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Modification Of Dental Materials By Silicon Nano-Sized Particles For The Purpose Of Complication Prophylaxis At The Orthopedist's.

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ABSTRACT

Production of the materials modified by nanoparticles of silver, copper, silicon, zinc, titanium, cobalt is considered to be an acute issue for prevention of complications at the dentist's, since their application as a modified additive allows improving physico-mechanical, physico-chemical and toxic-hygienic properties of dental materials. Recently, serious and focused attention has been paid to a perspective material – nano-sized silicon. Application of nano-sized silicon particles introduced into fixative dental materials leads to improvement of physico-chemical and physico-mechanical properties of crystallizing materials, whereas, low thermal conductivity of silicon may increase its working capacity and decrease heat release in the reaction of crystallization; this, in turn, will have an impact on prevention of complications after performed orthopedic procedures. Considering the fact that volume of procedures depends on these properties, it would be reasonable to reduce working time hardening to net time hardening when fixating orthopedic constructions on supporting teeth; this allows increasing the volume of manipulations with prepared mass without worsening its properties. Nano-sized silicon particles are reported to be co-catalysts of methylmethacrylate resulting in the decreased amount of residual monomer after the process of polymerization, thereby, increasing sanitary-chemical and toxic-hygienic characteristics of polymer; this fact has an impact on prevention of complications when using removable dentures.

Keywords: prophylaxis, prevention of complications, orthopedic dentistry, nano-sized particles, nano-silicon, fixating materials, polymers, scanning electron microscopy.

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TOPICALITY

Production of materials having a complex of improved or new properties beneficial for prevention of complications at the orthopedist's is reported to be one of the perspective trends in the dental material science in recent years [2,10,15]. They include novel types of dental materials, such as nano-cementum, nano-composites and nano-polymers that may be used in dentistry [11,26,37]. Development of national high-test, bio-compatible, high-technological fixating materials for fixed dental prostheses and polymers for removable dentures will undoubtedly influence prevention of complications when making prosthetic appliances for teeth and increase a quality of orthopedic care and patients' life [3,14,23,30].

Nano-structural materials are known to be extremely perspective, since application of nano-additives allow simultaneously improving such material properties as thermostability, impact resistance, chemical stability, reduction of permeability, solubility, surface porosity – and all this is achieved without increasing weight and density of the material [1,5,13,38,39]. Prevention of toxic and allergic stomatitis when applying removable dentures may be achieved only in complete bio-compatibility and increase of biodegradation properties of polymers [4,12,16,22].

Recently, serious and focused attention has been paid to a perspective material – nano-sized silicon [17,20,27,36]. Nano-sized silicon particles introduced into fixating dental materials lead to improvement of physico-chemical, physico-mechanical properties of crystallizing materials, whereas, low thermal conductivity of silicon may increase its working capacity and decrease heat release in the reaction of crystallization [6,18,29,31]. These properties exactly influence prevention of complications when fixing permanent dentures [4,7,28,32]. Development of high-test, bio-compatible, high-technological nano-composites is considered to be an acute issue of prevention of complications when making removable dentures [8,19,24,33]. Modification of acrylic polymer by nano-sized silicon particles gives an opportunity to improve such physico-mechanical properties as impact resilience, fracture strengths, temperature resistance, barrier improvement factors, and reduce the shrinkage of polymer at the polymerization stage [9,20,21,35]. Nano-sized silicon particles are reported to be co-catalysts of methylmethacrylate resulting in the decreased amount of residual monomer after the process of polymerization, thereby, increasing sanitary-chemical and toxic-hygienic characteristics of polymer; this fact has an impact on prevention of complications when using removable dentures [25,34].

Aim of study

The aim of study is to prevent orthopedic complications when making fixed and removable dentures by modifying dental materials with nano-sized silicon particles.

MATERIALS AND METHODS

To solve defined problems basic and clinical aspects of certain dental materials were modified, compared and studied. These materials included zinc-phosphate cement "Viscin" produced by "Raduga-R" (Voronezh, Russia), glass-ionomer materials «Fuji» (Japan), "Celitlonomer-FH" produced by "Celit" (Voronezh, Russia), polymers based on methylmethacrylate "Ftorax" (Ukraine), an acrylic polymer produced by "Raduga-R" (Voronezh, Russia), "Acry-free" (Israel) with standard formula. Porous silicon was used in this study as a modifying additive. It is a red-brown powder consisting of silicon microgranules sized 1-5 μm penetrated by nano-pores with diameter 1-10 nm (Figure 1).

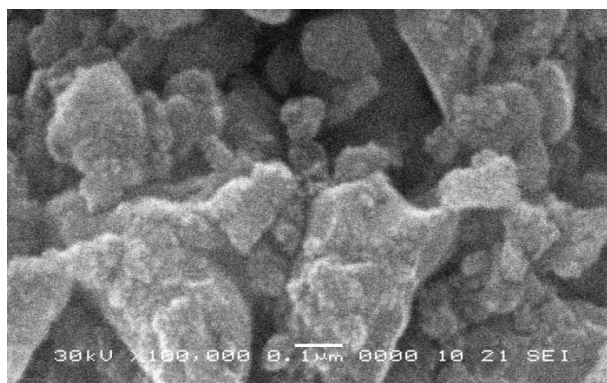


Figure 1: Scanning electron microscopy of nano-sized silicon particles JEOLJSM 6380 LV (X 100 000). Nano-sized silicon particles, sized 10-50 nm. Particles are in the void volume.

Nano-sized silicon particles were received by electrochemical etching of crystallized silicon followed by its ultrasound processing, by electrochemical etching of crystallized silicon in the solution on the basis of hydrofluoric acid (Figure 2). Scanning electron microscopy of the powder revealed particles of various shapes; this correlated with nano-sized silicon particles sized 10-50 nm. Particles were in the void volume.

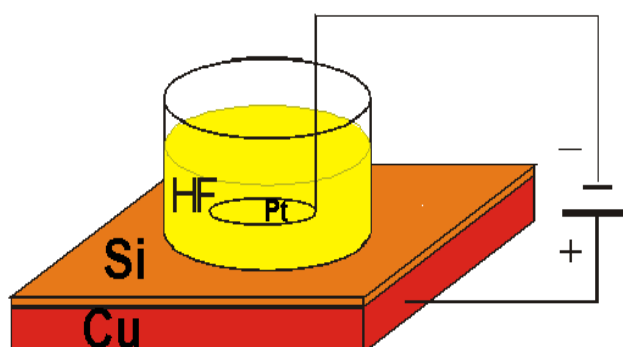


Figure 2: Synthesis parameters: electrolyte – HF + C₂H₅OH+H₂O, current density 80 mA/cm², time of etching – 40 min, monocrystallized plate p-type, resistance – 12 Ohm x cm, orientation (100).

To reduce size of particles a zinc-phosphate metal powder was additionally grounded in a ball drum, with further riddling via electric sieves with a cell size 25 μ m. At the final stage of the production nano-silicon was added to the ready powder using a vibroscreen (in the proportion 0.005%-1% to the powder weight).

Acrylic polymer was modified by nano-sized silicon particles that were added to a monomer using an electric mixer in the proportion 0.01%-0.3% to the powder weight. Nano-silicon was weighed using an analytical balance with an error of measurement equal 0.00001 g.

Physico-chemical parameters of changes that occurred after modification of the investigated materials by nano-sized silicon particles were studied using infra-red spectroscopy, an infra-red FT spectrometer "Vertex" produced by "Bruker" company, at the Department of Solid State and Nano-Structure Physics and the Department of Optics and Spectroscopy of the Voronezh State University. Scanning electron microscopy, i.e. a scanning electron microscope JEOLJSM 6380 LV, was used to assess chipping surface of standard and modified samples of investigated materials and to study their qualitative volumetric-spatial characteristics.

A tooth cut with a whole piece cap fixed on the modified fixating material was also studied. Electron microprobe analysis was used to qualitatively specify macro- and microcomponents in the investigated modified fixating dental materials of complex chemical composition. To assess planar distribution of several

chemical elements simultaneously relevant X-ray images were done in various colors and superimposed on each other – radiologic mapping was performed.

Physico-mechanical parameters of fixating materials and polymers were studied in accordance with common standards to dental cements on the basis of OOO “Celit” and OOO “Raduga-R” (Voronezh, Russia). The following parameters were specified for fixating dental materials: compressive strength, hardening time of materials, thickness of the formed film of fixating material, adhesive ability towards tooth dentine and solubility of the materials in fluids. The following parameters were specified for samples of the investigated polymers on the basis of methylmethacrylate: disruptive strength, bending strength, fracture resistance, water absorption and acid resistance.

AUTHORS’ RESEARCH RESULTS

Changes arising during the reaction of crystallization in the modification of fixating materials by silicon nano-particles were registered during the infra-red FT spectroscopy process. The most changes were observed in the proportion 0.06%-0.3% of the modifying additive to the weight of “Viscin” powder.

The graph demonstrated a peak in the area of wavenumbers in the range of 590 to 630 cm^{-1} ; that correlated with the formation of silico-phosphate gel (Figure 3). The graph of modified glass-ionomer material demonstrated a peak in the area of wavenumbers ranged from 1020 to 1150 cm^{-1} ; that correlated with the formation of silico-gel (Figure 4).

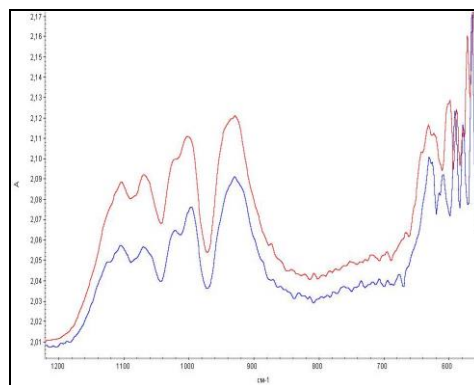


Figure 3: Spectrogram analysis of the investigated samples: red – initial material “Viscin”; blue – modified nSi “Viscin”. The graph demonstrated a peak in the area of wavenumbers in the range of 590 to 630 cm^{-1} ; this correlated with the formation of silico-phosphate gel.

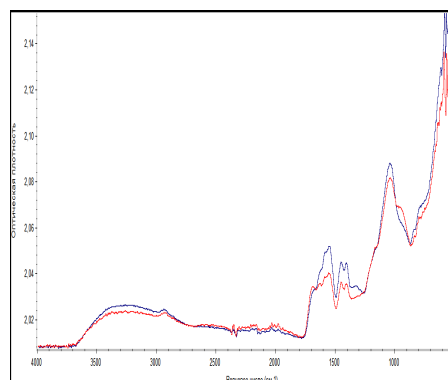


Figure 4: Spectrogram analysis of the investigated samples: blue – modified nSi “Celitlonomer-FH”, red - “Celitlonomer-FH”. The graph of modified glass-ionomer material demonstrated a peak in the area of wavenumbers ranged from 1020 to 1150 cm^{-1} ; that correlated with the formation of silico-gel.

Expressed changes were observed in the proportion 0.005%-0.01% of a modifying additive to the powder weight. The graph of an acrylic polymer modified by nano-silicon demonstrated main peaks of absorption in infra-red sample spectra in the frequency range 1723 cm^{-1} and 1141 cm^{-1} (Figure 5).

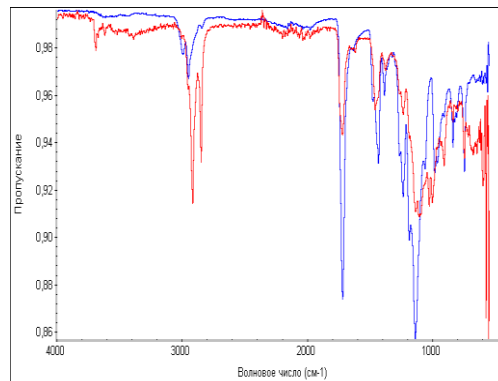


Figure 5: Spectrogram analysis of the investigated samples: red – acrylic polymer “Ftorax”, blue – acrylic polymer “Radacryl” with nSi. The graph of an acrylic polymer modified by nano-silicon demonstrated main peaks of absorption in infra-red sample spectra in the frequency range 1723 cm^{-1} and 1141 cm^{-1} .

The intensity of the main peak decreased after addition of nano-silicon. This means that nano-sized silicon particles are integrated into polymer chains and have a significant impact on polymer parameters, even despite a small amount of an additive.

Study of samples of fixating materials using a scanning optic microscope revealed improvement of structuring nature of modified materials in the hardening state, which manifested in smoother surface relief pattern, regular “gel-formation” and sharply-defined borders (Figure 6).

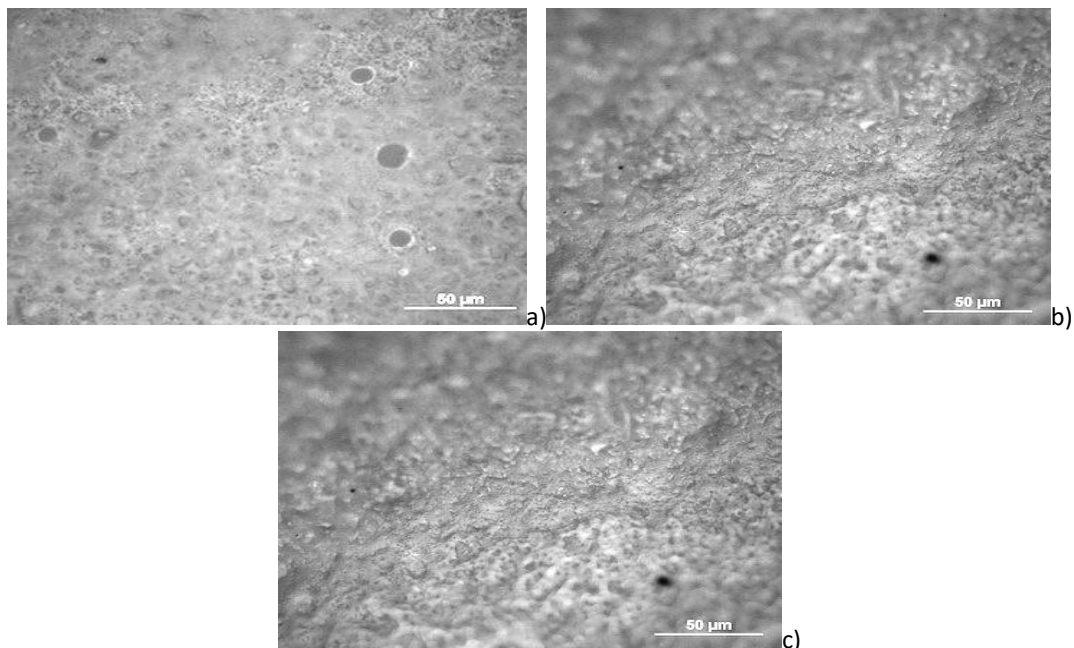


Figure 6: Optic microscopy (x 50000) a - “Celitlonomer-FH”, b – “Fuji”, c – modified “Celitlonomer-FH”. Study of samples of fixating materials using a scanning optic microscope revealed improvement of structuring nature of modified materials in the hardening state, which manifested in smoother surface relief pattern, regular “gel-formation” and sharply-defined borders.

When investigating samples of acrylic polymers, it was revealed that maximal changes of chipping surface of materials were registered in the addition of nano-sized silicon particles in the proportion of 0.01% -

0.05% to the powder weight (Figure 7). Moreover, this resulted in improvement of structuring nature of samples in polymerized state manifesting in smoother chipping surface relief pattern. Using scanning electron microscopy authors took pictures in the mode of secondary electron emission of tooth cross section, studied distribution of elements in the tooth cross section.

Authors performed radiologic color mapping of fixating materials modified by nano-silicon (Figure 8) and electron microprobe analysis (Figure 9). Investigation to specify nano-silicon in dentin thickness was also performed; it supported the lack of nano-silicon in the dentin (Figure 10).

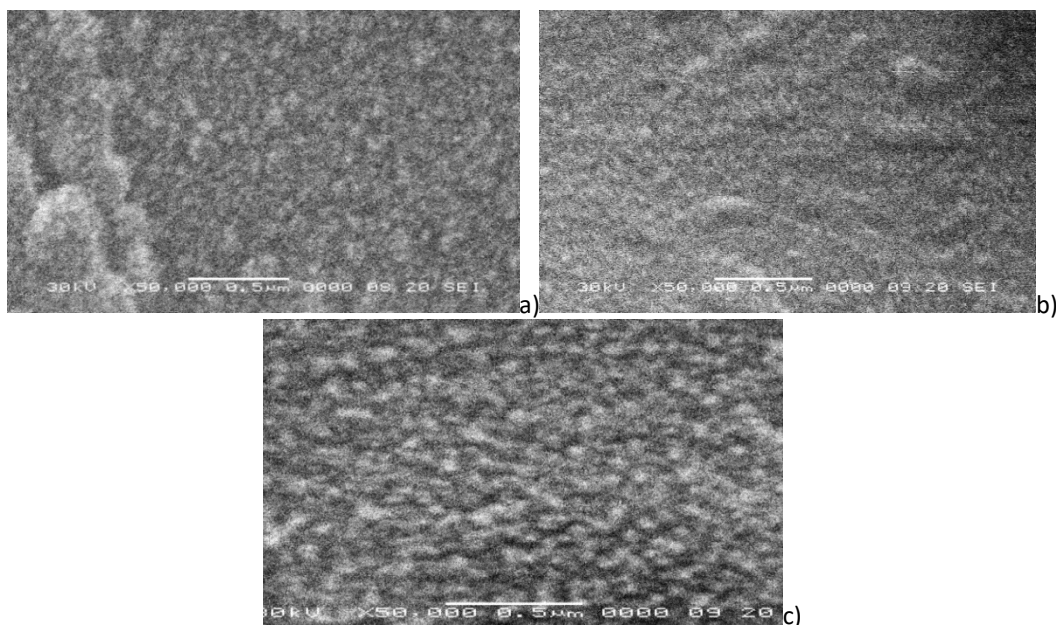


Figure 7: Scanning electron microscopy (x 50000): a) – acrylic polymer; b) – acrylic polymer modified by silicon nano-particles in the proportion 0.01% to the powder weight; c) – acrylic polymer modified by silicon nano-particles in the proportion 0.05% to the powder weight, characterized by smoother chipping surface relief pattern.

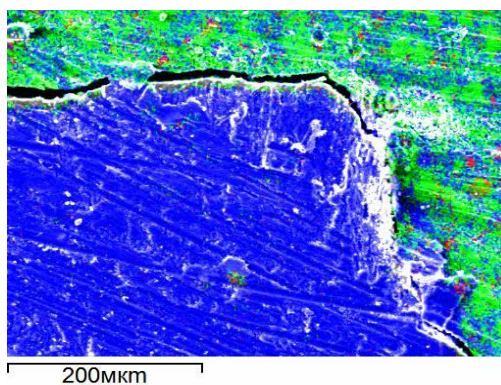


Figure 8: Radiologic color mapping of the studied zinc-phosphate cement modified by nano-silicon. JEOLJSM 6380 LV (X50 000). (Ca -blue, P -green, Si - red).

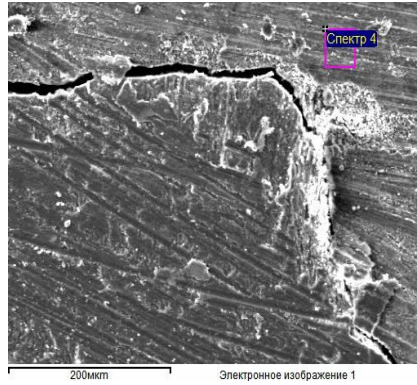
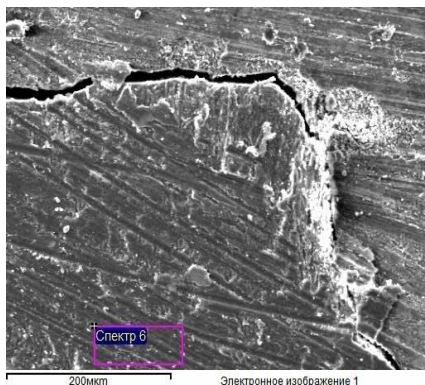


Figure 9: Electron microprobe analysis with detection of percentage of nano-silicon. JEOLJSM 6380 LV (X 50 000). Spectrum 4 – fixating material.

Microanalysis:

Element	Weighed %	Atomic%
CK	23.49	41.62
OK	29.40	38.90
MgK	0.75	2.40
SiK	0.37	0.31
PK	6.78	4.66
ZnK	34.69	11.29
BiM	1.69	0.17
Total	100.00	



Микроанализ:

Element	Weighed %	Atomic %
CK	23.58	38.14
OK	30.67	37.24
NaK	0.61	0.52
Mg K	0.12	0.10
P K	15.21	9.54
ClK	0.33	0.18
CaK	29.47	14.28
Total	100.00	

Figure 10: Electron microprobe analysis with detection of percentage of nano-silicon. JEOLJSM 6380 LV (X 50 000). Spectrum 7 – tooth dentin.

Modification of fixating materials by nano-silicon influenced changes of their physico-mechanical parameters, namely, increased strength of tooth characteristics on the borderline with fixating material. Improvement of this parameter by 15% was registered in samples of modified zinc-phosphate cement with nano-silicon content in the proportion 0.06% to the powder weight. It became possible to increase the studied parameter when modifying glass-ionomer fixating material and obtain an average compressive strength value equal to that of the widely applied imported fixating glass-ionomer material “Fuji” in the proportion of an additive 0.005% to the powder weight.

Investigation of the net time hardening demonstrated that this value in modified zinc-phosphate cement was by 35-40 sec higher than in the initial sample; and this value in modified glass-ionomer fixating materials with 0.005% content of nano-sized silicon particles was by 15-20 sec. higher; this allowed performing longer manipulations in the oral cavity. Dentine adhesion of modified samples of fixating materials increased in 2.5-3 times; this is, undoubtedly, beneficial and can increase efficiency and reliability of permanent denture

fixation. Exothermal reaction of crystallization of studied materials reduced by 3°C; this appeared to be one more positive issue regarding influence of temperature stimulus on the pulp of supporting teeth.

All polymer basic strength parameters increased when adding silicon nano-particles to acrylic polymer in the proportion 0.03%-0.05% to the powder weight. Thus, an average value of the disruptive strength limit increased by 15.6%, bend strength – by 8.5%, elasticity modulus – by 1,8%, a fracture resistance value increased by 12%. The obtained values of water absorption and acid resistance of an acrylic polymer “Radacryl” and its modifications decreased in 2.5 times in comparison with initial samples.

CONCLUSIONS

Thus, the analysis of the results obtained proves that modification of fixating materials by silicon nano-particles provide their better properties in comparison with the initial samples and increase quality of permanent denture treatment. This is especially important for prevention of complications when fixing permanent denture constructions. Study results of physico-mechanical parameters of acrylic polymers indicate that being in the oral cavity removable dentures produced from modified basic materials were less exposed to the moist environment influence expressed in the penetration of moisture with all its microorganisms and chemical compounds deep into the material; this apparently influence prevention of complications when making removable dentures. Biocompatibility of polymers nano-structured by nano-silicon has a great impact on the prevention of toxic and allergic stomatitis when making removable dentures.

REFERENCES

- [1] Abramyan A.A. Biocompatible materials. *Nanoindustriya [Nanoindustry]*, № 1, 2007, pp. 34-36. (In Russian)
- [2] Aleksandrjuk G. Comparative analysis of elastic materials for lining of removable dental prosthesis in vitro // *Ann Acad Med Stetin.* - 2002. J-Vol.48. - P. 163-78.
- [3] Buchler A. Laboratory strength of glass ionomer cement, compomers, and resin composites / A. Buchler [et al.] // *J. Prosthodont. Dent.* – 2002. –Vol. 11, № 2. – P. 86-91.
- [4] Zimin S.P. Porous silicon – a material with new properties. *Sorovskiy obrazovatel'nyy zhurnal [Soros educational journal]*, 2014, Vol. 8, № 1, pp. 101-107. (In Russian)
- [5] Chirkova N.V., Kunin A.A., Leshcheva Y.A. Nanokremniy v stomatologii [Nano-silicon in dentistry]. GBOU VPO «VGMA im.N.N. Burdenko» Minzdrava Rossii, 2013, 107 pages. (In Russian)
- [6] Chirkova N.V. The use of automatic image analyzing system in functional effectiveness investigation of general teeth-series prosthesis /N.V. Chirkova [et al.] // *Family Health in the XXI Century. Elat-Perm.* - 2008. – P. 388-391.
- [7] Ernst F. High-resolution imaging and spectrometry of materials. Springer, Berlin. - 2003. – P. 23-25.
- [8] Hoet P. Nanoparticles – known and unknown health risks, *J. Nanobiotechnology*, № 2, 2014, pp. 12-17.
- [9] Jian-Shu Kang, Cai-li Yu. Effect of Silane Modified SiO₂ Particles on Poly (MMA-HEMA) Soap-free Emulsion Polymerization. *Zhang Iranian Polymer Journal*, № 18 (12), 2009 pp. 927-935.
- [10] Gao J.C. Characteristics and properties of surface coated nano-TiO₂, *Trans Nonferrous Met Soc Chin.* - 2006. - P. 1252-1258.
- [11] Hamid J. Preparation and Properties of Triethoxyvinylsilane / J. Hamid, K. Akram, R. Ahmad // *Modified Styrene - Butyl Acrylate Emulsion Copolymers Turk J Chem* 31 (2007) , P. 257 – 269.
- [12] Hassel A.J. Correlation between self – ratings of denture function and oral health – related quality of Life in different age groups / A.J. Hassel, C. Rolko, A.C. Grossmann, B. Ohlmann, P. Rammelsberg // *Int. J. prosthodont.* - 2007. vol. 20, № 3 - P. 242.
- [13] Hoet P. Nanoparticles – known and unknown health risks, *J. Nanobiotechnology.* - № 2. – 2004. –P. 12-17.
- [14] Honda M. Correlation between the strength of glass ionomer cements and their bond strength to bovine teeth / M. Honda // *Dent. Mater. J.* – 2004. –Vol. 23, N 4 – P. 656-660.

- [15] Ikemura K. Multi-purpose bonding performance of newly synthesized phosphonic acid monomers. *Dent Mater J* 2007; 26: 105-115.
- [16] Jian-Shu Kang, Cai-li Yu. Effect of Silane Modified SiO₂ Particles on Poly(MMA-HEMA) Soap-free Emulsion Polymerization / Jian-Shu Kang, Cai-li Yu // *Zhang Iranian Polymer Journal* 18 (12), 2009. – P. 927-935.
- [17] Kheirandish S. Effect of surface polarity on wettability and friction coefficient of silicone rubber/poly (acrylic acid) hydrogel composite *Colloid Polymer Sci.* (2006) 284.
- [18] Kiyomi F. Multi-purpose, PMMA-type Adhesive Resin with Newly Synthesized Microcapsule of Radical Polymerization Initiators *Dental Materials Journal* 27(1) . - 2008. – P. 35-48.
- [19] Kunin A.A., Oleynik O.I., Korovkina A.N., Korovkin V.V. Personified prophylaxis and prevention of periodontal disease complications. *Vestnik instituta stomatologii [Journal of Institute of Dentistry]*, 2012, № 3(15), pp. 53-55. (In Russian)
- [20] Kunin A.A. Predictive research methods of enamel and dentine for initial caries detection. *The EPMA Journal*, 2013, Vol. 4, Suppl. 19
- [21] Kurtis B. Clinical examination and interleukin-1 β levels in gingival crevicular fluid in patients treated with removable partial dentures // *Int J Prosthodont.* - 2003. - Vol.16, №1. - P.59-63.
- [22] Lin BA. Isolating enzyme activities related to composite degradation. *J Dent Res.* 2004. Submitted for publication.
- [23] Li Y. P. Preparation and characterization of nano-SiO₂/acrylic resin composite latex. *Acta Polym Sin.*, 2006, pp.953-958.
- [24] Malachias M. Modified functional impression technique for complete dentures // *Braz. Dent. J* vol.16 no.2 Ribeirao Preto May/Aug. -2005. - P.231.
- [25] Massad JJ, Cagna DR. Relining extension-base removable partial dentures // *Compend Contin Educ Dent.* -2002. - Vol.23, №3. - P.24-29.
- [26] Michler G. Crazing in amorphous polymers: Formation of fibrillated crazes near the glass-transition temperature / Grellmann W, Seidler S (eds) // *Deformation and fracture behavior of polymers.* Springer, Berlin, 2003. – P. 193.
- [27] Moiseeva N.S., Ippolitov Y.A., Kunin D.A., Morozov A.N., Chirkova N.V. The use of led radiation in prevention of dental diseases. *The EPMA Journal*, 2016, Vol. 7, № S 1, pp.24.
- [28] Muhammad A., Abdul W. Synthesis and Characterization of Polymethyl methacrylate/SiO₂ Hybrid Membranes: Effect of Silica Contents on Membrane Structure *Jurnal Matematika Dan Sains*, Desember. – 2006. - Vol. 11, № 4. – P. 141-145.
- [29] Myers M.L. Comparison of luting cements for minimally retentive crown preparations/M.L. Myers [et al.] // *Quintessence Int.*–2002. –Vol. 33. – P. 95-100.
- [30] Nguyen D. New monomers for chemical vapor deposition polymerization of poly(p-xylylene). *Advances in Natural Sciences*, Vol. 7, No. 1&2. – 2006. – P. 107-119.
- [31] Oberdurster J. Nanotoxicology an emerging discipline discipline from studies of ultrafine particles, *Environmental Health Perspectives*, 2005. -v.113.P. 823-825.
- [32] Omi S. Nano/microcapsule technology. *Kogyo Zairyo* 2004; 52: 18-70.
- [33] Polyzois GL. Bonding of silicone prosthetic elastomers to three different denture resins//*Int J Prosthodont.* - 2002. - Vol.15, №6. – P. 535-538.
- [34] Ron' G.I. et al. Study of teeth chemical composition with application of electron microprobe analysis. *Problem stomatologii [Challenges of dentistry]*, № 5, 2008, pp. 13-17. (In Russian)
- [35] Rueggeberg F. Calibration of FTIR conversion analysis of contemporary dental resin composites. *Dent Mater* 2002. -P. 241–249.
- [36] Shindo D. Analytical electron microscopy for materials science. Springer, Tokyo. 2003. - P.34-36.
- [37] Tanaka K. Residual monomers (TEGDMA and Bis-GMA) of a set visible-lightcured dental composite resin when immersed in water. *J Oral Rehabil* 2005;18:353–362.
- [38] Qian XJ. Surface modification of the nano-SiO₂ with 1-octyl alcohol, *Chin J Inorg Chem.* №2. - 2004. -P. 335-338.



- [39] Zulfikar M.A. Synthesis and Characterization of Novel Porous PMMA/SiO₂ Hybrid Organic-Inorganic Membranes / M.A. Zulfikar, M.A.W. Mohammad, A.A. Khadum //Desalination, 2006. - P. 262-270.