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Challenges in Experimental Evaluation of Morphological, Chemo-Mechanical and Adhesive Properties of Glass-ionomer Based Dental Materials

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ABSTRACT

Changes in composition and new material characteristics require verification in clinical and experimental studies. Investigating glass-ionomer cements under laboratory conditions encounters problems in interpreting the results and in comparing them with other types of materials tested in the same way. As the connection between the glass-ionomer cements and the dental tissues is delicate, it is often the case that the impact of fractures and other artifacts is either underestimated or over-dimensioned when interpreting the results. A critical review was performed, with defining the main problems regarding the usage of SEM, EDX and nanoindentation techniques in glass-ionomer based materials evaluation.

Key words: *glass-ionomer, SEM, EDX; nanoindentation, surface characterization*

1. INTRODUCTION

Back in the middle of the previous century, with the launch of the modified ratio between aluminum and silica oxides in the silicate glass Wilson and Kent produced glass ionomer cements well-suited for numerous application in paediatric dentistry [1]. Glass-ionomer cements are a group of dental materials that contain glass with ion leaching properties, water soluble polyacrilic acid as a liquid component in the conventional form and photopolymerizable monomers in the resin based formulations [2, 3]. Glass-ionomer based materials exhibit several advantages compared to other restorative materials, such as the ability to chemically bond to enamel, both conditioned and wet dental substrate, antimicrobial activity and longstanding fluoride release, biocompatibility and acceptable thermal expansion coefficient [4-10]. This restorative material has been widely used for over 50 years because it does not require a complicated working technique. All these favorable properties validate their important position in everyday clinical practice. Then again, all these favorable properties are accompanied with some disadvantages such as the inability to achieve satisfactory surface polish, significant porosity and relatively poor physical properties, such as surface wear and brittleness when fully matured or set [2,6, 7, 9]. However, several studies of conventional glass-ionomer cements, both clinical and experimental, have proven that there are properties in need of correction, such as wear resistance, poor aesthetic level, relatively narrow clinical indications in contemporary restorative dentistry, sensitivity to moisture during application and cement reaction to definitive material stabilization, and sensitivity to fluid to powder ratio [2, 5, 8, 9]. Enhanced formulations of conventional glass-ionomer cements, have significant amounts of strontium in addition to fluoride, which has also been shown to have a strong anticariogenic potential [11, 12]. Changes in composition and new material characteristics require verification in clinical and experimental studies. There is a wealth of strong evidence for the therapeutic action of glass-ionomer materials in contemporary literature, supported

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by experimental studies that have shown reduced solubility in acidic environments and remineralization of solid dental tissues following the use of these materials [4, 13, 14]. Laboratory tests of glass ionomer cements using SEM most often give discouraging results due to cement damage caused by the drying of the material during sample preparation or during vacuum exposure necessary for SEM testing [15, 16]. Studies dealing with glass-ionomer cements under laboratory conditions encountered similar problems in interpreting the results and in comparing them with other types of materials tested in the same way. As the connection between the glass-ionomer cements and the dental tissues is delicate, it is often the case that the impact of fractures and other artifacts is either underestimated or over-dimensioned when interpreting the results.

The aim of this review was to retrospectively define the main problems regarding the usage of SEM, EDX and nanoindentation techniques in glass-ionomer based materials evaluation.

2.1 Microscopic techniques

Scanning electron microscope (SEM) is a powerful analytical tool in material evaluation that is widely used in dental investigations for quite some time since SEM allows the visualization of images and various topographical features at high magnifications in range of 50X-50000X and higher. [17]. The use of SEM in the study of glass-ionomer based materials permits direct visualization of the complete sample, whereas the third dimension examination and intensity of focus allow observation at the highest magnifications and present data on the spatial relations of the structures observed (Fig. 1). Our previous reports are related towards glass-ionomers topographical evaluation of three different experimental approaches: the material itself, glass-ionomer based fissure sealants and glass-ionomer based restoratives in primary teeth. The following features were analyzed in depth :1) topographical features of the material surface with respect to the storage media and material formulation ,2) hybrid layer between glass-ionomer and intact enamel and ground enamel and dentin, and 3) penetration and adaptation ability of glass-ionomer based fissure sealants and restoratives. [18-24]. Needless to say, each experimental approach has a different specimen preparation technique, evaluation criteria and scientific tasks. It has already clearly been pointed out that the analysis of glass-ionomer based materials using SEM unavoidably generates specimen failure, due to the damage produced by drying that happens during both the vacuum coating technique that is sometimes used but also during the establishing of the vacuum necessary for SEM examination. Investigators have a tendency to only in brief describe how the specimens were prepared, set and stored for SEM evaluation, which can have considerable effect on the data accuracy, research reproducibility and interpretation potential. Regrettably, majority of the authors did not consider that the type of preparation, storage, coating and sputtering used in analyses alters the results and interpretation. At this point, it is accepted that for standard imaging in SEM, samples must be electrically conductive, as a minimum at the material surface, and electrically grounded in order to prevent the accumulation of electrostatic charge at the surface. It is recognized that the presence of a hybrid layer at the connection between materials and dental tissues is not a sole feature of resin composites, nonetheless a comparable layer appears through the demineralization and ion exchange at the junction of the glass-ionomer based materials and dental tissues [15, 16, 20, 21].

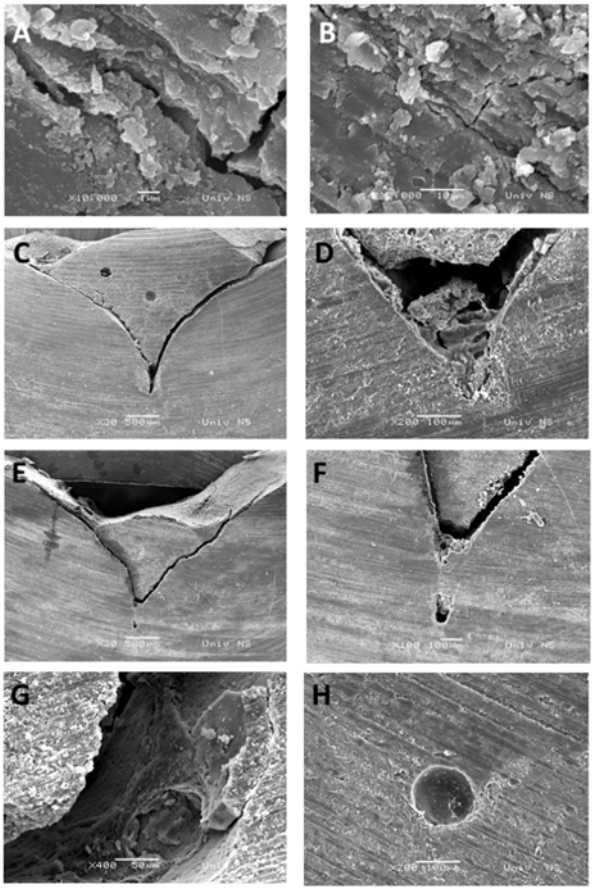

Fig. 1 Visualization of the hybrid layer, interfacial zone between enamel A, and dentin B. C- adhesive failure of the glass-ionomer fissure sealant D- adhesive failure and the crack within the material E,F- combination of cohesive and adhesive failures in two different magnifications.G- Complete cohesive failure at the enamel surface-air void intrapped at the interface zone[19,20,22,24].

In line with this observation, our previous reports demonstrated using the highest magnification in cases of good surface adaptation, the zone of the hybrid layer, the interconnection of the glass-ionomer and the surface of the enamel was visualized. [19, 20, 22, 24]. The adhesion of glass-ionomer based materials and the dental tissues is very subtle and the materials themselves have rather low cohesive strength. Consequently, cohesive cracks of glass-ionomer specimens, with the existence of a narrow layer of material firmly adhered to the tooth structure, are an occurrence that must be considered within the experimental evaluation of glass-ionomer based materials. As a result, these cohesive failures should not be

considered as a material failure, but rather a technique and sample preparation error. Although the preparation procedure is performed gently, sectioning the teeth with glass-ionomer material placed on it is a necessary step that can substantially affect the obtained data, since the diamond disc (despite the water cooling) goes through at least three different tissues, enamel, dentin and glass-ionomer with substantially different mechanical properties, and forces generated during these preparation steps cannot be anticipated. It is frequently reported that the sample preparation procedures resulted in significant rate of specimen failure. Adhesive failure was noticed around 15% of all specimens, while cohesive failures were observed in nearly 70% of entire glass-ionomer samples [20, 21]. It is worth mentioning that in the half of specimens, where conventional glass-ionomer materials had been used, specimen failure had been noticed even before the preparation for the SEM analysis had even started. Given that the interface between glass-ionomer and tooth structure is delicate (Fig. 2), there is a risk that the impact of these failures and other artefacts could be underestimated or amplified in results interpretations.

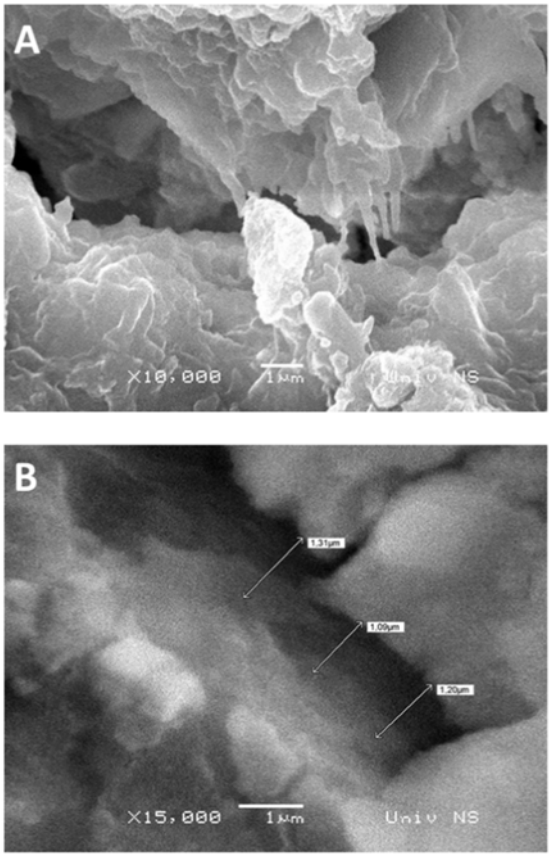

Fig. 2 A-Interface zone between the glass-ionomer and ground primary teeth enamel. B. Measurements of adhesive gap

2.2. *Spectroscopic techniques*

Investigating the morphological characteristics of the material and material-dental tissue adhesion solve only half of the problems in material analysis. Very often it is necessary to identify the elements on the surface of the test specimen. This identification is possible if the SEM is equipped with an EDS spectrometer. EDS is an analytical technique that uses x-radiation emitted by a sample when it is blasted by an electron beam to identify the structure by the elements of the test sample. Modern SEM/EDS devices are equipped with sophisticated software that enables automatic analysis and so-called "mapping" of the surface composition of the tested structure by elements. EDS analysis, as a semi-quantitative method, provides opportunities for evaluating the interaction of materials and dental tissues, but sample preparation and interpretation of results have some limitations. It is important to evaluate the exchange of ions at the interface between the material and tooth structure and incorporation of fluorine and strontium ions into the hard dental tissues since it would be evidence of the prophylactic, anticarigenic and therapeutic properties of the materials (Fig. 3).

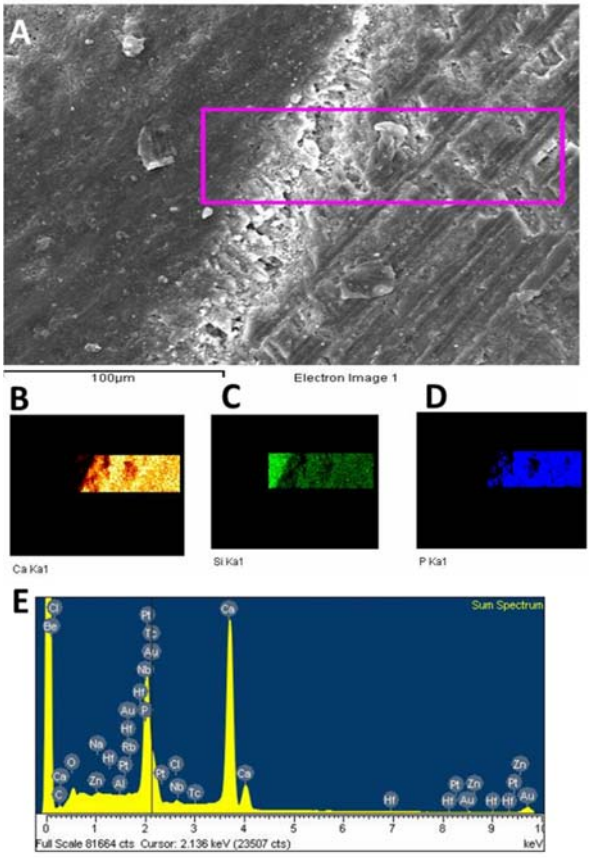

Fig. 3 *Hybrid layer between glass-ionomer based fissure sealant and intact enamel B, C, D- elemental mapping identifying calcium, silica and phosphorus content E-graph describing elemental composition of the adhesion zone*

Quantitative analysis of the adhesion zone of the glass-ionomer material and the enamel and dentine, as well as the ion exchange between the material and the dentin and enamel, is usually carried out at 2000x magnification using an acceleration voltage of 25 kV for identification of all elements, and a voltage of 10 kV for the identification of fluorine ions. Decrease in acceleration voltage sometimes resulted in lower resolution and

decreased image quality. Multiple and repeated analyses are performed at each cross section in both dentine and enamel. In order to avoid overlapping of the spectra, because the real identification range of the aforementioned spectrometer is about 3 μm, the phase shifting of the points is by the rule performed so that they were not located along one straight line. Each point should be at least 2μm farther from the intermediate zone than the previous one. On repeated analysis on the teeth on which conventional glass-ionomer material was placed 3 months prior to analysis, the presence of fluoride ions was detected at 2 sections[20]. This information must be taken with caution, although it speaks in favor of the continued long-term release of fluoride by the glass-ionomer and ion exchange at the intermediate interface with the enamel, since the absolute concentrations of fluoride in the enamel are extremely low (about 0.30 mg/cm3) and can be raised by topical application up to multiple values that still do not represent a significant constituent in the overall structure of the enamel (up to 12mg /cm3). In order to optimize EDS analysis, it is necessary to reduce the resolution of the SEM image and it is difficult to define the analysis points accurately. Then, EDS analysis requires ideally polished surfaces to prevent secondary diffraction.

Samples in all our previous reports were prepared on the recommendation of Dogan et al. to obtain samples of appropriate smoothness. Since glass-ionomer based materials are low-cohesive materials, polishing could result in a smear layer on the surface of the enamel. This layer, composed largely of glass-ionomers, could give false positive results for the presence of fluoride. These obstacles require finding solutions, but EDS analysis certainly has a future in examining the prophylactic characteristics and structure of glass-ionomer materials. Their values are stated to objectify the values for fluoride and strontium ions, because EDS does not offer the possibility of absolute quantitative analysis, but comparison of the detected values for as many elements present as possible gives valid data on differences in mass representation of a particular element at the test point (Fig. 4).

Finally, the assessment of the ion proportions at the surface of the material offers valuable information about the way that the initial material composition affects the ion dynamics into and from the solution. The fluoride content at the surface of the glass-ionomer based material is an important parameter in quantification of the release and recharge ability of the dental material [22-24].. Hadley demonstrated, using depth profiling, that the concentration of fluoride maximized at the surface of the samples [25]

2.3. Mechanical Characterisation

During the last three decades, mechanical and physical properties of glass-ionomer based materials have substantially improved as the result of the higher content of filler particle component, the incorporation of resin monomers into the cement, the addition of various nanomaterials into original formulation, and the combination of the abovementioned interventions.

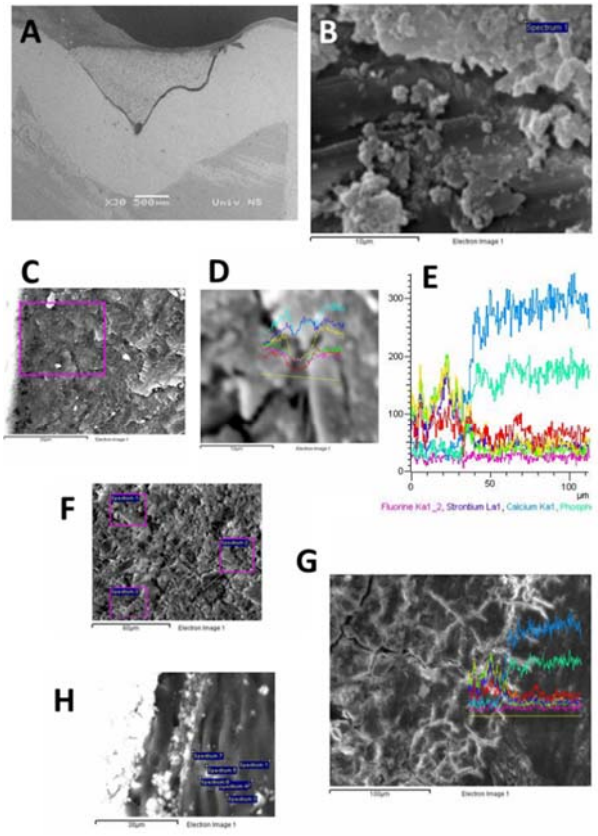

Fig. 4 A- Lower quality resolution with the decrease of acceleration voltage. B- Identification of the area for EDS analysis C-the surface covered with EDS analysis. D-Using higher magnification to evaluate ion exchange between glass-ionomer based material and primary teeth dentin. E. Elemental graph of the interface zone. F-The pattern of choosing the spots for analysis in the material G-The pattern of choosed representative spots at the dentinal surface. H-Line graph of elemental composition of the interface zone between glass-ionomer and primary teeth hard dental tissues.

Nanoindentation tests have been recognized as applicable methods for determination of the material mechanical and physical characteristics, such as nanomaterials used in dentistry, dental tissues and bone. For our set of indentation studies analyzing glass-ionomer based materials [26]. the prepared samples were mounted in the sample holder using adhesive tape or epoxy glue. Multiples indentations were always executed equally, distributed throughout the surface of the whole specimen. All performed tests were conducted with Agilent (Keysight) Nano indenter G200. This nanoindenter provides repeatable and consistent measurements. The system has resolution of load and displacement of less than 50 nN and 0.1 nm, respectively. In all our previous reports the same experimental setup has been employed with equipment parts as follows: 1) Berkovich three-sided pyramidal diamond tip, with the face angle of 65.27°. 2) Calibration indents were performed on fused silica. Examination of samples was performed at room

temperature and Poisson's ratio for all samples was set to be 0.38. The indents were located 25 μm apart to avoid the influence of residual stresses from adjacent impressions. Multiple indentations protocols were used, the first included at least 15 indentations per sample, while the second consisted of 100 indentations per sample. Using the first protocol, the obtained data was insufficient for adequate statistical analysis and relevant drawing of conclusions. The second protocol enabled results repeatability for the mechanical properties assessment of analyzed samples and relevant data. All tests from the first protocol were performed at max load of 1 mN while for the second max load was set up at 30 mN. Both protocols used same following parameters: one indentation per place, 1 s peak hold time and time to load of 15 s.

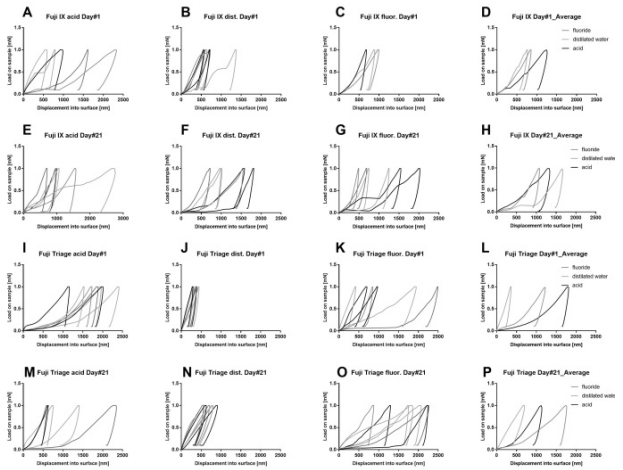

Fig. 5 *Nanoindentation test with usage of first protocol*

Immense variations with respect to mechanical and physical properties of glass-ionomer based materials have been reported, the differences described in the literature are sometimes multiple fold higher or lower compared to the manufacturers descriptions and specifications. As a result, there were suggestions to standardize evaluation protocols, and sometimes even clearly emphasized that the obtained results regarding mechanical properties of glass-ionomer based materials were valid only for aqueous solutions. Acquired results of the experiments where the first protocol on nanoindentation was used, were in fractional agreement with existing works data. Acquired values for hardness and Young modulus are to some extent either significantly lower or marginally lower compared to results available in some experimental works (Fig. 5). Using the second protocol resulted in more uniformed results and clearly visible behavior pattern of tested materials (Fig. 6).

3. CONCLUSIONS

Glass-ionomer based materials are in constant process of clinical evaluation and new formulation development. At the same time, they are frequently subjected to criticism mainly due to lack of standardization of in vitro material testing. The present review shows the series of challenges and obstacles in glass-ionomer based materials testing with respect to adhesion, chemical structure and mechanical properties. It is important to take into consideration all the factors related to the use of specific analytical equipment, peculiarities of specimen preparation, distinctiveness and demands of testing procedures before generalization of the obtained data and extrapolation of the results to real clinical circumstances. Data presented in this review could be used by clinicians and material science researchers with the aim of optimization and standardization of dental materials assessment.

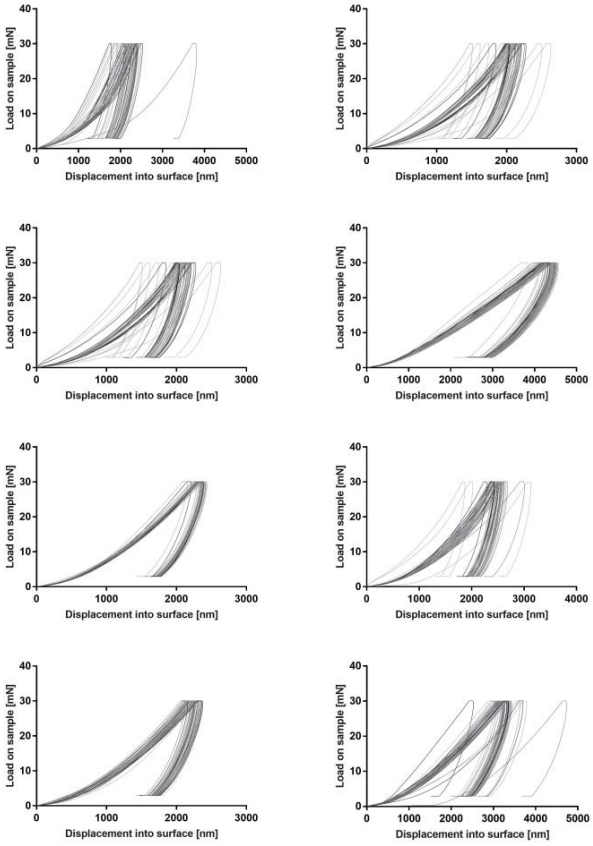

Fig. 6 *Nanoindentation test with usage of second protocol*

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REFERENCES

[1] Wilson, A., Kent, B., (2007) The glass-ionomer cement, a new translucent dental filling material. *Journal of Applied Chemistry and* Biotechnology, 21(11), 313-313, DOI: 10.1002/jctb.5020211101.

[2] Akashi, A., Matsuya, Y., Unemori, M., Akamine, A., (1999) The relationship between water absorption characteristics and the mechanical strength of resin-modified glass-ionomer cements in long-term water storage. *Biomaterials, 20(17),* 1573-1578, DOI: 10.1016/s0142-9612(99)00057-5.

[3] Dunne, S. M., Goolnik, J. S., Millar, B. J., (1996) Caries inhibition by a resin-modified and a conventional glass ionomer cement in vitro. *J Dent, 24(1-2),* 91-94, DOI: 10.1016/0300-5712(95)00051-8.

[4] Featherstone, J. D. B., (1999) Prevention and reversal of dental caries: role of low level fluoride. *Community Dent Oral Epidemiol, 27,* 31-40, DOI: 10.1111/j.1600-0528.1999.tb01989.x.

[5] Mount, G. J., Buonocore, (1994) Memorial Lecture. Glass-ionomer cements: past, present and future. Oper Dent., 19, 82-90.

[6] Zoergiebel, J., Ilie, N., (2013) Evaluation of a conventional glass ionomer cement with new zinc formulation: effect of coating, aging and storage agents. *3. Clin Oral Investig., 17(2),* 619-626, DOI: 10.1007/s00784-012-0733-1.

[7] Naasan, M. A., Watson, T. F., (1998) Conventional glass ionomers as posterior restorations. A status report for the American Journal of Dentistry. *Am J Dent., 11,* 36-45.

[8] Ilie, N., Hickel, R., Valceanu, A., Huth, K., (2012) Fracture toughness of dental restorative materials. *Clin Oral Invest., 16,* 489-498, DOI: 10.1007/s00784-011-0525-z.

[9] Sidhu, S., (2011) Glass-ionomer cement restorative materials: a sticky subject? *Australian Dental Journal, 56,* 23-30, DOI: 10.1111/j.1834-7819.2010.01293.x.

[10] Zafer, C., Cehreli, C., Altay, N., (2000) Effects of a nonrinse conditioner and 17% ethylenediaminetetraacetic acid on the etch pattern of intact human permanent enamel. *Angle Orthod., 77(1),* 22-27, DOI: 10.1043/0003-3219(2000)070<0022:EOANCA>2.0.CO;2.

[11] Tam, L. E., Chan, G. P., Yim, D., (1997) In vitro caries inhibition effects by conventional and resin-modified glass-ionomer restorations. *Oper Dent., 22,* 4-14.

[12] Massara, M. L. A., Alves, J. B., Brandao, P. R. G., (2002) Atraumatic restorative treatment: clinical, ultrastructural and chemical analysis. *Caries Res., 36, 430-6,* DOI: 10.1159/000066534.

[13] Randall, R. C., Wilson, N. H. F., (1999) Glass-ionomer restoratives: A systematic review of a secondary caries treatment effect. *J Dent Res.,* 78, 628-637, DOI: 10.1177/00220345990780020101.

[14] Birkenfeld, L. H. Schulman, A. (1999). Enhanced retention of glassionomer sealant by enamel etching: A microleakage and SEM study. *Quint Int. 30, 712-719*.

[15] Ngo, H., Mount, G. J., Peters, M. C. (1997). A study of glass-ionomer cement and its interface with enamel and dentin using a low-temperature, high-resolution scanning electron microscopic technique. *Quint Int 28,* 63-69.

[16] Milicich, G., (2005). A resin impression SEM technique for examining the glass–ionomer cement chemical fusion zone. *Journal of Microscopy 217,* 44-48, DOI: 10.1111/j.0022-2720.2005.01432.x.

[17] Paradella, T. C., Bottino, M. A., (2012) Scanning electron microscopy in modern dentistry research. *Braz Dent Sci, 15(2),* 43-48, DOI: 10.14295/bds.2012.v15i2.798.

[18] Markovic, D., Peric, T., Petrovic, B., (2018) Glass-ionomer fissure sealants: Clinical observations up to 13 years. *J Dent.,* 79, 85-89, DOI: 10.1016/j.jdent.2018.10.007.

[19] Markovic, D., Petrovic, B., Peric, T., Miletic, I., Andjelkovic, S., (2011) The impact of fissure depth and enamel conditioning protocols on glass-ionomer and resin-based fissure sealants penetration. *Journal of Adhesive Dentistry, 13*, 171-178, DOI: 10.3290/j.jad.a19006.

[20] Petrović, B., Perić, T., Marković, D., (2008) Analiza međuspoja glasjonomernog materijala i gleđi i dentina mlečnih zuba. *Hemijska industrija, 62,* 211-216.

[21] Markovic, D., Petrovic, B., Peric, T., Blagojevic, D., (2012) Microleakage, adaptation ability and clinical efficacy of two fluoride releasing fissure sealants. *Vojnosanitetski pregled, 69,* 320-325.

[22] Petrović, B., Marković, D., Filipović, D., (2007) Efikasnost glasjonomera kao profilaktičkih sredstava u stomatologiji. *Hemijska industrija, 61(2),* 90-95.

[23] Markovic, D. Lj., Petrovic, B. B., Peric, T. O., (2008) Fluoride content and recharge ability of five glassionomer dental materials. *BMC Oral Health, 8, 21,* DOI: 10.1186/1472-6831-8-21.

[24] Markovic, D., Petrovic, B., Peric, T., Mandic, J., (2008) Prophylactic properties of fluoride-releasing materials. *Metalurgija - Journal of Metalurgy, 14,* 111-120.

[25] Hadley, P. C., Milella, E., Cerardi, C., Hill, R. G., Bilington, R. W., (2001) Distribution of fluoride in glass-ionomer cement determined using SIMS. *Biomater, 22*, 1563-1569, DOI: 10.1016/s0142-9612(00)00316-1.

[26] Petrović, B., Marković, D., Kojić, S., Perić, T., Dubourg, G., Drljača, M., Stojanović, G., (2019) Characterization of Glass Ionomer Cement Stored in Variouse Solutions, *Materiali in Tehnologie, 53(2),* 286-293, DOI: 10.17222/mit.2018.159.