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Original article

AFM and SEM/EDS characterization of surfaces of fluorine-releasing bulk-fill restorative materials aged in common liquids

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Abstract

Purpose: This study investigated the surface roughness (SR), surface microhardness (SH), and chemical composition of recently developed fluoride-releasing restorative materials aged in common liquids.
Methods: A total of 276 disc-shaped samples with a diameter of 8 mm and a height of 2 mm were prepared by using four restorative materials: alkasite, Activa, Equia Forte, and Zirconomer. Atomic force microscopy (AFM) and the Vickers microhardness test were used to measure SR and SH, respectively. Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM/EDS) was used for elemental analysis of the materials. The prepared samples were divided into 3 subgroups and immersed in coffee, cola, and saliva for 1 week at 37°C and 100% humidity.
Results: Cola and coffee significantly increased the SR of all materials except Zirconomer immersed in coffee ($P < 0.05$). The microhardness of alkasite and Activa significantly decreased in all liquids ($P < 0.05$) The percentage of fluorine (F) in the materials significantly changed after immersion for some liquids ($P < 0.05$).
Conclusion: Aging differentially affected the surface characteristics and elemental mass ratios of the studied materials.

Keywords: AFM, bulk-fill, EDS, microhardness, roughness

Introduction

Fluoride-releasing restorative dental materials suppress caries formation, reduce or prevent demineralization, and support remineralization of dental hard-tissue structures [1]. Although resin composites have satisfactory physical properties, most lack fluoride-releasing ability and have a limited capacity to prevent secondary caries and remineralization [2]. Therefore, new restorative materials with robust protective properties are being developed. Hybrid materials have been marketed that overcome challenges associated with conventional glass ionomers and composite resins, while maintaining their clinical benefits. [3]. These beneficial properties, including fluoride release and use of bulk-fill, and increased demand has led to development of glass-ionomer cements (GIC).

Alkasite, a material that emerged from these studies, contains calcium fluorosilicate glass fillers in a methacrylate resin matrix. The powder portion contains various alkaline fillers that release fluoride, calcium, and hydroxyl, which neutralize acidic ions around the restoration. The liquid consists of monomers that increase the fluidity of the material and allow it to adapt to the smear layer [4]. Activa, another bioactive restorative material, contains bioactive glass and increases pH by releasing Ca, P, and fluoride and is claimed to be more bioactive than conventional glass ionomers [5]. Equia Forte Fil, a type of high-viscosity glass-ionomer cement (HVGIC), is less sensitive to moisture of the material, and has better abrasion resistance and hardness, than conventional glass ionomers. Thus, it is more suitable for the posterior region, where chewing forces are strong [6]. Zirconomer, also known as white amalgam (HVGIC), includes zirconia particles that resist higher compressive and bending forces and achieves lower occlusal abrasion and a rapid curing reaction [7]. Zirconomer is as strong as amalgam, does not contain mercury, and has the beneficial properties of GIC [8].

In addition to fluoride release and low pH-balancing ability, these materials must be resistant to forces in the oral cavity and have strong abrasion resistance, to be considered clinically successful. The low pH of acidic foods and beverages causes considerable chemical wear on dental materials and teeth [9]. Acid resistance of the tooth structure can be improved by a remineralization process that requires calcium (Ca), phosphorus (P), and fluoride, which are components of saliva [10]. Most evidence indicates that beverages with low pH and colorants, such as tea, coffee, cola, red wine, fruit juices, and energy drinks, adversely affect restorative materials [11,12]. Hardness was correlated with the abrasion resistance of materials, and frequent exposure to low-pH beverages reduced abrasion resistance of teeth and restorations [13]. Roughness and irregularities on the surface of a restorative material create an area of adhesion for gradual accumulation of plaque, which can cause gum irritation, discoloration of the restoration, and deterioration of its coherence with the tooth structure [14]. Surface properties of restorations, such as hardness and roughness, are determinants of clinical success [15]. The capacity of restorative materials to withstand acid exposure is critical to the life span of restorations.

Rising consumption of acidic beverages is increasing the need for continued improvement of esthetic restorative materials. The popularity of acidic beverages among young adults and the increasing use of resin-based materials for persons of all ages has led to considerable research. However, knowledge of the mechanical properties of these new materials and their behavior in acidic beverages is limited.

This study investigated the surface roughness (SR), surface hardness (SH), and elemental structure of the fluoride-releasing restorative materials alkasite, Activa, Equia Forte, and Zirconomer after aging in beverages with different pH values. The null hypotheses tested were that there would be no difference between the surface properties of the materials and that the surface properties and elemental structure of the materials would not differ in relation to beverage exposure.

Materials and Methods

This study was approved by the Çukurova University Faculty of Medicine Clinical Research Ethics Committee (approval no. 2021/108.43).

Experimental groups

The composition and application of the investigated materials are shown in Table 1. On the basis of previous studies [4,14], a power analysis for roughness and microhardness using G*Power 3.1 (Heinrich Heine University, Düsseldorf, Germany) indicated that a minimum sample size of 10 for each group ensured a power of 80% to detect differences at a significance level of 0.05. The study of Ruengrungsom et al. [4] was used to determine the sample size for scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM/EDS) analysis.

A total of 276 samples ($n = 69$ for each restorative material) were prepared by using Teflon molds (diameter, 8 mm; thickness, 2 mm). Sixty samples were used for analysis of SR and SH ($n = 10$), and the remaining nine samples ($n = 3$) were used for SEM/EDS analysis for all groups. All materials in this study were applied and polymerized in accordance with

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Table 1 Brand name, content, and polymerization methods of the restorative materials

Material	Specification	Composition	Application
Alkasite (Cention N; Ivoclar Vivadent AG, Schaan Liechtenstein) Shade: A2 Lot: Z0054T	alkasite, self-adhesive restorative material	powder: calcium fluoro-silicate glass, barium glass, calcium-barium-aluminum fluoro-silicate glass, iso-fillers, ytterbium trifluoride, initiators and pigments liquid: dimethacrylates, initiators, stabilizers, additives and mint flavor	Manually mix one measuring spoon of powder and one drop of resin until a smooth consistency is achieved; mixing time should not exceed 60 s; setting time, 5 min.
Activa (Pulpdent, Watertown, MA, USA) Shade: A2 Lot: 191212	bioactive glass ionomer	blend of diurethane and other methacrylates with modified polyacrylic acid (44.6%), amorphous silica (6.7%), and sodium fluoride (0.75%)	Applied to the mold with a gun and polymerized with a FreeLight 2 curing unit (3M Oral Care, MN, USA) for 20 s at 1,200 mW/cm^2 power LED
Equia Forte Fil (GC Corp., Tokyo, Japan) Shade: A2 Lot: 1803121	high viscosity glass ionomer	fluoroalumino silicate glass, hybrid glass particles, polyacrylic acid powder, polyacrylic acid, polybasic carboxylic acid, distilled water	Capsule was activated just before mixing and was placed in the amalgamator immediately; the restorative material mixing time was 10 s and the setting time was 2 min 30 s after placing into the cavity. Then, Equia Forte Coat was applied to the surfaces with a disposable microtip applicator; all coated surfaces were light cured with FreeLight 2 curing unit (3M Oral Care) for 20 s at 1,200 mW/cm^2
Zirconomer (Shofu, Kyoto, Japan) Shade: Universal Lot: 10200185	high viscosity glass ionomer	powder: fluoro-aluminosilicate glass, zirconium oxide, pigments and others liquid: polyacrylic acid solution and tartaric acid	Powder to liquid ratio, 3.6/1.0 g (3.6:1.0 m/m); dispense two level scoops of powder with the measuring scoop provided by the manufacturer, and dispense one drop of liquid onto a mixing pad separately; the dispensed powder and liquid are mixed for 5-10 s with a plastic spatula; setting times 3 min.

Table 2 Brand name, content, and pH value of the liquids

Liquids	Composition	pH
cola (The Coca Cola, Atlanta, GA, USA)	carbonated water, sugar, caramel color, phosphoric acid, natural flavors, caffeine	2.53
coffee (Nescafe Classic, Nestle, Switzerland)	10 g/200 mL of boiling water and cooled to 60°C	4.50
artificial saliva (Malatya, Turkey)	1.160 g/L sodium chloride, 0.600 g/L calcium chloride, 0.600 g/L potassium phosphate, 1.491 g/L potassium chloride, 0.050 g/L sodium fluoride, trace of sodium hydroxide	6.93

the manufacturers' instructions, as shown in Table 1. Overflow of excess material was achieved by placing a transparent mylar strip and glass layer on the upper surface of the Teflon mold. The samples were kept in distilled water for 24 h at 37°C to complete polymerization. The upper surfaces of all samples were sequentially polished with medium, fine, and superfine aluminum oxide-impregnated discs (Sof-Lex, 3M Oral Care, St. Paul, MN, USA), in accordance with the manufacturers' instructions, by using a low-speed handpiece rotating at 12,000 rpm (30 s for each step). A marked box was created on the upper polished surface to ensure that all measurements were made at the same area before and after immersion in the liquids. The bottom surface of each sample was marked with a number and a code to identify the material.

Surface roughness

Analysis of SR was performed in semi-contact mode with an atomic force microscope (AFM; Park Nx10, Suwon, Republic of Korea). Three-dimensional (3D) topographic images of 10 × 10 μm^2 of the samples were obtained by scanning with a silicon probe tip at a scanning rate of 1 Hz and a scanning resolution of 256 × 256 pixels. Three measurements were obtained from each sample, and average roughness (nm) was calculated.

Surface microhardness

SH was measured by using the Vickers tip of a microhardness device (Buehler MMT-3, Waukegan, IL, USA). A force of 100 g was applied to three points in the defined region on the surface of each sample for 15 s. Diagonal measurements were taken from the corners of notches on the surface, and the Vickers microhardness number (VHN) was calculated with the device by using the formula VHN = 1.8544 × F/d^2, where F is applied force and d is the mean diagonal length in mm.

Scanning electron microscopy-energy dispersive X-ray spectroscopy

Elemental analysis of the samples was performed by using SEM/EDS (FEI, Quanta 650 FEG, Eindhoven, The Netherlands). An area of 20 × 20 μm of the samples was examined at 500× magnification. A spectrum was obtained that illustrated the elements in the basic composition of the material as peaks. No coating material was used on Equia Forte for the SEM/EDS analysis.

After initial measurements of SR, SH, and SEM/EDS, the samples were divided into three subgroups according to liquid type. The contents and pH values of the liquids used for aging—coffee, cola, and saliva—are shown in Table 2. During the experiment, the samples were placed in plastic test tubes filled with 5 mL of liquid for each group, and pH was measured with a pH meter (Inolab WTW, Weilheim, Germany). The samples were stored in the incubator at 37°C and 100% humidity for 7 days (168 h), and liquids were replaced daily. Samples removed from the liquids were washed with distilled water and dried with a blotter before measurements, and roughness, microhardness, and EDS were again measured in the same manner as the initial measurements. In addition, a random sample selected before and after immersion from each group underwent SEM scanning at 5,000× magnification.

Statistical analysis

Statistical analysis was performed by using the SPSS program for Mac version 26 (IBM SPSS Inc., Chicago, IL, USA). The Shapiro-Wilk test was used to examine the data distribution. The Kruskal-Wallis and Mann-Whitney U tests were used to analyze differences in data for SR and SH. The Wilcoxon test was used for paired comparison of data for SR and SH pre- and post-immersion. SEM/EDS data were analyzed by 1-way ANOVA and the Tukey *post hoc* tests. All data were evaluated with a 95% of confidence interval ($P = 0.05$).

Results

Surface roughness

The mean (SD) SR (nm) values of the materials before and after immersion (pre-Ra and post-Ra) are shown in Table 3. Pre- and post-immersion AFM and SEM images of the investigated materials are shown in Figs. 1-4. Analysis of differences among pre-Ra values of the restorative materials revealed that Zirconomer had the highest pre-Ra value, 175.04, which was significantly higher than the values for alkasite (144.22), Activa, (131.64), and Equia Forte (120.29) ($P = 0.014$, $P < 0.001$ $P < 0.001$, respectively). Pre-Ra was higher for alkasite than for Equia Forte ($P = 0.001$). Cola and coffee significantly increased the SR of all materials except Zirconomer immersed in coffee ($P < 0.05$). However, pre-Ra and post-Ra values did not significantly differ for saliva for any material ($P > 0.05$).

Vickers microhardness

The mean (SD) SH values of the materials before and after immersion are shown in Table 4. Zirconomer had the highest pre-VHN SH value, 56.76, which was significantly higher than the values for Activa (33.75) and Equia Forte (43.41) ($P < 0.001$ for both). The pre-VHN value for Activa was significantly lower than those for alkasite (51.79), Equia Forte, and

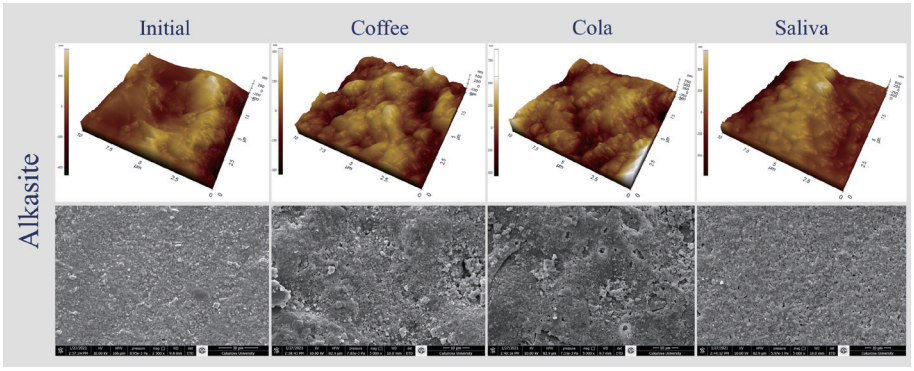


Fig 1 AFM and SEM images of alkasite. In randomly selected AFM images, the initial elevation of 200 nm increased to 500 nm in coffee and saliva and to 750 nm in cola after immersion. An increase in surface irregularity was observed topographically after immersion in coffee and cola. The initial and saliva subgroups of the 3D surface images are similar, as was the case in the SEM images.

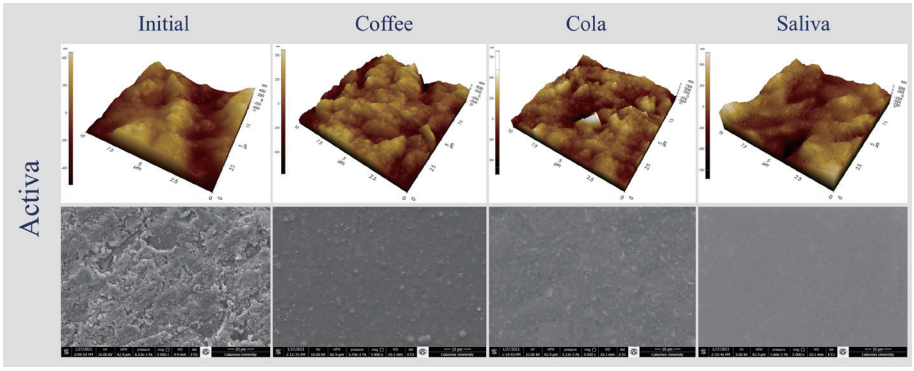


Fig 2 AFM and SEM images of Activa. In randomly selected AFM images, the initial elevation of 400 nm increased to 500 nm in coffee and saliva and to 750 nm in cola after immersion. SEM images of Activa after immersion are similar and indicate that the surface properties changed after contact with all of the liquids. In addition, the micro-porous structure observed in post-immersion SEM images can be attributed to the low amount of inorganic filler of the material and high water absorption of the resin matrix.

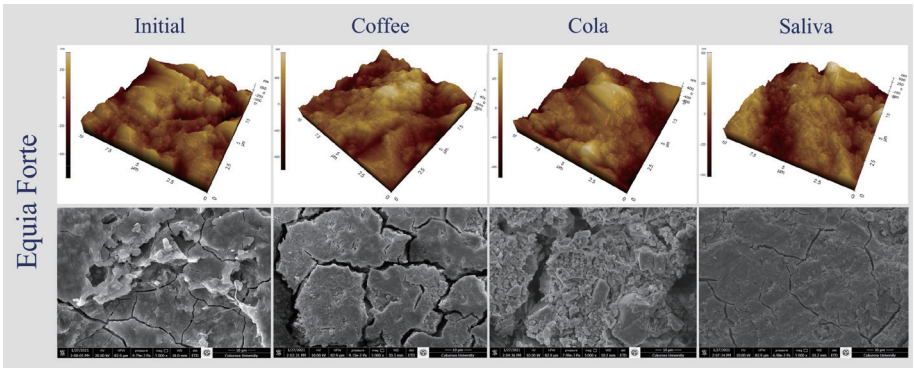


Fig 3 AFM and SEM images of Equia Forte. In randomly selected AFM images, the initial elevation of 250 nm increased to 400 nm in coffee and cola and to 500 nm in saliva after immersion. Although the first three topographic AFM images show a rough surface, Equia Forte had fewer elevations at the nm level than the other groups. Moreover, while fine cracks were observed on the surface in SEM images of the initial and saliva subgroups, deep fissures were formed by exposure to coffee and cola.

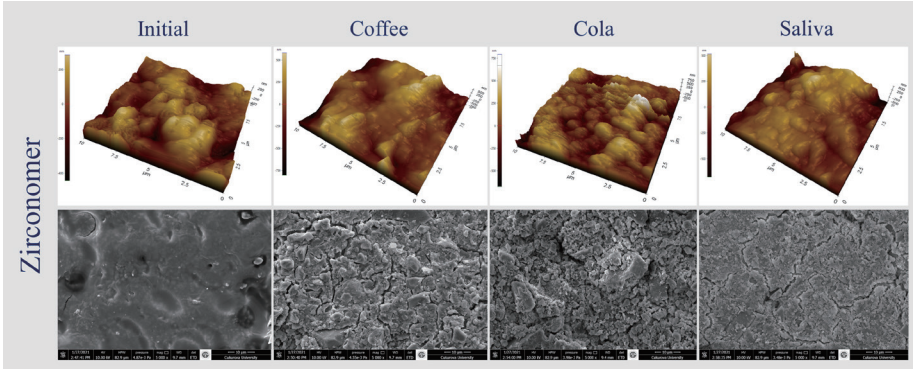


Fig 4 AFM and SEM images of Zirconomer. In randomly selected AFM images, the initial elevation of 200 nm increased to 500 nm in coffee and saliva and to 750 nm in cola after immersion. The cola subgroup had the greatest surface roughness. SEM images of the initial subgroup indicated wide, shallow pits. However, surface irregularities increased after immersion in all liquids, especially cola. The surfaces in SEM images of saliva and coffee are similar.

Table 3 Surface roughness values (nm) of the restorative materials pre- and post-immersion

Materials	Groups	Liquids			
		Coffee	Cola	Saliva	
Alkasite	pre-Ra	$144.58 \pm 21.89^{A,a}$	$147.65 \pm 32.11^{A,a}$	$140.44 \pm 23.93^{A,a}$	$P = 0.870$
	post-Ra	$180.77 \pm 22.51^{B,a}$	$195.46 \pm 32.55^{B,a}$	$147.72 \pm 22.52^{A,b}$	$P = 0.001$*
		$P = 0.011$*	$P = 0.000$*	$P = 0.285$	
Activa	pre-Ra	$133.81 \pm 27.24^{A,a}$	$139.92 \pm 21.38^{A,a}$	$121.19 \pm 20.60^{A,a}$	$P = 0.204$
	post-Ra	$175.01 \pm 24.15^{B,a}$	$180.51 \pm 34.83^{B,a}$	$134.74 \pm 29.07^{A,b}$	$P = 0.003$*
		$P = 0.002$*	$P = 0.007$*	$P = 0.232$	
Equia Forte	pre-Ra	$125.84 \pm 21.84^{A,a}$	$121.74 \pm 17.03^{A,a}$	$113.29 \pm 17.51^{A,a}$	$P = 0.334$
	post-Ra	144.92 ± 21.75^{a}	150.21 ± 17.08^{a}	118.31 ± 18.77^{b}	$P = 0.002$*
		$P = 0.006$*	$P = 0.000$*	$P = 0.413$	
Zirconomer	pre-Ra	$162.06 \pm 29.48^{A,a}$	$187.04 \pm 32.16^{A,a}$	$176.03 \pm 31.82^{A,a}$	$P = 0.218$
	post-Ra	$193.94 \pm 34.17^{A,a}$	$220.60 \pm 32.10^{B,a}$	$186.30 \pm 31.85^{A,a}$	$P = 0.065$
		$P = 0.080$	$P = 0.017$*	$P = 0.475$	

Different capital letters represent a significant difference between pre- and post-immersion (pre-Ra and post-Ra) values. Different lowercase letters represent a significant difference among liquids. *$P < 0.05$ was defined as significant

Table 4 Vickers microhardness values of the restorative materials pre- and post-immersion

Materials	Groups	Liquids			
		Coffee	Cola	Saliva	
Alkasite	pre-VHN	$54.48^{A,a} \pm 5.28$	$50.84^{A,a} \pm 6.52$	$50.03^{A,a} \pm 5.63$	$P = 0.105$
	post-VHN	$40.86^{B,a} \pm 5.47$	$31.82^{B,b} \pm 5.35$	$42.52^{B,a} \pm 7.06$	$P = 0.001$*
		$P = 0.008$*	$P = 0.000$*	$P = 0.028$*	
Activa	pre-VHN	$34.53^{A,a} \pm 3.80$	$35.56^{A,a} \pm 3.07$	$31.16^{A,a} \pm 4.95$	$P = 0.092$
	post-VHN	$15.55^{B,a} \pm 4.30$	$13.76^{B,a} \pm 2.70$	$23.49^{B,b} \pm 4.00$	$P = 0.000$*
		$P = 0.000$*	$P = 0.005$*	P = 0.007*	
Equia Forte	pre-VHN	$40.68^{A,a} \pm 4.48$	$46.20^{A,a} \pm 7.90$	$43.34^{A,a} \pm 7.69$	$P = 0.218$
	post-VHN	$34.87^{B,ab} \pm 6.27$	$33.60^{B,a} \pm 5.85$	$40.26^{A,b} \pm 6.13$	$P = 0.016$*
		P = 0.021*	$P = 0.005$*	P = 0.103	
Zirconomer	pre-VHN	$54.84^{A,a} \pm 4.46$	$56.71^{A,a} \pm 4.96$	$58.71^{A,a} \pm 6.99$	$P = 0.625$
	post-VHN	$48.45^{A,a} \pm 6.28$	$42.53^{B,a} \pm 7.36$	$53.18^{A,b} \pm 3.29$	P = 0.004*
		$P = 0.051$	$P = 0.005$*	$P = 0.059$	

Different capital letters represent a significant difference between pre- and post-immersion (pre-VHN and post-VHN) values. Different lowercase letters represent a significant difference among the liquids. *$P < 0.05$ was defined as significant

Zirconomer ($P < 0.001$, $P = 0.007$, and $P < 0.001$, respectively). All liquids caused a significant decrease in microhardness for alkasite and Activa ($P < 0.05$), coffee and cola caused a significant decrease for Equia Forte ($P < 0.05$), and only cola reduced the SH of Zirconomer ($P = 0.005$).

Scanning electron microscopy-energy dispersive X-ray spectroscopy

The representative SEM/EDS spectrum, which shows the chemical compositions of the 4 restorative materials, is shown in Fig. 5. The percentage weights of the essential elements of each material are shown in Table 5. Carbon (C), oxygen (O), sodium (Na), aluminum (Al), silicon (Si), Ca, and F were found in all materials. The ratio of F in the materials before immersion was 6.47 for alkasite, 1.78 for Activa, 8.33 for Equia Forte, and 8.25 for Zirconomer. The ratio of F was significantly lower in Activa than in the other materials ($P < 0.001$). The element P was observed in all materials except alkasite.

Coffee significantly reduced the ratio of F in alkasite ($P = 0.027$). Coffee and cola decreased the ratio of Na in alkasite ($P = 0.023$ and 0.026, respectively). Coffee and saliva decreased the ratio of F and Na in Activa ($P < 0.05$). The ratios of C, O, Na, and Al in Equia Forte were significantly decreased by all liquids ($P < 0.05$). Cola and saliva decreased the ratio of F in Equia ($P < 0.001$ for both of them). Coffee dramatically increased the ratio of P in Equia Forte ($P < 0.001$). Coffee, cola, and saliva significantly reduced the F ratio in Zirconomer ($P = 0.002$, 0.010, and 0.009, respectively). Coffee and cola decreased the ratio of Na in Zirconomer ($P = 0.05$). The liquids had no significant effect on the other structural elements of Zirconomer.

Discussion

This study examined the effects of common liquids on the surface properties of pristine restorative materials. Because the liquids changed the surface roughness, hardness, and elemental structure of the materials, the study hypotheses are rejected.

In previous studies, materials were exposed to liquids for different durations. One study [16] estimated that the annual exposure of tooth enamel to soft drinks was 90,000 s (1,500 min or 25 h). The present study thus used 168 h of liquid exposure, approximately 7 years, as a reasonable estimate of adult exposure.

Various artificial saliva formulations are described in the literature, but there is no consensus on which is most similar to human saliva. However, a common feature of the different formulations is that they minimize the effect of pH attacks by acting as a buffer on the tooth surface [17]. Therefore, an artificial saliva formula was used as a positive control group in this study [14].

By providing a 3D topographic image at nanometer resolution, AFM can be used to collect fundamental data on particle and particle–surface interactions and investigate surface heterogeneity. SEM and AFM provide micromorphological and microtopographic images that allow reliable evaluation of dental materials [18,19]. Thus, AFM was preferred for analysis of long-term interactions of frequently consumed beverages with the surfaces of the materials and for investigating surface topography. Analysis of data on surface properties revealed that surface roughness values for AFM and SEM analysis were similar.

In this study, SR was similar for alkasite, Activa, and Equia Forte but significantly higher for Zirconomer. Although SR is similar for resin-modified GIC and HVGIC [20], the present results for Zirconomer may be attributable to the protruding structure of hard zirconia glass fillers, a result of polishing. In roughness studies of HVGIC and composite resin, the low roughness values for Equia Forte were attributed to the resin coat [21]. Bollen et al. [22] reported that an SR of less than 0.2 μm is optimal for preventing plaque accumulation and caries formation. Roughness values increased with exposure to beverages, but all materials except Zirconomer were within clinically acceptable limits. Deterioration and surface roughness of restorative materials increased after exposure to beverages [23,24]. The increase in the SR of resin-based materials was attributed to water absorption by the material. Water caused the loss of polymer components by softening and hydrolyzing bonds of the material [25]. In addition, strong acids, such as carbonic acid in cola, damage the material surface by

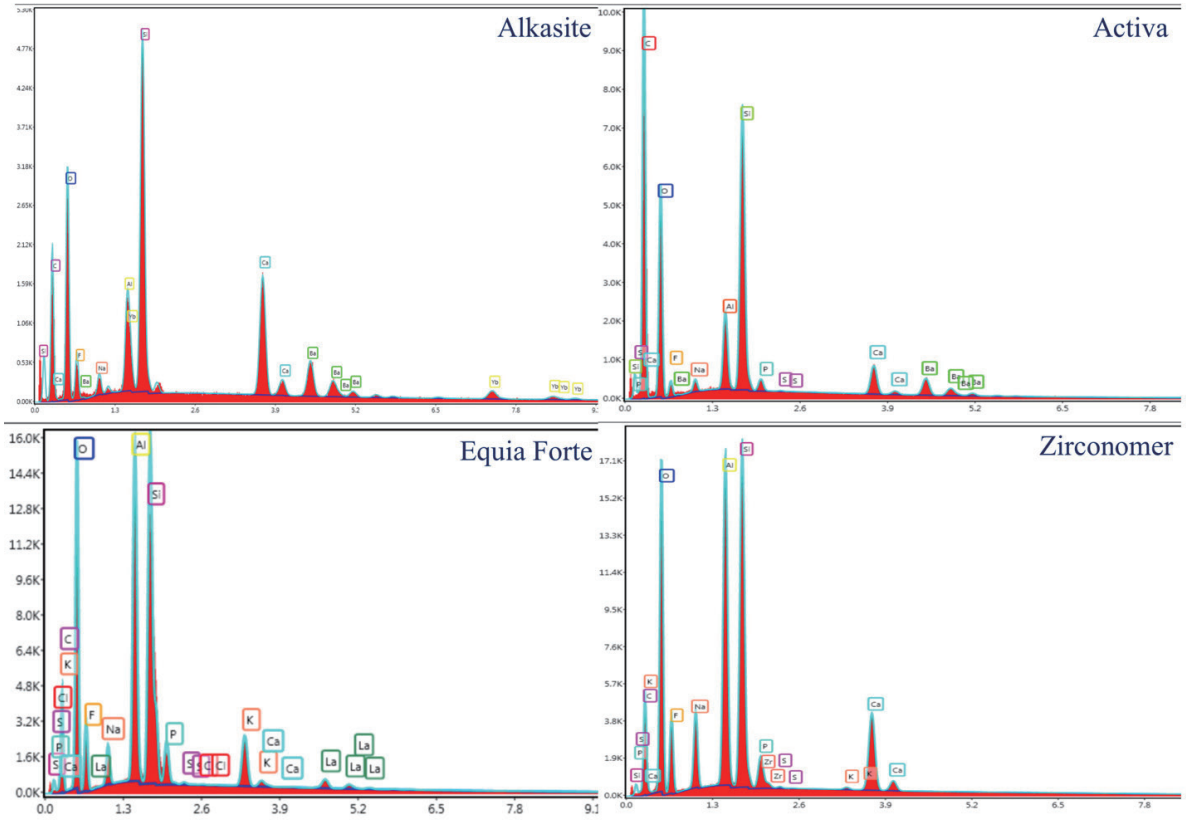


Fig 5 The energy dispersive spectroscopy (EDS) spectrum of the present restorative materials before immersion in liquids. In all materials, the elements carbon, oxygen, silicon, and aluminum had the highest peaks. Yb and Ba in alkasite, Ba in Activa,La in Equia Forte, and Zr in Zirconomer were specific to the materials. Al content was high in Equia Forte and Zirconomer but not in the other materials. Moreover, the low Fluorine peak in Activa distinguished it from the other materials.

Table 5 Percentage weights of elements detected in the restorative materials pre- and post-immersion

		C	O	F	Na	Al	Sİ	P	Ca	La	Ba	Yb	Zr
Alkasite	initial	29.17 (8.61)	30.71 (3.08)	6.46 (0.66)	1.33 (0.20)	2.63 (0.56)	11.71 (2.30)	-	6.04 (2.09)	-	7.72 (1.95)	4.05 (0.38)	-
	coffee	33.50 (2.36)	39.84 (2.07)	4.31 (0.94)	0.55 (0.14)	1.85 (0.97)	9.25 (2.12)	-	4.05 (1.78)	-	4.84 (1.36)	1.73 (1.73)	-
	cola	32.62 (5.04)	39.31 (1.71)	7.11 (0.53)	0.54 (0.43)	1.71 (0.15)	9.88 (1.52)	-	0.51 (0.13)	-	5.83 (1.21)	1.95 (0.27)	-
	saliva	35.18 (9.21)	35.95 (2.50)	8.26 (0.68)	1.05 (0.15)	2.33 (0.82)	7.93 (3.07)	-	1.52 (0.65)	-	4.28 (2.39)	3.21 (0.70)	-
Activa	initial	48.23 (2.46)	31.70 (1.71)	1.78 (0.17)	0.77 (0.07)	2.36 (0.14)	8.77 (0.55)	0.48 (0.06)	1.58 (0.17)	-	4.28 (0.56)	-	-
	coffee	45.59 (0.57)	30.72 (0.91)	1.36 (0.15)	0.49 (0.04)	2.71 (0.17)	10.39 (0.49)	0.56 (0.03)	2.00 (0.31)	-	6.16 (0.79)	-	-
	cola	45.58 (2.11)	30.93 (1.47)	1.48 (0.12)	0.63 (0.03)	2.66 (0.07)	10.13 (0.36)	0.53 (0.01)	1.99 (0.15)	-	6.02 (0.38)	-	-
	saliva	45.77 (0.53)	30.56 (0.42)	1.36 (0.13)	0.54 (0.10)	2.67 (0.11)	10.31 (0.19)	0.59 (0.04)	2.17 (0.17)	-	6.00 (0.50)	-	-
Equia Forte	initial	25.15 (2.53)	35.43 (0.80)	8.32 (0.23)	2.22 (0.16)	10.16 (0.95)	10.13 (2.30)	1.63 (0.35)	0.17 (0.06)	1.85 (0.11)	-	-	-
	coffee	19.80 (0.26)	38.62 (0.79)	7.64 (0.47)	1.09 (0.10)	0.65 (0.10)	10.82 (0.24)	12.65 (0.41)	1.50 (0.09)	2.22 (0.15)	-	-	-
	cola	39.41 (0.63)	41.53 (0.57)	1.61 (0.08)	0.07 (0.01)	3.00 (0.13)	10.67 (0.46)	2.51 (0.39)	0.37 (0.12)	0.47 (0.16)	-	-	-
	saliva	13.48 (0.81)	30.71 (0.53)	4.50 (0.36)	9.76 (0.58)	6.46 (0.51)	10.22 (0.75)	3.72 (0.20)	1.40 (0.20)	1.36 (0.09)	-	-	-
Zirconomer	initial	25.73 (4.41)	35.60 (1.49)	8.25 (1.27)	4.15 (0.55)	9.49 (1.17)	10.55 (1.08)	0.99 (0.12)	4.50 (0.48)	-	-	-	0.63 (0.02)
	coffee	27.76 (9.68)	40.72 (6.10)	2.87 (0.86)	1.56 (1.07)	5.67 (1.94)	15.45 (7.31)	1.15 (0.34)	2.50 (1.33)	-	-	-	1.04 (0.39)
	cola	23.30 (8.28)	41.65 (2.69)	4.18 (1.40)	1.52 (0.55)	8.52 (2.10)	11.84 (2.54)	3.29 (3.59)	3.60 (0.77)	-	-	-	0.74 (0.09)
	saliva	20.21 (3.47)	41.05 (3.58)	4.10 (0.90)	2.41 ((1.47)	9.17 (0.20)	13.74 (1.16)	3.00 (2.49)	3.60 (1.73)	-	-	-	1.02 (0.19)

C, carbon; O, oxygen; F, fluorine; Na, sodium; Al, aluminum; Sİ, silicon; P, phosphor; Ca, calcium; La, lanthanum; Ba, barium; Yb, ytterbium; Zr, zirconium

softening and abrading it. Because of its low pH, cola exposure resulted in the highest SR of the restorative materials [26]. Previous studies reported that GIC-based materials absorb acidic liquids, causing material degradation and dimensional changes. [14,27]. A study of Equia Forte and alkasite reported significant increases in SR after exposure to acidic pH for 1 week [27]. In the present study, alkasite, which had satisfactory initial roughness, had post-immersion Ra values similar to those of GIC-based materials, most likely because the material was set in self-cure mode. Past and present results show that saliva does not have a significant effect on roughness, while exposure to cola and coffee increased the roughness of all materials.

Restorative materials must have adequate hardness to successfully resist chewing forces and temperature and pH changes in the oral cavity. In this study, Zirconomer had the highest SH and Activa had the lowest SH. Although both are HVGIC materials, initial SH was significantly higher for Zirconomer than for Equia Forte, perhaps because of the different filler/volume ratio of the materials and the presence of polycrystalline ceramic zirconia fillers in Zirconomer. Material content, filler size, filler/volume ratio, resin type, and particle size were found to affect the surface properties of restorative materials [28], and a resin coating reduced the hardness of Equia Forte [4]. In this study, Activa had the lowest hardness value in the initial SH measurement. In studies of composite resin and HVGIC materials, Activa had the lowest hardness [29,30]. These results are consistent with those of the present study. The fact that SH was significantly higher for alkasite than for Equia Forte and Activa is likely attributable to its 78.4% inorganic filler content [31].

Studies of resin composite and glass ionomer–containing materials reported decreased SH after immersion in coffee, cola, and energy drinks and that the magnitude of the decrease varied in relation to the material

structure [26,32,33]. The SH of materials containing resin markedly decreased in solutions with a low pH [2,34]. Awliya et al. [35] reported no significant difference in the microhardness of resin-based materials before and after immersion in coffee. In contrast, the SH of resin-containing Activa and alkasite greatly decreased in all liquids in the present study. The 2-hydroxyethylmethacrylate (HEMA) resin component of Activa increases water absorption, causing hydrolysis between the resin matrix and filler particles and consequent weakening of the structure of the material. The decrease in the SH of alkasite can be attributed to its inability to form a homogeneous surface with its powder-liquid structure and self-curing mode. However, the SH of Equia Forte decreased in coffee and cola, while the SH of Zirconomer decreased only in cola. Saliva had no effect on HVGIC materials. Perhaps the acidic pH of cola affected the HVGIC materials.

Alkasite, Equia Forte, and Zirconomer had similar ratios of F, while F content was much lower for Activa. The high solubility of GICs caused the material to be dissolved more easily in the solutions; however, GICs were reported to encourage more F ion release from the material [4]. The reduction in Al and F ions in Equia Forte and Zirconomer might be caused by hydrolysis of Al-O-Si bonds in fluoroaluminosilicate glass. This release of F ions indicates that the materials formed fluorapatite structures [36]. Ca ions decreased in alkasite, and bioactive materials exhibited an exchange with H ions in solution, suggesting that it induces hydroxyapatite formation [36,37]. In addition, octacalcium phosphate apatite was formed in an alkasite environment in the presence of sufficient phosphate, whereas calcium fluoride was formed when there was insufficient phosphate [36]. In this study, the above finding might be explained by the presence of fewer F ions in the structure of alkasite in phosphate-free coffee than in phosphate-containing cola and saliva. Although alkasite has less bioactive glass filler than Activa, Al release was higher than in Activa after immersion in cola because the glass filler in alkasite had a higher Al/Si ratio and its glass fillers were more reactive [38]. Tiskaya et al. [36] concluded that Activa contains fluoroaluminosilicate glass but that it was not a bioactive material since it was unable to form apatite. In addition, less fluoride was released in Activa than in GIC-containing materials [3]. The present EDS results are consistent with the characteristics of the materials. The F ratios of Equia and Zirconomer were lower, especially in cola, which has a low pH. Other EDS studies of the same materials reported elemental mass percentages that were similar to those of the present study [4].

Limitations of this in vitro study include the inability to simulate the pH cycle and buffering capacity of the oral cavity. In addition, the materials were evaluated without mechanical loading, and current hygiene procedures such as brushing affect the oral cavity. The finishing and polishing process was completed with abrasive discs; rubber polishers were not included. The present results therefore require confirmation by long-term clinical studies.

The present AFM and SEM/EDS analysis contributes to the literature by clarifying the effects of commonly consumed beverages on the surface characteristics of recently developed fluorine-releasing bulk-fill restorative materials. Immersion in liquids with different pH values increased the surface roughness and decreased the surface hardness of all materials. Because of their acceptable surface features and high fluorine content, Equia Forte and Zirconomer are recommended for use in adults at high risk of caries. Alkasite was found to be a promising bioactive material with suitable characteristics, while the properties of Activa were unsatisfactory.

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Conflicts of interest

The authors have no conflicts of interest to declare.

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