Topical fluoride application is able to reduce acid susceptibility of restorative materials

Hao YU[1], Wolfgang BUCHALLA[2], Hui CHENG[1], Annette WIEGAND[2] and Thomas ATTIN[2]

[1]Department of Prosthodontics, School and Hospital of Stomatology, Fujian Medical University, Yangqiao Zhong Road 246, Fuzhou 350002, China
[2]Clinic for Preventive Dentistry, Periodontology and Cariology, University of Zurich, Plattenstrasse 11, Zurich 8032, Switzerland
Corresponding author, Hui CHENG; E-mail: huicheng.fjmu@yahoo.com and ch.fj@163.com

This study aimed to investigate the effect of topical fluoride application on the acid susceptibility of restorative materials. Four restorative materials were investigated in this study: 2 composite resins (Tetric EvoCeram and Filtek Silorane), a polyacid-modified resin composite (Dyract Extra), and a conventional glass-ionomer cement (Ketac Fil Plus). The samples were treated once with 1 of 8 different fluoride solutions (TiF_4, NaF, AmF, and SnF_2, each at native pH or pH 4) for 3 min or remained untreated (control). The samples were then eroded by citric acid (pH 2.6) for 5 days (6×1 min daily). Erosive substance loss, surface topographic and compositional changes were investigated using surface profilometry, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS), respectively, after fluoride pretreatment and after erosion. The results indicate high-concentrated AmF solution at native pH was effective in inhibiting erosion in the conventional glass-ionomer cement and polyacid-modified resin composite.

Keywords: Fluoride, Erosion, Restorative material

INTRODUCTION

In recent years the effects of fluoride agents on prevention of dental erosion have been widely investigated. Generally speaking, the strategy of the fluoride application is to render the tooth tissue more resistant against acid attacks[1]. In literature, a number of studies showed that fluoride application is able to reduce erosive substance loss, calcium release, and surface softening of enamel and dentine[2-7]. Overall, although clinical studies regarding the erosion-inhibiting potential of fluoridation are not yet available, the protective effect of fluoride application on erosion progression have been shown both *in vitro* and *in situ*. Therefore, based on the current evidence, fluoridation is considered a promising preventive strategy for patients suffering from erosion[8,9].

In addition to erosion of tooth hard tissues, the erosion of restorative materials has also received attention from researchers[10,11]. It has been shown that erosion induced substance loss, surface degradation, and reduced abrasive-resistance of restorative materials[12-15]. Although restorative materials are less susceptible to erosive attacks compared to enamel, the erosive attack can induce, at least to some extent, the degradation of the matrix and fillers of restorative materials[11,16]. On the assumption that fluoride application is an interceptive method to prevent erosion on dental hard tissues, getting better understanding of the effect of fluoride regimen on acid resistance of restorative materials would be advantageous. There is some evidence that fluoride application might have a detrimental effect on restorative materials, causing changes in surface morphology and abrasive-resistance[17,18]. Additionally, it was reported that fluoride might cause depolymerization of the matrix-filler interface and filler loss of dental materials[18-21].

Although the mechanism is still not clear, the deleterious effects of fluoride on restorative materials are thought to be due to the acidity of fluoride solutions and chemical erosion by a prolonged or frequent contact with the fluoride solution[18,22,23]. However, in a previous study using profilometric analysis[11], an infra-additive interaction between erosion and toothbrushing with fluoridated toothpaste was observed, possibly suggesting the protective effects of fluoride in the erosion process of some restorative materials. Based on the current literature, it can be speculated that the acid resistance of dental materials may vary after fluoride application depending on the composition of the respective material. However, only one published study showed that the surface roughness of the polyacid-modified resin composite and conventional glass-ionomer cement increased after APF application and subsequent erosive attacks[22]. Moreover, it has been found that the pH of fluoride solution plays an important role in the efficacy of fluoride agents against erosion of dental hard tissue[24]. During application of fluoride compounds on the dental hard tissues, contact of existing restorations with the fluoride agents could not be avoided. However, limited information, regarding the role of the pH of fluoride agents on erosion of restorative materials, is available.

Therefore, the objective of this study was to investigate the effects of topical fluoride application on erosion of tooth-colored restorative materials using surface profilometry, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). Two hypotheses were proposed: 1) different fluoride agents have a different effect on erosion of restorative materials; 2) fluoride agents at native and buffered pH have a different effect on acid resistance of restorative materials.

MATERIALS AND METHODS

Four tooth-colored restorative materials were investigated in this study: 2 composite resins (Tetric EvoCeram, Ivoclar Vivadent, Schaan, Liechtenstein, and Filtek Silorane, 3M ESPE, St. Paul, MN, USA), a polyacid-modified resin composite (Dyract Extra, Dentsply DeTrey, Konstanz, Germany), and a conventional glass-ionomer cement (Ketac Fil Plus, 3M ESPE, Seefeld, Germany). Shade A2 was selected for all the restorative materials.

Study design

The samples from each group were treated once with 1 of 8 different fluoride solutions for 3 min (titanium tetrafluoride (TiF_4), stannous fluoride (SnF_2), amine fluoride (AmF), and sodium fluoride (NaF), each at native pH and pH 4, for each of 8 fluoride solutions: $n=20$) and then subjected to a five-day pH cycling procedure. The specimens were eroded with citric acid at pH 2.6 for 6×1 min daily and were immersed in artificial saliva during the remaining time. The effect of fluoride treatment and erosion were analyzed using surface profilometry ($n=10$), SEM ($n=4$), and EDS ($n=6$).

Additionally, to test the effect of pH on erosion, another 80 specimens of each material were pretreated for 3 min with fluoride-free buffer solutions at pH 1.2, 2.7, 4, 7.8, analogous to the pH of fluoride solutions used in this study. Subsequently, the samples were subjected to the pH cycling and measurements in the same manner as described above.

Specimen preparation

For each type of restorative material, 260 specimens were fabricated using ring-shaped ceramic moulds (3 mm diameter, 3 mm thickness). The ceramic moulds were cut from a ceramic tube (Degussit, Friatec/Degussa, Düsseldorf, Germany) using a water-cooled low speed diamond saw (Isomet, Buehler, Lake Bluff, IL, USA). The ceramic moulds were positioned on a glass plate, slightly overfilled with the material, and pressed flat with a microscopic glass slide to extrude the excess material. For Dyract Extra, Tetric EvoCeram, and Filtek Silorane, the specimens were light cured from both sides for 40 s using a LED curing light (high power setting; Bluephase, Ivoclar Vivadent, Schaan, Liechtenstein). Ketac Fil Plus was prepared in accordance with the manufacturer's instruction and left undisturbed for 8 min. Following removal of the glass plate, the surface of the glass-ionomer cement was coated with a resin bonding agent (Heliobond, Ivoclar Vivadent, Schaan, Liechtenstein), which was light cured for 20 s. All specimens were stored in distilled water for 24 h and then polished wet with carborundum discs progressively (FEPA-P 1200, 2400 and 4000).

The polished specimens were cleaned in distilled water in an ultrasonic cleaner (M. Scherrer, Wil, Switzerland) for 1 min to remove any debris. Prior to testing, all specimens were stored in distilled water for 7 days[25].

Fluoride application

The fluoride solutions used in this *in vitro* study were: 1) native TiF_4 solution (0.48 M F, pH 1.2); 2) buffered TiF_4 solution (0.48 M F, pH 4); 3) native SnF_2 solution (0.48 M F, pH 2.7); 4) buffered SnF_2 solution (0.48 M F, pH 4); 5) native AmF solution (0.48 M F, pH 4.6); 6) buffered AmF solution (0.48 M F, pH 4); 7) native NaF solution (0.48 M F, pH 7.8); 8) buffered NaF solution (0.48 M F, pH 4). The preparation procedure has been described in detail previously[24]. All the solutions were prepared freshly before used.

The specimens were fixed in plastic chambers separately and then the chambers were filled with 5 mL of the respective fluoride solution and left undisturbed for 3 min. After pretreatment, all samples were rinsed with distilled water for 30 s. Specimens of the control group remained untreated during this procedure.

An additional experiment was performed in order to investigate the effect of the pH, where specimens were pretreated with fluoride-free solutions at different pH (pH 1.2, 2.7, 4 and 7.8, $n=20$) for 3 min. The fluoride-free buffer solution at pH 1.2 was prepared by mixing 9 mL 0.1 M disodium citrate with 91 mL 0.1 M HCl. The fluoride-free buffer solution at pH 2.7 was obtained by mixing 36 mL 0.1 M disodium citrate with 64 mL 0.1 M HCl. The fluoride-free buffer solution at pH 4 was prepared by mixing 55 mL 0.1 M disodium citrate with 45 mL 0.1 M HCl. The fluoride-free buffer solution at pH 7.8 was made by mixing 7.5 mL 0.07 M KH_2PO_4 with 92.5 mL 0.07 M Na_2HPO_4. The samples were rinsed in the same manner as described above.

pH cycling

The pH cycling included erosive acid attacks 6 times daily and storage in artificial saliva for the remaining time. The samples were eroded by 2 mL citric acid (pH 2.6) for 1 min and rinsed with distilled water for 30 s. Afterwards, the eroded samples were immersed in 5 mL artificial saliva for 1 h. The artificial saliva was mixed according to the formulation given by Klimek *et al.*[26]. Five hundred millilitres of artificial saliva contained 0.001 g ascorbic acid, 0.015 g glucose, 0.290 g NaCl, 0.085 g $CaCl_2$, 0.080 g NH_4Cl, 0.635 g KCl, 0.080 g NaSCN, 0.165 g KH_2PO_4, 0.100 g carbamide, 1.350 g mucin, and 0.170 g Na_2PO_4. Every day after 6 cycles, the specimens were stored in artificial saliva overnight. Specimens of the control group were maintained in artificial saliva for the entire experimental period. The artificial saliva for storage was renewed every day.

Profilometric analysis

Substance loss was measured using a stylus profilometer (Perthometer S2/GD 25, Mahr, Göttingen, Germany) after fluoride pretreatment and after erosion. The profilometry system has been reported to have a detection limit of 0.105 μm and high reproducibility[27]. The procedure has been described in detail elsewhere[11]. Briefly, three profiles were performed on each specimen *via* scanning from one reference surface (rim of the ceramic mould) across the treated surface to the opposite

reference surface. Profiles before and after treatment were exactly matched using a custom-designed software (4D client) so that the difference between the profiles could be determined. An average of these three readings (µm) was obtained and used for data analysis.

SEM and EDS analysis
For each kind of restorative materials, 4 samples from each group were randomly selected for SEM examination after fluoride pretreatment and after erosion. The specimens were mounted on aluminum stubs and sputter-coated with platinum, and then examined using a Supra 50 VP Scanning Electron Microscope (Carl Zeiss NTS, Oberkochen, Germany) with an acceleration voltage of 2 kV.

Quantitative changes of the surface composition of the fluoride-treated and eroded samples were evaluated using EDS. The EDS analysis was performed with the same SEM equipped with an EDAX PV7715/89 ME energy-dispersive X-ray spectrometer. Six specimens from each group were sputter-coated with carbon and the respective EDS spectra were obtained in a 200×200 µm area with an acceleration voltage of 15 kV. The spectra were then analyzed using the EDAX Genesis Spectrum software package (EDAX, Mahwah, NJ, USA).

Statistical analysis
The data were analyzed using the SPSS statistical software package (SPSS 13.0 for Windows, SPSS, Chicago, IL, USA). The Kolmogorov-Smirnov test was used for checking the normal distribution of the data. The results from profilometry and EDS were analyzed by two-way analysis of variance (ANOVA) followed by Tukey HSD multiple comparison tests. All statistical analyses were carried out at a significance level of 0.05.

RESULTS

All the three categories of materials tested (glass-ionomer cement, polyacid-modified resin composite, and composite resin) behaved differently following fluoride application and erosive challenge. However, the two composite resins (Filtek Silorane and Tetric EvoCeram) showed similarity in substance loss, changes in surface structure and composition after fluoride pretreatment and erosion.

Surface profilometry
The surface profile changes due to topical fluoride application and erosion were all under the detection limits of the profilometer for all the composite resin samples (Filtek Silorane and Tetric EvoCeram). Generally, the native TiF_4 solution induced the most pronounced substance loss of Dyract Extra and Ketac Fil Plus (Table 1). However, for Dyract Extra, the application of the native and buffered TiF_4 (82% reduction and 59% reduction compared to controls, respectively), native SnF_2 (58% reduction compared to controls) and native AmF (75% reduction compared to controls) significantly reduced the erosive substance loss compared to the fluoride free control group. Likewise, for Ketac Fil Plus, the application of native SnF_2 (61% reduction compared to controls), native AmF (76% reduction compared to controls) and native NaF (63% reduction compared to controls) significantly decreased the erosive substance loss compared to the respective controls. However, with regard to the total loss due to fluoride application and acid attack, only the application of native AmF was able

Table 1   Means (standard deviations) of substance loss [µm] for the fluoride-treated groups and control group

Materials	Groups	pH-value of the respective solution		Substance loss after pretreatment		Substance loss after erosion		Total substance loss	
		Native	Buffered	Native pH	Buffered pH	Native pH	Buffered pH	Native pH	Buffered pH
Dyract Extra	TiF_4	1.2	4.0	0.34(0.07)a	0.11(0.03)a,b,c,d	0.14(0.10)a	0.31(0.07)a,b	0.48(0.12)a,b	0.43(0.07)a,b
	SnF_2	2.7	4.0	0.26(0.09)a,b	0.04(0.06)b,c,d	0.32(0.05)a,b	0.75(0.23)b,c,d	0.56(0.11)a	0.78(0.19)a
	AmF	4.6	4.0	−0.17(0.13)d	0.25(0.10)a,b	0.19(0.04)a,b	0.47(0.01)a,c,d	0.05(0.15)b	0.76(0.06)a
	NaF	7.8	4.0	−0.11(0.09)c,d	0.13(0.10)a,b,c	0.57(0.07)b,c,d	0.55(0.10)b,c,d	0.46(0.16)a,b	0.68(0.18)a
	Control	–	–	0.00(0.04)b,c,d	–	0.76(0.20)d	–	0.77(0.22)a	–
Ketac Fil Plus	TiF_4	1.2	4.0	2.39(0.24)a	0.67(0.15)b	0.92(0.26)a,b,c	1.70(0.23)b,c,d	3.31(0.31)a	2.37(0.29)a,b
	SnF_2	2.7	4.0	0.48(0.09)b	0.27(0.18)b	0.67(0.20)a	2.05(0.37)b	1.13(0.16)d,e	2.32(0.21)a,b,c
	AmF	4.6	4.0	0.25(0.17)b	0.59(0.26)b	0.41(0.29)a	0.95(0.37)a,b,c	0.67(0.22)e	1.54(0.42)b,c,d,e
	NaF	7.8	4.0	0.24(0.10)b	0.31(0.21)b	0.64(0.32)a	1.16(0.33)a,b,c,d	0.89(0.24)d	1.46(0.44)b,c,d,e
	Control	–	–	0.07(0.10)b	–	1.74(0.13)c,d	–	1.82(0.12)b,c,d	–

Positive values indicate substance loss of the respective group. Comparisons of substance loss are made between all groups within the same column (pretreatment, erosion and total), values marked with the same letter were not significantly different. The substance loss due to fluoride pretreatment and subsequent erosive attack of Filtek Silorane and Tetric EvoCeram was below the detection limit of the profilometry and, therefore, is not shown.

Table 2   Means (standard deviations) of substance loss (in µm) for the fluoride-free groups and control group

Materials	Groups	Substance loss after pretreatment	Substance loss after erosion	Total substance loss
Dyract Extra	Fluoride-free buffer (pH1.2)	0.49(0.06)a	0.56(0.13)a	1.04(0.18)a
	Fluoride-free buffer (pH2.6)	0.22(0.11)a,b	0.68(0.12)a	0.88(0.19)a,b
	Fluoride-free buffer (pH4)	0.16(0.05)b,c	0.59(0.09)a	0.77(0.17)a,b
	Fluoride-free buffer (pH7.8)	0.02(0.05)c	0.62(0.11)a	0.64(0.12)b
	Distilled water	0.00(0.04)c	0.76(0.20)a	0.77(0.22)a,b
Ketac Fil Plus	Fluoride-free buffer (pH1.2)	2.01(0.77)a	1.63(0.45)a	3.65(1.06)a
	Fluoride-free buffer (pH2.6)	0.53(0.16)b	1.75(0.47)a	2.34(0.35)a,b
	Fluoride-free buffer (pH4)	0.29(0.15)b	1.88(0.26)a	2.19(0.31)b
	Fluoride-free buffer (pH7.8)	−0.02(0.05)b	1.78(0.53)a	1.76(0.52)b
	Distilled water	0.07(0.10)b	1.74(0.13)a	1.82(0.12)b

Comparisons of substance loss are made between all groups within the same column (pretreatment, erosion and total), values marked with the same letter were not significantly different. The substance loss due to fluoride-free buffer pretreatment and subsequent erosive attack of Filtek Silorane and Tetric EvoCeram was below the detection limit of the profilometry and, therefore, is not shown.

to significantly decrease the substance loss of Dyract Extra and Ketac Fil Plus compared with the fluoride free control groups.

Application of the solution with pH 1.2 on Dyract Extra and Ketac Fil Plus samples pretreated with fluoride-free solutions led to significantly higher erosive substance loss compared with pH 2.6, pH 4 and pH 7.8, and distilled water. The substance loss due to fluoride application was similar to that caused by the application of fluoride-free buffer at the same pH. However, no significant differences were found in the erosive substance loss of the specimens treated with fluoride-free solutions at different pH (Table 2). Filtek Silorane and Tetric EvoCeram showed no detectable substance loss after pretreatment with fluoride-free solution and after erosion.

SEM and EDS
The control groups of all materials showed a relatively smooth and intact surface morphology with the exception of Ketac Fil Plus, which revealed dehydration cracks due to specimen preparation. After application of native TiF_4 on Dyract Extra, most of the fillers were partially debonded or completely removed form the matrix. The porosity of surface was increased and randomly distributed. After application of buffered TiF_4, native and buffered AmF, buffered SnF_2, and buffered NaF, precipitations have formed on the surface of Dyract Extra (Figs. 1C, E, G and 2A, E). The precipitates varied in their appearance. Dissolution and loss of filler particles were typical findings in conventional glass-ionomer cement and polyacid-modified resin composite after erosion. A significant less etching effect of citric acid on the surface of Dyract Extra was found on buffered TiF_4-treated, native SnF_2-treated, and native AmF-treated samples compared with the specimens from other groups (Fig. 1).

Native TiF_4 had the most severe degradation effect

on the surface of Ketac Fil Plus, while the application of buffered SnF_2 and AmF led to the formation of surface precipitates (Fig. 3A, C, and E). After erosion using citric acid, all Ketac Fil Plus samples had severely eroded surfaces with pitting and cracking except for the AmF-treated samples (Fig. 3).

In general, fluoride solutions increased the surface fluoride concentration of Ketac Fil Plus and Dyract Extra (Table 3 and 4). The application of TiF_4 and SnF_2 significantly increased the surface titanium and tin contents, respectively. Ketac Fil Plus and Dyract Extra showed a similar surface composition after erosive cycling, irrespectively of whether or not the samples were pretreated with fluoride.

Composite resins (Filtek Silorane and Tetric EvoCeram) presented the least affected surface morphology and composition, regardless of the fluoride solutions used. Further, 30 min erosion caused negligible changes in the surface structure and composition of the composite resins tested (data not shown).

Pretreatment with fluoride-free solutions at different pH did not have a significant influence on surface structure and composition after erosive cycling (data not shown).

DISCUSSION

Based on the above results, the hypotheses that different fluoride agents have a different effect on restorative material erosion and that the pH of fluoride agents affects erosion of restorative materials under the testing conditions, were therefore accepted.

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. In the present study, the *in vitro* erosive pH-cycling model was adopted to mimic the clinical condition with short time
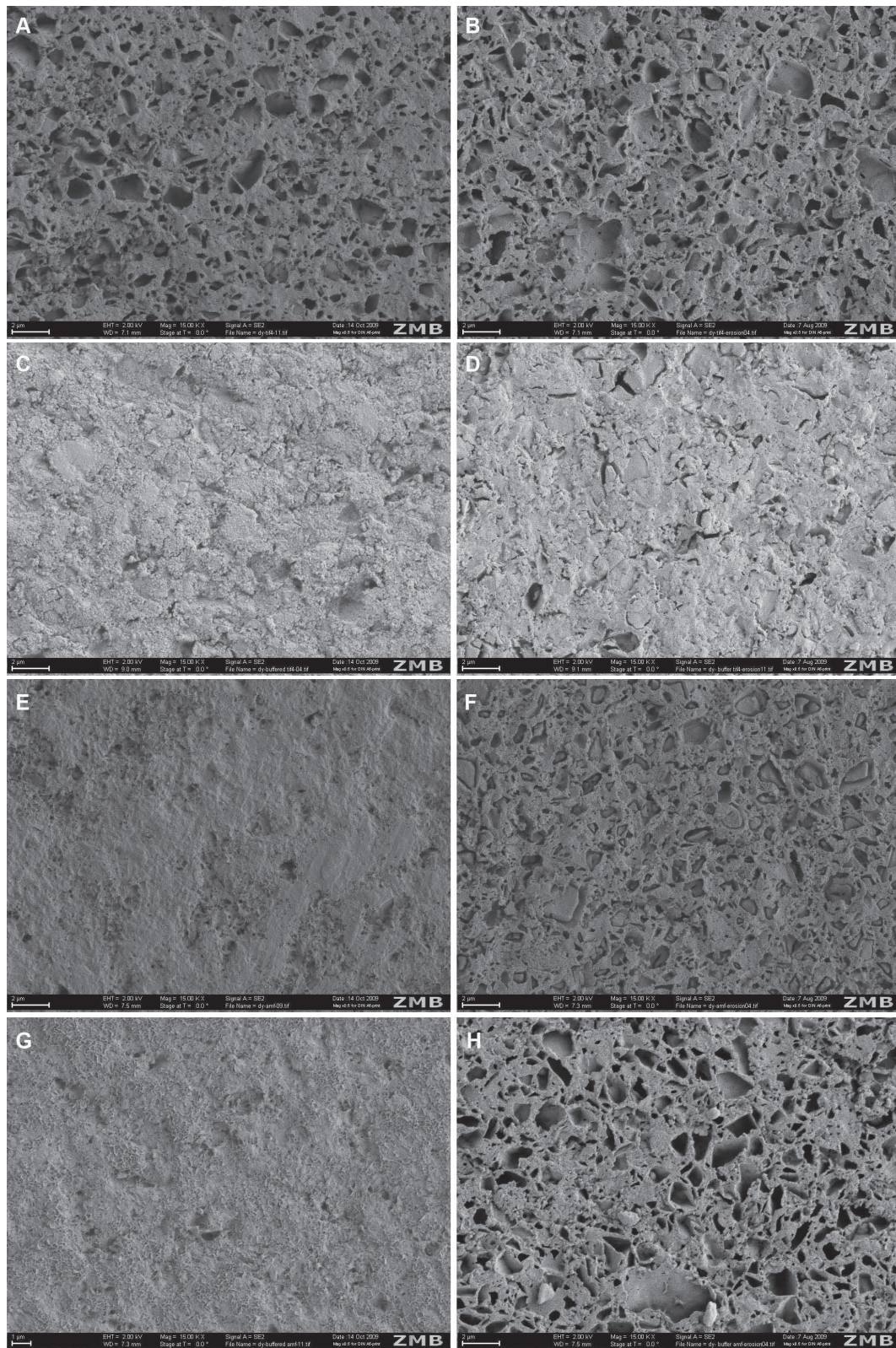
Fig. 1   Representative SEM images of Dyract Extra (15,000×).
A: after native TiF_4 pretreatment; B: native TiF_4-treated surface after erosion; C: after buffered TiF_4 pretreatment; D: buffered TiF_4-treated surface after erosion; E: after native AmF pretreatment; F: native AmF-treated surface after erosion; G: after buffered AmF pretreatment; H: buffered AmF-treated surface after erosion.
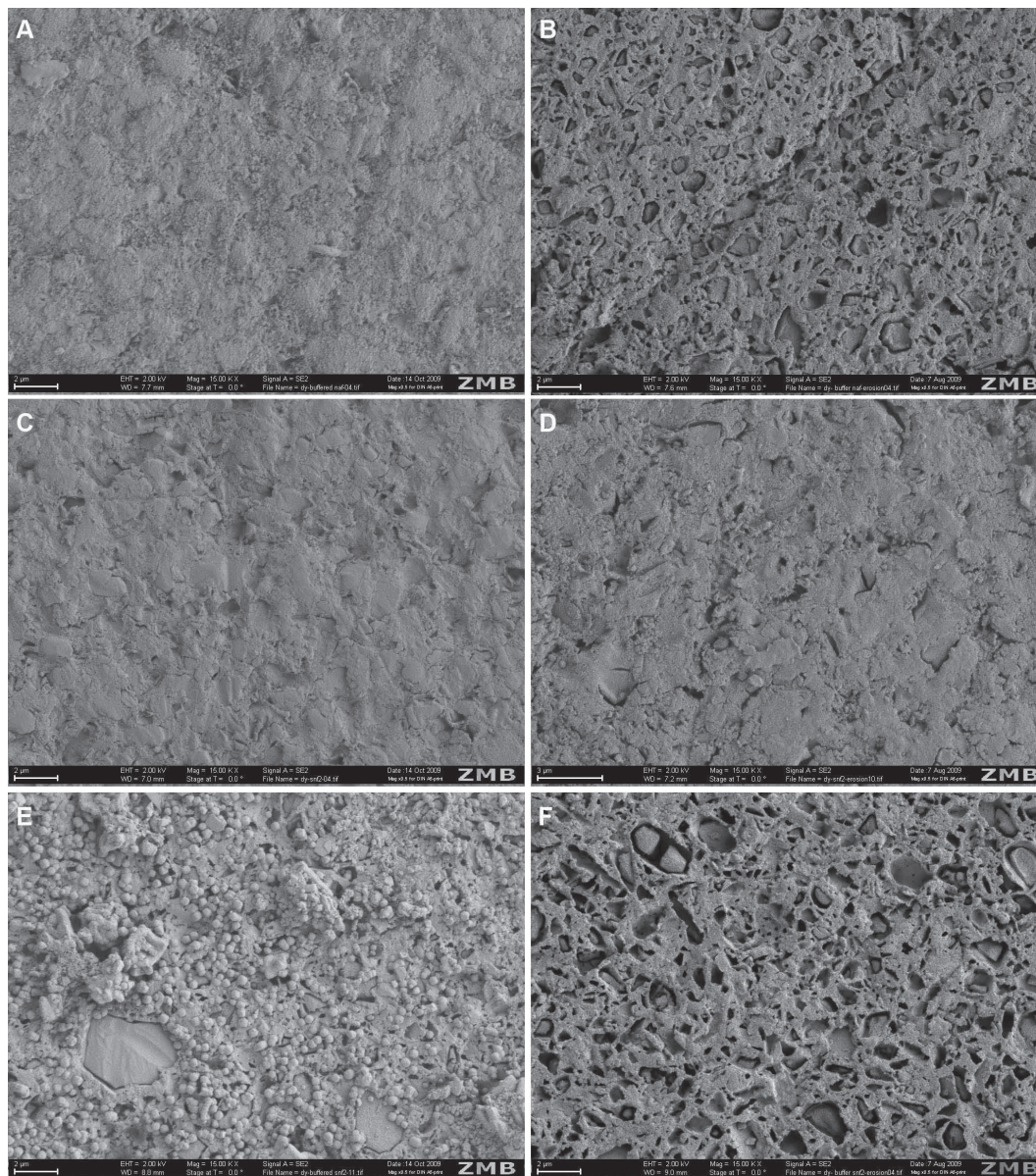
Fig. 2 Representative SEM images of Dyract Extra (15,000×).
A: after buffered NaF pretreatment; B: buffered NaF-treated surface after erosion; C: after native SnF_2 pretreatment; D: native SnF_2-treated surface after erosion; E: after buffered SnF_2 pretreatment; F: buffered SnF_2-treated surface after erosion.

consumption of acidic beverage several times daily. The ceramic moulds were used to provide an mechanically and chemically stable reference surface in the profilometrical assessment[11,27]. Further, the ceramic moulds were employed to minimize the possible shrinkage effects of the materials on the results of the present study[27].

It has been reported that the acid susceptibility of dental hard tissue is generally greater than those of restorative materials. Although erosion-inhibiting effects of fluoride measures have been reported by many studies, there is limited information concerning clinically relevant changes to the restorative materials that may take place when restored teeth are subjected to erosive attack and therapeutic application of fluoride solution is performed. The present study could be considered the first investigation in this regard.

As shown previously[28-30], many fluoride preparations affected the morphology and composition of conventional glass-ionomer cement and polyacid-modified resin composite. Based on the current findings, the substance loss caused by fluoridation is mainly due to the acidity of the fluoride solution. The morphologic and compositional patterns obtained from the materials were dependent on
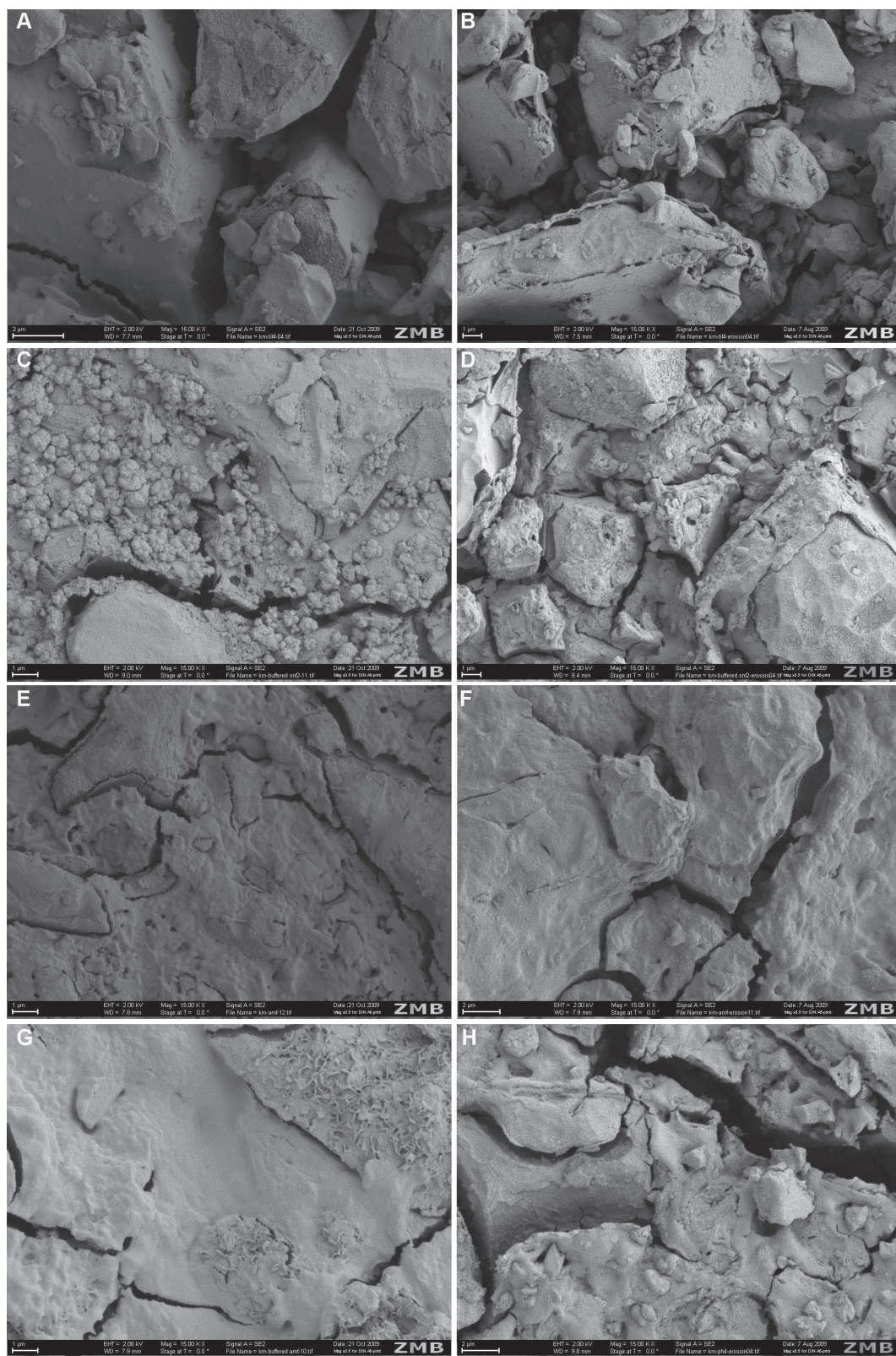
Fig. 3 Representative SEM images of Ketac Fil Plus (15,000×).
A: after native TiF_4 pretreatment; B: native TiF_4-treated surface after erosion; C: after buffered SnF_2 pretreatment; D: buffered SnF_2-treated surface after erosion; E: after buffered AmF pretreatment; F: Buffered AmF-treated surface after erosion; G: after native AmF pretreatment; H: Native AmF-treated surface after erosion.

Table 3 Changes in surface concentration [wt%] of the respective elements for Dyract Extra after erosion by EDS analysis (200×200 µm)

	C	F	Al	Si	Sr	Ca	Sn	Ti
Native TiF$_4$	3.08%	−1.35%	−1.15%	1.17%	−1.70%	−0.01%	–	0.09%
Native SnF$_2$	4.92%	−2.15%	−2.18%	1.93%	−2.56%	0.06%	−1.29%	–
Native AmF	10.99%	−5.58%	−2.33%	0.01%	−4.98%	−0.12%	–	–
Native NaF	14.89%	−4.27%	−3.50%	−0.17%	−5.44%	−0.05%	–	–
Buffered TiF$_4$	10.99%	−6.74%	−3.40%	1.41%	−6.23%	−0.08%	–	−0.27%
Buffered SnF$_2$	18.72%	−15.74%	−3.73%	2.30%	−5.75%	−0.10%	−2.05%	–
Buffered AmF	13.22%	−9.86%	−2.38%	1.60%	−8.10%	−0.08%	–	–
Buffered NaF	13.72%	−13.82%	−3.48%	2.00%	−4.42%	−0.07%	–	–
Water	12.68%	−3.48%	−3.22%	−0.11%	−4.68%	0.03%	–	–

Positive values indicate increase in surface concentration of the elements after erosion. "–" means that the concentration of the respective element was below the detection limit.

Table 4 Changes in surface concentration [wt%] of the respective elements for Ketac Fil Plus after erosion by EDS analysis (200×200 µm)

	C	F	Al	Si	Sr	P	Ca	La	Sn	Ti
Native TiF$_4$	0.82%	−2.31%	−0.91%	2.86%	−3.00%	−0.03%	−0.06%	−0.90%	–	−0.42%
Native SnF$_2$	0.84%	−1.92%	−1.52%	3.10%	−1.07%	−0.23%	−0.39%	0.23%	−3.03%	–
Native AmF	8.52%	−4.18%	−1.95%	0.88%	−2.17%	−0.28%	−0.99%	−0.34%	–	–
Native NaF	3.78%	−3.23%	−1.31%	1.83%	−1.10%	−0.03%	−1.27%	0.57%	–	–
Buffered TiF$_4$	0.99%	−6.13%	−0.18%	2.56%	−1.17%	0.04%	−1.84%	0.38%	–	−0.09%
Buffered SnF$_2$	5.01%	−14.54%	−0.92%	5.32%	0.64%	0.32%	−1.61%	0.68%	−1.33%	–
Buffered AmF	8.66%	−12.07%	−1.71%	3.10%	−4.90%	0.18%	−1.82%	−0.16%	–	–
Buffered NaF	6.67%	−16.55%	−0.95%	2.51%	4.10%	0.57%	−0.88%	2.82%	–	–
Water	2.89%	−1.10%	−2.17%	2.95%	−2.04%	−0.35%	−1.35%	−0.06%	–	–

Positive values indicate increase in surface concentration of the elements after erosion. "–" means that the concentration of the respective element was below the detection limit.

the type of the fluoride solution and the restorative materials used. It is noteworthy that the acid resistance of conventional glass-ionomer cement and polyacid-modified resin composite were elevated after topical application of some fluoride solutions (AmF, SnF$_2$, etc). This phenomenon was probably related to the formation of F-rich material on the surface, although some of the changes were not detectable under SEM. The finding that the surface fluoride level increased after fluoride application support this hypothesis. The present study did not determine what kind of compound was precipitated, but it is clear that the compound must be different from, or at least additional to, calcium fluoride (CaF$_2$). This conclusion was based on the finding that only little amount of calcium (around 0.20 wt%) was found on the surface and the structure of the deposits was, with the more amorphous appearance, different from the typical globular appearance of pure CaF$_2$[31]. The mechanism of the precipitate formation following application of fluoride solutions is not clear. Probably, in contact with specific fluoride solution, the fluoride ion

can compete with carboxylate groups to form complexes with the Al^{3+} ions, leached from glass particles[32]. However, further studies are needed to confirm this hypothesis.

Importantly, for conventional glass-ionomer cement and polyacid-modified resin composite, the application of native AmF was more effective in protecting erosive substance loss compared to other fluoride solutions. This is possibly because the precipitates formed by application of native AmF had less solubility in citric acid thus providing a protective barrier to conventional glass-ionomer cement and polyacid-modified resin composite surface against erosive attack[3]. Further, the surfactant properties of AmF might contribute to its superior erosion-prohibiting potential compared to other fluoride measures[33].

Under the current experimental setting, TiF$_4$ and SnF$_2$ also exhibited some erosion-inhibiting potential on conventional glass-ionomer cement and polyacid-modified resin composite. The application led to an increase of surface titanium and tin contents,

respectively. The elevated acid resistance of treated conventional glass-ionomer cement and polyacid-modified resin composite specimens might not only be attributed to the F-rich layer, but also to the incorporation of metal cations into the material surface[24,34]. However, further studies are needed to verify this issue.

Among all materials tested, Ketac Fil Plus showed the most significant surface degradation and substance loss after fluoride pretreatment. This finding was in agreement with a previous study[35]. In contrast to previous findings[36], there was no significant difference in surface appearance and composition of composite resins before *vs.* after treatment with fluoride preparations. This may be due to the different application time between the previous and the present study (8 h *vs.* 3 min). Application time for fluoride solution in the present study was selected in order to simulate clinical conditions[2,24,37].

It appears that the pH of fluoride solution plays an important role in the efficacy of fluoride agents against erosive challenges on conventional glass-ionomer cement and polyacid-modified resin composite. In contrast to previous findings on enamel[3,24], the native fluoride solutions provided better protection against erosive substance loss compared to the respective buffered solutions. The different results seem to be related to the distinct composition and structure of enamel and restorative materials.

In the present study, even the short-term application (3 min) of native TiF_4 resulted in a severe surface disintegration on conventional glass-ionomer cement and polyacid-modified resin composite. This might be because of the high acidity of native TiF_4 solution (pH 1.2). This hypothesis can be confirmed by the finding that the substance loss due to native TiF_4 solution and fluoride-free buffer at pH 1.2 were similar (2.39 μm *vs.* 2.01 μm).

Only 4 materials from 3 types of restorative materials (composite resin, glass-ionomer cement, and polyacid-modified resin composite) were investigated in the current study. Given that there is a great variation in the composition of different restorative materials even within the same categories, it is rather difficult to generalize the results. Extrapolation from the present findings and the literature[11,38] indicated that composite resin has the best resistance to both erosive attack and fluoride application among the 3 types of restorative materials tested. Based on the present and past evidence[11,39], conventional glass-ionomer cement might be more vulnerable to acid attack and fluoride application than polyacid-modified resin composite. However, these hypotheses needed to be explained with caution and clarified with further studies.

If the situation at the restoration margin is analyzed, not only the wear of restorative material but also the wear of tooth hard tissue should be taken into account. Under the same experimental setting, it was found that AmF was the most effective agent in protecting enamel erosion among all fluoride agents tested[24]. After fluoride application and 30 erosion cycles (1 min/ cycle), the total

substance loss of native AmF-treated enamel was 0.17 μm, which is close to the substance loss of native AmF-treated conventional glass-ionomer cement (0.05 μm) and composite resin (remain unchanged). Therefore, in the case of native AmF application is adopted as a symptomatic therapy of dental erosion, the conventional glass-ionomer cement, composite resin restoration and the natural tooth surface might erode at relatively similar speed and a step between the tooth surface and restoration can develop without producing a gap. However, extrapolation of laboratory research into *in vivo* condition is difficult as the absence of pellicle and saliva. Further *in situ* or *in vivo* studies are needed to determine the effect of topical fluoride regimes on the acid resistance of restorative materials.

CONCLUSION

Within the limitation of this *in vitro* study, it suggests conventional glass-ionomer cement and polyacid-modified resin composite restorations exhibit greater acid resistance following application of native AmF solution, although the application of acidic fluoride solutions lead to a certain surface degradation, due to the acidity rather than the fluoride content an chemical composition. Composite resin has the best resistance to fluoride treatment and erosive attack among all the materials tested. Fluoride solution at native pH provided better protection against erosion compared to the respective solution at buffered pH.

ACKNOWLEDGMENTS

REFERENCES

1) Lussi A, Hellwig E, Ganss C, Jaeggi T. Buonocore Memorial Lecture. Dental erosion. Oper Dent 2009; 34: 251-262.
2) Yu H, Wegehaupt FJ, Zaruba M, Becker K, Roos M, Attin T, Wiegand A. Erosion-inhibiting potential of a stannous chloride-containing fluoride solution under acid flow conditions *in vitro*. Arch Oral Biol 2010; 55: 702-705.
3) Wiegand A, Bichsel D, Magalhaes AC, Becker K, Attin T. Effect of sodium, amine and stannous fluoride at the same concentration and different pH on *in vitro* erosion. J Dent 2009; 37: 591-595.
4) Hara AT, Gonzalez-Cabezas C, Creeth J, Parmar M, Eckert GJ, Zero DT. Interplay between fluoride and abrasivity of dentifrices on dental erosion-abrasion. J Dent 2009; 37: 781-785.
5) Ganss C, Schlueter N, Hardt M, Schattenberg P, Klimek J. Effect of fluoride compounds on enamel erosion *in vitro*: a comparison of amine, sodium and stannous fluoride. Caries Res 2008; 42: 2-7.
6) Magalhaes AC, Levy FM, Rios D, Buzalaf MA. Effect of a single application of TiF(4) and NaF varnishes and solutions on dentin erosion *in vitro*. J Dent 2010; 38: 153-157.
7) Lagerweij MD, Buchalla W, Kohnke S, Becker K, Lennon AM, Attin T. Prevention of erosion and abrasion by a high fluoride concentration gel applied at high frequencies. Caries Res

2006; 40: 148-153.

8) Wiegand A, Attin T. Influence of fluoride on the prevention of erosive lesions —a review. Oral Health Prev Dent 2003; 1: 245-253.

9) Magalhaes AC, Wiegand A, Rios D, Honorio HM, Buzalaf MA. Insights into preventive measures for dental erosion. J Appl Oral Sci 2009; 17: 75-86.

10) Rios D, Honorio HM, Francisconi LF, Magalhaes AC, de Andrade Moreira Machado MA, Buzalaf MA. *In situ* effect of an erosive challenge on different restorative materials and on enamel adjacent to these materials. J Dent 2008; 36: 152-157.

11) Yu H, Wegehaupt FJ, Wiegand A, Roos M, Attin T, Buchalla W. Erosion and abrasion of tooth-colored restorative materials and human enamel. J Dent 2009; 37: 913-922.

12) Aliping-McKenzie M, Linden RW, Nicholson JW. The effect of Coca-Cola and fruit juices on the surface hardness of glass-ionomers and 'compomers'. J Oral Rehabil 2004; 31: 1046-1052.

13) Kuybulu FI, Gemalmaz D, Pameijer CH, Yarat A, Alcan T. Erosion of luting cements exposed to acidic buffer solutions. Int J Prosthodont 2007; 20: 494-495.

14) Buchalla W, Attin T, Hellwig E. Brushing abrasion of luting cements under neutral and acidic conditions. Oper Dent 2000; 25: 482-487.

15) Attin T, Buchalla W, Trett A, Hellwig E. Toothbrushing abrasion of polyacid-modified composites in neutral and acidic buffer solutions. J Prosthet Dent 1998; 80: 148-150.

16) Francisconi LF, Honorio HM, Rios D, Magalhaes AC, Machado MA, Buzalaf MA. Effect of erosive pH cycling on different restorative materials and on enamel restored with these materials. Oper Dent 2008; 33: 203-208.

17) Attin T, Buchalla W, Hellwig E. Effect of topical fluoride application on toothbrushing abrasion of resin composites. Dent Mater 2006; 22: 308-313.

18) El-Badrawy WA, McComb D. Effect of home-use fluoride gels on resin-modified glass-ionomer cements. Oper Dent 1998; 23: 2-9.

19) Bowen RL, Cleek GW. A new series of x-ray-opaque reinforcing fillers for composite materials. J Dent Res 1972; 51: 177-182.

20) Kula K, Nelson S, Thompson V. *In vitro* effect of APF gel on three composite resins. J Dent Res 1983; 62: 846-849.

21) Kula K, McKinney JE, Kula TJ. Effects of daily topical fluoride gels on resin composite degradation and wear. Dent Mater 1997; 13: 305-311.

22) Avsar A, Tuloglu N. Effect of different topical fluoride applications on the surface roughness of a colored compomer. J Appl Oral Sci 2010; 18: 171-177.

23) Yip HK, To WM, Smales RJ. Effects of artificial saliva and APF gel on the surface roughness of newer glass ionomer cements. Oper Dent 2004; 29: 661-668.

24) Yu H, Attin T, Wiegand A, Buchalla W. Effects of Various Fluoride Solutions on Enamel Erosion *in vitro*. Caries Res 2010; 44: 390-401.

25) Yu H, Li Q, Lin Y, Buchalla W, Wang Y. Influence of carbamide peroxide on the flexural strength of tooth-colored restorative materials: an *in vitro* study at different environmental temperatures. Oper Dent 2010; 35: 300-307.

26) Klimek J, Hellwig E, Ahrens G. Fluoride taken up by plaque, by the underlying enamel and by clean enamel from three fluoride compounds *in vitro*. Caries Res 1982; 16: 156-161.

27) Attin T, Becker K, Roos M, Attin R, Paque F. Impact of storage conditions on profilometry of eroded dental hard tissue. Clin Oral Investig 2009; 13: 473-478.

28) Hadley PC, Billington RW, Pearson GJ, Williams JA. Effect of monovalent ions in glass ionomer cements on their interaction with sodium fluoride solution. Biomaterials 2000; 21: 97-102.

29) Billington RW, Hadley PC, Towler MR, Pearson GJ, Williams JA. Effects of adding sodium and fluoride ions to glass ionomer on its interactions with sodium fluoride solution. Biomaterials 2000; 21: 377-383.

30) Papagiannoulis L, Tzoutzas J, Eliades G. Effect of topical fluoride agents on the morphologic characteristics and composition of resin composite restorative materials. J Prosthet Dent 1997; 77: 405-413.

31) ten Cate JM. Review on fluoride, with special emphasis on calcium fluoride mechanisms in caries prevention. Eur J Oral Sci 1997; 105: 461-465.

32) De Witte AM, De Maeyer EA, Verbeeck RM. Surface roughening of glass ionomer cements by neutral NaF solutions. Biomaterials 2003; 24: 1995-2000.

33) Arweiler NB, Auschill TM, Baguley N, Netuschil L, Sculean A. Efficacy of an amine fluoride-triclosan mouthrinse as compared to the individual active ingredients. J Clin Periodontol 2003; 30: 192-196.

34) Wiegand A, Magalhães AC, Attin T. Is titanium tetrafluoride (TiF4) effective to prevent carious and erosive lesions? A review of the literature. Oral Health Prev Dent 2010; 8: 159-164.

35) el-Badrawy WA, McComb D, Wood RE. Effect of home-use fluoride gels on glass ionomer and composite restorations. Dent Mater 1993; 9: 63-67.

36) Dionysopoulos P, Gerasimou P, Tolidis K. The effect of home-use fluoride gels on glass-ionomer, compomer and composite resin restorations. J Oral Rehabil 2003; 30: 683-689.

37) van Rijkom H, Ruben J, Vieira A, Huysmans MC, Truin GJ, Mulder J. Erosion-inhibiting effect of sodium fluoride and titanium tetrafluoride treatment *in vitro*. Eur J Oral Sci 2003; 111: 253-257.

38) Shabanian M, Richards LC. *In vitro* wear rates of materials under different loads and varying pH. J Prosthet Dent 2002; 87: 650-656.

39) Setty JV, Singh S, Subba Reddy VV. Comparison of the effect of topical fluorides on the commercially available conventional glass ionomers, resin modified glass ionomers and polyacid modified composite resins —an *in vitro* study. J Indian Soc Pedod Prev Dent 2003; 21: 55-69.