Surface Analysis of Contemporary Aesthetic Dental Filling Materials after Storage in Erosive Solutions

ANDREEA BORS[1], IULIAN ANTONIAC[2], COSMIN COTRUT[2], AURORA ANTONIAC[2*], MELINDA SZEKELY[1]

[1]University of Medicine and Pharmacy, Faculty of Dental Medicine,67A Gheorghe Petrascu,031593,Tîrgu Mures, Romania

[2] University Politehnica of Bucharest,Materials Science and Engineering Faculty, 313 Splaiul Independentei,060042,Bucharest, Romania

Clinical performance of restorative materials and their adhesive interfaces can be affected by erosion after rehabilitation of erosive lesions. The aim of the present in vitro study was to evaluate the erosive wear resistance and adhesive bond strength of direct restorative materials, using four different testing tools. Four aesthetic dental filling materials were included in the study: a universal nano-filled composite, a light curing posterior filling composite resin, a tooth-coloured polyacid modified composite resin (compomer) and a coloured compomer indicated in restorations of deciduous teeth. Fifteen specimens were prepared according to each of the four tested restorative materials. Following manufacturers' instructions for the manipulation/ mixing of the materials, adhesive systems and unset pastes were placed in cavities of 4mm length, 3mm width and 1mm depth prepared in bovine extracted teeth and cured. After 24 hours of rehydration in distilled water, each group was immersed in erosive solutions chosen for testing: 1% citric acid and 0.02% phosphoric acid. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used in order to analyze the degrees of erosive wear of the materials following exposure to the various erosive solutions. Also, microtensile bond strength (μTBS) was made and the obtained data was analyzed by one-way ANOVA test and two-sample t-test, with a level of significance that was set at $p<0.05$. Experimental results reveal that the dental filling materials showed different behaviour under the same erosive conditions. These findings suggest that erosive wear resistance of direct dental restoratives could influence their longevity in intraoral acidic conditions.

Keywords: dental materials, composites, erosive, wear, microscopy, bond strength.

The improvement in life quality and longevity with the consequent longer maintenance of the teeth in the oral cavity, significantly increased the prevalence and severity of tooth wear in the world population. In addition to that, the combination of factors such as higher consumption of acidic foods and the presence of psychosomatic eating disorders transformed dental erosion in a disorder of great concern to dentists and also in an important and increasing issue worldwide addressed by the researchers [1]. Defined as an irreversible loss of dental hard tissue due to chemical mechanisms, dental erosion does not involve acids derived from oral bacteria, such as the dental caries, but, chelating substances and acids derived from the diet, medication and occupational intrinsic sources [1, 2]. With the development of adhesive systems and within the concepts of minimally invasive restorative treatment the direct composite restorations are conservative procedures that can rehabilitate teeth affected by erosion [3]. Furthermore, it is conceivable that patients will fall back into their old *erosive behaviour* after the application of restoratives [2, 4, 5], therefore the clinical performance of the dental materials and adhesive interfaces can be affected.

Many previous reports have found dental erosion to be significantly associated with the diet factors [6], particularly soft drinks consumption [7]. Unfortunately, consumption of acidic soft drinks has increased continuously during the recent decades in both developed and developing countries [2] and might have led to the increased prevalence of dental erosion [3, 8]. The harmful effects of these beverages include enamel or dentin erosion, dental material and adhesion alteration [9, 10]. Hence, a number of studies described erosion dynamics by acidic beverages, associated or not with abrasion on enamel [8-11, 13] or dentine [12, 14]. Conversely, there is less evidence on the impact of erosive drinks on aesthetic coloured restoratives and on adhesive bond strength between tooth and material [1, 15, 16].

Only few studies have been conducted to investigate any detectable damage on the adhesion of hybrid composite resin samples or other tooth-coloured materials under persisting erosive conditions using dietary acids [1, 17]. Given the growing use of these restoratives and the wide spread use of soft drinks in diet it seemed worthwhile to conduct further studies in this regard.

The aim of this study was to determine the surface changes of contemporary dental direct restoratives subjected to an erosive challenge and the quality of the aesthetic material-tooth structure bonded interfaces using scanning electron microscopy, atomic force microscopy and microtensile bond strength. It was aimed to provide information on aesthetic dental filling materials regarding their relative abilities to resist to erosive attack. The tested experimental hypothesis was that exposure to erosive solutions would influence surface degradation, chemical composition and the created resin–dentine interfaces of the evaluated dental restoratives.

Experimental part

Material and methods

Four aesthetic dental filling materials (shown in table I) were included in the study: (1) a universal nano hybrid composite; (2) a light curing posterior filling composite resin; (3) a tooth-coloured polyacid modified composite

---

* *email: antoniac.aurora@gmail.com; Phone: 0745206509* *All authors have participated equally in developing this study*

resin (compomer), and (4) a coloured compomer indicated in restorations of deciduous teeth.

Sixty bovine teeth were stored in 0.5 % chloramine solution at 4 °C until the beginning of the experiment. A low-speed diamond saw (Isomet, Buehler Ltd., IL, USA) was used to create standardized cavity moulds of 4mm length, 3mm width and 1mm depth and the surface was cleaned with wet cotton in distilled/deionized water to remove any remnants. An all in one adhesive system was applied in the dental cavities according to manufacturers' instructions and light cured. The polymerization procedure was carried out for the manufacturers' recommended exposure time, using a light-curing equipment (Demetron II, Kerr Corporation). Following instructions for the manipulation/mixing of the materials, unset pastes were placed in the cavity moulds covered with celluloid bands and cured. Each increment of ≈ 1 mm thick was light cured using Demetron II lamp and the light intensity was monitored by means of radiometer (Curing Light Meter 105, Demetron Research Corporation, USA). Fifteen specimens were prepared according to each of the four tested restorative materials, using the same adhesive system.

The erosive solutions chosen for testing were: 1% citric acid and 0.02% phosphoric acid, respectively. These solutions represent the most common acids found in soft drinks. The using of generic formulae for solutions preparation was used as the citric and phosphoric acid concentration of beverages varies between batches and is difficult to preserve for prolonged periods: (1) 1.0% citric acid (*p*H 3.6) as proposed by Shellis et al.[22]; (2) 0.02% solution of phosphoric acid, found to result in a *p*H of 2.74, which is the *p*H of most of the traditional cola drinks [23].

The specimens (n=60) were stored individually for 24 hours in distilled water to achieve rehydration and dried with filter paper. Each sample group consisting of dental materials previously presented (G$_{1;}$ n=15, G$_{2;}$ n=15, G$_{3;}$ n=15, G$_{4;}$ n=15) was randomly distributed to three subgroups (n=5): two groups were assigned to one of the immersion media used and the third was the control group (CG) which was not subjected to erosive treatment. The subgroup specimens were immersed individually in 40 mL of 1% citric acid (CA) and 0.02% phosphoric acid (PA), respectively for a period of 8 h. The containers were incubated at 37°C under constant slow agitation using an Orbital Incubator (Biosan, Latvia).

The specimens were air dried, mounted on aluminum stubs and then examined using a scanning electron microscope type FEI QUANTA 3D FEG dual beam in high vacuum using EDT detector. The SEM images were used to view surface damage on dental materials. The surface details at higher level of the sample, for controls (CG) and for CA and PA treated specimens, have been acquired in air with a commercial AFM instrument (Veeco, Germany) operating in tapping mode.

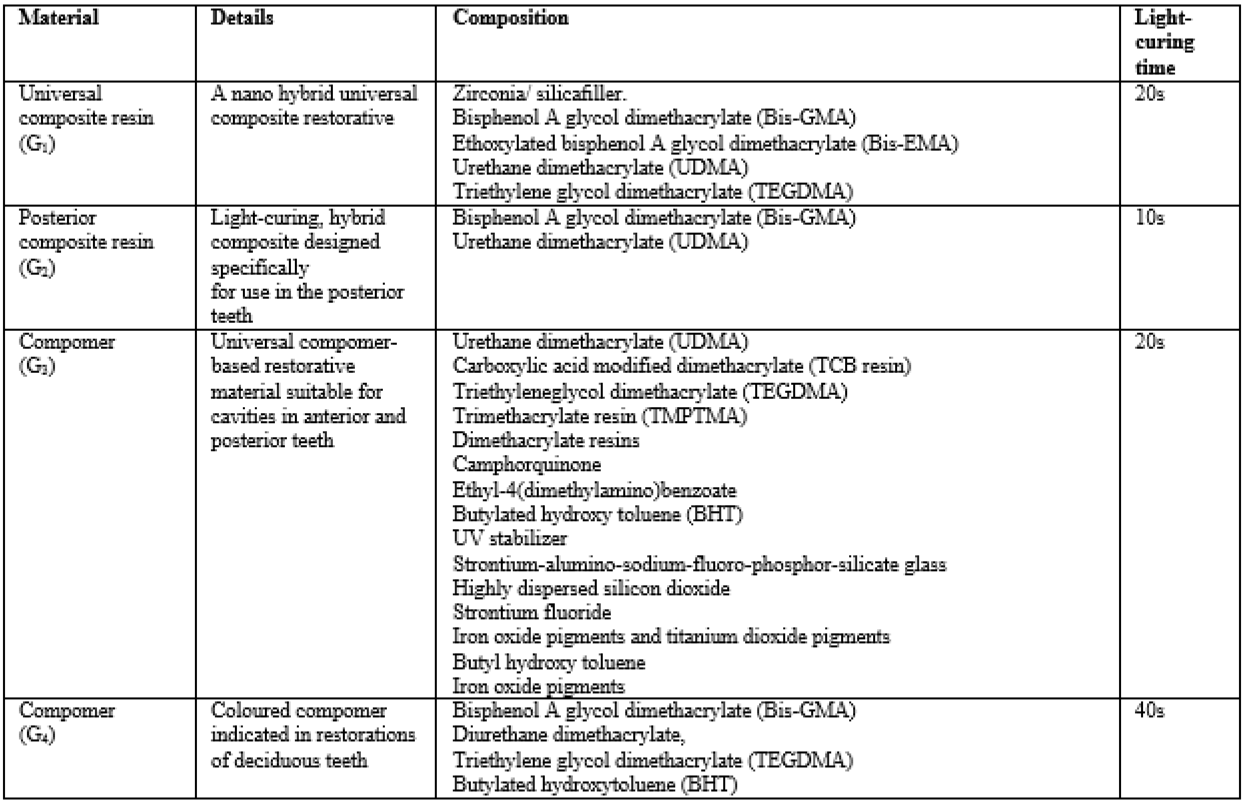
The teeth were individually fixed to a sectioning block mounted on an acrylic resin. Each specimen was serially sectioned in the occlusogingival direction producing 3 mm thick slabs, free from the root and were termed as beams. For group-G$_1$ and G$_2$ beams consisted of resin composite in the upper third and dentin in the lower two thirds while in group G$_3$ and G$_4$ beams were made of compomers upper and dentine lower. Fifteen specimens of each group were taken for micro-tensile bond strength test having cross-sectional area 3 mm × 3 mm. The beams were then attached to a custom made Jig Prepared by Electrical Discharge Machine by cyanoacrylate glue. The jig with specimen was fixed in a micro-tester. Micro-tensile force was applied parallel to long axis of each specimen at a crosshead speed of 1 mm/min until the beam fractured. The tensile load at which the fracture occurred was recorded.

Results and discussions

The experimental results obtained after the surface analysis using scanning electron microscopy and atomic force microscopy are shown in figure 1-4, for each type of dental materials in similar storage conditions.

Table 1

EXPERIMENTAL MATERIALS USED IN THIS STUDY FOR DIFFERENT GROUPS



Material	Details	Composition	Light-curing time
Universal composite resin (G$_1$)	A nano hybrid universal composite restorative	Zirconia/ silicafiller. Bisphenol A glycol dimethacrylate (Bis-GMA) Ethoxylated bisphenol A glycol dimethacrylate (Bis-EMA) Urethane dimethacrylate (UDMA) Triethylene glycol dimethacrylate (TEGDMA)	20s
Posterior composite resin (G$_2$)	Light-curing, hybrid composite designed specifically for use in the posterior teeth	Bisphenol A glycol dimethacrylate (Bis-GMA) Urethane dimethacrylate (UDMA)	10s
Compomer (G$_3$)	Universal compomer-based restorative material suitable for cavities in anterior and posterior teeth	Urethane dimethacrylate (UDMA) Carboxylic acid modified dimethacrylate (TCB resin) Triethyleneglycol dimethacrylate (TEGDMA) Trimethacrylate resin (TMPTMA) Dimethacrylate resins Camphorquinone Ethyl-4(dimethylamino)benzoate Butylated hydroxy toluene (BHT) UV stabilizer Strontium-alumino-sodium-fluoro-phosphor-silicate glass Highly dispersed silicon dioxide Strontium fluoride Iron oxide pigments and titanium dioxide pigments Butyl hydroxy toluene Iron oxide pigments	20s
Compomer (G$_4$)	Coloured compomer indicated in restorations of deciduous teeth	Bisphenol A glycol dimethacrylate (Bis-GMA) Diurethane dimethacrylate, Triethylene glycol dimethacrylate (TEGDMA) Butylated hydroxytoluene (BHT)	40s

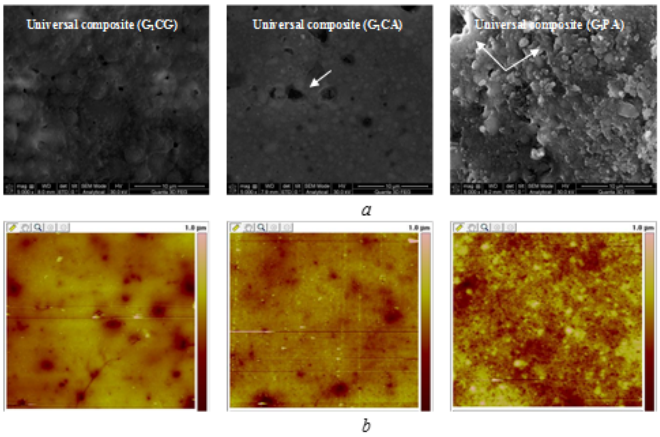


Fig. 1 Result of microscopically surface analysis illustrating the differences on the morphological pattern compared to control group (CG) of restoratives after cycling in citric acid (CA) and phosphoric acid (PA). A–C: Universal composite resin showing an eroded surface with loss of filler particles (white arrows) (magnification 5000×)

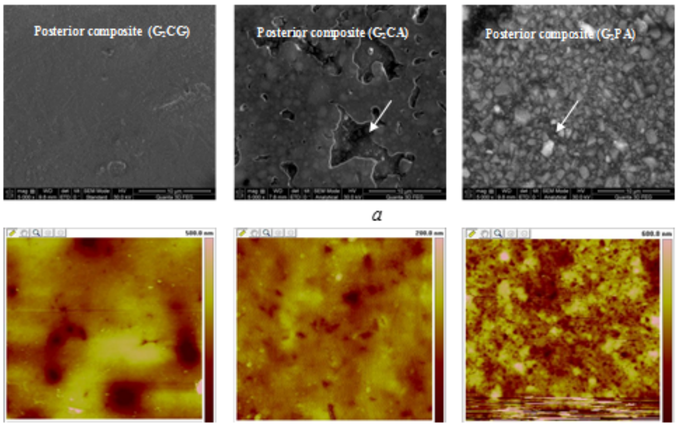


Fig. 2. Result of microscopically surface analysis illustrating the differences on the morphological pattern compared to control group (CG) of restoratives after cycling in citric acid (CA) and phosphoric acid (PA): a) SEM results (magnification 5000×); AFM results

Scanning electron microscopy images micrographs of nanohybrid universal restorative exposed to CA and PA (fig. 1) showed extensive surface changes associated with missing areas of some particles.

The posterior hybrid composite resin showed minimal surface changes in group exposed to CA as compared to CG (fig. 2). Filler particles on the control group appeared unaffected for the first three tested materials showing a relatively smooth surface without evidence of matrix degradation.

The aesthetic polyacid modified resin exhibited reduced changes in filler particles when exposed to CA and PA (fig. 3).

For coloured polyacid modified resin small particles were completely missing in the CG, whereas large particles experienced considerable surface loss which extended into the interface between particles and matrix, when exposed to CA and PA (fig.4).

Among the four restorative materials tested, the most severe changes in the surface morphology were found in coloured compomer caused by erosive attacks, followed by universal composite and posterior composite.

The microtensile bond strength data expressed as mean and standard deviation (SD) are shown in table 2.

The increased occurrence of dental erosion combined with the lack of research on erosive resistance of adhesively fixed direct dental resotratives, led to the decision to carry out this in vitro study. In 2011 Sauro et al [15] investigated using confocal microscopy (CLSM), AFM nano-indentation and microtensile bond strength test (TBS) the quality of the resin–dentin interfaces conditioned with phosphoric acid or EDTA. It was found that HEMA-containing adhesive applied onto H_3PO_4-etched ethanol or water-wet dentin created hybrid layers with the lowest biomechanical nano-properties. Zimmerli et al. evaluated the influence of different surface preparation techniques on long-term bonding effectiveness to eroded dentin [16].

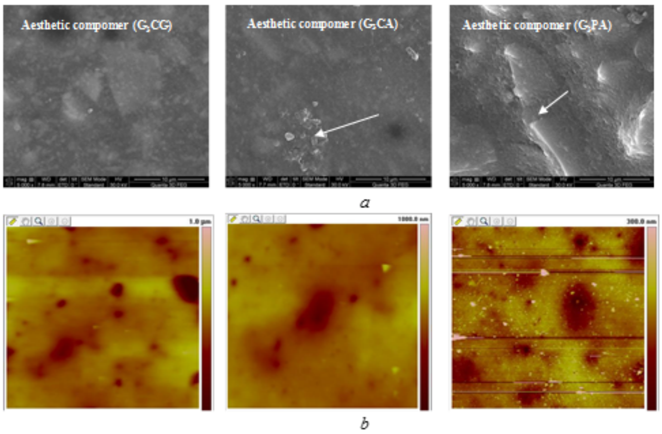


Fig. 3. Result of microscopically surface analysis Representative SEM images illustrating the differences on the morphological pattern compared to control group (CG) of restoratives after cycling in citric acid (CA) and phosphoric acid (PA). G–I: Aesthetic compomer different degrees of erosive wear. (magnification 5000×).

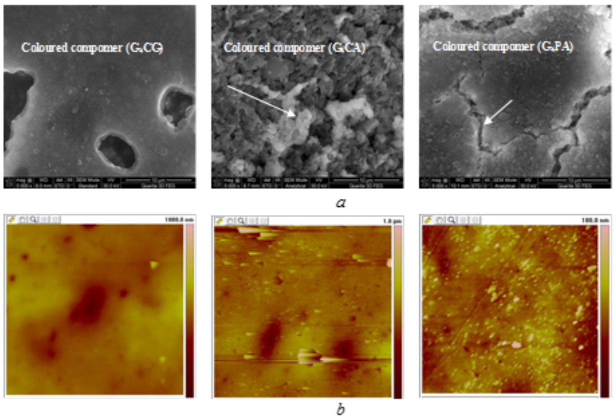


Fig. 4. Result of microscopically surface analysis Representative SEM images illustrating the differences on the morphological pattern compared to control group (CG) of restoratives after cycling in citric acid (CA) and phosphoric acid (PA). J–L: Coloured samples showing eroded areas (white arrows) in the surface of the restoration; (magnification 5000×)

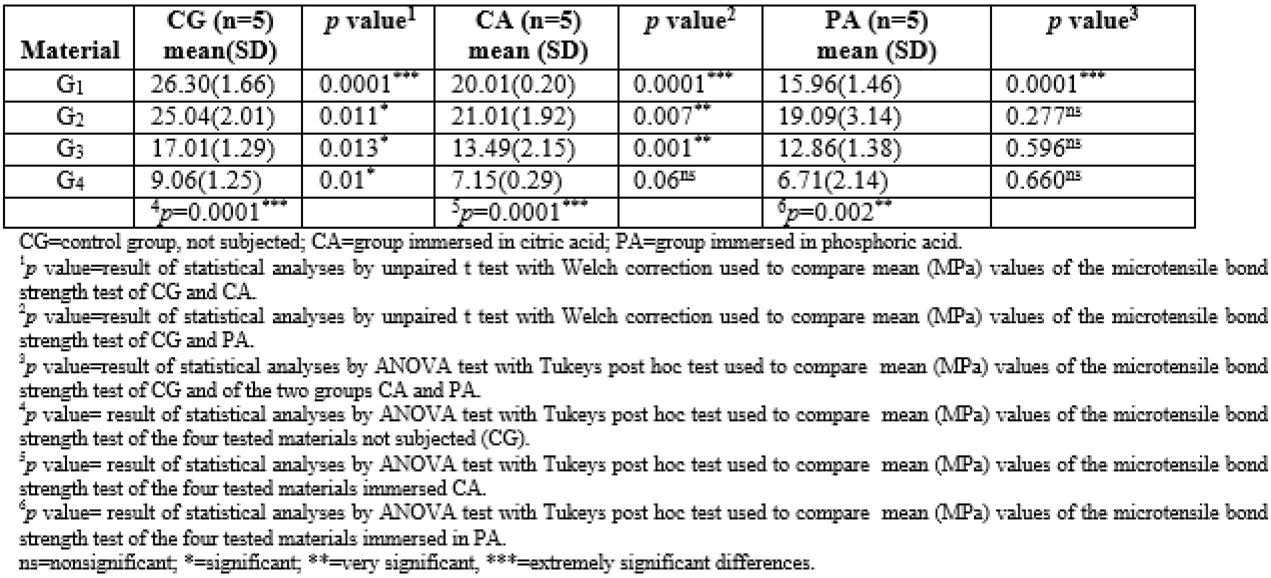
A review published in 2013 by Attin and Wegehaupt regarding the impact of erosive conditions on tooth-coloured restoratives, mentioned that in literature information on the behaviour of dental filling materials under still persisting erosive conditions are limited [2].

In all the fields of science and technology the relationship between the structure, chemical composition and properties of a material is a critical issue for its desired functionality. Nowadays it is possible to investigate this relationship with the strength of the nanoscale, and recently also the field of dental materials is undergoing extensive application of nanoscience and nanotechnology concepts, including atomic force microscopy [18 - 21].

The samples that were pH cycled presented significant mineral and morphological changes. The three-

Table 2

MEAN (MPa) AND STANDARD DEVIATION (SD) VALUES OF THE MICROTENSILE BOND STRENGTH TEST



Material	CG (n=5) mean(SD)	p value[1]	CA (n=5) mean (SD)	p value[2]	PA (n=5) mean (SD)	p value[3]
G_1	26.30(1.66)	0.0001^{***}	20.01(0.20)	0.0001^{***}	15.96(1.46)	0.0001^{***}
G_2	25.04(2.01)	0.011^{*}	21.01(1.92)	0.007^{**}	19.09(3.14)	0.277^{ns}
G_3	17.01(1.29)	0.013^{*}	13.49(2.15)	0.001^{**}	12.86(1.38)	0.596^{ns}
G_4	9.06(1.25)	0.01^{*}	7.15(0.29)	0.06^{ns}	6.71(2.14)	0.660^{ns}
	[4]$p=0.0001^{***}$		[5]$p=0.0001^{***}$		[6]$p=0.002^{**}$	

CG=control group, not subjected; CA=group immersed in citric acid; PA=group immersed in phosphoric acid.

[1] p value=result of statistical analyses by unpaired t test with Welch correction used to compare mean (MPa) values of the microtensile bond strength test of CG and CA.

[2] p value=result of statistical analyses by unpaired t test with Welch correction used to compare mean (MPa) values of the microtensile bond strength test of CG and PA.

[3] p value=result of statistical analyses by ANOVA test with Tukeys post hoc test used to compare mean (MPa) values of the microtensile bond strength test of CG and of the two groups CA and PA.

[4] p value= result of statistical analyses by ANOVA test with Tukeys post hoc test used to compare mean (MPa) values of the microtensile bond strength test of the four tested materials not subjected (CG).

[5] p value= result of statistical analyses by ANOVA test with Tukeys post hoc test used to compare mean (MPa) values of the microtensile bond strength test of the four tested materials immersed CA.

[6] p value= result of statistical analyses by ANOVA test with Tukeys post hoc test used to compare mean (MPa) values of the microtensile bond strength test of the four tested materials immersed in PA.

ns=nonsignificant; *=significant; **=very significant, ***=extremely significant differences.

dimensional representation of the surface gives a realistic impression of a relatively smooth surface for the aesthetic compomer, with some flat narrow grooves for the coloured compomer. The surface quality of the products investigated differs significantly. During erosive degradation, calcium from the restoratives are dissolved, which eventually leads to a collapse of the surface structure [22-24]. Therefore, determination of chemical dissolution by assessing the amount of calcium is important for assessing dental materials erosive behaviour [24]. The results of the present study showed that G_2 and G_3 had significantly lower degree of chemical degradation compared to G1 and G4 after acid exposure.

Although erosion-inhibiting effects of fluoride have been reported by many studies [25, 26], there is limited information concerning clinically relevant changes to the restorative materials that may take place when restored teeth are subjected to erosive attack. In previous studies, amount of mineral dissolved by erosive drinks, acids and foodstuffs was assessed [24, 27].

SEM images showed differences on the morphological pattern of the tested materials. Among all materials tested, the coloured compomer (developed for the restoration of deciduous teeth) showed the most significant surface degradation and substance loss. Based on the above results, the experimental hypotheses that different erosive agents have a different effect on restorative materials composition affecting their adhesion with the dental hard structures under the testing conditions, were therefore accepted.

The findings are in agreement with a previous study [23] demonstrating the effectiveness of resin containing materials in providing protection of enamel in advanced cases of erosion. Composite resin and porcelain restorations had the best chemical resistance to erosion among all the materials (composite resin, glass ionomers, resin modified glass ionomers and porcelain) in the study conducted in 2010 by Wan Bakar [23].

In contrast to the present study results, other studies revealed significant differences in surface appearance and composition of composite resins and polyacid modified resins. Aliping and McKenzie [28] assessed the effect of Coca-Cola and fruit juices on the surface hardness of glass–ionomers and ‘compomers’. The results showed that all materials presented similar results, sharp reductions in surface hardness in acidic beverages [28]. This may be due to the different application time between the previous and the present study (1 week, 1, 3, 6, 12 month *vs.*8 h) or related to the distinct composition and structure of the tested restorative materials.

There are important variations in the composition of different dental restorative materials, even within the same categories, and it is rather difficult to generalize the results as only four materials out of two types of dental restoratives (composite resins and compomers) were investigated in the current study. However, extrapolation from the present findings indicated that posterior composite resin and aesthetic compomer have the best resistance to erosive attack among the tested restorative materials. Based on the present evidence, coloured compomers might be more vulnerable to acid attack than aesthetic polyacid-modified resin composites. However, these hypotheses need to be explained with caution and clarified with further studies.

The SEM images showed that all the materials had morphological surface changes after erosive attack. In the present study, atomic force microscope (AFM) was used as a tool to study at high level of magnification and on some small areas the surface structural morphology and roughness of direct dental restoratives subjected to erosion. AFM is not only a tool to image and characterize the topography of solid surfaces at high resolution. In this study, AFM was selectively used to characterize the structural changes of erosively demineralized dental filling materials because it has an advantage over the other ultra-high vacuum measuring equipments, such as SEM [29-33].

Erosion was shown to negatively affect the bond strength, as also reported previously by Zimmerli et al. [16]. For the adhesive system evaluated, the adhesion to dentin was compromised. In our study the bond strength evaluation revealed the highest values for G_1 and the lowest for G_4.These results should be considered before the restorative treatment in patients with erosive behaviour.

In vitro studies are generally difficult to extrapolate to conditions *in vivo* but they have the advantage that individual parameters such as erosion time, erosive agents and pH values can be controlled. However, extrapolation of laboratory research into *in vivo* condition is difficult as the absence of pellicle and saliva. The saliva is considered the most important biological factor influencing dental erosion due to its ability to act directly on the erosive agent itself by diluting, clearing, neutralizing, and buffering acids. The saliva also plays a role in forming a protective membrane, and to reduce the demineralization rate and enhance remineralization to eroded enamel and dentine [27, 34].

The present results have to be interpreted within the frame of the study design. Both acid exposure regimens may represent exaggerated clinical conditions and our study can therefore only be assumed as a pilot for further studies and for clinical approaches in particular. Further *in situ* or *in vivo* studies are needed to determine the acid resistance of restorative materials.

Conclusions

Within the limitation of this *in vitro* study, we concluded that aesthetic polyacid modified resins exhibit greater erosive resistance than coloured compomers and universal nano hybrid restoratives. Therefore material selection should be considered when planning restorations in patients who experiencing erosive tooth surface loss. AFM has proven to be an efficient tool capable to characterize the changes in surface of dental restorative materials and the variations in surface nano-mechanical properties enabling more clear understanding of the structural/ properties correlation associated with erosive factors.

Acknowledgment.The study was supported by the Internal Research Grant no. 5/30.01.2013 of the University of Medicine and Pharmacy of Tîrgu Mures.

References

1. RAMOS T.M., RAMOS-OLIVEIRA T.M., DE FREITAS, Lasers Med Sci., **30(1)**, 2015, p.17.
2. ATTIN T, WEGEHAUPT F.J., Dent Mater., **S0109-5641(13)**, 2013, p.181.
3. WANG X, LUSSI A., Dent Clin N Am, **54**, 2010, p.565.
4. CORRER GM, ALONSO RCB, CORREA MA, CAMPOS EA, BARATTO-FILHO F, PUPPIN-RONTANI RM., J Dent Child, **76**, 2009, p.181.
5. ELTON V, COOPER L, HIGHAM SM, PENDER N., J Dent, **7**, 2009, p.336.
6. GURGEL CV, RIOS D, DE OLIVEIRA TM, TESSAROLLI V, CARVALHO FP., Int J Paediatr Dent, **21**, 2011, p.50.
7. LI H, ZOU Y, DING G., PLoS ONE, **7(8)**, 2012, p.42626.
8. LUSSI A, JAEGGI T, ZERO D., Caries Res, **38(S1)**, 2004, p.34.
9. NAVARRO R, VICENTE A, ORTIZ AJ, BRAVO LA., Eur J Orthod, **33(1)**, 2011, p.60.
10. YIP HH, WONG RW, HAGG U. World J Orthod, **10(1)**, 2009, p.33.
11. BARBOSA CS, MONTAGNOLLI LG, KATO MT, SAMPAIO FC, BUZALAF MAR., J Dent., **37(12)**, 2009, p.913.
12. KATO MT, BUZALAF MAR., J Appl Oral Sci, **20(3)**, 2012, p.318.
13. JAWALE BA, BENDGUDE V, MAHULI AV, DAVE B, KULKARNI H, MITTAL S., J Contemp Dent Pract., **13(2)**, 2012, p.201.
14. BARBOSA CS, KATO MT, BUZALAF MAR., Aust Dent J., **56(3)**, 2011, p.317.
15. SAURO S, OSORIO R, WATSON TF, TOLEDANO M., Dent Mater., **28(6)**, 2012, p.622.
16. ZIMMERLI B, DE MUNCK J LUSSI A, LAMBRECHTS P, VAN MEERBEEK B., Clin Oral Investig., **16**, 2012, p.1451.
17. FATIMA N, ABIDI SY, QAZI FU, JAT SA., Saudi Dent J., **25(1)**, 2013, p.29.
18. HABELITZ S, BALOOCH M, MARSHALL SJ, BALOOCH G, MARSHALL GW., Journal of Structural Biology, **138**, 2002, p.227.
19. BALOOCH M, HABELITZ S, KINNEY J, MARSHALL S, MARSHALL G. Journal of Structural Biology, **162**, 2008, p.404.
20. FAWZY AS, AMER MA, EL-ASKARY FS., Journal Adhesive Dentistry, **10**, 2008, p.135.
21. SHARMA S, CROSS S, HSUEH C, WALI R, STIEG A, GIMZEWSKI J., Int J Mol Sci, **11**, 2010, p.2523.
22. SHELLIS RP, GANSS C, REN Y, ZERO DT, LUSSI A., Caries Res, **45(S1)**, 2011, p.69.
23. WAN BAKAR WZ, MCINTYRE JM., Saarbrucken, Lambert Academic Publishing, 2010.
24. SOARES LE, LIMA LR, VIEIRA LDE S, DO ESPIRITO SANTO AM, MARTIN AA., Microsc Res Tech., **75(6)**, 2012, p.703.
25. YU H, BUCHALLA W, CHENG H, WIEGAND A, ATTIN T. , Dent Mater J , **31(3)**, 2012, p.433.
26. WIEGAND A, SCHNEIDER S, SENER B, ROOS M, ATTIN T. Caries Res, **48(2)**, 2014, p.154.
27. DOMICIANO SJ, COLUCCI V, SERRA MC., J Biomed Mater Res Part B: Appl Biomater., **93B**, 2010, p.304.
28. ALIPING-MCKENZIE M, LINDEN RWA, NICHOLSON JW., Journal of Oral Rehabilitation, **31**, 2004, p.1046.
29. JANDT KD., Surface Science, **491**, 2001, p.303.
30. MANOLEA H., ANTONIAC I., MICULESCU M., RICA R., PLATON A., MELNICENCO R., J. Adhes. Sci. Technol., **30(16)**, 2015, p.1-11.
31. ANTONIAC I., BURCEA M., IONESCU R.D., BALTA F., Mat. Plast., **52,** no.1, 2015, p.109-112.
32. GAREA S.A., MIHAI A.I., GHEBAUR A., Mat. Plast., **52,** no.3, 2015, p.275
33. MARINESCU R., ANTONIAC I., LAPTOIU D., ANTONIAC A., GRECU D., Mat. Plast., **52,** no.3, 2015, p. 340
34. LUSSI A, LUSSI J, CARVALHO TS, CVIKL B., Eur J Oral Sci, **122(5)**, 2014, p.353.

Manuscript received: 21.03.2016