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RESEARCH ARTICLE

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Evaluation of the microhardness of different resin-based dental restorative materials treated with gastric acid: Scanning electron microscopy–energy dispersive X-ray spectroscopy analysis

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Abstract

The aim of this study is to evaluate the microhardness, relative surface roughness, and elemental changes of resin-based dental restorative materials (RDRMs) after gastric acid treatment. Five different RDRMs (Group 1 [Filtek Z550], Group 2 [Beautifil II], Group 3 [Vertise Flow], Group 4 [Dyract XP], Group 5 [Fuji II LC]) were used. Samples were formed by using plexiglass molds of 10 mm diameter and 2 mm thickness. A total of 50 samples ($n = 10$) for microhardness tests and a total of 15 samples ($n = 3$) for scanning electron microscopy (SEM)–energy dispersive X-ray spectroscopy (EDX) analysis were prepared. All samples of each group were treated to gastric acid, simultaneously. A Vickers microhardness tester was used to evaluate the microhardness of the upper surfaces of each sample. SEM–EDX system was used for microstructure and elemental composition detection. The SEM–EDX, microhardness and relative surface roughness analysis were made prior to treatment in gastric acid for 14 days and analysis were repeated on the 14th day. As the difference in the microhardness values of RDRMs was compared, the time-dependent variation in all RDRMs was found to be statistically significant. It was observed that a drastic decrease in microhardness values was in Beautifil II, Filtek Z550, Vertise Flow, Fuji II LC, and Dyract XP, respectively. Average decrease rate of microhardness values compared to the initial state can be listed from high to low as Beautifil II (%35.72), Vertise Flow (% 28.88), Fuji II LC (% 21.09), Dyract XP (%17.60), and Filtek Z550 (% 16.58). As a result, in in-vitro conditions gastric acid decreased microhardness while increasing the relative surface roughness of RDRMs.

KEYWORDS
gastric acid, microhardness, relative surface roughness, SEM–EDX

1 | INTRODUCTION

Dental erosion (DE) is defined as the progressive, irreversible loss of dental hard tissues by acid dissolution without bacterial involvement. Extrinsic and intrinsic factors play a role in the etiology of DE. Various medications and acid containing food & beverages can be the examples of extrinsic factors. Additionally, vomiting & regurgitation caused by psychological disorders such as anorexia and blumia and gastro-esophageal reflux (GER) are the examples of intrinsic factors (Jaeggi & Lussi, 2006; Johansson, Omar, Carlsson, & Johansson, 2012). Gastric

acid can repeatedly reach the oral cavity and teeth due to frequent vomiting, persistent GER and regurgitation. The pH value of gastric acid being around 1–1.5 triggers the formation of DE (Johansson et al., 2012; Scheutzel, 1996). When the pH of the oral environment reaches the critical threshold value of pH 5.5, demineralization of tooth enamel may occur (Hicks, Garcia-Godoy, & Flaitz, 2005). The enamel surface softens due to the demineralization and thus a decrease in micro hardness values can be observed (Zanatta, Esper, Valera, Melo, & Bresciani, 2016). If the acid effects for a long time, clinically visible defects may occur and the physical and mechanical properties of the teeth may also change. Teeth are considered to be mechanically weakened by the reduction in microhardness (Ganss, 2006).

One of the important points to be considered in the selection of dental restorative materials is their mechanical properties. Restorative materials used to replace the missing tooth structure must be strong enough to withstand the forces associated with chewing (Hengtrakool, Kukiattrakoon, & Kedjarune-Leggat, 2011). Microhardness tests can be used to evaluate these mechanical properties. Microhardness is related to the compositional properties of the materials tested and is affected by aging, water absorption and reactions of the material surface (Prabhakar, Jibi Paul, & Basappa, 2010). Microhardness measurements are performed using indentation tests (Vickers or Knoop), which can provide good determination of resistance to local plastic deformation (Deniz Arısu et al., 2018). Another test used in evaluating the mechanical properties is surface roughness tests. SR of the restorative materials adversely affects their marginal integrity and abrasion, and it causes the coloration of restoration, plaque accumulation and gingival irritation, leading to clinical failure (Joniot, Gregoire, Auther, & Roques, 2000; Reis, Giannini, Lovadino, & dos Santos Dias, 2002). Evaluation of surface roughness could be made with qualitative & (semi) quantitative methods such as profilometer, atomic force microscopy, SEM, and surface profile analysis.

The aim of this in vitro study is to evaluate the microhardness, relative surface roughness and elemental analysis results of dental restorative materials after gastric acid treatment. The null hypothesis of our research was that exposure of these dental materials to gastric acid for a long time would cause changes in both microhardness values and elemental structures.

2 | MATERIALS AND METHOD

In this study, five different resin-based dental restorative materials (RDRMs) with different monomer and filler contents were evaluated. Technical profiles of RDRMs were shown in Table 1. The power analysis of the study was performed to determine the sample size, it was decided to take 10 specimens to each group and the power of the test was found to be $p = .90640$.

A total of 50 samples ($n = 10$) for microhardness tests and a total of 15 samples ($n = 3$) for scanning electron microscopy (SEM)–energy dispersive X-ray spectroscopy (EDX) analysis were prepared. Samples were formed by using plexiglass molds of 10 mm diameter and 2 mm thickness. After the materials were placed in the mold, mylar strips were placed on both surfaces. Excess material that overflowed was removed by applying pressure with a glass sheet. Subsequently, the samples were polymerized with an LED light device (Elipar S10, 3 M ESPE, St. Paul, MN) with a wavelength of 430–480 nm and a light intensity of 1.200 mW/cm^2. All samples were extracted from plastic molds and stored in distilled water for 24 hr. Thick, medium, fine and super fine grained aluminum oxide discs (Sof-Lex Polishing Discs, 3 M ESPE, St. Paul, MN) were used, respectively, for the finishing and polishing of the samples under running water. After each polishing procedures, the samples were washed for 10 s to remove debris and air-dried for 5 s. Finally, all samples were dried with blotter paper.

2.1 | Preparation of gastric acid and treatment procedure

According to the reference of the previous study (Guler & Unal, 2018) in which the surface properties of dental restorative materials were investigated, an artificial gastric acid solution with a pH value of 1.2 was prepared in Sivas Cumhuriyet University, Faculty of Science, Department of Chemistry. During the experiment, samples were stored in tubes filled with 3 ml of freshly prepared gastric acid solution. Samples were treated for 14 days at 37°C, 18 hr in gastric acid and 6 hr in distilled water per day (Guler & Unal, 2018). Gastric acid solution was replenished every day. Treated samples were washed with distilled water and dried with a blotter prior to measurements.

2.2 | Microhardness tests

The microhardness values of dental restorative materials were determined by microhardness test. With a digital microhardness tester (Shimadzu HMV-M3, Kyoto, Japan), a 300 g load was applied through the Vickers indentation for 15 s. Measurements were made on different regions of the upper surfaces of each sample and the average of five measurements was calculated.

2.3 | Evaluation of the relative surface roughness

The relative roughness of the surface profile was examined with the post process program in SEM, Mira TC. The area of 100*100 μm^2 was determined and the average surface profile was evaluated according to the electron beam histogram on the device (Soygun, Varol, Ozer, & Bolayir, 2017).

2.4 | SEM and EDX analysis

SEM photographs were taken from samples randomly selected samples of each group on the initial, seventh and 14th day. Samples were coated with (Quorum Q150R ES, Quorum Technologies, UK) gold and evaluated with SEM (Tescan MIRA3 XMU, Brno, Czech Republic). The entire surface of sample was scanned and the most representative

TABLE 1 The technical profiles of resin based dental restorative materials

Materials	Type	Composition	Filler ratio (weighted)	Particle size	Manufacturer	Lot number
Beautifil II	Giomer	Bis-GMA, TEGDMA, S-PRG, aluminofluoro-borosilicate glass, Al_2O_3, DL-camphorquinone	%83.3	0.8 μm	Shofu Inc., Kyoto, Japan	071528
Dyract XP	Polyacid modified composite (compomer)	UDMA, TCB resin, TEGDMA, trimethacrylate resin, carboxylic acid camphorquinone, ethyl-4 dimethylaminobenzoate, butylated hydroxy toluene (BHT), UV stabilizer, strontium aluminosodiumfluoro-phosphor-silicate glass, highly dispersed silicon dioxide, strontium fluoride (2.5–10%), iron oxide and titanium dioxide pigments	%47	0.8 μm	Dentsply, DeTrey, Konstanz, Germany	1,511,000,295
Filtek Z550	Nanohybrid composite resin	Bis-GMA, Bis-EMA, PEGDMA, TEGDMA, UDMA, surface-modified zirconia/silica fillers 3,000 nm (3 μm or less), nonagglomerated/nonaggregated surface-modified silica particles 20 nm	%81.8	0.02 μm	3 M/ESPE, St. Paul, MN	N636062
Fuji II LC	Resin modified glass ionomer cement (RMGIC)	Distilled water, polyacrylic acid, HEMA, urethane dimethacrylate, camphorquinone, fluoroaluminosilicate filler	%58	5.9 μm	GC corporation, Tokyo, Japan	1,601,271
Vertise Flow	Self-adhering flowable composite resin	GPDM, HEMA, prepolymerized filler, 1 mm barium glass filler, nano-sized colloidal silica, Nano-sized ytterbium fluoride	%70	1 μm	Kerr, Orange, CA	5,842,135

Abbreviations: Bis-EMA, ethoxylated bisphenol A dimethacrylate; Bis-GMA, bisphenol A glycidyl methacrylate; GPDM, glycero-phosphate dimethacrylate; HEMA, 2-hydroxyethyl methacrylate; PEGDMA, polyethylene glycol dimethacrylate; S-PRG, surface pre-reacted glass-ionomer; TEGDMA, triethylene glycol dimethacrylate; UDMA, urethane dimethacrylate.

areas showing structural surface changes were photographed at 1kx, 2kx, and 5kx magnification with 10 kV acceleration voltage.

To evaluate the chemical composition and surface structure, randomly selected samples from each group were examined with an energy dispersive X-ray spectroscopy (EDX, Inca, Oxford Inst.) system for surface elemental analysis. In the present study, EDX measurements made from the surface of the materials were examined to determine the elemental distribution of RDRMs.

2.5 | Statistical analysis

The data obtained from the present study were evaluated with the SPSS 22.0 (Statistical Package for Social Science Version: 22) program. For evaluation of the data, Kolmogorov-Smirnow and the paired sample *t* test were used. *p*-values equal to or less than .05 were considered statistically significant.

3 | RESULTS

3.1 | The EDX analysis results

The surfaces at the initial, 7th and 14th days-treated samples were evaluated with SEM and the images of samples at magnification of 2kx were shown in Figure 1. All sample surfaces were gold (Au) coated for conductivity but Au was not included in EDX quantification.

EDX measurements made from the surface of the materials to determine the elemental distribution of RDRMs were shown in Figure 2. The yellow and red spectra in Figure 2 represent the elemental distribution of RDRMs at initial and after 14th days of gastric acid treatment. While the yellow spectra represent the initial analysis results, the red spectra represent the analysis results on the 14th day.

In Beautifil II group, B, O, F, Al, Si decreased and C increased after 14 days of gastric acid treatment shown in Figure 2a. When the SEM photographs were examined with EDX analysis, no glass particles were observed. Due to the effect of gastric acid, the outermost part of the material can be said dissolved and the particles mentioned on the polymer surface have been removed.

In the Dyract XP group, after 14 days of gastric acid treatment each particle with sharp corners was completely detached from the surface shown in Figure 1b." Sr, Al, Na, F are related compounds dissolved in solution after gastric acid treatment shown in Figure 2b.

In Fuji II LC group, for the initial condition in Figure 1c the coarse silica inorganic particles are seen and many microcracks are visible around them. Since the coarse particles are sharp and irregularly shaped, it may be expected to dissolve faster by detaching from the polymer surface. After the gastric acid treatment, Al, F decreased while Si, O, and C increased and is shown in Figure 2c.

In the Vertise Flow group, glass silica fillers such as barium silicate, ytterbium fluoride, alumina silicate bound to polymers are seen as sharp diagonal particles shown in Figure 1d. These particles appear to be detached from the structure shown in Figure 1d′ by the effect of gastric acid. After the gastric acid treatment, Ba, Yb, Si, Al decreased while O and C increased and is shown in Figure 2d.

In the Filtek Z550 group by examining the EDX results, no significant changes were raised which can be interpreted as the dissolution of all elements at the same time or no significant dissolution may occur to smoothen the surface to an extent as shown in Figure 2e.

3.2 | The microhardness & relative surface roughness results

When initial and 14th day microhardness measurement values were compared in all groups, the difference was found statistically significant. It is seen that the highest decrease in microhardness values is in Beautifil II, Filtek Z550, Vertise Flow, Fuji II LC, Dyract XP. Average decrease rate of microhardness values compared to the initial state can be listed from high to low as Beautifil II (%35.72), Vertise Flow (% 28.88), Fuji II LC (% 21.09), Dyract XP (%17.60), and Filtek Z550 (% 16.58). Accordingly, the materials with the highest decrease in microhardness values proportionally are Beautifil II, Vertise Flow, Fuji II LC, Dyract XP, and Filtek Z550, respectively (Table 2).

The post process program of SEM device named as Mira TC was used to evaluate the relative roughness determination of the surfaces of samples before and after the gastric acid treatment. The procedure was done by drawing a rectangle of 100*100 μm^2 to evaluate the areal roughness of imaged surface. The image histogram was adjusted accordingly for obtaining the best image results to show hills and valleys simultaneously. Then, the averaged roughness diagram was obtained in jpeg form and shown under each image, respectively. The highest point was subtracted from the lowest point and was multiplied by 100 then divided to the highest one for obtaining an analytical value of percentage deviation as roughness on surface.

As seen from Figure 1a, for Beautifil II, 17% of deviation was found on surface as relative roughness due to surface regularity before the gastric acid treatment. After the gastric acid treatment, as clearly seen from the corresponding Figure 1a related pictures, this value increased up to 20% for seventh day in Figure 1a′ while increasing up to 24% in Figure 1a**”** due to deeper pores on surface which makes the surface to behave as hill. So the maximum and minimum levels are re-arranged and the roughness value increases from 17 to 24%. This roughness decrease may also cause the microhardness values to decrease by forming deep pores and easily fracturing pores by losing the interconnectivity of polymers.

Figure 1b represents the surface features of Dyract XP before gastric acid treatment while Figure 1b′ and b″ stands for after the gastric acid treatment for 7 and 14 days, respectively. The surface was seen to be smoother with some polishing grooves on it to form possibly hills and valleys that was evaluated as 16% relative roughness for Figure 1b, %17 for Figure 1b′ and repeating 17% for Figure 1b**”.** This slight roughness divergence may come from the forming of very tiny holes on surface which in turn due to erosion and removal of nanofiller materials from surface by dissolving into gastric acid solution. The resultant microhardness is aimed to decrease by this removal and hard particle-free surface of polymeric structure.

Figure 1c shows the surface of Fuji II prior to gastric acid treatment and Figure 1c′ and c″ shows the afterwards. Fuji was seen as the roughest surface of all by having a relative roughness of 33% by post process, afterwards the roughness was increased up to 43% with

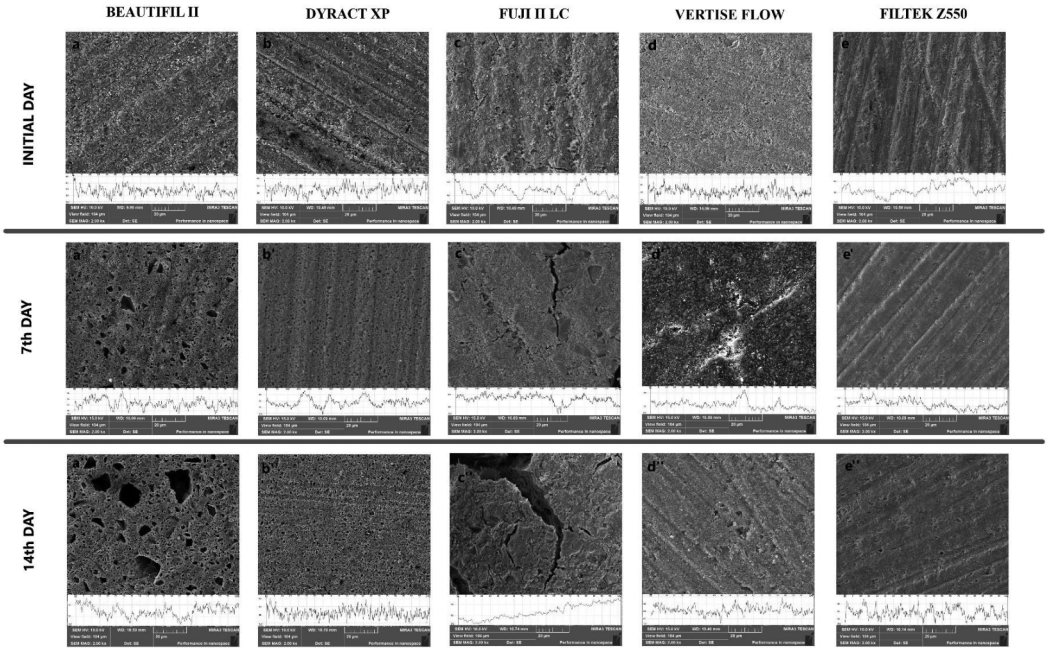
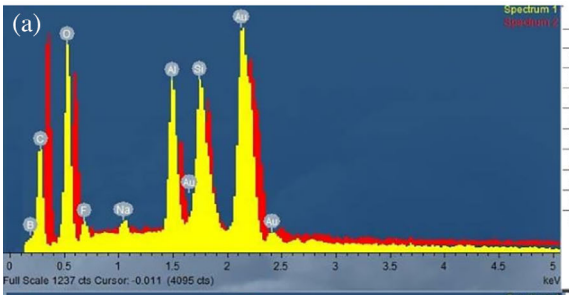
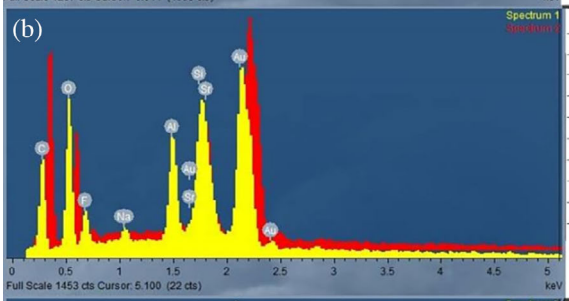


FIGURE 1 SEM photographs and relative surface roughness profiles of RDRMs prior and after 7th & 14th days of gastric acid treatment. SEM, scanning electron microscopy



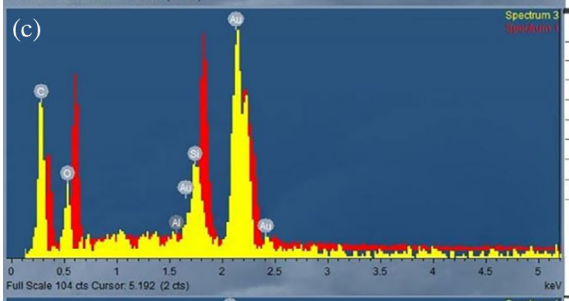
Beautifil II SEM-EDX Analysis Results

	INITIAL DAY		7th DAY		14th DAY	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
B	21.19±2.72	26.87	20.11±1.91	24.47	18.19±1.92	21.97
C	35.79±1.70	40.86	47.31±1.83	50.28	51.19±1.49	55.65
O	27.82±1.26	23.85	24.83±0.75	19.45	22.46±0.89	18.33
F	3.50±0.55	2.53	2.48±0.34	1.77	0.88±0.38	0.61
Na	0.62±0.14	0.37	0.22±0.07	0.12	0.10±0.09	0.06
Al	5.69±0.30	2.89	3.48±0.27	1.75	2.69±0.16	1.30
Si	5.39±0.34	2.63	4.94±0.12	2.16	4.48±0.23	2.08
Totals	100.0	100.0	100.0	100.0	100.0	100.0



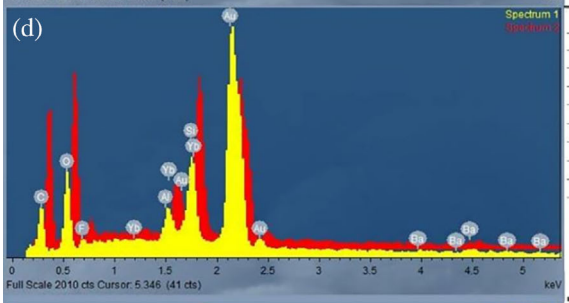
Dyract XP SEM-EDX Analysis Results

	INITIAL DAY		7th DAY		14th DAY	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C	34.51±1.21	49.17	51.74±1.03	59.76	55.11±1.35	64.88
O	29.46±0.96	31.52	30.91±0.89	29.79	31.10±1.16	27.48
F	8.76±0.78	7.89	5.05±0.86	5.02	3.95±0.91	2.94
Na	0.84±0.18	0.63	0.34±0.03	0.21	0.28±0.22	0.17
Al	5.67±0.27	3.60	0.99±0.07	0.58	0.67±0.21	0.35
Si	7.56±0.40	4.61	7.61±0.64	4.25	8.02±0.46	4.04
Sr	13.20±0.93	2.58	2.35±1.05	0.39	0.87±1.03	0.14
Totals	100.0	100.0	100.0	100.0	100.0	100.0



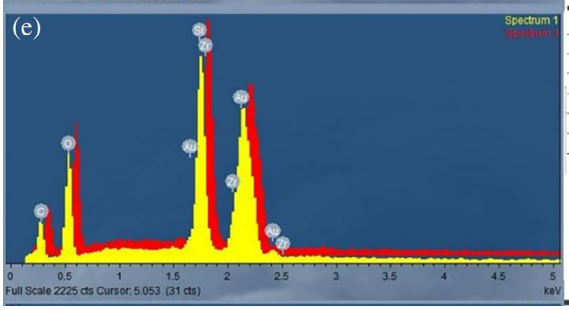
Fuji II LC SEM-EDX Analysis Results

	INITIAL DAY		7th DAY		14th DAY	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C	35.27±1.51	46.60	35.73±1.61	47.29	37.37±1.20	47.59
O	32.38±1.25	32.11	41.17±1.84	42.31	44.47±1.07	42.52
F	10.05±1.17	8.39	0.85±0.44	0.87	-	-
Na	0.44±0.28	0.30	0.05±0.01	0.04	-	-
Al	10.53±0.48	6.19	2.91±0.98	1.85	0.28±0.17	0.16
Si	11.33±0.62	6.40	11.98±0.85	7.64	17.88±0.54	9.74
Totals	100.0	100.0	100.0	100.0	100.0	100.0



Vertise Flow SEM-EDX Analysis Results

	INITIAL DAY		7th DAY		14th DAY	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C	27.78±1.66	45.27	33.81±0.91	48.71	35.73±1.20	51.70
O	30.01±1.46	36.71	30.91±1.44	36.05	32.09±1.05	34.86
F	4.82±1.32	4.96	4.81±0.56	4.71	4.92±0.90	4.50
Al	1.98±0.36	1.43	0.78±0.41	0.5	0.68±0.22	0.44
Si	12.59±0.70	8.77	12.01±0.17	7.93	11.07±0.43	6.85
Ba	9.48±2.11	1.35	4.52±2.02	0.62	3.86±1.24	0.49
Yb	13.34±1.69	1.51	13.08±1.65	1.48	11.66±1.07	1.17
Totals	100.0	100.0	100.0	100.0	100.0	100.0



Filtek Z550 SEM-EDX Analysis Results

	INITIAL DAY		7th DAY		14th DAY	
Element	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C	28.29±1.52	41.18	28.08±0.98	41.01	29.07±1.46	41.58
O	39.14±1.27	42.77	39.91±1.14	43.06	40.26±1.26	43.23
Si	22.75±0.75	14.16	21.99±1.21	14.08	22.24±0.72	13.60
Zr	9.82±1.48	1.88	8.84±1.56	1.85	8.43±1.45	1.59
Totals	100.0	100.0	100.0	100.0	100.0	100.0

FIGURE 2 Comparative EDX spectrums of RDRMs as initial and 14th days and their corresponding quantification results on initial, 7th & 14th days of gastric acid treatment. EDX, energy dispersive X-ray spectroscopy; RDRMs, resin-based dental restorative materials

surface deformation and high level of erosion that left deep valleys on surface after 14 days of immersion. The Day 7 can be concluded as the roughness decrease down to 28% due to the dissolution of particles as well as polymer structure to form a relatively smooth surface and beginning of surface cracks to some extent. This phenomenon may be derived to be unsuitable for surface roughness decrease or increase but the surface becomes more sensitive to the environmental factors. The corresponding roughness may also lead to drastic decrease in microhardness by deterioration of surface integrity. The initial microcracks on the surface can favor the formation of highly deformed surface by high level of removal of glassy sharp shaped particles and leaving polymer structure was affected by solution ions.

TABLE 2 Microhardness values of resin based dental restorative materials prior and after the gastric acid treatment

Materials	Treatment period	Microhardness values (Mean–*SD*)	Change in microhardness values (Mean–*SD*)	Results
Filtek Z550	Initial	98.91 ± 4.75	16.41 ± 1.39	$t = 37.74$ $p = .001^*$
	14th day	82.50 ± 3.84		
Dyract XP	Initial	59.58 ± 5.16	10.50 ± 1.06	$t = 31.20$ $p = .001^*$
	14th day	49.08 ± 5.52		
Fuji II LC	Initial	57.36 ± 6.95	12.10 ± 2.41	$t = 15.90$ $p = .001^*$
	14th day	45.26 ± 5.84		
Beautifil II	Initial	71.77 ± 6.06	25.64 ± 1.94	$t = 41.74$ $p = .001^*$
	14th day	46.12 ± 7.07		
Vertise flow	Initial	56.39 ± 5.76	16.30 ± 3.51	$t = 14.69$ $p = .001^*$
	14th day	40.09 ± 2.91		

Note: $^*p < .05$ was accepted as significance level.

The surface microhardness therefore tend to decrease to a high extent.

Figure 1d represents Vertise Flow's surface before the gastric acid treatment while Figure 1d′ and d″ stands for after the gastric acid treatment for 7 and 14 days, respectively. The polishing grooves are also evident on the surface which produces 11.5% of relative roughness for Figure 1d, 13% for Figure 1d′ while Figure 1d″ increases up to 14.5% relative roughness due to pore formation and deterioration of integrity of polymer surface. This also decreases the microhardness which was caused by particle removal from surface.

Contrary to all surfaces, in Figure 1e, Filtek Z550 showed a reverse relative roughness change. As very well known, Filtek Z550 is designed by zirconia and silica fillers in a polymer matrix and hard materials are in high amount. Due to this structure, the Filtek Z550 was hard to polish and relatively high amount of grooves with a hill–valley formation was observed and 19% relative roughness value was found prior to gastric acid treatment. After the gastric acid treatment, for Figure 1e′, it was seen as 15.5% and this value decrease down to 12% for Figure 1e" which may be attributed to the surface groove etching by gastric acid. This etching produces smoother surface than prior and improves the roughness. This phenomenon also approves the decrease in microhardness from 98 HV to 82 HV. This can be attributed to production of small area after first indentation by groove height and afterwards, the disappearing those grooves produced higher area for indentation which also results in decrease in microhardness.

4 | DISCUSSION

According to the results of our study, it was seen that gastric acid did not affect the organic content of the materials, especially since the polymers are resistant to organic acid. However, it was observed that microhardness decreased and cracks started to progress due to the dissolution of inorganic particles after the gastric acid treatment in the long term. For these reason, the null hypothesis was accepted.

Various dental restorative materials for protective and restorative purposes are used in dentistry. Nowadays, nanocomposites with advanced mechanical properties in both superior esthetics and high stress areas have been produced (Sakaguchi & Powers, 2012). Filtek Z550, which is a nanohybrid group composite resin that has advanced mechanical properties in both esthetic and high stress areas and is frequently used in the literature and the Vertise Flow, a self-adhering flowable composite resin that can be applied directly to the cavity were included in the present study. Glass ionomer cement (GIC) is well accepted in pediatric patients with high caries risk activity, due to its chemically bonding ability to the tooth structures (Smith, 1992), fluoride release capacity (Davidovich, Weiss, Fuks, & Beyth, 2007; Kotsanos, Topitsoglou, Tatsi, & Thanouri, 2007), antibacterial effect (Davidovich et al., 2007; Hallgren, Oliveby, & Twetman, 1992), and potential for remineralizing hydroxyapatite crystals (Davidovich et al., 2007; Hallgren et al., 1992). Resin modified GIC (Fuji II LC), polyacid modified composite (Dyract XP) and giomer (Beautifil II) were used in the present study.

In some studies evaluating the effectiveness of liquids with different pH values on the mechanical and physical properties of dental restorative materials different immersing periods were planned. Researchers used different immersing periods ranging from 1 day to 1 month (Bayrak, Ozalp, & Okte, 2011; De Paula, De Fúcio, Alonso, Ambrosano, & Puppin-Rontani, 2014; Honório et al., 2008), or 1 month to 1 year (Aliping-McKenzie, Linden, & Nicholson, 2004; Dos Santos, Garcia, De Oliveira, Chinelatti, & Palma-Dibb, 2010; von Fraunhofer & Rogers, 2004; Wongkhantee, Patanapiradej, Maneenut, & Tantbirojn, 2006). von Fraunhofer and Rogers (von Fraunhofer & Rogers, 2004) reported that the 336-hr (14 days) test period used in their study corresponded to a period of 13 years approximately, which is a reasonable time period to evaluate the response of the patients to various beverages. In the present study, to obtain more realistic results that reflect the pH cycle of the oral environment in in vitro conditions; a 14-day immersion period (18 hr in gastric acid and 6 hr in distilled water per day) was planned (Guler & Unal, 2018). And thus, we aimed to evaluate the long-term effects of gastric acid on the elemental composition and microhardness of RDRMs.

One of the most important parameters used in evaluating the mechanical properties of materials is the microhardness. The hardness of dental restorative materials correlates well with compressive strength, resistance to intraoral softening and degree of polymerization. A low surface microhardness value is largely related to *insufficient* wear resistance and proclivity to scratching which can compromise fatigue strength and lead to failure of the dental restoration (Badra, Faraoni, Ramos, & Palma-Dibb, 2005; De Moraes et al., 2008; Say, Civelek, Nobecourt, Ersoy, & Guleryuz, 2003; Uhl, Mills, & Jandt, 2003).

Beautifil II showed drastic changes in microhardness compared to other resin-based materials used in this study. This may be due to the higher acid resistance of polymer matrix of other RDRMs (Yu et al., 2009). Likewise, in a previous study in which the change in the physical properties of the restorative materials of various acidic beverages was evaluated, the microhardness of Beautifil II was changed and decreased more compared to other materials (Choi, Lee, Oh, & Kim, 2019). The negative change in the microhardness of the polymer composite can be due to the loss of chemical and physical bonds as a result of water absorption and hydrolysis between the resin matrix and filler particles (EL-Sharkawy, Zaghloul, & Ellkappaney, 2012).

In present study, Fuji II LC showed more decrease in microhardness values compared to Filtek Z550 group which is a nanohybrid composite; this can be attributed to the dissolution of siliceous hydrogel layer surrounding the glass particles in the glass ionomer (Rios et al., 2008; Tursi, Hara, Serra, & Rodrigues Jr, 2002; Yu et al., 2009). In addition, some studies have reported that the fluoride release of glass ionomer cements is increased, especially under acidic conditions in the long term (De Moor & Verbeeck, 1998; Fukazawa, Matsuya, & Yamane, 1990; Luo, Billington, & Pearson, 2009; Verbeeck et al., 1998). Similarly, in the present study, it was determined that the concentrations of F ions on their surfaces decreased after gastric acid treatment in glass ionomer based Beautifil II and Fuji II LC groups.

Yu et al. (2009) reported that composite resin was the most resistant material to erosion among glass ionomer and composite resin sample groups immersed in citric acid (pH 2.3). In a previous study (Gupta et al., 2018) in which restorative materials such as composite, compomer and glass ionomer were immersed in different acidic beverages, it was reported that the material with the lowest change in microhardness values was composite resin. The results of present study are consistent with these studies. Composite resins are more stable, nano-sized and organized due to the material formulation and morphology of the filler particles. This allows them to have a higher inorganic volume and thus composites are less affected by acidic conditions (Attar, 2007; Candan & Ünal, 2021).

In another study evaluating the effects of different beverages on the physical properties of restorative materials, composites were reported as the most resistant material to acidic beverages. The authors also noted that that low-pH beverages affected GIC and compomers more. When they compared the GIC and the compomer, it was found that the compomer was more affected, but there was no statistically significant difference between them (Hamouda, 2011). Unlike Hamouda's study (Hamouda, 2011), the compomer used in our study was less affected. This situation may be due to the different brand of the compomer used in our study.

Compomer and GIC have the ability to buffer the storage media (Aliping-McKenzie et al., 2004) and this could explain their main susceptibility to acid attacks. The decrease in microhardness of the compomers when they come into contact with the acid may be due to the dissolution of the structural ions in the glass phase (Narsimha, 2011).

Since the restorative materials used in present study contain barium glass and zirconia fillers; possible reasons for the decrease in the surface hardness of these materials when immersed in an acidic environment is that Barium containing glass particles dissolve more easily than quartz particles and the failured bonding of spherically shaped zirconia / silica fillers to the resin matrix (AU Yap, Low, & Ong, 2000; AUJ Yap et al., 2001). Also, the acid penetrates into the resin matrix of the material, promoting the release of unreacted monomers. As a result, this may cause a decrease in microhardness (Aliping-McKenzie et al., 2004). Another reason for the decrease in the surface hardness of composite resins immersed in organic acids is the softening of bisphenol-A-glycidyl methacrylate (Bis-GMA) based polymers. This is also thought to be caused by the leaching of diluent agents such as triethylene glycol dimethacrylate (TEGDMA; Francisconi et al., 2008; Lee, Huang, Lin, & Shih, 1998; Rios et al., 2008). Consequently, all these could be shown as the reasons for the decrease in the microhardness of the used RDRMs in this study.

Bis-GMA resin in dental restorative composites is hydrophobic and incompatible with the aqueous environment in the GIC. Therefore, hydrophilic 2-hydroxy-ethyl-methacrylate (HEMA) is used in most of resin modified GICs (Gasser, 1994). Although the composite contains resin ranging from 30% to 50%, the amount of hydrophilic resin in resin modified GIC varies around 5%. In Dyract, the acidic polymerizable monomer TCB makes up 28% of the composition. The high amount of resin in the composition of the compomer may be the reason for the close behavior of this material to composites (Abubakr, Han, Okamoto, & Iwaku, 2000). Similarly, in present study, Dyract XP behaved close to Filtek Z550.

When SEM–EDX analysis results were evaluated; in the Beautifil II group, gastric acid removed the particles on the polymer surface as a result of the dissolution of the outermost region and gastric acid treatment. In the Dyract XP group, Sr, Al, Na, F related compounds dissolved in solution after gastric acid treatment. Since, the inorganic material dissolved in solution during the immersion period, the remaining main polymeric surface can be the reason of increasing C content in structure detected by EDX. In the Fuji II LC group, Na and F disappeared mainly due to dissolution in gastric acid. Also, it can form hydroxyl groups on the alumina surface, resulting in separation from the surface. Compounds such as alumina silicate, sodium fluoride, aluminum fluoride dissolved in solution after application of gastric acid and the remaining material can be considered as silica, which can be in the form of crystalline quartz. Alumina silicate is a hard and sharp particulate compound and can be thrown into solution, so the O and Si elements, possibly also in the form of silica called quartz, have increased. After 14 days of gastric acid treatment in the Vertise Flow

group, alumina-silicate and fluoride based nanoparticles as well as macro-sharp particles tend to dissolve into gastric acid solution by departing from the polymeric structure which surrounded the particles. Since, sodium alumina silicates as well as ytterbium fluoride were affected by hydrochloric acid in gastric solution, possibly in ionic form of chlorine. In the Filtek Z550 group, no significant changes were raised which can be interpreted as the dissolution of all elements at the same time or even no significant dissolution occurred to smoothen the surface to an extent.

5 | CONCLUSION

Within the limitations of the present in vitro study;

- Mechanical properties such as microhardness and surface roughness of RDRMs were affected after gastric acid treatment.
- The microhardness values of all RDRMs decreased. RDRMs can be considered to be mechanically weakened by the reduction in microhardness.
- Clinically, this situation may cause aesthetic and functional problems in dental restorations.
- Consequently, RDRMs should be carefully selected for restorative procedures in patients with chronic GER, recurrent vomiting, or regurgitation.

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CONFLICT OF INTEREST

The authors deny any conflicts of interest related to this study.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in [repository name e.g "figshare"] at http://doi.org/[doi], reference number [reference number].

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