Microhardness and Surface Roughness of Glass Ionomer Cements after APF and TiF_4 Applications

Topaloglu-Ak A * / Cogulu D ** / Kocatas Ersin N *** / Sen BH ****

Objective: *To evaluate whether TiF_4 solution and APF gel had any adverse effects on the surface morphology of newly developed glass ionomers.* ***Study Design:*** *Fifteen disc-shaped specimens of Fuji IX Extra, Fuji II LC and Ketac N100 were prepared and stored in 2 ml of artificial saliva at 37°C for 8 weeks. Specimens of each material were divided randomly into three subgroups as 1 and 4 minutes application of 1.23% APF gel and 1 minute application of 1% TiF_4 solution. Specimens were reaged for another 8 weeks. Microhardness, surface roughness values and surface morphology were evaluated by using Vicker's hardness test, surface profilometry and scanning electron microscopy (SEM) for all time interventions, respectively. One-way Anova test was performed and differences were compared by Tukey's HSD and Dunnet T3 test.* ***Results:*** *APF and TiF_4 applications decreased microhardness significantly in Fuji II LC. In Fuji IX Extra microhardness decreased significantly after 1- and 4-min APF applications. Ketac N100 showed no difference in microhardness after APF and TiF_4 applications. Surface roughness was not affected at any time interval for three restorative materials.* ***Conclusion:*** *Within the limitations of this vitro study, it was revealed that, potential adverse effects of APF and TiF_4 applications might be material dependant. Hence, restorative materials should be selected in accordance with kind, frequency and application time of fluoridation to avoid deteriorations of the restorations.*

Keywords: *microhardness, surface roughness, APF, TiF_4*
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INTRODUCTION

Glass ionomer cements (GIC) have evolved as the demands have changed over the course of time in dentistry. Today, clinicians aim to elevate not only mechanical properties and esthetics, but also resistance of the restorative materials to chemical wear for a long lasting clinical success.[1-3]

Developments in GIC resulted in wide range of alternatives for clinical application such as resin modified glass ionomers (RMGIC). However, improvements in mechanical and physical properties of restorative materials go on with the application of nanotechnology in the field of dental materials.[4] More recently, a new RMGIC have been introduced in the market which is also classified as nano-ionomer because its formulation is based on bonded nano-filler technology. In addition to improved mechanical properties, it is claimed to release high fluoride as well.[5-6]

These restorative materials are often recommended for patients with a high caries risk who receive preventive treatments based on fluoride containing dentrifices, mouth rinses and topical applications of fluoride gels.[7]

Today in the market, there are different alternatives for professionally applied fluoride gels with different composition and pH values which may alter the surface morphology of restorative materials. Sodium fluoride (NaF), acidulated phosphate fluoride (APF), stannous fluoride (SnF_2) and amine fluoride (AmF) are fluoride agents selected over the years for caries prevention. Many other agents have been investigated for caries prevention.[8] Today, TiF_4 is suggested as an alternative in preventing hypersensitivity and erosion.[9–11] However its effect on restorative materials have not been investigated up to date. Currently, ideal concentration and required time for fluoride agents is still questionable for interfering demineralization and avoiding any damage to the restorations in the oral cavity.[12]

* Asli Topaloglu-Ak, DDS, PhD, Assoc. Professor, Department of Pedodontics, Ege University, School of Dentistry, Bornova, Izmir, Turkey.
** Dilsah Cogulu, DDS, PhD, Assoc. Professor, Department of Pedodontics, Ege University, School of Dentistry, Bornova, Izmir, Turkey.
*** Nazan Kocatas Ersin DDS, PhD, Assoc. Professor, Department of Pedodontics, Ege University, School of Dentistry, Bornova, Izmir, Turkey.
**** Bilge Hakan Sen, DDS, PhD, Professor, Divison of Endodontology, Ege University, School of Dentistry, Bornova, Izmir, Turkey.

Send all correspondence to: Dr. Asli Topaloglu-Ak, Ege University School of Dentistry Pedodontics Department, Bornova, Izmir, Turkey, PK: 35100

Phone: 00 90 532 33 181 33
Fax : 00 90 232 323 03 25

E-mail: aslitopaloglu@yahoo.com

There is a clear need of research on the possible adverse effects of topical fluoride agents on newly developed glass ionomer restorative materials. Therefore, the aim of the present study was to investigate the effects of 1 and 4 minutes application of 1.23% APF gel and 1 minute application of 1% TiF_4 solution on the mechanical and physical properties of a high viscosity glass ionomer; Fuji IX GC Extra (GC Int. Corp., Tokyo, Japan), nano-ionomer; Ketac N 100 (3M ESPE, Seefeld, Germany) and a resin based glass ionomer Fuji II LC (GC Int Corp., Tokyo, Japan).

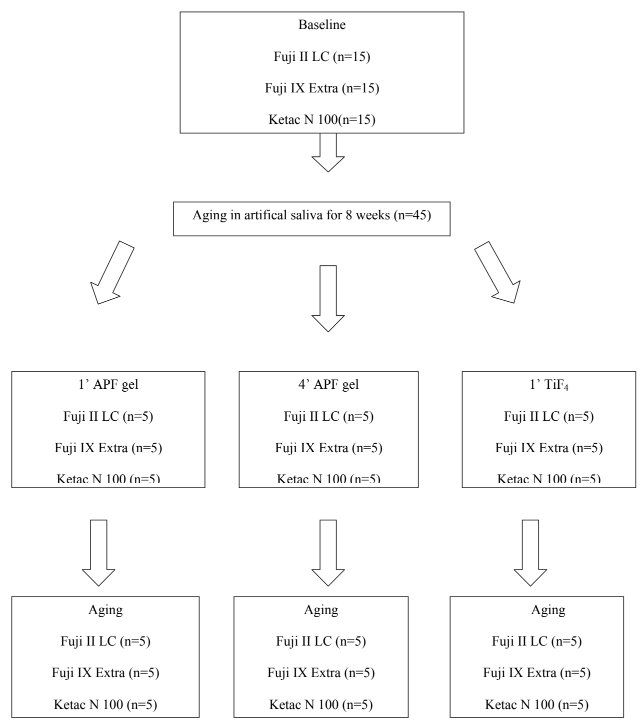
MATERIALS AND METHOD

Fifteen disc-shaped specimens of Fuji IX Extra, Fuji II LC and Ketac N100 were prepared according to manufacturer´s instructions and placed into disposable, Teflon moulds (5 mm diameter X 2 mm thickness) and then pressed between two Mylar-covered glass slides. The resin ionomer cements were light cured from both ends of the moulds for 40 seconds using LED (Bluephase, Ivoclar, Vivadent, Liechtenstein). The distance between the light source and sample was standardized by using a 1 cm glass plate. The light tip was in close contact with the restoration surface during polymerization. All specimens were allowed to set initially for an hour. After setting a total of 45 specimens were removed from their moulds and then baseline microhardness and surface roughness were evaluated from upper and lower sides respectively. Following the measurements, they were placed in small polypropylene vials containing 2 ml of artificial saliva solution (0.05 M acetate buffer with 2.2 mM $CaHPO_4$ adjusted with glacial acetic acid to pH 5.0). The vials were kept at a constant temperature of 37°C. The solutions were replaced daily for 8 weeks. Each time, the specimens were rinsed thoroughly with distilled water. At the end of 8 weeks, all specimens were rinsed with distilled water and evaluated for their microhardness and surface roughness from upper and lower sides again. Following the second measurements, five specimens of Fuji IX Extra, Fuji II LC and Ketac N100 were randomly selected for 1 min. application of 1.23% APF gel, 4 min. application of 1.23% APF gel and 1 min. application of 1% TiF_4 solution respectively (Table 1). Immediately after the fluoride applications, specimens were rinsed with distilled water until there were no remnants of APF gel and TiF_4 solution and they were once again evaluated for their microhardness and surface roughness from upper and lower sides for the third time. After the measurements, they were replaced in small polypropylene vials containing 2 ml of artificial saliva solution for the final aging at a constant temperature of 37°C for another 8 weeks. Solutions were replaced daily and each time and the specimens were rinsed thoroughly with distilled water as previously. Following the aging, final microhardness and surface roughness from upper and lower sides were completed for all the specimens.

Microhardness Evaluation

Microhardness measurements of the investigated surfaces of the specimens were determined by using Vicker's Hardness

Table 1. The study design showing the number of specimens at each time intervals.



Testing Machine (Shimadzu Micro Hardness Tester HMV-2, Shimadzu Corporation, Kyoto, Japan). The Vicker's surface microhardness test method consisted of indenting the test material with a diamond tip, in the form of a right pyramid with a square base and Vicker's microhardness readings were undertaken using a load of 50 g for 20 seconds. Three indentations were made at random on each specimen and a mean value was calculated.

Surface Roughness Evaluation

Surface roughness measurements were recorded for each fresh and aged specimen after 8 weeks and those coated with 1.23%APF gel for 1 and 4 minutes, and 1 minute with 1% TiF_4 solution and after a total of 16 weeks. The Ra was automatically determined using the graphical-centerline method with a cut-off 80 µm according to the ASME Standard Y14.36 (2002).

Scanning Electron Microscopy Evaluation

One specimen from each restorative group (Fuji II LC, Fuji IX Extra, Ketac N 100) was selected at random for all time intervals (baseline, aging, 1 min. APF gel, 4 min. APF gel, 1 min. TiF_4 solution and final aging) in order to evaluate the changes under a scanning electron microscope (SEM). The specimens were mounted on brass stubs, placed in a desiccator containing phosphorous pentoxide for overnight and then sputter-coated with 20 nm-thick gold. All specimens were examined mainly at 500X magnifications.

The data were statistically analyzed first using one-way ANOVA. Then, Tukey's HSD and Dunnet T3 tests were used for multiple comparisons.

RESULTS

The microhardness values per restorative materials and per surface treatments are listed in Table 2, 3 and 4. For all three restorative materials, microhardness increased with aging in buffered artificial saliva however this increase was statistically significant for Fuji II LC and Ketac N100 group (p=0.00). In Fuji II LC group, 1 and 4 min 1.23% APF applications and 1 min. 1% TiF_4 applications decreased microhardness significantly (p=0.00). In Fuji IX group, after 1 and 4 min. APF applications there was a statistically significant decrease in mean microhardness. 1 min. 1% TiF_4 application did not have a significant decreasing effect in microhardness of Fuji IX Extra. Ketac N100 showed no significant difference in the mean microhardness value after APF and TiF_4 applications.

Application time 1 vs 4 min. of APF was found to have no statistically significant difference for microhardness values for Fuji II LC, Fuji IX Extra and Ketac N100. Final aging in artificial saliva generally caused no change in microhardness for Fuji II LC and Fuji IX Extra whereas a statistically significant decrease was noted in Ketac N 100 group.

Surface roughness values for Fuji II LC, Fuji IX Extra and Ketac N100 were reported to show no statistically significant difference after aging in artificial saliva and fluoride applications, (Table 5).

Table 2. Mean microhardness values for Fuji II LC at all time intervals

	Fuji II LC
Baseline	$46,2 \pm 3,18^{a}$
Aging	$67,7 \pm 4,75^{a,b,c,d,e,f,g}$
APF 1 min	$35,5 \pm 6,20^{b}$
APF 4 min	$34,0 \pm 5,08^{c,h,l}$
TiF_4 1min	$43,9 \pm 2,48^{d,h,j}$
APF 1 min + aging	$34,3 \pm 4,12^{e}$
APF 4 min + aging	$33,2 \pm 2,10^{f,j,k}$
TiF_4 1min + aging	$42,8 \pm 3,17^{g,i,k}$

^{a,b,c,d,e,f,g,} **p=0.00** ^{h,i} **p=0.44** ^{j,k}**p=0.43**

Table 3. Mean microhardness values for Fuji IX Extra at all time intervals

	Fuji IX Extra
Baseline	$59,9 \pm 12,46$
Aging	$86,3 \pm 18,79^{a,b,c,d,e}$
APF 1 min	$44,1 \pm 14,68^{a}$
APF 4 min	$38,8 \pm 13,61^{b,f}$
TiF_4 1min	$73,5 \pm 9,32^{f,g}$
APF 1 min + aging	$40, 7 \pm 9,63^{c}$
APF 4 min + aging	$36,4 \pm 10,71^{d,g}$
TiF_4 1min + aging	$50,7 \pm 8,10^{e}$

^{a,b,c,d}**p=0.00** ^{f,g}**p=0.017**

Table 4. Mean microhardness values for Ketac N 100 at all time intervals

	Ketac N 100
Baseline	$32,6 \pm 1,41^{a,b,c,d}$
Aging	$59,5 \pm 4,07^{a,e,f,g}$
APF 1 min	$57,0 \pm 5,09^{b,h,i,j}$
APF 4 min	$56,1 \pm 3,71^{c,k,l,m}$
TiF_4 1min	$58,6 \pm 3,50^{d,n,o,p}$
APF 1 min + aging	$40,6 \pm 4,25^{e,h,k,n}$
APF 4 min + aging	$39,1 \pm 1,0^{f,i,l,o}$
TiF_4 1min + aging	$36,2 \pm 3,02^{g,j,m,p}$

^{a,b,c,d,e,f,g,h,i,j,k,l,m,n,o,p}**p=0.00**

Table 5. Mean surafce roughness values for restorative materials at all time intervals

	Fuji II LC	Fuji IX Extra	Ketac N 100
Baseline	0.12 ± 0.02	0.34 ± 0.07	0.09 ± 0,04
Aging	0.13 ± 0.07	0.34 ± 0.11	0.17 ± 0,17
APF 1 min	0.15 ± 0.06	0.33 ± 0.08	0.18 ± 0,04
APF 4 min	0.15 ± 0.04	0.38 ± 0.17	0.32 ± 0,10
TiF_4 1min	0.10 ± 0.03	0.36 ± 0.08	0.23 ± 0,09
APF 1 min + aging	0.24 ± 0.05	0.57 ± 0.21	0.30 ± 0,09
APF 4 min + aging	0.19 ± 0.11	0.37 ± 0.12	0.37 ± 0,17
TiF_4 1min + aging	0.18 ± 0.07	0.44 ± 0.17	0.25 ± 0,09

SEM findings revealed degradation of glass particles after APF gel and TiF_4 applications for all the restorative materials (Figure 1, 2 and 3). For 1 min. application of APF gel, moderate degradation with pitting or slight cracking of the glass particles and limited number of voids were observed (Figure 1b, 2b and 3b). Generally, 4 min. APF application resulted with more severe cracking and pitting of glass particles whereas considerable numbers of voids were present in the matrix (Figure 1c, 3c). After TiF_4 application, surface coating with microcracks corresponding to the titanium deposits were noted (Figure 1d, 2d and 3d).

DISCUSSION

Glass ionomer cements are susceptible to changes in surface morphology when treated with topical agents.[13-17] Studies revealed that various APF topical agents etches and reacts with the restorative materials due to the hydrofluoric acid used in the preparation of APF.[15,18,19] In earlier conventional GIC's, the glass particles were either lost or left protruded after 4 minutes application of APF gel.[20] It is reported that, the amount of surface material lost is proportional to the time of exposure.[12,21] Yet the application time of the APF gel is recommended in a range of 1 to 4 minutes which might have different effects on the surface morphology of the restorative materials. Hence in the present study 1 and 4 minutes application of 1.23% APF were chosen. However,

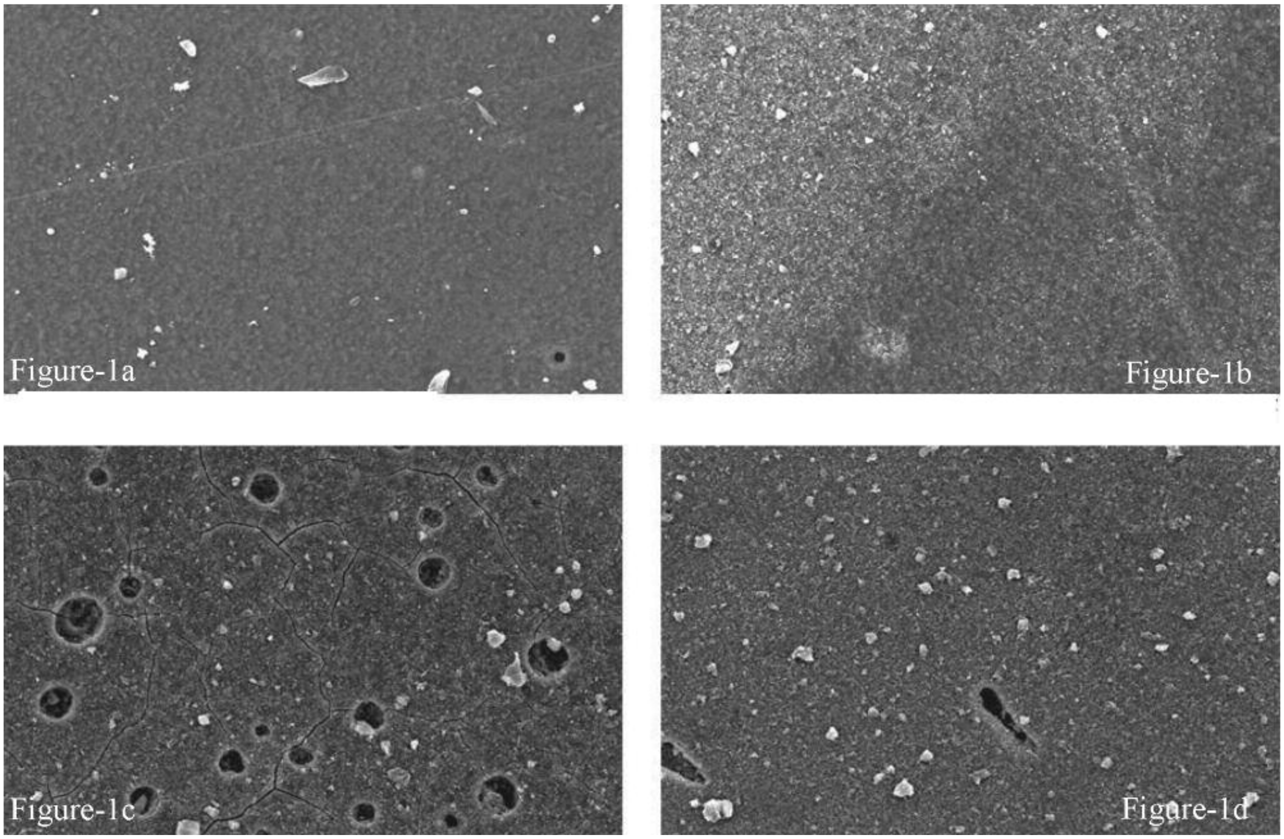


Figure 1a. Fuji II LC at baseline at 500X
Figure 1b. Fuji II LC after 1 min 1.23% APF application at 500X
Figure 1c. Fuji II LC after 4 min 1.23% APF application at 500X
Figure 1d. Fuji II LC after 1 min 1% TiF4 application at 500X

there is incosistency in dental literature about the application time of TiF_4 varying among 1 min., 2 min. and 4 minutes.[8,10,11] Since it is well established that glass ionomers exhibit degradation when subjected to low pH or acidic environment. 1% TiF_4 solution with an application time of 1 minute was preferred in the present study. This is the first study to investigate the effects of TiF_4 on newly developed glass ionomer restorative materials and compare it with professionally applied 1.23% APF gel.

In order to imitate the oral cavity, samples were immersed in artificial saliva at 37°C. It has been reported that different formulations of artificial saliva and storage media have different effects on the mechanical and physical properties of the restorative materials.[22-24] The artificial saliva used in our study (0.05 acetate buffer with 2.2 mM $CaHPO_4$ adjusted with glacial acetic acid to pH 5.0) have been used previously to test surface roughness and microhardness.[13,14] There are number of techniques and methods to imitate the oral cavity. However it is well known that in order to stimulate the biological condition in the mouth using currently available measuring techniques, in situ studies are more feasible.

In the present study after aging in buffered artificial saliva, microhardness increased for all restorative materials. However, this increase was significant only for RMGIC and nanoionomer. Our results are in line with the previous studies which reveal that during cements maturation phase, glass ionomer cements surface hardness increases due to exchange of ions in saliva.[25] Following APF applications, both HVGIC and RMGIC decreased significantly. After TiF_4 application decrease was noted only for RMGIC. There was no significant change in microhardness for nanoionomer after APF and TiF_4 applications. This could be attributed to the nanotechnology used in the nanoionomers which is claimed to be more resistant.[26] It is also well known that, the number and size of voids incorporated during mixing and placement of restorative materials affect their mechanical characteristics.[27]

In the present study, TiF_4 solution did not show aggressive effect on the restorative materials based on our results and SEM findings. This could be attributed to the application of 1% TiF_4 solution. It has been reported that the application method may be of considerable importance.[8] In the present study we applied the 1% TiF_4 solution without any rubbing action. In a pilot study by van Rijkom *et al*, TiF was applied by using a cotton pellet with rubbing action as described by Büyükyılmaz *et al* [28] and profilometric analysis showed that there was a loss of 6-8 μm loss of surface ena-

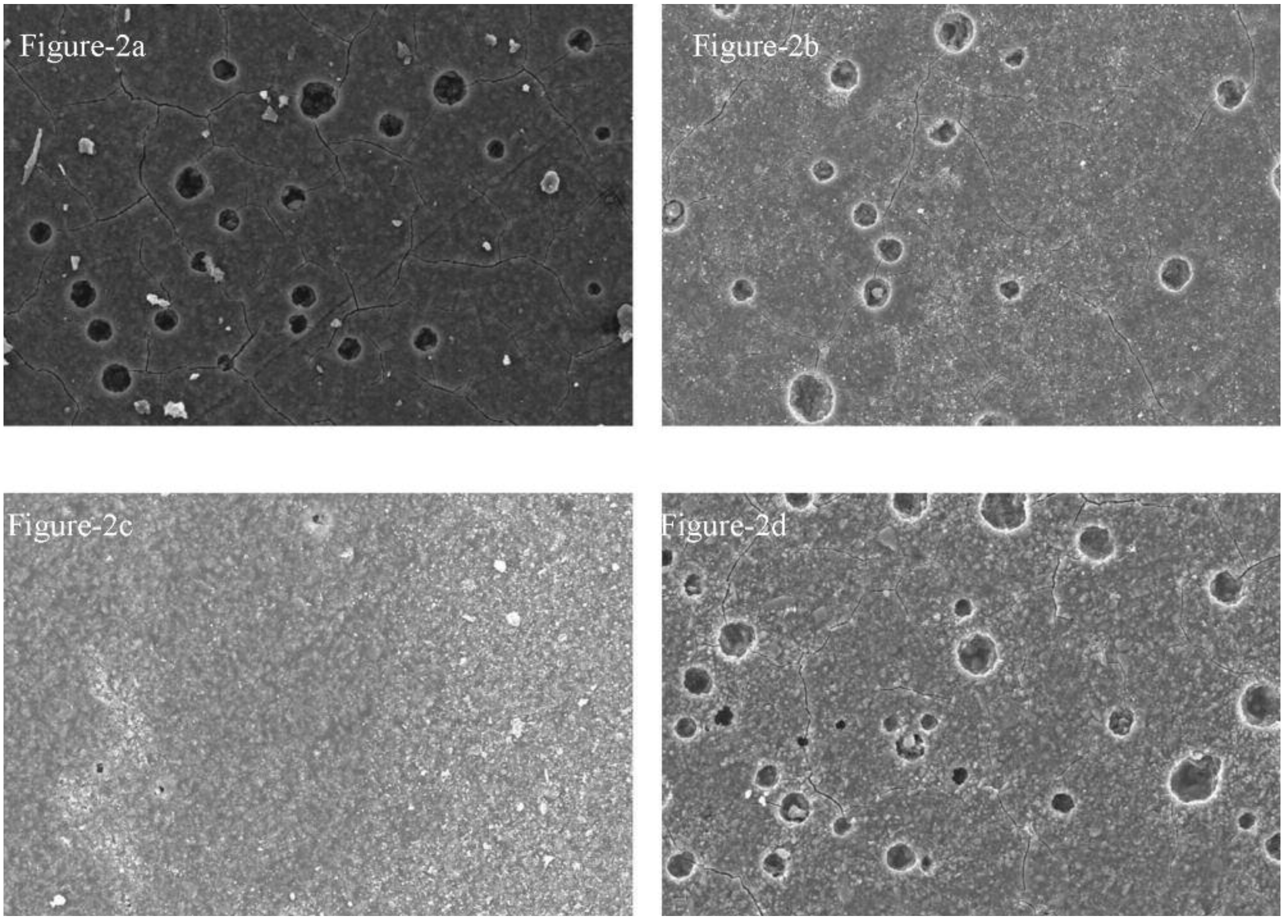


Figure 2a. Fuji IX Extra at baseline at 500X
Figure 2b. Fuji IX Extra after 1 min 1.23% APF application at 500X
Figure 2c. Fuji IX Extra after 4 min 1.23% APF application at 500X
Figure 2d. Fuji IX Extra after 1 min 1% TiF4 application at 500X

mel.[8] In the present study, no rubbing action was used and left on the surface of the restorative material for 1 minute only.

After final reaging, there was no difference in microhardness for HVGIC and RMGIC. This finding is also supported by El-Badrawy's *et. al* showed that saliva may in some way protect the material surface immediately before and after fluoride application.[15] In contrast to this finding, microhardness of nanoionomer decreased at the final reaging. We assume that, HVGIC and RMGIC might have exhibited an earlier acidic reaction when exposed to APF or TiF_4 compared to nanoionomer.

Our results also indicated APF application time (1'vs 4') had no effect on microhardness or surface roughness values for all the restorative materials tested. This finding is in line with Godoy *et. al* study which evaluated 1 and 4 minutes application time effect for APF foam on HVGIC and RMGIC.[12]

Increase in surface roughness of dental materials encourages plaque retention.[29] The critical mean surface roughness for adhesion and colonization of bacteria has been reported to be 0.2 µm.[30] It was suggested that phosphoric acid in APF gel formed large complexes with metal ions leading to increased surface roughness of GIC.[15] Yip *et al.* showed that APF gel increases the surface roughness of restorative materials generally in rank order from the resin composite and polyacid modified resin composites to the conventional glass ionomer cements.[13,14] In the present study, there was no significant difference found in surface roughness of all the restorative materials following APF and TiF_4 applications.

One versus 4 minutes exposure time of APF gel has no difference on newly developed glass ionomers. Mechanical characteristics of Fuji II LC seemed to be influenced more severely compared to Fuji IX Extra and Ketac N100 after 1.23 % APF and 1%TiF_4 applications. Thus, it is concluded that the potential adverse effects of APF and TiF_4 applications might be material dependant.

CONCLUSION

Within the limitations of this *in vitro* study, it was revealed that, potential adverse effects of APF and TiF_4 applications might be material dependant. Hence, restorative materials

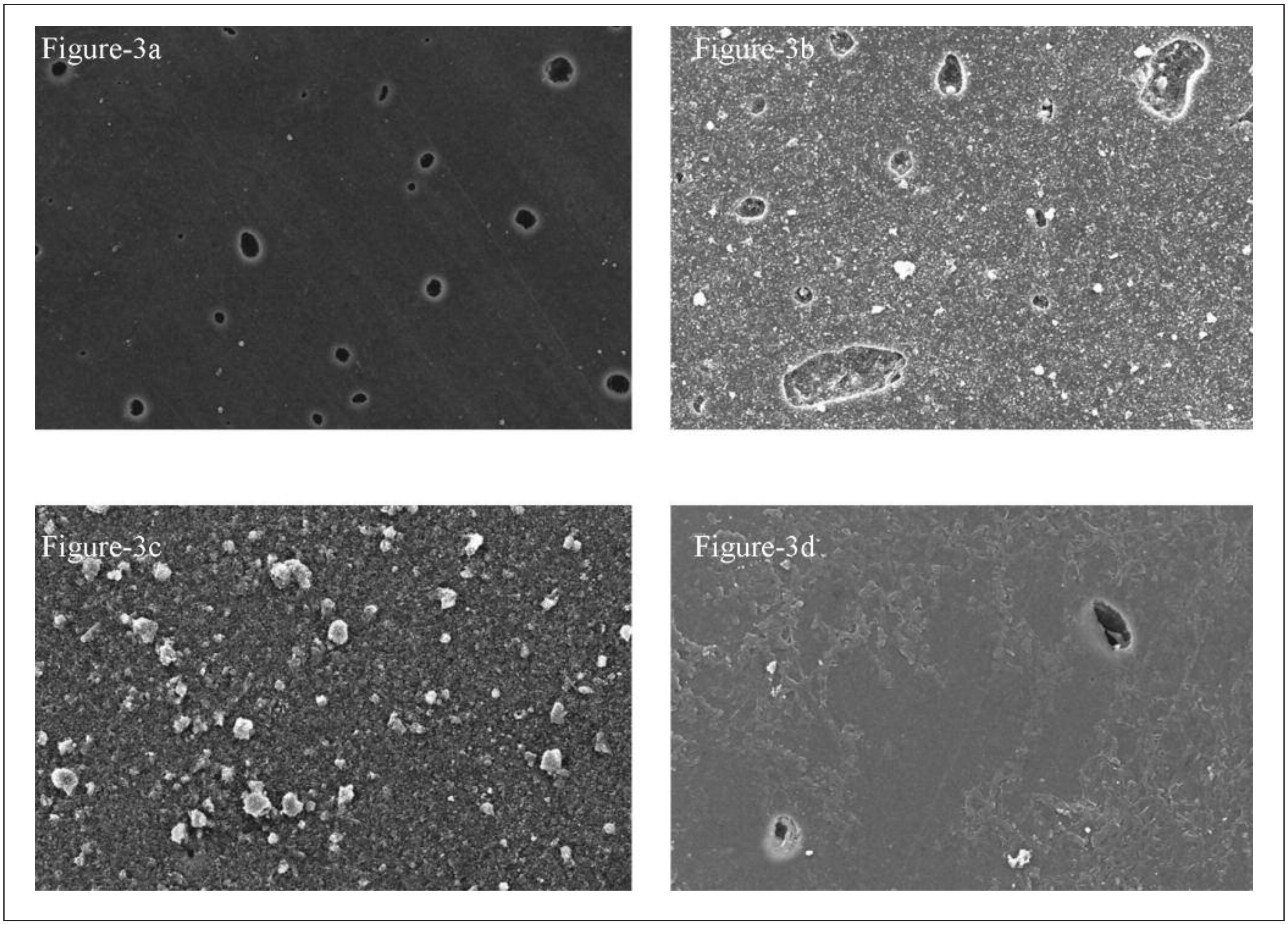


Figure 3a. Ketac N100 at baseline at 500X
Figure 3b. Ketac N100 after 1 min 1.23% APF application at 500X
Figure 3c. Ketac N100 after 4 min 1.23% APF application at 500X
Figure 3d. Ketac N100 after 1 min 1% TiF4 application at 500X

should be selected in accordance with kind, frequency and application time of fluoridation to avoid deteriorations of the restorations.

Further studies both in situ and in vivo are required to conclude about the effects of different fluoride regimens to different restorative materials used in pediatric dentistry.

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