# Influence of Initiation System and Filler Ratio on the Properties of New Flowable Dental Composites

STANCA BOBOIA[1,2*], MARIOARA MOLDOVAN[1], CRISTINA PREJMEREAN[1], CODRUTA SAROSI[1], ALEXANDRA ROMAN[2], IOAN ARDELEAN[3]

[1] „Babes Bolyai" University, "Raluca Ripan" Chemistry Research Institute, Department of Polymer Composites, 30 Fantanele Str., 400294, Cluj-Napoca, Romania

[2] University of Medicine and Pharmacy "Iuliu Haţieganu", Faculty of Dental Medicine,  Department of Dental Propaedeutics, 32 Clinicilor Str., 400006, Cluj-Napoca, Romania

[3] Tehnical University of Cluj-Napoca, Physics and Chemistry Department, 103-105 Muncii Blv.., 400641, Cluj-Napoca, Romania

*The goal of this study was to measure and analyze the water sorption and mechanical properties of 5 experimental flowable composites with different filling ratios and two types of initiation systems: self cured and light-cured. The samples were analysed, in order to observe the influence of initiation type and the amount of filler on the properties required to satisfy the conditions for dentistry use. We have determined the water sorption and mechanical properties (compressive strength, flexural strength, diametral tensile strength) according to ISO 4049/2000 and international norms "American Dental Association's Specification No.27. The measurements were done using a mechanical testing machine Lloyd Instruments-LR5k Plus. Increased water absorption weakens the bonds in the polymer matrix, causing separation of filler by the polymer matrix, filler hydrolytically degrade, leading ultimately to reducing the mechanical resistance, which represents a major step in the characterization of dental materials to be used in dentistry. Among all the mechanical stress from oral cavity, the compression and the tension are the predominant forces, during which are developing the highest forces that dental hard tissues are subject to. The results of this study highlight the relationship between the composition, initiation system of the dental materials and their properties.*

*Keywords: flowable dental composites, water sorption, compressive strength, flexural stiffness, tensile strength.*

The flowable dental composite materials have in their composition less amount of fillers or a higher proportion of diluent monomer, giving a lower viscosity to dental material, a better adaptation to the internal walls of the dental hard tissues, an easy insertion and a higher elasticity module compared to conventional composites. Compared to traditional hybrid composites, flowable composites have inferior mechanical properties, thus discouraging their use in high stress applications [1]. However, the mixtures with a lower filler content and/or with a lower elasticity showed a better marginally sealing in class V restorations, compared to mixtures with a higher content of filler [2,3], reducing the cervical gap and the marginal leakage formation. In addition, flowable composites with a relatively low elastic modulus have been used to reduce stress on the adhesion interface, generated by the occlusal forces associated with cervical lesions [4].

A particularly important feature of dental materials refers to their tendency to resist forces, that are applied during mastication, to break or deformation. This behaviour can be measured by a number of mechanical properties like: tensile strength, impact strength, hardness, compression, traction, shear, torsion, which are the key step in the characterization of a dental material to be used in dentistry. Also, the dental materials are used in an oral cavity where the materials are in continuous contact with saliva and oral fluid, which can be absorbed by the polymer matrix could cause filler–matrix debonding or even hydrolytic degradation of the fillers, and may affect composite materials by reducing their mechanical properties [5,6].

Therefore water absorption and solubility must be evaluated for a good characterization of dental materials.

The current state of dental composites fluid includes a variety of materials with a wide range of mechanical properties, handling characteristics, and esthetic possibilities. This highly competitive field continues to evolve, with major emphasis on the issue of the necessary amount of filler that does not influence the viscosity of the material and does not produce any failures on the mechanical properties of the restoration. In the present work, water absorption and solubility as well as the mechanical properties of 5 samples of dental flowable composites will be investigated. Absorption and solubility studies reflect the degradation over a period of 3 months, during which the samples were immersed in water and alcoholic solution (according to ISO 4049/2000 [7]).

**Experimental part**

The studies have been performed on samples with similar composition as commercial composites on the market, based on Bis-GMA aromatic monomer (density:1140; Viscosity at 60°C: 1300 CP; refractive index: 15100) (synthesized in Department of Polymer Composites) and TEGDMA diluted monomer (Aldrich), obtaining the matrix in which is dispersed the powdered inorganic filler. 5 types of powers with different particles sizes and different mass ratios are added to give various characteristics for our dental experimental flowable composites.

For the curing approach of the flowable composite samples we used two mechanisms distinguised as self

* email: stancabobo@yahoo.com, Tel: 0757939232

| Samples (wt %) | Organic Phase | | Inorganic Phase | | | | | Chemical Initiation System | | Photochemical Initiation System | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Bis-GMA | TEGDMA | Quartz | Glass with Sr | FAP | TCP | SiO₂ | DHEPT (% from Paste 1) | BPO (% from Paste 2) | CQ | DM AEM |
| S1a | 34 | 11 | 22 | 19 | 5.5 | 5.5 | 3 | 1 | 2 | | |
| S1b | 34 | 11 | 22 | 19 | 5.5 | 5.5 | 3 | 0.7 | 1.2 | | |
| S2a | 19 | 16 | 26 | 23 | 6.5 | 6.5 | 3 | 1 | 2 | | |
| S2b | 19 | 16 | 26 | 23 | 6.5 | 6.5 | 3 | 0.7 | 1.2 | | |
| SP | 34 | 11 | 22 | 19 | 5.5 | 5.5 | 3 | | | 0.5 | 1 |

Bis-GMA: 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy) phenyl]propane (synthesized in Department of Polymer Composites laboratory)

TEGDMA: Triethyleneglycol dimethacrylate (Aldrich).

FAP: Glass with Sr and Fluoridated hydroxylapatite (synthesized in Department of Polymer Composites)

SiO₂: Colloidal silica (Degusa)

BPO: Benzoyl peroxide (Merck),

CQ: camphorquinone (Aldrich)

DMAEM: dimethylaminomethylmetacrylate (Aldrich)

DHPET: N,N-dihydroxyethyl-p-toluidine (Aldrich).

TCP: Ca₃ (PO₄)₂: Tricalciumphosphate (synthesized in Department of Polymer Composites)

cure and light cure. The samples 1 and 2 with self cure types are two-paste systems, which require mixing thorough that the activator N,N-dihydroxyethyl-p-toluidine from paste 1 comes into contact with the initiator which is benzoyl peroxide from paste 2. These specimens were fabricated using a ratio of 1:1 paste1 to paste2, the waiting autopolymerization time beeing from 4 to 7 min.

The sample SP is a light-cure dental composite with one-paste systems, which contains a photo-initiator (camphorquinone) that is achieved using an Optilux lamp for 40 seconds. The compositions of the samples subject to our research are shown in table 1.

*Absorption and solubility*

According to ISO 4049/2000, for specimen preparation, the experimental dental composites were cured into a Teflon matrix with 15±1 mm diameter and 1 mm thickness. Eight specimens were fabricated for each subgroup. The polymerized specimens were removed from the matrix and excesses were eliminated with a sheet of sandpaper. The specimens were placed in desiccators and kept at 23°C until a constant weight is reached [8]. The samples were then immersed in labeled bottles of 25 mL distilled water (4 specimens), or 25 mL alcoholic solution (4 specimens) at a temperature of 37°C for 3 months [9]. During the first 7 days and afterwards on day 14, 28, 60 and 90, the discs were removed from the bottles, dried with absorbent paper and then weighed, using an analytical balance, then carefully placed back in their bottles. The values of water absorption (A) and solubility (S) can be calculated for each disc as follows:

$$A = \frac{m_2 - m_3}{V} \qquad S = \frac{m_1 - m_3}{V} \qquad (1)$$

Here $m_1$, $m_2$ are the masses of the specimen before and after immersion in water whereas $m_3$ represents the mass of the specimen kept in a desiccator until a constant weight is reached. V is the volume of the specimen.

*Mechanical properties*

Flowable composites are indicated not only as an intermediate layer, but also as a restorative material for minimally invasive cavities, sealing cracks or as a restorations repair composite. For these indications, specific mechanical properties are required. These properties were determined according to the method described in ANSI/ADA Specification No. 27-1993 [10] for composite materials or ISO 4049. The testing was performed on a Lloyd Instruments- LR5k Plus mechanical testing machine controlled using the Nexygen Software on a Windows PC. The behaviour of the material was assessed by measuring the flexural strength, compressive strength and diametral tensile strength. Each sample set consisted of ten specimens for each group.

*Flexural strength and elasticity modulus*

Flexural strength reflects the rigidity and the resilience of composite biomaterials to deformation or rupture due to mechanical stress, thus providing an indication of dimensional stability and restorations breaking trend. According to International Organization for Standardization (ISO) standard 4049, ten rectangular bar specimens of each material, measuring 25 mm in length, 2 mm in width and 2 mm in height, were prepared in a Teflon mould, and then cured. After polymerization, the specimens were stored in distilled water at 37°C for 24 h[11]. A three-point bending test was performed using a universal testing machine at a cross-head speed of 0.5 mm/min. The flexural strength (FS) in MPa was calculated as:

$$FS = \frac{3}{2} \frac{PL}{bd^2} \qquad (2)$$

Here P is the ultimate load at fracture (N), L is the distance of the supports (20 mm), b is the width of the specimen (mm), and d is the thickness of the specimen (mm).

The modulus of elasticity, which describes the rigidity of the material, is provided from flexural test [12]. For each dental material with different clinical situations use, the elasticity modulus demands different values. Several authors have reported a significant correlation between the modulus of elasticity and the percentage of dental materials fillers [13-15]. The elastic modulus (E, in GPa) was calculated by:

$$E = \frac{P}{db} \frac{\Delta l}{l} \frac{1}{10^3} \qquad (3)$$

where $\Delta l$ is the increase in specimen length $l$ [16].

*Compressive strength*

Compressive strength is a relative indicator of abrasion resistance, such that high values of compressive strength provide good resistance to abrasion. The resistance to abrasive assesses the substance loss due to wear over time, during chewing act and due to the friction tooth surface under the action of food, toothpaste and brushing [17]. For the compressive strength tests, the specimens were cured in cylindrical Teflon molds with diameter of 4 mm and height of 6 mm. After completing the polymerization process, the specimens of each group were stored in water at 37°C for 24 h prior to the test. The compressive strength was then determined with the universal testing machine at a cross-head speed of 1 mm/min. The compressive strength (MPa) is calculated as:

$$CS = \frac{9.81}{0.785}\frac{P}{D^2} \qquad (4)$$

Here P is the ultimate load at fracture (N), and D is specimen diameter (mm).

*Tensile strength*
In the literature [18-20] the method of tensile strength is described as a diametrical compression test, where a disc of material is compressed on the diameter until it is broken. The compressive stress applied to the sample induces a tensile stress in the load application plane, which is directly proportional to the applied compressive load. The preparation and testing approach of tensile strength is similar to that described for compressive strength, except that the cylindrical specimens used have dimensions of 0.3 cm thick and 0.6 cm diameter. The tensile strength (MPa) is calculated as:

$$TS = \frac{2P}{\pi Dd} \qquad (5)$$

Here the P is the ultimate load at fracture (N), D is the specimen diameter (mm), and d is the specimen thickness (mm).

## Results and discussions
*Absorption and solubility*
Water absorption is a diffusion controlled process that occurs in the matrix resin where water reacts with the fillers favoring its separation from the polymer matrix. The values of A and S, calculated using eq. (1), in the case of water and alcohol solution at 37°C for 3 months, are depicted in figure 1 and 2 respectively. The absorption values depend mainly on the resin constituents of the dental material composition. Resins containing hydrophilic molecules or portions of molecules have high water absorption. In this case, the based resin, Bis-GMA, is a relatively large molecule which is not very fast solved in water. Consequently, the sample S1 with a higher concentration of based volume monomer, shows a higher solubility compared to the samples where the dilution monomer proportions are higher which modifies the handling properties of the dental materials.

If we use the same type and amount of monomers, water absorption may depend on the content of the fillers. The factors that affect solubility values include the quantity, the size and the surface of the filler particles but also the coupling agents. Thus, the composites marked with *a* (larger amount of chemical initiator system) show a lower absorption than the composites marked with *b* (smaller amount of chemical initiation system). Therefore, the high value of water absorption is influenced by the high degree of conversion which depends on the type of polymerization reaction and also on the curing time. Degradation of the matrix resin depends to a large extent on the degree of conversion of the C = C, because a sufficient increase in the degree of polymerization and the density of the network, reduce the solubility and diffusion of water into the matrix. However, the specimens with more filler, had a higher water absorption than which would be expected on the basis of the resin content. This increase in the water uptake was largely due to the presence of porosity and filler particle aggregates in the microstructure of composites, although the adsorption of some water onto the filler surface has not been ruled out.

The polymeric matrix of the samples shows a greater affinity to the alcoholic solution in which they are immersed as compared with the water because in both cases the samples showed higher A and S values in alcoholic solution [21].

*Mechanical Properties*
The results were recorded with the Lloyd Instruments NEXYGEN software program, which also provides a descriptive statistics system for all tested samples from a group of 10 specimens. The specimens that were strayed over 15% from the mean value were not taken into account. If more than 4 samples were disregarded, the whole sequence was repeated.

*Flexural strength and elasticity modulus*
The results of a 3-point test are summarized in figure 3a. Analyzing the results, one can observe that the highest strength values could be attributed to the high concentrations of fillers (sample S2a). However, comparing the samples, we can also conclude that increasing the amount of basic monomer in comparison with the dilution
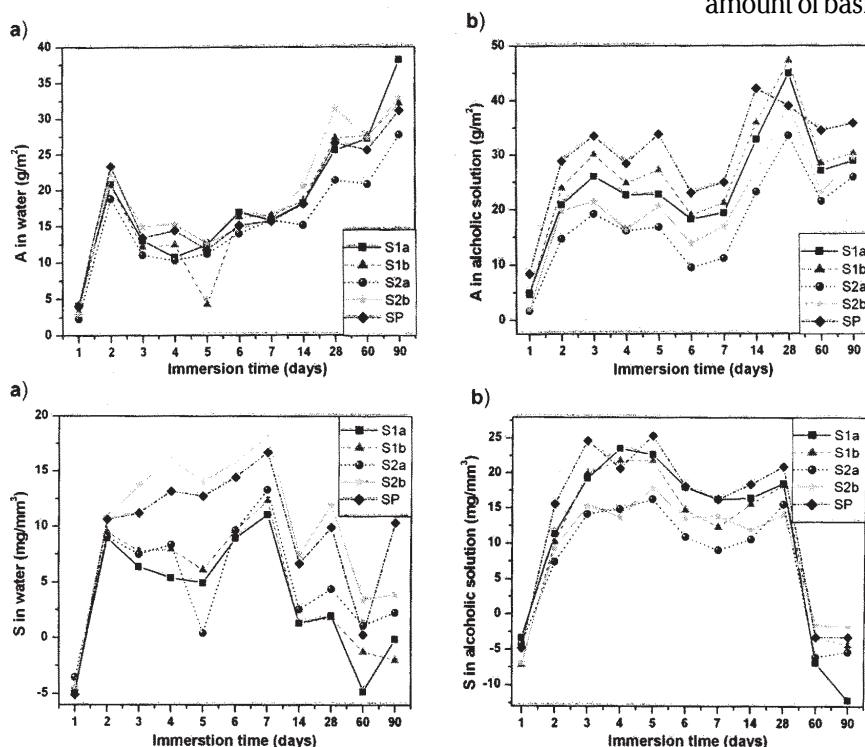


Fig.1. The values of water absorption (A) calculated according with Eq. (1) in the case of samples immersed in water (a) and alcohol solution (b) for 3 months at a temperature of 37°C



Fig.2. The values of water solubility (S) calculated according with Eq. (1) in the case of samples immersed in water (a) and alcohol solution (b) for 3 months at a temperature of 37°C
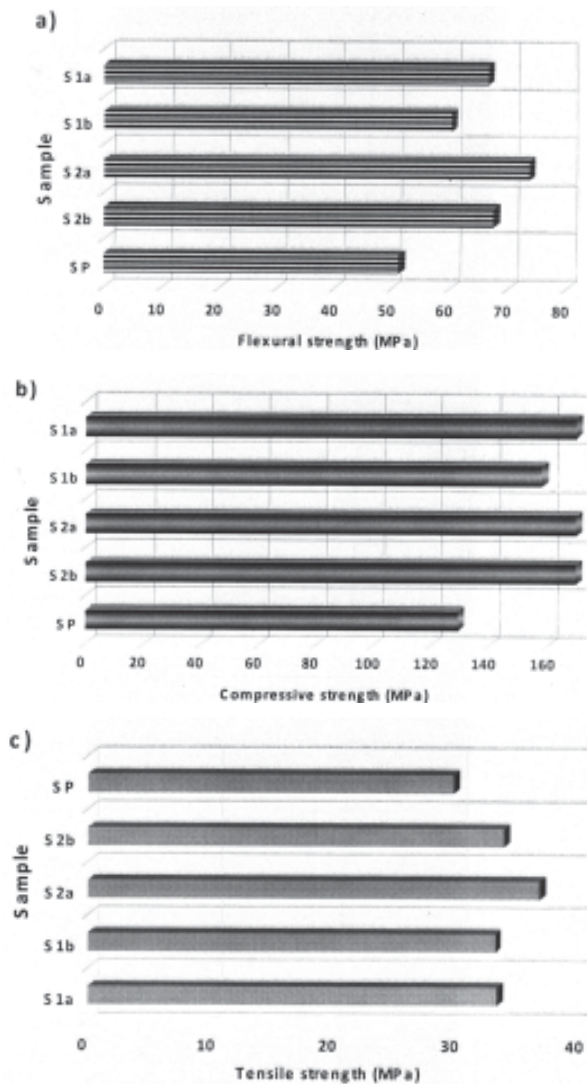
Fig.3. Mechanical properties of the investigated samples: a) Flexural strength; b) Compressive strength; c) Tensile strength

monomer leads to a greater flexural resistance [22]. Since the fracturing, as a result of flexural request, occurs along filler particles, the flexural strength reflects also the adhesion forces established in the composite/filler interface [23]. Consequently an improved interfacial bond between the filler particles and the organic phase was obtained by using a silane coupling agent.

Table 2 shows the descriptive statistics of the elastic modulus and the flexural strength for all the samples. As expected, the sample which contains the lowest filler amount has the weakest mechanical properties, including a low modulus of elasticity. The sample S2 exhibited a higher mean elastic modulus and a higher mean flexural strength compared to the S1 and SP, having the highest values among all samples. These values may be explained by the increase of dilution amount of TEGDMA monomer which is a flexibile monomer that creates a dense and flexible polymeric structure that increases the composite elastic deformation. At the same time the samples S2, with the largest amount of filler in the structure reveals higher values both for the flexural strength and the elastic modulus. Consequently, increasing the volume of the inert material present in a composite (inorganic or organic filler) may increase the mechanical properties. Note however that higher filler loading also produces a high degree of stiffness, therefore the increase in the filler volume fraction does not invariably produces a good elastic modulus.

*Compressive strength*

The values of the compressive strength composites obtained under investigation are plotted in figure 3b. The higher values of resistance to compression are recorded on sample S1a (186 MPa) and S2a (181 MPa), respectively with the difference between them of only 3%. The lower values correspond to the composition of sample SP (135 MPa). These differences, in the compressive strength between the composites investigated, is due to the size distribution, because the very small particles of powder are added between the higher particles, leading to reduction of the interstitial space between them [24]. The very small particles inserted, contribute to the reducing of compression fracture incidence.

*Tensile strength*

Table 2 and figure 3c show the results of tensile properties of the investigated samples. The best results were achieved in the composite S2a followed by S2b> S1a> S1b> SP. As can be observed the lowest resistance was recorded in composite SP. The organic phase composition, the nature and the proportion of the monomers and the polymerization system significantly influences the mechanical properties of the composite. The measurements show an improvement of the mechanical properties for the composites with a higher ratio of chemical initiation systems. The tensile strength of dental composites can be also influenced by the homogeneous distribution of the filler particles in the organic phase [25]. If there are many pores into the curing dental composite samples, the tensile strength may decrease up to 30% of the optimum value.

**Table 2**
MEAN, STANDARD DEVIATION, MINIMUM AND MAXIMUM VALUES OF
ELASTIC MODULUS (GPa) AND FLEXURAL STRENGTH (MPa)

| Material | N | Studied variable | Mean | Studied deviation | Minimum | Maximun |
|---|---|---|---|---|---|---|
| S1a | 10 | Flexural strength | 66,589 | 1,356 | 64,560 | 68,963 |
| | | Elastic modulus | 11,785 | 1,697 | 9,661 | 13,816 |
| S1b | 10 | Flexural strength | 60,225 | 2,129 | 59,725 | 63,662 |
| | | Elastic modulus | 11,345 | 2,190 | 9,174 | 11,983 |
| S2a | 10 | Flexural strength | 73,767 | 1,325 | 72,261 | 77,487 |
| | | Elastic modulus | 14,210 | 1,995 | 13,975 | 16,738 |
| S2b | 10 | Flexural strength | 67,285 | 2,184 | 64,178 | 69,504 |
| | | Elastic modulus | 14,831 | 1,309 | 13,296 | 15,074 |
| SP | 10 | Flexural strength | 52,397 | 2,2658 | 51,272 | 56,555 |
| | | Elastic modulus | 9,630 | 1,667 | 8,354 | 10,708 |

## Conclusions

Flowable composites can offer significant advantages when used as intermediate layers. They can be also used to improve the adaptation of the surface of the cavity in the areas which are difficult to reach, but for that purpose they have to fulfil several conditions concerning absorption of water and their mechanical properties. The differences in the strength of different types of dental composites are due to their size distribution. When small particles of powder are inserted between the larger particles this leads to a reduction of the interstitial spaces between them. The very small particles inserted contribute to the reducing of the fracture incidence. The measured strength values emphasize that a good mixture of composite fillers gives higher mechanical properties, hybrid fillers showing an improvement in mechanical properties.

According to the results of the present tests we have concluded that the sample containing high inorganic phase in which the ratio of based monomer composition and the dilution monomer is the largest, offers the best properties. The materials tested in this study provide a wide range of properties reflecting the fact that they can offer optimal solubility and high mechanical strength even though the fillers ratio is lower, in order to give a controlled flow, and thus, an easier clinical handling.

## References

1. BAYNE S.C., THOMPSON J.Y., SWIFT J.R.E.J., STAMATIADES P., WILKERSON M., JADA **129**, 1998, p.567
2. KEMP-SCHOLTE C.M., DAVIDSON C.L., J. Dent. Res. **67**, 1988, p.841
3. KEMP-SCHOLTE C.M., DAVIDSON C.L., J. Dent. Res., **69**, 1990, p.1240
4. HEYMANN H.O., STURDEVANT J.R., BAYNE S., WILDER A.D., SLUDER T.B., BRUNSON W.D., J. Am. Dent. Assoc. **122**, 1991, p.41
5. SATTERTHWAITE J.D., ALSHALI R., SILIKAS N., Dent. Mat. **29**, 2013, p.116
6. PAUL S.J., LEACH M., RUEGGEBERG F.A., PASHLEY D.H., J. Dent. **27**, 1999, p.209
7. **8 Dental resin-based restorative materials. International Standard Organization, ISO **4049,** 2000
8. FONG H., J. Appl. Polym. Sci. **94**, 2004, p.492
9. JACOBSEN T., SODERHOLM K.J., Dent. Mat. **11**, 1995, p.132
10. *** American Dental Association's Specification, Direct Filling Resins **27,** 1993
11. TANIMOTO Y., KITAGAWA T., AIDA M., NISHIYAMA N., Acta Biomater. **2**, no.6, 2006, p.633
12. CRAIG R.G., POWERS J.M., WATAHA J.C., Dental Materials: Properties and manipulation **8**, 2004, p.4
13. O'BRIEN W.J., Dental Materials and Their Selection, Second ed. Quintessence Publishing Co, 1997, p.86
14. MENG T.R., LATTA M.A., J. Contemp. Dent. Pract. **6**, 2004, p.93
15. MCCABE J.F., WALLS A.W.G., Applied Dental Materials, 8th Ed. Blackwell Science, Oxford, 1998, p.97
16. ANUSAVICE K.J., PHILLIPS R.W., Phillips' Science of Dental Materials, 11th ed. St. Louis, WB Saunders, 2003, p. 83
17. KIM K.H., ONG J.L., OKUNO O., J. Prosthet. Dent. **87,** no.6, 2002, p.642  18. ATTAR N., TAM L.E., MCCOMB D., J.Can. Dent. Assoc. **69**, no.8, 2003, p.516
19. BRAEM M., FINGER W., VANDOREN V.E., LAMBRECHRS P., VANHERLE G., Dent. Mater. **5**, no.5, 1989, p.346
20. SUMINO N., TSUBOTA K., TAKAMIZAWA T., Acta Odontol. Scand. **71**, 2013, p.820
21. WU W., MCKINNEY J.E., J. Dent. Res. **61**, 1982, p.1180
22. HIRASAWA T., HIRANO S., HIRABAYASHI S., HARASHIMA I., NASU I., KUROSAWA T., Shika Rikogaku Zasshi **22**, no.59, 1981, p.187
23. RAPTIS C.N., FAN P.L., POWERS J.M., J. Am. Dent. Assoc. **99**, no.4, 1979, p.631
24. SCHULZE K.A., ZAMAN A.A., SÖDERHOLM K.J., J. Dent. **31**, no.6, 2003, p.373
25. BALOS S., PILIĆ B., PETRONIJEVIĆ B., MARKOVIĆ D., MIRKOVIĆ S., SARCEV I., Vojnosanit Pregl. **70**, no.5, 2013, p.477