree of conversion for the adhesive material can be determined with the use of FTIR data [11]. To do this it is required to determine the ratio of integral intensities for the bands related to aliphatic (C = C) bonds/aromatic (C = C) bonds before the process of polymerization and after its completion. The part of aliphatic C = C bonds can be determined from intensity of vibrations near 1637 cm^{-1}, while the part of aromatic (C = C) bonds can be determined from intensity of vibrations near 1610 cm^{-1}. Calculations were performed for 10 samples of standard Bis-GMA adhesive and each of the 10 biomimetic adhesive specimens in the samplings. After that mean values for the degree of conversion for each group of the specimens were determined and standard deviation was calculated which did not exceed 2%.

Results of the calculation show that in case of the use of original adhesive based on BisGMA the share of non-polymerized bonds is of about 22.0±1.4%, thus coinciding with the calculations presented for the adhesive on the basis of Bis-GMA/HEMA from [11]. At the same while adding nano-c-HAp the value of the degree of conversion (polymerization) starts increasing, attains its maximum at ~93%, while after that a decrease of polymerization degree (degree of conversion) is observed.

Spline-curves of microhardness and degree of polymerization for the samples in a dependence on nano-c-HAp in the composition of biomimetic adhesive are presented together in figure 1. It can be easily seen that both values representing as mechanical as molecular properties of the synthesized biomimetic adhesives are of the similar character in a dependence on the filler content. Simultaneous graphical analysis makes it possible to determine the range of the optimal compositions for bioadhesive providing maximal value of as microhardness as the value of the degree of conversion during polymerization. From the calculations it follows (see Fig. 1) that the content of nanocrystalline hydroxyapatite with characteristic morphological characteristics (20×20×50 nm) should be within the vicinity of the value ~0.125–0.135 g per 250 ml of Bis-GMA (Fig. 1).

Before our work has been performed it was shown that involvement of nanoparticles resulted in improvement of a number of mechanical properties for dental composites. Addition of the fillers (silicon nanoparticles) to the adhesion systems has an impact on the improvement

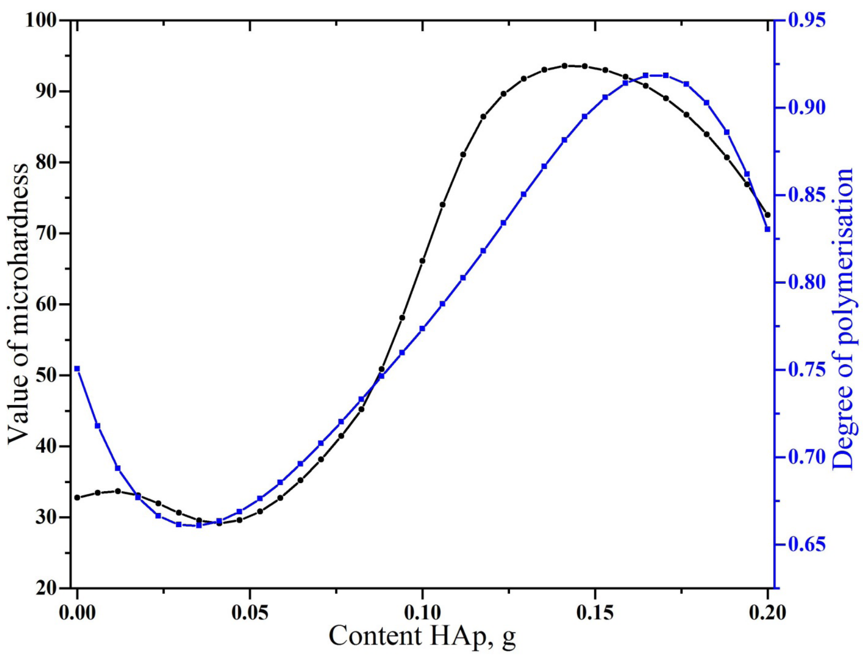

Fig. 1. Comparison of the microhardness value *H*μ (HV) and Degree of conversion for biomimetic adhesives in a dependence of nanofiller admixture

of mechanical properties and elastic modulus, improved the distribution of stresses caused by polymerization [12]. Results of modification for the adhesive systems on the basis of Bis-GMA, TEGDMA and HEMA with the use of HAp nanocrystallites from the work by Vicente Castelo Branco Leitune el al [9] correlate well with the dependence of mechanical properties of adhesive under increase of nanofiller addition observed in our research work. It was demonstrated that using HAp nanoparticles with the mean size of ~ 27 nm the enhanced values of microhardness can be attained somehow in the range of ~ 32,35 MPa. After that with an increase of HAp nanoparticles content in adhesive characteristic decay of mechanical properties was obtained. However, in our work we managed to get even greater values of microhardness (HV) with the account of increasing value of the conversion degree that considerably exceeds the value of 63.84%. The latter one was attained in the work by Vicente Castelo Branco Leitune el al for the addition of 1% HAp by mass [9].

As it follows from the obtained results (see Fig. 1) while modifying Bis-GMA with the use of nano-cHAp it is possible to attain the value of Vicker hardness exceeding dentin hardness but less than for dental enamel [13,14]. This would probably redistribute natural loads between the anatomic tissues in the efficient manner.

It was repeatedly noted that an important factor of the process is the size of nanofiller particles. The particles of large size can lead to agglomeration of the particles and degradation of mechanical properties of the interface [15]where nanoparticles (minimum size ~3 nm. However, the type of nanofiller has also a great impact on the final properties of the modified material. Unlike of the number of the previous similar investigations where HAp nanoparticles and other inorganic nanomaterials were applied for the filling of adhesion system, in our work used nanocrystals of carbonate-substituted hydroxyapatite with the mean sizes of 20×20×50 nm obtained according to our elaborated technology [4]. These nanocrystals are characteristic for the native dental tissue. Uniform distribution of nano-cHAp filler in the adhesive matrix as well the interaction with the filler molecular groups favors the changes in molecular bonds that is confirmed by FTIR data; as a result, this considerably improved mechanical characteristics of the material.

4. Conclusions

With the use of light-curing Bis-GMA (Bis-phenol-A glycidylmethacrylate) adhesive and nanocrystalline carbonate-substituted calcium hydroxyapatite (nano-cHAp), corresponding by an aggregate set of characteristics to the apatite of human enamel and dentin obtained from the biogenic source of calcium – egg's shell of birds biomimetic Bis-GMA/nano-cHAp adhesives were synthesized.

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This result would provide a considerable influence on the following application of the developed biomimetic adhesives and clinical successes of teeth restoration with the use of these composites.

Author Contributions

Seredin P. V. – conceived and designed the experiments, analysed the data, performed the experiments, contributed reagents/materials/analysis tools and wrote the manuscript. Goloshchapov D. L. – contributed reagents/materials/analysis tools, performed the experiments, analysed the data, prepared the figures and/or tables and wrote the manuscript. Ippolitov Yu. A. – contributed reagents/materials/analysis tools and wrote the manuscript. AlZubaidi Asaad. A. H., Kashkarov V. M., Buylov N. S., Ippolitov Yu. A., Vongsvivut J. – performed the experiments. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest

References

1. Zafar M. S., Amin F., Fareed M. A., Ghabbani H., Riaz S., Khurshid Z., Kumar N. Biomimetic aspects of

restorative dentistry biomaterials. *Biomimetics*. 2020;5(3): 34. https://doi.org/10.3390/biomimetics5030034

2. Alhenaki A. M., Attar E. A., Alshahrani A., Farooq I., Vohra F., Abduljabbar T. Dentin bond integrity of filled and unfilled resin adhesive enhanced with silica nanoparticles – an SEM, EDX, Micro-Raman, FTIR and micro-tensile bond strength study. *Polymers*. 2021;13(7): 1093. https://doi.org/10.3390/polym13071093

3. Timpe N., Fullriede H., Borchers L., Stiesch M., Behrens P., Menzel H. Nanoporous silica nanoparticles with spherical and anisotropic shape as fillers in dental composite materials. *BioNanoMaterials*. 2014;15(3–4): https://doi.org/10.1515/bnm-2014-0010

4. Seredin P. V., Goloshchapov D. L., Prutskij T., Ippolitov Yu. A. Fabrication and characterisation of composites materials similar optically and in composition to native dental tissues. *Results in Physics*. 2017;7: 1086–1094. https://doi.org/10.1016/j.rinp.2017.02.025

5. Goloshchapov D. L., Gushchin M. S., Kashkarov V. M., Seredin P. V., Ippolitov Y. A., Khmelevsky N. O., Aksenenko A. Yu. XPS and XANES studies of biomimetic composites based on B-type nano-hydroxyapatite. *Results in Physics*. 2018;9: 1386–1387. https://doi.org/10.1016/j.rinp.2018.04.065

6. Goloshchapov D., Buylov N., Emelyanova A., Ippolitov I., Ippolitov Y., Kashkarov V., Khudyakov Y., Nikitkov K., Seredin P. Raman and XANES spectroscopic study of the influence of coordination atomic and molecular environments in biomimetic composite materials integrated with dental tissue. *Nanomaterials*. 2021;11(11): 3099. https://doi.org/10.3390/nano11113099

7. Provenzi C., Leitune V. C., Collares F. M., Trommer R., Bergmann C. P., Samuel S. M. Interface evaluation of experimental dental adhesives with nanostructured hydroxyapatite incorporation. *Applied Adhesion Science*. 2014;2(1): 2. https://doi.org/10.1186/2196-4351-2-2

8. Lezaja M., Jokic B. M., Veljovic D. N., Miletic V. Shear bond strength to dentine of dental adhesives containing hydroxyapatite nano-fillers. *Journal of Adhesion Science and Technology*. 2016;30(24): 2678–2689. https://doi.org/10.1080/01694243.2016.1197086

9. Leitune V. C. B., Collares F. M., Trommer R. M., Andrioli D. G., Bergmann C. P., Samuel S. M. W. The addition of nanostructured hydroxyapatite to an experimental adhesive resin. *Journal of Dentistry*. 2013;41(4): 321–327. https://doi.org/10.1016/j.jdent.2013.01.001

10. Al-Hamdan R. S., Almutairi B., Kattan H. F., Alresayes S., Abduljabbar T., Vohra F. Assessment of hydroxyapatite nanospheres incorporated dentin Aadhesive. A SEM/EDX, micro-Raman, microtensile and micro-indentation study. *Coatings*. 2020;10(12): 1181. https://doi.org/10.3390/coatings10121181

11. Daood U., Swee Heng C., Neo Chiew Lian J., Fawzy A. S. In vitro analysis of riboflavin-modified, experimental, two-step etch-and-rinse dentin adhesive: Fourier transform infrared spectroscopy and micro-Raman studies. *International Journal of Oral Science*. 2015;7(2): 110–124. https://doi.org/10.1038/ijos.2014.49

12. Kasraei S., Khamverdi Z. Effect of nanofiller addition to an experimental dentin adhesive on microtensile bond strength to human dentin. *Journal of Dentistry of Tehran University of Medical Sciences*. 2009;6(2): 1–5.

13. del Pilar Gutiérrez-Salazar M., Reyes-Gasga J. Microhardness and chemical composition of human tooth. *Materials Research*. 2003;6(3): 367–373. https://doi.org/10.1590/S1516-14392003000300011

14. Aydın B., Pamir T., Baltaci A., Orman M. N., Turk T. Effect of storage solutions on microhardness of crown enamel and dentin. *European Journal of Dentistry*. 2015;09(02): 262–266. https://doi.org/10.4103/1305-7456.156848

15. Souza G. M. D. Nanoparticles in restorative materials. In: *Nanotechnology in Endodontics*. Kishen A. (ed.). Springer International Publishing; 2015. pp. 139–171. http://link.springer.com/сГАПter/10.1007/978-3-319-13575-5_8

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Received 04.04.2022; approved after reviewing 01.07.2022; accepted for publication 15.07.2022; published online 25.09.2022.

Translated by Pavel Seredin