# Correlation between morphology, structure and composition at the glass ionomer bioadhesive materials

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The objective of the present study was to determine the physical properties of two hybrid restorative materials as compared with two conventional glass ionomers cements (GICs) and two metal-reinforced GICs. The roughness surface of GICs materials, in descending order, was achieved subsequent to the use of metal-reinforced glass ionomers, resin modified glass ionomers and conventional GICs. The material with most heterogeneous structure is metal-reinforced GICs MM (GC). The size of the hybrid layer is influenced by the structure of material. EDS analysis evidenced no important difference beetwen the fluor contenu of investigated materials was found.

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## 1. Introduction

The morphologies, microstructures and compositions of some bioadhesive materials were systematically investigated by scaning electron microscopy (SEM), optical microscopy (MO), Energy-dispersive X-ray spectroscopy (EDS) and atomic force microscopy (AFM) analysis [1, 2, 3].

Evolution of dental plastics materials is in continuous expansion. Characteristics of an ideal restorative material are numerous. The most important aspects are given by their biological properties and by their capacity for adhesion.

Glass ionomers cements (GIC) are materials most suitable in terms of biocompatibility but their increased degree of roughness, low wear resistance and low aesthetics restricts their widespread use. GIC are polyacrylates complex, resulting from the interaction of aqueous solutions of homo-or copolymers of acrylic acid or polialchenoic with a double silicate of aluminum and calcium.

GICs materials are based on the reaction of silicate glass powder and polyalkenoic acid. GICs are commonly classified into many types: GIC conventional, Resin Modified Glass Ionomer Cements (RMGI), tri-cure glass ionomer cements and Metal-reinforced GICs.

Conventional GlCs were first introduced in 1972 by Wilson and Kent [4]. They are derived from aqueous polyalkenoic acid such as polyacrylic acid and a glass component that is usually a fluoroaluminosilicate. As they bond chemically to dental hard tissues and release fluoride for a relatively long period, modern day applications of GICs have expanded. [5, 6, 7, 8 and 9]

Metal-reinforced GICs were first introduced in 1977. The addition of silver-amalgam alloy powder to conventional materials increased the physical strength of the cement and provided (radiodensity).

Developed in 1992, RMGI are conventional GlCs with addition of Hydroxyethyl methacrylate (HEMA). Tri-cure glass ionomer cements have also incorporated a chemical curing tertiary amine-peroxide reaction to polymerize the methacrylate double bonds along with the photo-initiation and acid-base ionic reaction. The chemical cure component of tri-cure cements has been shown to have a significant effect on their overall strength. Photo-initiated cements cannot be used in cases involving opaque structures such as metal substrates. The RMGI generally have a much lower release of fluoride which is favorable for remineralization than the conventional glass ionomer materials [10, 11, and 12]. These materials are intended to overcome the disavantages of conventional glass ionomers (short working time, long setting time, and sensitivity to water during the early stages of setting) while preserving their clinical advantages (esthetics, self-adhesion, to dental tissues, fluoride release, and termal insulation) [13, 14]. The number of application steps of this materials in the restorative process is drastically reduced, which shortens chair time. They were also initially intented to serve as metal-free amalgam substitutes [15]. Since these hybrids restorative materials are all light-curable, they do lengthen the working time and shorten the setting time, and they can be wet finished and polished immediately after placement [16, 17]. The hybrid restorative materials have also been claimed to have better physical, mechanical, and esthetic properties than do conventional glass ionomers [10, 17]. Furthermore, the hybrid restorative materials have shown higher bond strength to enamel and dentin than have conventional glass ionomers [10, 12, 14, and 19]. The high finishing ability a basic material is a goal to be attained by each material. Retention capacity of the dental bacterial plaque increases with the material roughness. The roughness of the material is related to particle size fillers. As filler particle size is greater the degree of roughness of the material is more also and the capacity for hybridization of the dental hard tissue is low.

The objective of the present study was to determine the physical properties of two hybrid restorative materials

as compared with two conventional GICs and two metal-reinforced GICs.

## 2. Experimental

Two hybrid restorative materials, two conventional GICs and two metal-reinforced GICs were investigated, as listed in Table 1.

*Table 1. Lists of investigated materials.*

| Catego-ry | Brand Name | Co-de | Manufactu-rer | Setting Mecha-nism |
|---|---|---|---|---|
| C-GICs | Fuji IX | FuIX | GC Tokyo, Japan | AB |
| C- GICs | Kavitan | Ka | SpofaDental, Praha | AB |
| RM- GICs | Fuji II LC hand-mix | FuII LC | GC Tokyo, Japan | L+AB+C |
| RM-GICs | Vitre-mer | Vi | 3M ESPE | L+AB+C |
| Metal reinfor-ced C-GICs | Miracle Mix | MM | GC Tokyo, Japan | AB |
| Metal reinfor-ced C- GICs | Argecem | Ar | JSC VladMiVa, Belgorod, Russia | AB |
| C- conventional, GICs- glass ionomers cements, RM- resin modified, L-Light-curing; AB-Acid-base,reaction; C- Additional chemical curing. | | | | |

### 2.1. Surface characterization by scanning electron microscopy (SEM), optic microscopy (MO), and Energy-dispersive X-ray spectroscopy (EDS) analysis

Fifteen caries-free molars and premolars were extracted from orthodontically and periodontologically reasons. The teeth were obtained from patients who required an extraction as a routine part of their treatment. The research was conducted with the agreement of the Ethics Commission of the Iasi University of Medicine and Pharmacy (UMF Gr.T. Popa).

The teeth were mechanically brushed with a non-fluorurate abrasive paste, rinsed with dionised water and stored in 0.5% chloramine solution at $4^0$ C. Tweenty standard cavities were performed at each tooth: 2.5 mm depth and 4 mm wide. Cavities were performed M (mechanically) at slow and high speed under water spray with round and cylindrical diamond burs no:1. The teeth were randomly assingned in four equal groups and than were prepared and restored according to the manufacturers instruction as follows: Group 1 filled with FuIX (GC); Group 2 filled with FuII LC (GC); Group 3 - filled with Vi (3MESPE); Group 4- filled with MM (GC).

The samples were cut longitudinaly (mesio-distal) with diamond disc under water cooling and then washed with ethanol. The samples are submitted to a mechanically polishing process using diamond (particles size – 3μm) and Syton (particles size – 20nm) under continuous irrigation. The role of this step is to bring the materials to the same length on the surface and to obtain very smooth surfaces. After each polishing step, the AAO surface is visualized with the SEM microscope. The samples were etched with $H_3PO_4$ 35% for 4 seconds and washed for two minutes with distilled water as presented in Ref. 6 [18].

The teeth were then stored in saline solution 48 hours. SEM and EDS observation was done with JEOLJSM 6390ª Japan and MO was done with ZEISS – AXIO with AXIO-CAM-MRC 5. The modality by adhesion was characterized by SEM and MO. The measure was performed at walls of the restauration in at least three different points, making the average for each sample.

### 2.2. Surface roughness and topography characterization

Six sample of different material was made. The materials were prepared in conformity with manufacturer indication for one drop. After preparation the materials were put between two matrix strips of celluloid (Nr. 437 Alfred Becht GmbH-D 7600 Offenburg, Germany) and then between two glasses plates to obtain a flat surface. The materials samples with photo initiator were light-cured for 40 seconds through the glass slide with a conventional quartz halogen lamp (QTH), power density 570mW/cm$^2$ (3MESPE). After polymerization the materials were removed and analyzed. The microstructures and the composition of biomaterials were characterized by SEM (JEOLJSM 6390ª Japan). The roughness and the topography of the surface were characterized by AFM (Park SYSTEMS XE -100). AFM was used in non-contact mode using single crystal silicon tip (with nominal radius < 10 nm), which was connected to a fixed substrate on a canti-lever. The images were recorded with a scan rate of 0.5 Hz and a resolution of 256 × 256 pixels. For each specimen, two scans were carried out at each specimen surface quadrant at a scanning area of 10 μm × 10 μm. The collected 3D topographical data was analyzed with data analysis software (XEI - Image Processing and Analysis). For each group, the surface roughness was calculated in nm.

### 2.3.Statistical analysis

Statistical analysis was performed with one-way ANOVA and Bonferoni posthoc test with the significance level of for difference between means $p<0.05$ ( SPSS – 14) for SEM and MO

## 3. Results and discussions

The results of the tests are listed in table 2.

### 3. 1. Surface roughness

After specimens were activated, the lowest surface roughness was measured for the RMGI – FuII LC (GC) for the groups is shown in Table 2.

*Table 2. Analysis of the surface roughness Ra [nm] for 10 µm obtained from AFM images.*

| Material | *Ra* [nm] |
|---|---|
| FuIX | 25.747 |
| Ka | 25.13 |
| FuII LC | 0.041 |
| Vi | 105.038 |
| MM | 62.031 |
| Ar | 21.716 |

There were differences in surface roughness among the RMGI cements (Table 2). But their values were significantly different in favor of FuII LC (GC). The roughness of the conventional GICs was 50 times higher than that of the FuII LC (GC) but lowest 4 times than that of the Vi (3MESPE). The roughness of the metal reinforced GICs was 120 times higher than that of the FuII LC (GC) but only approximate 3 times than that of the conventional GICs. The Vi is higher roughness of the surface.

### 3.2. Surface topography characterization

Morphologically, by AFM, the particle of the Vi (3MESPE) materials appeared to be exposed to a higher degree than the particle of the conventional GICs Selected AFM images of the surfaces of materials are presented in (Fig. 1. a-f). AFM images show a relatively smooth natural surface at FuII LC (GC) material (Figure 1b). Increased surface irregularities are observed in the AFM images of other materials. (Fig. 1 a, c-f).

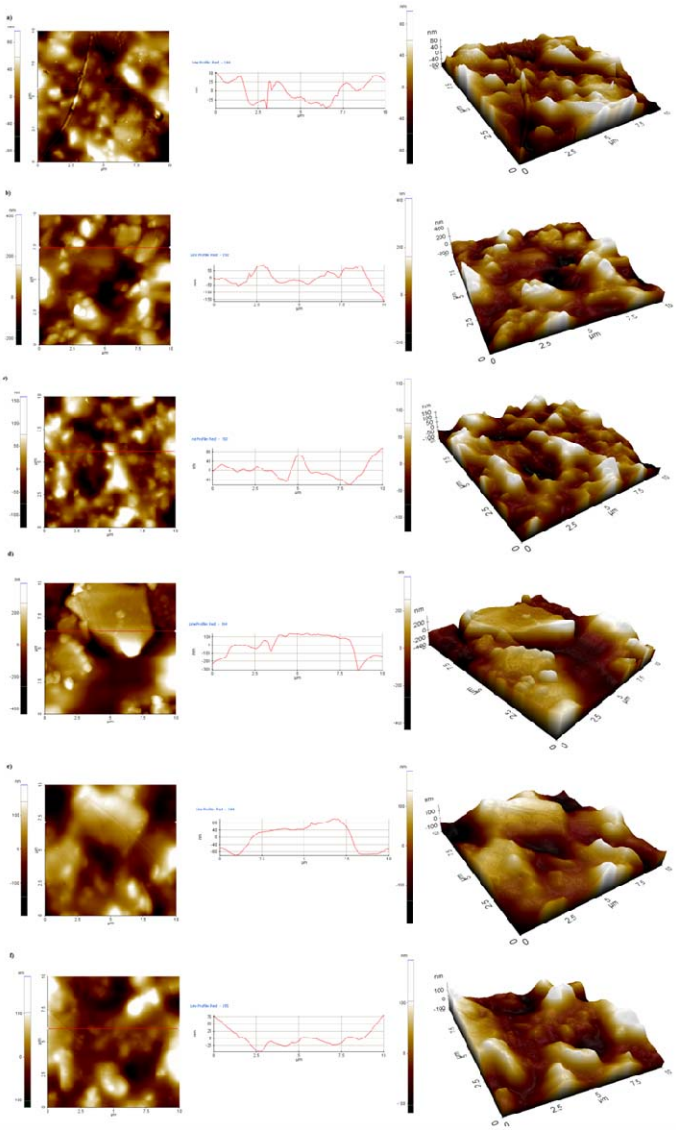


*Fig. 1. AFM of template filled with with FuIX(GC) (a), filled with FuII LC (GC) (b), filled with Ka (SpofaDental) (c) filled with Vi(3MESPE) (d) filled with MM (GC )(e), filled with Ar (JSC VladiMiVa) (f)*

### 3.3. Compositional characterization by Energy-dispersive X-ray spectroscopy (EDS) analysis.

The EDS spectra show that all the materials studied contain aluminum, silica and gold in different percents. The metal-reinforced GICs presents also silver 0. 37 Atom% for MM (GC) and 0.50 Atom% for Ar (JSC VladMiVa) (Fig. 2 e and Fig. 2 f). The major different are between fluoride contain in favor of Vi (3MESPE) (6.35Atom %) (Figure 2d) materials followed by FuIX (GC) (6. 15 Atom %) (Figure 2b), FuII LC (GC) (5. 21 Atom %) (Figure 2c), MM (GC) (4. 24 Atom %) (Fig. 2e) and Ar (JSC VladMiVa) (3,62 Atom %), (Fig. 2f).

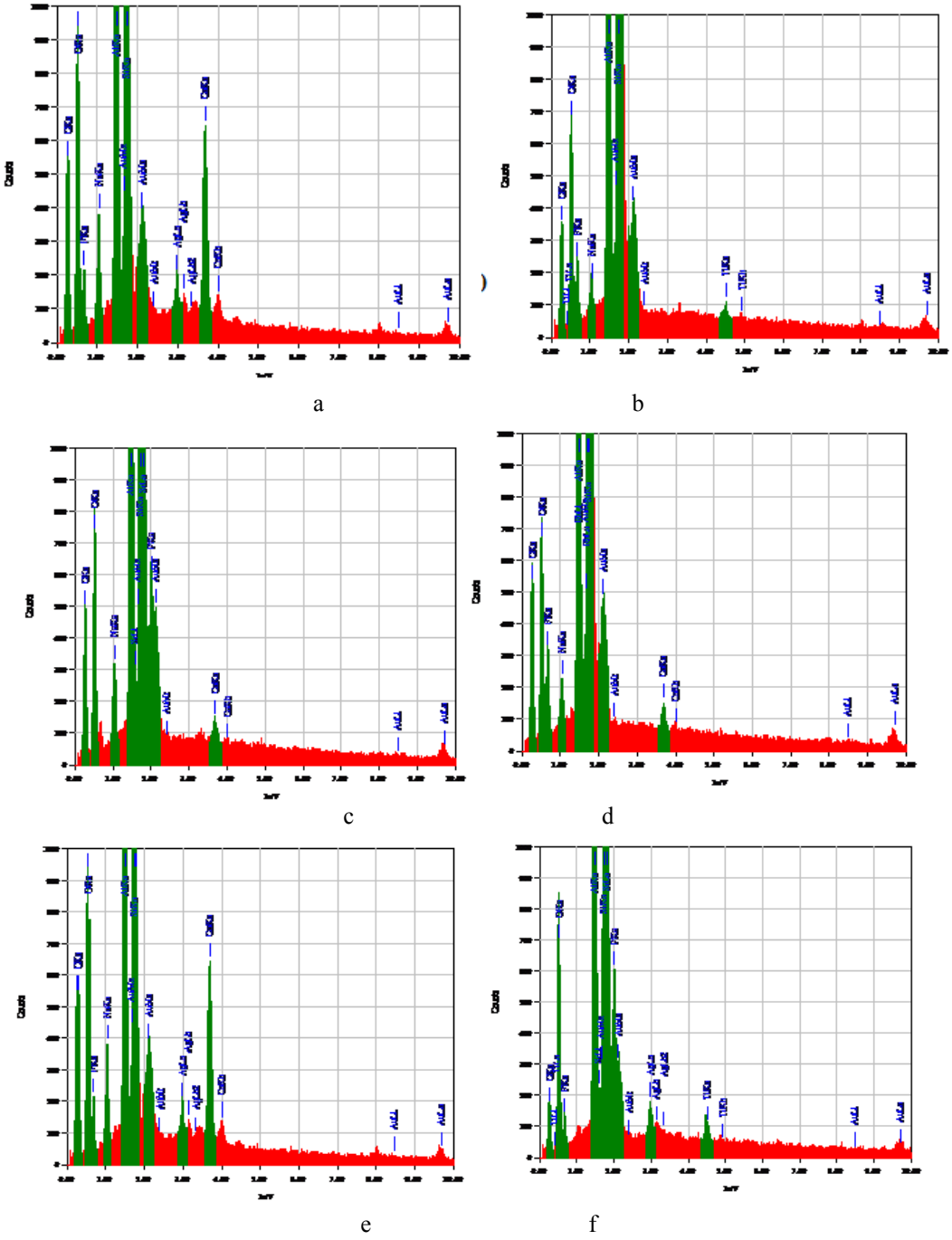



*Fig. 2. EDS analisys of template filled with FuIX (GC) (a), filled with FuII LC (GC) (b), filled with Ka (SpofaDental) (2 c) filled with Vi (3MESPE) (d) filled with MM (GC) (e), filled with Ar (JSC VladMiVa) (f)*

### 3.4. Surface characterization by SEM and MO analysis

Surface characterization by SEM and MO showed the microstructures and morphologies of the GICs materials is different (Fig. 3).

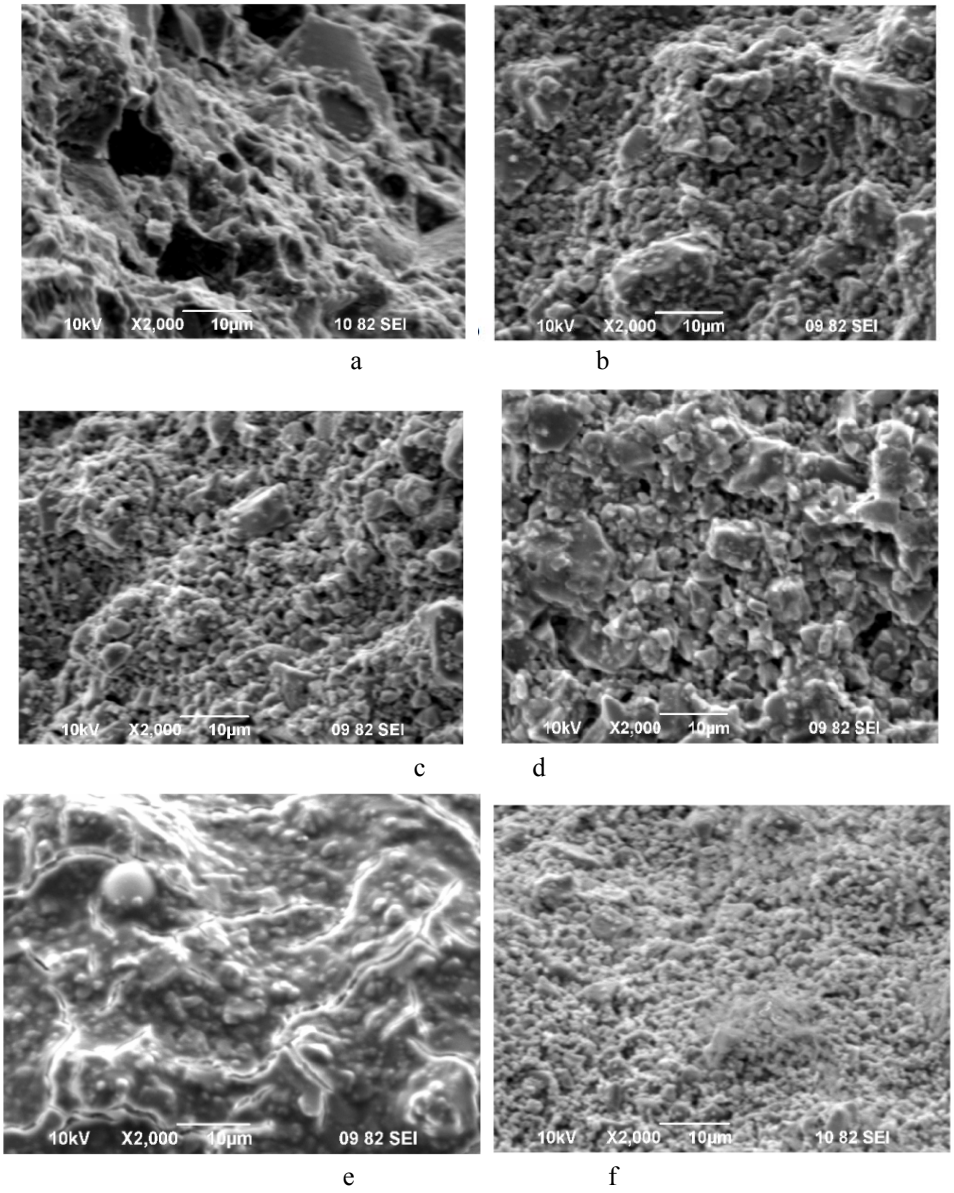



*Fig. 3. Top-view SEM photomicrographs of a template filled with FuIX (GC) (a), filled with Fu II (GC) (b), filled with Ka (SpofaDental)(c) filled with Vi (3MESPE)(d) filled with MM (GC) (e), filled with Ar (JSC VladMiVa) (f)*

*Table 3. Multiple comparisons Dependent Variable: Mean of the hybrid layer*

| (I) GR. | (J) GR. | MD (I-J) | SE | Sig. | 95% Confidence Interval | |
|---|---|---|---|---|---|---|
| | | | | | Lower | Upper |
| 1 | 2 | 14.56 (*) | .780 | .000 | 12.21 | 16.91 |
| | 3 | 16.56 (*) | .780 | .000 | 14.21 | 18.91 |
| | 4 | 14.98 (*) | .780 | .000 | 12.63 | 17.33 |
| 2 | 1 | -14.56 (*) | .780 | .000 | -16.91 | -12.21 |
| | 3 | 1.99 | .780 | .126 | -.35 | 4.34 |
| | 4 | .41 | .780 | 1.00 | -1.93 | 2.76 |
| 3 | 1 | -16.56 (*) | .780 | .000 | -18.91 | -14.21 |
| | 2 | -1.99 | .780 | .126 | -4.34 | .35 |
| | 4 | -1.58 | .780 | .358 | -3.93 | .76 |
| 4 | 1 | -14.98 (*) | .780 | .000 | -17.33 | -12.63 |
| | 2 | -.41 | .780 | 1.00 | -2.76 | 1.93 |
| | 3 | 1.58 | .780 | .358 | -.76 | 3,93 |

Bonferroni
* The mean difference is significant at the .05 level.
Group (Gr), D-dentin, Gr1(FuIX-D), Gr.2 ( FuII LC-D), Gr.3 (Vi-D), Gr.4 (MM-D), Mean Difference (MD), Standard errors (SE)

Morphologically, by SEM, micrograph shows the fact that the diameter and the shape of micro particles of the GICs are different. Conventional GICs has a particle size smaller components. Filler particle size range from 0.72 µm to 2.4 µm for Kavitan and from 1,26 µm to 8,54 µm for FuIX. Also these materials are homogeneous. Top-view SEM micrographs of a sample filled with FuII LC (GC) is present in Figure 1a and for Ka (SpofaDental) materials in Figure 1 c. RMGI cements have a heterogeneous structure with variety filler particle size. Filler particle size for FuII LC (GC) material is range from 0.8 µm to 2.4 µm (Figure 3 b) and for Vi (3MESPE) the range is from 1.49 µm to 6.42 µm ( Figure 3 d). Metal-reinforced GICs presents also heterogeneous structure. Filler particle size range from 2.38 µm to 60 µm for MM (GC) (Figure 3 e) and from 0.66 µm to 0.95 µm for Ar (JSC VladMiVa), (Fig. 3 f).

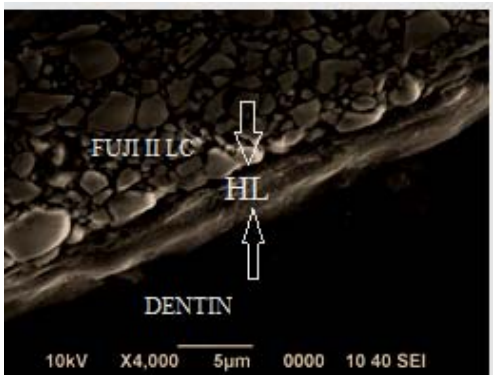
The highest thickness and therefore the best results were obtained for Group 1=18,26 (±2,35)µm, followed by Group 2=3,69 (±0.17)µm, Group4=3.28(±0.69)µm and Group 3=1.70 (±0.23)µm. The equality of variances test (Levene test) was positive at the p-value of $p$ =.000 with semnificative differences between the averages. The ANOVA tests showed statistically significant differences between the groups $p$ =.000, showing that the restoration material influence the dimensional level of hybrid layer F=196.385. Bonferroni test was used to evidence the differences betweeen the groups: $p$ =.000. No evidence diference was found beetween the same type of materials respectivelly group 2 (FuII LC,GC) and group 3 (Vi, 3MSPE) and also beetwen group 2 and group 4 (Tab.3).

Fig. 4 shows the top-view MO micrographs of the template filled with FuIX (GC) (GC) (Figure 4 a), SEM micrographs of the template filled with Fuji II LC (GC) (Figure 4 b), SEM micrographs of the template filled with Vi (Fig. 4 c) MO micrographs of the template filled with MM (GC)(Fig. 4 d).

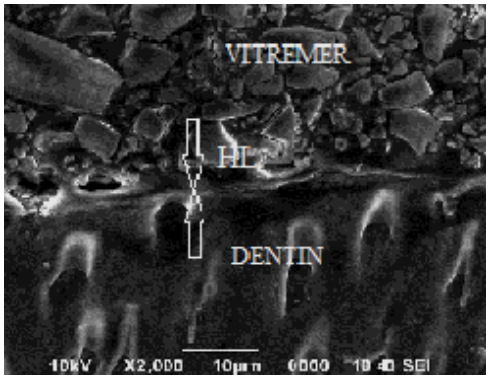
Surface finish quality of tooth-colored restorations is a determinant factor in the esthetics and longevity of such restorations [21, 22]. Restorations with rough surfaces enhance plaque accumulation and stain retention and may cause gingival irritation and dental caries. The results of the present study indicated that all the materials have a certain degree of roughness.

AFM has several advantages for surface analysis, including higher resolution and the ability to provide 3D topographic images of the surface and suitability for qualitative and quantitative comparison of surface texture and roughness [23]. As it can be observed in figure 4, the surface roughness has the same trend in GICs – FuIX (GC)(GC) and RMGI cements FuII(GC). However there is a difference between the GICs FuIX (GC) (GC) and RMGI cements Vi (3MESPE) in favor of conventional cements. The highest surface roughness values, in descending order, were observed at MM (GC) followed by Vi (3MESPE). Vi is a biphasic restorative material and each of the phases differs in hardness values with no uniform abrasion.


a




b




C


d

*Fig. 4. Top-view MO photomicrographs of the template filled with FuIX (GC) (a), SEM photomicrographs of the template filled with FuII LC (GC) (b), SEM micrographs of the template filled with Vi (3MESPE) (c) MO micrographs of the template filled with MM (GC) (d)*

Baghery R. et al, demonstrate that: FuIX (GC), GC showed the least susceptibility to staining by all stains especially coffee, red wine and tea when was compared with Photac Fill, 3MESPE and Fuji II LC, GC. [24]

The surface roughness of the giomer specimens treated with all prophylaxis methods was greater than 0.2 μm, which is a threshold value for bacterial adherence [25].

Our study showed that the composition of glass ionomers materials is different. The differences appear as into same type of material and also between conventional GICs and resin modified GICs. The powder of GIC is an acid-soluble calcium fluoroaluminosilicate glass similar to that of silicate but with a higher alumina-silicate ratio that increases its reactivity with liquid. The fluoride portion acts as a "ceramic flux". Lanthanum, Strontium, Barium or Zinc Oxide additives provide radioopacity. The glass is ground into a powder having particles into a powder in the range of 15 to 50 μm. Typical percentages of the raw materials are: Silica 41.9%, Alumina 28.6%, Aluminium Fluoride 1.6%, Calcium Fluoride 15.7%, Sodium Fluoride 9.3%, and Aluminium Phosphate 3.8%. EDS analysis showed that metal reinforced GICs contain low quantity of fluoride 4.24% for MM and 3.62% for Ar (JSC VladMiVa) .

The differences in the substrate of materials can be considered as another reason for the observed differences in our results. It has been reported that the hardness, the initial surface roughness, filler size, filler content and water absorption of the substrate affect wear resistance [26, 27, 28, 29, and 30]. The mechanical properties of GICs were closely related to their microstructures. Factors such as the integrity of the interface between the glass particles and the polymer matrix, the particle size, and the number and size of voids have important roles in determining the mechanical properties. [31]

Analysis of the size of the hybrid layer resulted from RMGI restoration was discussed in several specialized studies, some of which demonstrating the presence, in dentine, of some microfilaments, resulting in the formation of an optimum hybrid layer, [32, 33, and 34] while other studies [35, 36, and 37] showed their absence. Other contributions outlined that marginal micropercolation at dentine level in the case of restorations with RMGI occurred in only 19% of cases [38].

The lower mean size of the hybrid layer in case Gr. 1=1.70(±0.23) μm, when RMGI – Vitremer (3MESPE) was employed as an obturation material may be attributed to the viscolelasticity of the material. [39]

Other studies [38] show that, at dentine level, RMGI - Vitremer achieved a good penetration of the material FujiIILC şi Vitremer, with a maximum thickness of the hybrid layer of 25 μm. The differences beetwen the material who appears into same classes respectively RMGI cements might be related to substrate's conditioning, made with polyacrylic acid for Fuji II LC (GC), and with primer, respectively, for Vitremer (3MESPE), once known that the blatter one ameliorates surface humidity [40].

The large differences recorded among the values obtained in various studies may be attributed to the

working conditions, *i.e.* to a correct dosage of compounds. Introduction of a lower amount of powders will induce a higher substrate moisturing, as a result of its higher yield, which will nevertheless be detrimental to the mechanical proprieties of the material.

## 4. Conclusions

Given the results of the current study, further investigations on the surface roughness and abrasion resistance of glass ionomers materials restoratives materials are warranted. Within the limitations of this study it was concluded that the use the roughest surface of glass ionomers cements materials, in descending order, was achieved subsequent to the use of metal-reinforced glass ionomers, resin modified glass ionomers and conventional GICs. The material with most heterogeneous structure is metal-reinforced GICs MM (GC).

The size of the hybrid layer is influenced by the material structure, so the conventional GICs materials show a higher wetting capacity of the substrate, which is translated into a higher average size of the hybrid layer than in materials with resin or with metalic particle filler.

No important difference beetwen the fluor contenu of investigated materials was found.

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