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Evaluation of Monomer Elution and Surface Roughness of a Polymer-Infiltrated Ceramic Network CAD–CAM Material After Er,Cr:YSGG Laser-assisted Tooth Bleaching

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Clinical Relevance

Bleaching treatment with Er,Cr:YSGG laser or the conventional technique is a safe procedure as regards to monomer elution and surface roughness of resin composites and resin–ceramic computer-aided design–computer-aided manufacturing materials.

SUMMARY

Purpose: The aim of this in vitro study was to examine the effect of Er,Cr:YSGG laser-assisted tooth bleaching treatment on the elution of monomers and surface roughness of a hybrid computer-aided design–computer-aided manufacturing (CAD–CAM) material, and to compare it with a resin composite for direct restorations.

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Methods and Materials: Forty specimens of a hybrid CAD–CAM material (Enamic) and forty of a conventional resin composite (Tetric) were fabricated and randomly divided into four groups (n=10). Half of the specimens of each material were stored in distilled water and the other half in artificial saliva for 7 days. At the end of this period, the storage medium was analyzed by high-performance liquid chromatography (HPLC), and the surface roughness parameters of the specimens were evaluated by optical imaging noncontact interferometric profilometry. Afterwards, half of the specimens of each tested material received a conventional in-office tooth bleaching treatment and the other half an Er,Cr:YSGG laser-assisted bleaching treatment, and then they were again incubated in distilled water and artificial saliva for an additional 7-day time period. At the end of this period, the effect of the bleaching treatments on elution of monomers and surface roughness of the tested materials was evaluated.

Results: Bisphenol A (BPA), urethane dimethacrylate (UDMA), triethylene glycol dimethacrylate (TEGDMA), and bisphenol A-glycidyl dimethacrylate (BisGMA) were eluted from the conventional resin composite into both the solutions tested. Only TEGDMA was eluted from the hybrid CAD–CAM material. However, no statistically significant differences were found among the surface roughness parameters of both materials. Both the conventional and Er,Cr:YSGG laser-assisted tooth bleaching treatments affected the monomer elution from the composite resin. However, there were no statistically significant differences ($p<0.05$) between the treatments.

Conclusions: According to the results of this study, tooth bleaching with Er,Cr:YSGG laser or conventional technique is safe, even if the bleaching agent comes in contact with hybrid CAD–CAM restorations.

INTRODUCTION

Computer-aided design–computer-aided manufacturing (CAD–CAM) and laser technologies have increased their popularity among dental clinicians. Dental applied science continues to expand, as more dental practitioners gain access to the evolving technology and as long as there are significant developments in dental materials.[1] Often, CAD–CAM indirect restorations that have been fabricated with resin composites, or hybrid CAD–CAM materials may accidentally come in contact with a bleaching gel during tooth bleaching treatments. Tooth bleaching is a popular choice among patients due to increased aesthetic demands for whiter teeth. There are several categories of tooth bleaching treatments including: (1) over-the-counter bleaching gels, (2) hydrogen peroxide (H_2O_2) strip systems, (3) at-home bleaching, (4) power bleaching, (5) assisted or waiting room bleaching, and (6) in-office dual-activated techniques.[2] Most of the predictable tooth bleaching treatments seem to be the at-home and the in-office dual-activated technique. At-home bleaching treatment is carried out by the patient but under dental supervision, while in-office bleaching treatments are performed by the dentist at the dental office in one or more visits.[3]

The bleaching gels contain peroxide compounds like H_2O_2 and carbamide peroxide ($NH_2CONH_2 . H_2O_2$). These bleaching agents in the presence of water break down and produce oxidizing agents, which diffuse within enamel micropores. The oxidative radicals that are released degrade the extracellular matrix and oxidize the chromophores located in the enamel and dentin, causing the tooth color change.[4]

Several light sources can accelerate the bleaching procedure by heating the carbamide peroxide or the hydrogen peroxide and also by increasing the production of oxygen-free radicals.[5] Currently, the most commonly used light sources for the tooth bleaching procedure are the light-emitting diodes (LEDs) and the diode lasers. The latter produce controlled heating on the gel and exclude the risk of pulpal irritation due to their monochromatic nature.[6] Recently, erbium-family lasers such as Er:YAG (2940 nm)[5-7] and Er,Cr:YSGG (2780 nm)[8-10] take more attention in terms of laser-assisted tooth bleaching techniques. The purported advantage of the Er,Cr:YSGG laser is that it offers a fast, gentle, and effective bleaching procedure.[11,12] Moreover, the wavelength of the Er,Cr:YSGG laser (2780 nm) has a high affinity for tooth hydroxyapatite and the nearly highest absorption in water of any dental laser wavelengths, which results in the absence of additional absorbing particles in the bleaching gel – so it can be used with all water-based bleaching agents.[13] Moreover, the high absorption of the Er,Cr:YSGG laser irradiation prevents the penetration of the laser energy in the depth of hard tissues, making the bleaching procedure minimally invasive and safe.[13]

There are some concerns regarding the negative effects of the bleaching agents on the surface of the restorative materials. In particular, H_2O_2 may affect the stability of polymer networks in composite materials, since it can react with single (C–C) and double (C=C) carbon bonds.[14] This phenomenon may influence the physical and chemical properties of composites materials, leading to increased surface roughness[15] and increased elution of monomers and compounds.[16] The elution of monomers from restorative resin composites after tooth bleaching treatments have been adequately investigated.[17,18] On the contrary, there is a little evidence about the effect of bleaching agents on the hybrid CAD–CAM materials. The elution of residual methacrylates or other degraded monomers that leach into the oral environment can cause allergic reaction or other oral tissue pathology issues that are potentially dangerous to human health.[19-21]

Surface roughness of restorative materials is an indispensable factor in ensuring the absence of discoloration of the restorations, the lacking of periodontal inflammation, and the decrease in biofilm formation.[22] The surface roughness of ceramic restorative materials is usually lower than composite materials.[23,24] Nevertheless, the changes in surface roughness and morphology of the recently introduced hybrid ceramic materials after the influence of different tooth bleaching protocols have not sufficiently investigated.

Therefore, this *in vitro* study aimed to evaluate surface roughness changes and monomer leaching patterns of a hybrid ceramic CAD–CAM material and a nanohybrid resin composite after conventional and Er,Cr:YSGG laser-assisted tooth bleaching treatments. Three null hypotheses were set in this study: $H_0$1 was that between the two tested materials there are no differences in surface roughness change and elution of monomers after the bleaching procedures; $H_0$2 was that the bleaching procedure does not affect these two properties of the materials; and $H_0$3 was that Er,Cr:YSGG laser irradiation does not influence these two properties in comparison with the conventional bleaching technique.

METHODS AND MATERIALS

In the present study a polymer-infiltrated ceramic network (PICN) CAD–CAM material—Vita Enamic (VITA Zahnfabrik, H Rauter GmbH & Co KG) and a nanohybrid composite resin—Tetric (Ivoclar Vivadent AG, Shaan, Lichteinstein) were tested. Detailed information about the composition of the materials and the manufacturers are presented in Table 1.

Preparation of the Specimens

Each CAD–CAM block was sectioned vertically, using a 0.3-mm thick, diamond-coated, low-speed precision sectioning saw (IsoMet 1000; Buehler, Lake Blu, IL, USA) under copious water coolant resulting in 40 rectangular-shaped specimens with dimensions of 14 mm in length, 12 mm in width, and 1 mm in height. For the composite material, 40 rectangular-shaped specimens were also prepared by overfilling a customized Teflon mold with the same dimensions as the CAD–CAM specimens used in this experiment. The composite was inserted in the mold in one increment and polyester matrix strips (Polydentia SA, Messovico, Switzerland), 0.05 mm in thickness, were placed on both sides of the mold. Glass microscope slides were placed over the polyester strips and clamped to produce a standardized smooth surface, to remove excess of the material and to prevent oxygen-inhibited layer formation. Subsequently, the top and bottom surfaces of each specimen were irradiated for 20 seconds using

Table 1: *Technical Characteristics of the Tested Materials According to the Manufacturer*

Materials	Type	Composition	Manufacturer	Lot No
Enamic	PICN, CAD–CAM	Monomers: UDMA, TEGDMA (14% wt-25% v/v) Fillers: Feldspar ceramic enriched with aluminium oxide (75% v/v, 86% wt)	Vita Zahnfabrik, H Rauter GmbH & Co KG, Germany	56802
Tetric	Nanohybrid composite	Monomers: Bis-GMA, TEGDMA, UDMA(18.8 wt%) Fillers: Barium glass filler, Ytterbium trifluoride, mixed oxide (63.5 wt%), polymer (17 wt%), additive, catalysts, pigments, stabilizers (0.7 wt%) Particle size: 0.04-3 μm	Ivoclar Vivadent Schaan, Liechtenstein	V23649

Abbreviations: PICN, Polymer-infiltrated ceramic network material, CAD–CAM: Computer-aided designed–computer-aided manufactured; UDMA, Urethane dimethacrylate; TEGDMA, Triethylene glycol dimethacrylate; Bis-GMA, Bisphenol A glycidyl dimethacrylate.

a dental LED light-curing unit (Bluephase G2, Ivoclar Vivadent AG, Schaan, Lichtenstein) at 1200 mW/cm^2, according to the manufacturer's specifications. The light intensity of the LED device was checked with a Bluephase Meter II (Ivoclar Vivadent AG, Schaan, Lichtenstein).

Both the CAD–CAM and composite specimens were wet polished, with fine (1000-grit) and superfine (3000-grit) silicon carbide abrasive papers. Immediately after the polishing of the specimens, they were immersed in 1 ml human pooled saliva for 3 days at 37°C, in order to resemble the aging of the materials intraorally. Then half of the specimens of each material were suspended individually using a silk thread in 10 ml of distilled water and the other half in 10 ml of artificial saliva for 7 days. The composition of the artificial saliva was as follows: $CaCl_2$ (0.6 g), KH_2PO_4 (0.26 g), NaCl (0.552 g), CH_4N_2 (Urea, 1.0 g), and distilled water (1000 mL), at neutral pH.

Using a thin silk thread that was passed through a hole in the middle of each specimen and with the help of a screw cap that was placed firmly on top of the glass vessel, the samples could be fully immersed and hung inside the bottles with both surfaces in direct contact with the solution.

Experimental Groups of the Study

Following this 7-day period of storage, the 40 specimens of each material were randomly divided into 4 groups (n=10). The specimens of the groups were submitted to one of two bleaching treatments.

Group A1 and A2 specimens received a conventional in-office tooth bleaching treatment using a bleaching agent (Opalescence Xtra Boost, Ultradent Products, South Jordan, UT, USA), which contained 40% H_2O_2 and also 3% potassium nitrate and 1.1% fluoride ions (10,000 ppm); pH=7. The mixing conditions of the gel and the parameters of the procedure complied with the manufacturer's instructions. More specifically, the bleaching gel was applied on the surface of the specimens in a layer approximately 1-mm thick, for 40 minutes, and then it was removed carefully with a spatula and swabbed with a cotton stick without the use of water in order to avoid washing out monomers from the specimens' surface. Subsequently, Group A1 specimens were incubated separately in 10 ml of distilled water and Group A2 specimens in 10 ml of artificial saliva, at 37°C for an additional 7-day period.

Group B1 and B2 specimens received the same in-office tooth bleaching protocol using Er,Cr:YSGG laser (solid state) irradiation to catalyze the chemical reaction of H_2O_2 breakdown. Er,Cr:YSGG (2780 nm) laser (Waterlase MD Turbo, BIOLASE, Irvine, CA, USA) had a Z-type glass tip (MZ8) with an 800-μm diameter and 6-mm length, and was used with the gold handpiece of the laser system. The laser parameters that were selected were as follows: average output power of 1.25 W, pulse duration of 700 μs (S-mode), and pulse repetition rate of 10 Hz without water- or air-flow. The laser treatment of the bleaching agent consisted of two intervals of 15 seconds for each specimen, keeping the handpiece of the laser device at a distance of 2.5 cm from the surface with the use of a custom-made spacer and positioned perpendicularly to the surfaces. The fluence of every laser pulse using the above laser parameters was 0.45 J/cm^2, which is far below the ablation threshold for enamel. To minimize the effect of operator variability, the same researcher carried out the bleaching procedures. Afterwards, Group B1 specimens were incubated in distilled water and Group B2 specimens in artificial saliva, at 37°C for an additional 7-day period.

Evaluation of Monomer Elution

At the end of the initial 7-day period, before the bleaching treatments, an aliquot of 20 μL of the storage medium was analyzed by high-performance liquid chromatography (HPLC). The technical characteristics of the chemicals used in this method are presented in Table 2. This measurement was performed in order to investigate the elution of monomers without the effect of the bleaching agent (control). A second measurement was performed after the bleaching treatments at the end of the second 7-day period.

The mobile phase was composed of acetonitrile and water (CH_3CN:H_2O, 70:30%, v/v), employing a Shimadzu (Kyoto, Japan) LC-10AD pump. The method used was previously developed and used authors' research group[25]; however, two more analytes were included. The pressure observed was 150 bar, while the flow rate was set at 1.5 mL/min. Sample injection was performed via a Rheodyne 7125 injection valve (Rheodyne, Cotati CA, USA) with a 20 μL loop. Detection was achieved by an SSI 500 UV-Vis detector (SSI, State College, PA, USA) at a wavelength of 215 nm and a sensitivity setting of 0.002 AUFS. The monomers were identified by comparison of their retention times with those of the reference compounds under the same HPLC conditions. The retention time for BPA was 5.5 minutes, for TEGDMA 9 minutes, for UDMA 21.5 minutes, and for *Bis*-GMA 22.5 minutes. Calibration curves were constructed using peak areas of eluted peaks of BPA, TEGDMA, UDMA, and *Bis*-GMA. A typical chromatogram is illustrated in Figure 1.

Table 2: *Technical Characteristics of the Chemicals used for HPLC Method*

Chemicals	Name	Chemical Type	Molecular Weight	CAS Number	Purity	Manufacturer
BPA	Bisphenol A	$C_{15}H_{16}O_2$	228.29	80-05-7	95%	Sigma–Aldrich LLC
Bis-GMA	Bisphenol A glycidyl Dimethacrylate	$C_{29}H_{36}O_6$	513	1565-94-2; LOT: MKBR2670V	99%	Sigma–Aldrich LLC
TEGDMA	Triethylene glycol Dimethacrylate	$C_{14}H_{22}O_6$	286.32	109-16-0; LOT: 09004BC-275	99%	Sigma–Aldrich LLC
UDMA	Urethane dimethacrylate	$C_{23}H_{38}N_2O_8$	470.56	72 869-86-4; LOT:12430KC	99%	Sigma–Aldrich LLC
Acetonitrile		CH_3CN	41.05	75% v/v, ethanol; CAS:75-05-8; LOT:0001245593	HPLC grade	PanReac AppliChem
Distilled water				CAS:7732-18-5; LOT:0001118157	HPLC grade	PanReac AppliChem
Artificial Saliva		H_2O(distilled) CH_4N_2O(urea) NaCl $CaCl_2$ KH_2PO_4				Sigma–Aldrich Merck KGaA, Darmstadt, Germany

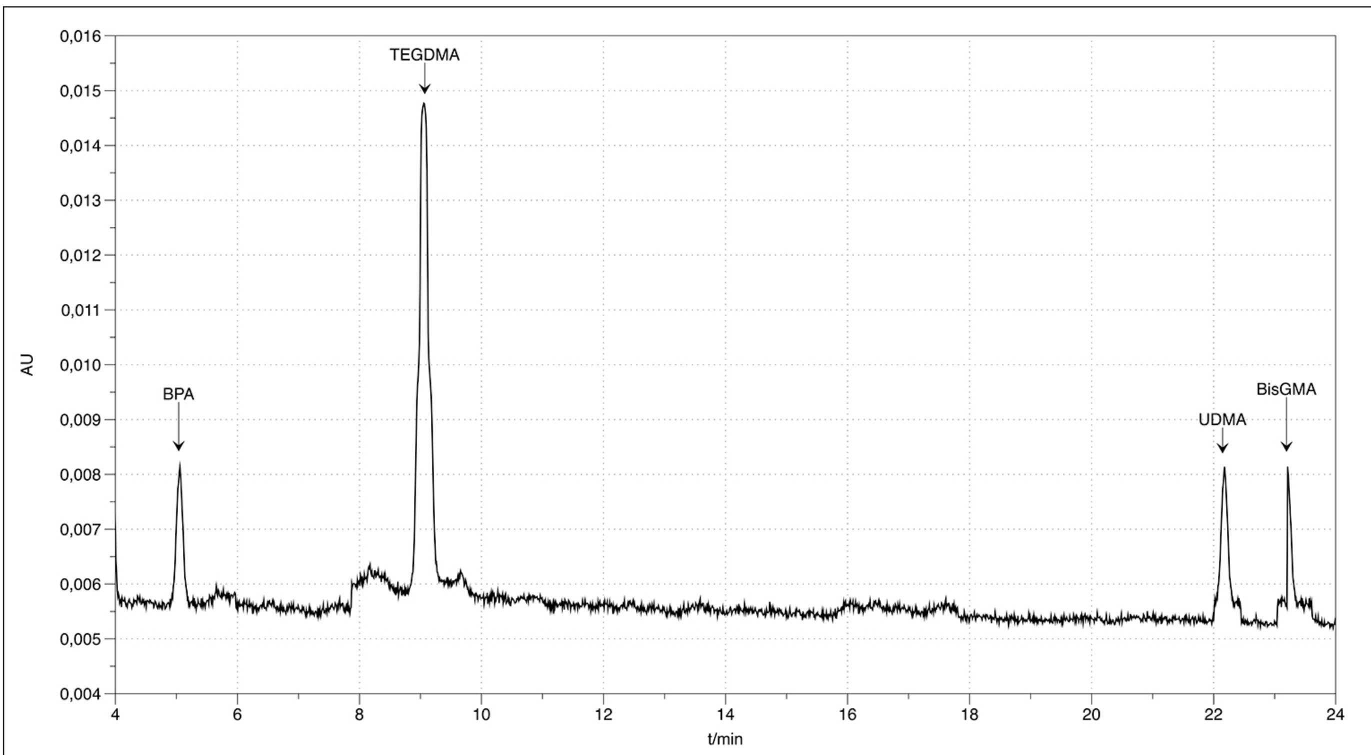

Figure 1. *Representative high-performance liquid chromatograms at 1 ng/mL standard solution of BPA, TEGDMA, UDMA, and Bis-GMA. Bis-GMA: Bisphenol A glycidyl dimethacrylate; BPA: Bisphenol A; TEGDMA: triethylene glycol dimethacrylate; UDMA: urethane dimethacrylate.*

Analytical Procedure

The linearity of the analytical method was studied using mixtures of ethanolic standard solutions covering the entire working range. Limit of detection (LOD) values were calculated from the calibration curve according to the formula LOD=S/N and limit of quantification (LOQ) values according to the formula LOQ=10S/N, where S=signal and N=noise. The corresponding value of the LOD was 0.2 ng/μL for BPA, TEGDMA, *Bis*-GMA, and UDMA monomers. The LOQ was calculated to 0.06 ng/μL for BPA, TEGDMA, *Bis*-GMA, and UDMA monomers.

Evaluation of Surface Roughness

Surface roughness parameters of the tested materials were evaluated by optical imaging noncontact interferometric profilometry. The 3D optical profiler (3D Optical Surface Metrology System Leica DCM8, Leica Microsystems CMS GmbH, Mannheim, Germany) was used under the following conditions: vertical scanning mode, Leica lens, 20× magnifications (800×650 μm^2 analysis area), tilt correction, 5 μm Gaussian high-pass filter to remove surface waviness. The following surface roughness parameters were evaluated before and after the bleaching treatment: the absolute profile deviation versus the average over a 3D surface; S_a, the average difference between the five highest peaks and the five lowest valleys; S_z, the root mean square roughness over the entire 3D surface; S_q and the developed interfacial area ratio, expressed as the percentage of the additional surface area contributed by the texture compared to an ideal plane of the same size; S_{dr}. The surface roughness parameters S_a and S_q represented an overall measure of the texture, and S_{dr} differentiated the surface of similar amplitudes and average roughness. The surface parameter S_z defined the sum of the largest peak height value and the largest pit depth value of a defined area.

Statistical Analysis

Normality of the data distribution was checked by the Kolmogorov–Smirnov test, while the homogeneity of the variances was examined by the Levene test. The comparisons of the mean values of the leaching monomers (ng/μL) and the roughness parameters (S_a, S_q, S_z, and S_{dr}) that followed a normal distribution were evaluated with one-way analysis of variance (ANOVA) and Tukey honest significant difference (HSD) *post hoc* test. For those specimens that did not follow a normal distribution mean values were analysed with the use of nonparametric Wilcoxon test and one-way ANOVA with multiple comparisons using Dunn test or independent sample test. The statistical significance for all the tests was set at a = 0.05.

RESULTS

Mean values and standard deviations of each monomer released from the materials tested before and after tooth bleaching periods are presented in Tables 3 and 4 for distilled water and artificial saliva, respectively. Accordingly, in Tables 5 and 6, the mean values and standard deviations of surface roughness parameters before and after the bleaching procedures of each experimental group are shown for distilled water and artificial saliva, respectively. Mean concentrations of the monomers eluted in both the solutions from the materials tested before and after the bleaching treatment with or without the Er,Cr:YSGG laser effect are illustrated in Figure 2.

Monomer Elution

Monomer Elution from Composite Resin in Distilled Water

BPA was eluted from Tetric before and after both conventional and laser-assisted bleaching treatments. After the Er,Cr:YSGG laser bleaching treatment, BPA release was decreased significantly (p=0.011). However, the conventional bleaching treatment did not affect the release of BPA (p=0.393). TEGDMA was also released from the Tetric before and after both bleaching treatments. Nevertheless, the bleaching treatments had no statistically significant effect on the release of this substance (conventional: p=0.511, laser-assisted: p=0.601). UDMA and *Bis*-GMA monomers were released only before the bleaching treatments, and there were no traces of those monomers in the distilled water after the treatments.

Monomer Elution from Composite Resin in Artificial Saliva

BPA was eluted from the composite specimens in the artificial saliva before and after the bleaching treatments but in lower concentrations compared to those stored in distilled water (p<0.05), except for B2 group specimens before the bleaching treatment (p=0.823). However, there was no statistical significance of the effect of bleaching treatments on BPA elution (p>0.05). Similarly, TEGDMA was also eluted from the composite specimens in the artificial saliva before and after the bleaching treatments in lower concentrations compared to those stored in distilled water (p<0.05). Only after the laser-assisted bleaching treatment, there was an increase in the release of this monomer (p=0.009). No statistically significant differences were detected among the other experimental groups regarding TEGDMA release (p>0.05). UDMA and *Bis*-GMA were released from the composite specimens

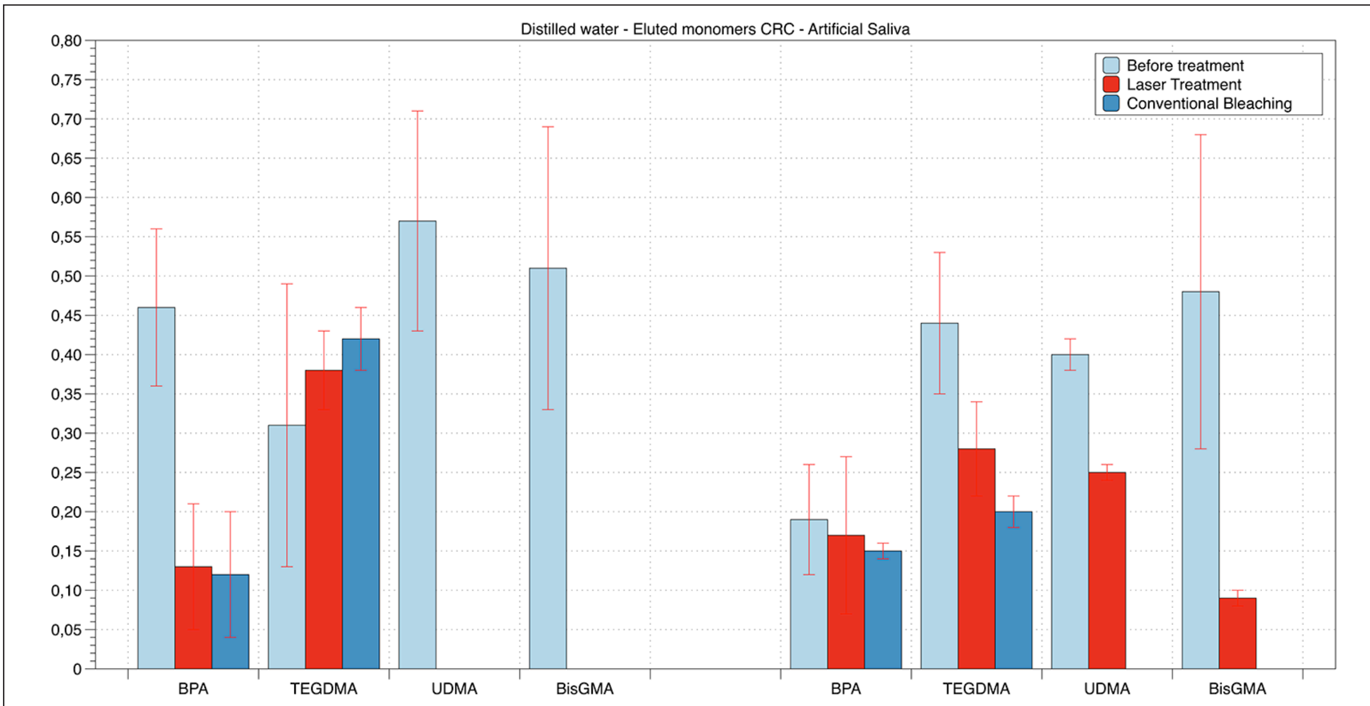

Figure 2. *Bar chart illustrating the mean values and standard deviations of the eluted monomers from the composite resin before the bleaching treatment, after the laser treatment with Er,Cr:YSGG laser, and after the conventional bleaching treatment.*

before the treatments. After the conventional bleaching technique, no traces were detected for either monomer, while after the laser-assisted bleaching treatment there was a significant decrease in UDMA and *Bis*-GMA release ($p<0.001$). UDMA and *Bis*-GMA also exhibited lower concentrations in artificial saliva than in distilled water ($p<0.05$) (Figure 3).

Monomer Elution from Hybrid CAD–CAM Material in Distilled Water and Artificial Saliva

TEGDMA was the only monomer that was released into the distilled water and artificial saliva from the specimens of Enamic before the beaching treatments. However, after the bleaching treatments no traces of TEGDMA were detected. Tooth bleaching treatments

Table 3: *Means and Standard Deviations (ng/μL) of the Eluted Monomers after Incubation in Distilled Water Before and after the Bleaching Treatments*[a]

Distilled Water	**Monomer**	**Er,Cr:YSGG Laser Bleaching Treatment**		**Conventional Bleaching Treatment**	
ng/μL		Before treatment	After treatment	Before treatment	After treatment
Enamic	BPA	ND	ND	ND	ND
Tetric	BPA	0.46 ± 0.20 a	0.13 ± 0.08 b	0.36 ± 0.05 a	0.42 ± 0.16 a
Enamic	UDMA	ND	ND	ND	ND
Tetric	UDMA	0.27 ± 0.04 a	ND	0.58 ± 0.18 a	ND
Enamic	TEGDMA	0.39 ± 0.02 a	ND	0.38 ± 0.05 a	ND
Tetric	TEGDMA	0.32 ± 0.05 a	0.39 ± 0.08 a	0.32 ± 0.02 a	0.41 ± 0.14 a
Enamic	Bis-GMA	ND	ND	ND	ND
Tetric	Bis-GMA	0.51 ± 0.28 a	ND	0.32 ± 0.10 a	ND

ND: not detected = amounts lower than method's limit of quantification (LOQ), as quantified by standard addition method.

Table 4: *Means and Standard Deviations (ng/μL) of the Eluted Monomers after Incubation in Artificial Saliva Before and after the Bleaching Treatments*[a]

Artificial Saliva	**Monomer**	**Er,Cr:YSGG laser Bleaching Treatment**		**Conventional Bleaching Treatment**	
ng/μL		Before treatment	After treatment	Before treatment	After treatment
Vita Enamic	BPA	ND	ND	ND	ND
Tetric	BPA	0.19 ± 0.07 a	0.17 ± 0.10 a	0.15 ± 0.06 a	0.15 ± 0.01 a
Vita Enamic	UDMA	ND	ND	ND	ND
Tetric	UDMA	0.44 ± 0.19 a	0.25 ± 0.01 b	0.60 ± 0.12 a	ND
Vita Enamic	TEGDMA	0.58 ± 0.08	ND	ND	ND
Tetric	TEGDMA	0.26 ± 0.04 a	0.43 ± 0.02 b	0.24 ± 0.07 a	0.20 ± 0.02 a
Vita Enamic	Bis-GMA	ND	ND	ND	ND
Tetric	Bis-GMA	0.48 ± 0.20 a	0.09 ± 0.01 b	0.34 ± 0.03 a	ND

[a]Same lowercase superscripts in rows indicate no statistically significant differences among the groups (p>0.05). ND: Not detected = Amounts lower than method's limit of quantification (LOQ), as quantified by standard addition method.

did not affect elution of the other monomers from the hybrid CAD–CAM material in either storage media (Table 6).

Surface Roughness

Representative images (20× magnification) obtained from the PICN CAD–CAM material and the conventional resin composite before and after the Er,Cr:YSGG laser bleaching treatment are shown in Figure 4. No surface morphology alterations were observed after the treatments.

Surface Roughness of Composite Resin

For the composite specimens stored in distilled water, there were no statistically significant differences among the experimental groups in all the surface roughness parameters (S_a, S_q, S_z, and S_{dr}) before and after the bleaching treatments ($p>0.05$). On the other side, the specimens of Tetric stored in artificial saliva showed a statistically significant increase only in parameter S_z for the laser-assisted bleaching technique ($p=0.037$).

Surface Roughness of Hybrid CAD–CAM Material

There were no statistically significant differences in the surface roughness parameters (S_a, S_q, S_z, and S_{dr}) for the hybrid CAD–CAM material, before and after the bleaching treatments. More specifically, there was no statistical significance before and after the Er,Cr:YSGG laser bleaching treatment for the specimens of Vita Enamic either stored in distilled water ($p=0.855$ for S_a,

Table 5: *Means and Standard Deviations of Surface Roughness Parameters (S_a, S_q, S_z, and S_{dr}) of the Specimens after Incubation in Distilled Water Before and after the Bleaching Treatments*[a]

Distilled Water	**Surface Parameter**	**Er,Cr:YSGG Laser Bleaching Treatment**		**Conventional Bleaching Treatment**	
		Before treatment	After treatment	Before treatment	After treatment
Vita Enamic	S_a (μm)	1.14 ± 0.02 a	1.18 ± 0.01 a	1.29 ± 0.40 a	1.98 ± 0.47 a
Tetric	S_a (μm)	0.67 ± 0.09 a	0.45 ± 0.07 a	0.44 ± 0.09 a	0.51 ± 0.08 a
Vita Enamic	S_q (μm)	1.42 ± 0.02 a	1.49 ± 0.01 a	1.61 ± 0.05 a	1.89 ± 0.31 a
Tetric	S_q (μm)	0.87 ± 0.10 a	0.60 ± 0.10 a	0.59 ± 0.12 a	0.66 ± 0.10 a
Vita Enamic	S_z (μm)	8.72 ± 0.06 a	8.96 ± 0.19 a	9.55 ± 0.28 a	9.44 ± 0.22 a
Tetric	S_z (μm)	5.62 ± 0.50 a	4.04 ± 0.74 a	3.60 ± 0.70 a	4.30 ± 0.53 a
Vita Enamic	S_{dr} (%)	9.91 ± 0.43 a	10.05 ± 0.47 a	11.30 ± 0.45 a	10.97 ± 0.35 a
Tetric	S_{dr} (%)	3.00 ± 1.19 a	1.94 ± 0.74 a	1.89 ± 0.78 a	2.48 ± 0.75 a

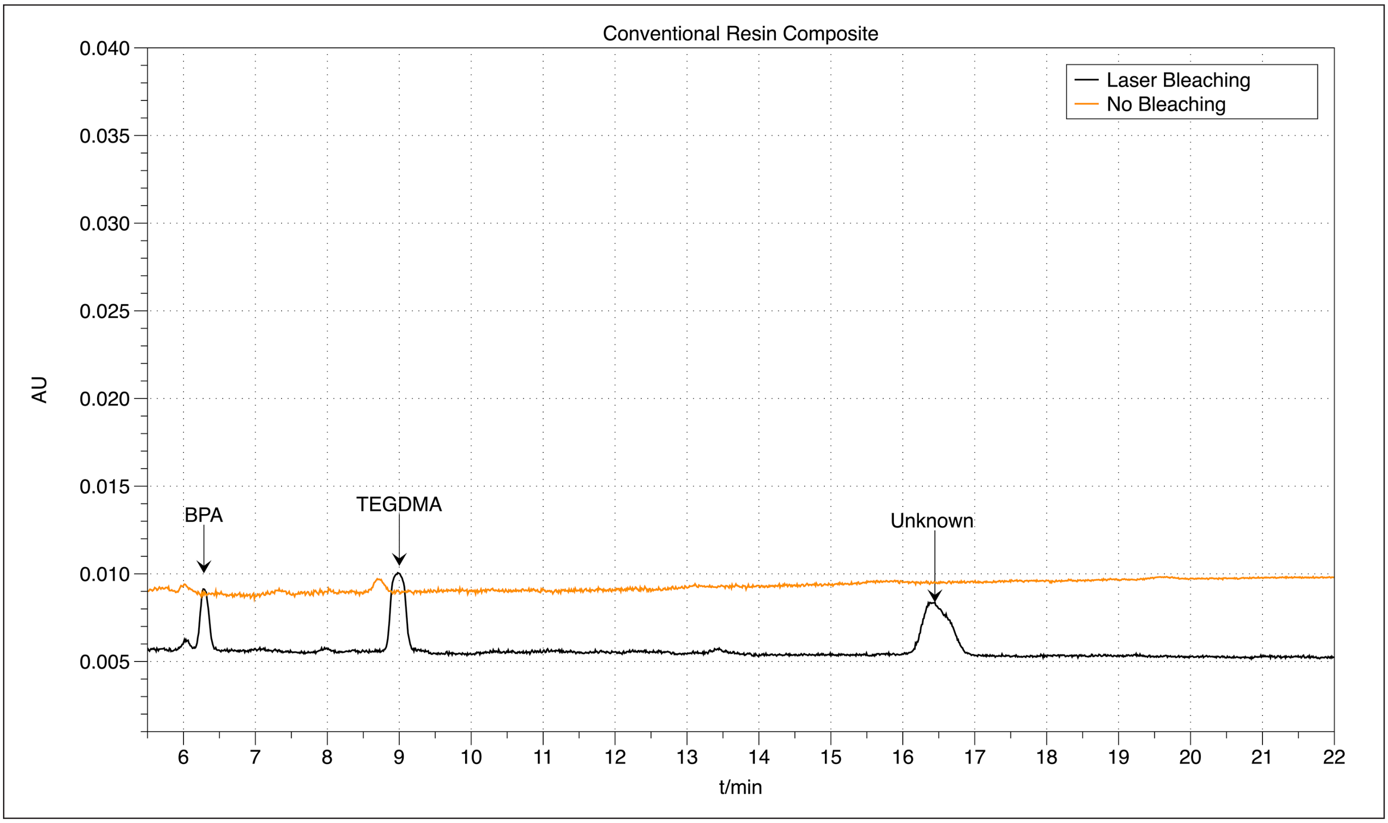

Figure 3. *Representative high-performance liquid chromatograms of a conventional composite resin specimen before and after the laser-assisted bleaching treatment. BPA: Bisphenol A; TEGDMA: triethylene glycol dimethacrylate.*

p=0.103 for S_q, p=0.237 for S_z, and p=0.591 for S_{dr}) or for those stored in artificial saliva (p=0.518 for S_a, p=0.486 for S_q, p=0.119 for S_z, and p=0.175 for S_{dr}).

DISCUSSION

According to the results of this study, H_01 was rejected since more monomers were eluted into the solutions from the conventional composite resin compared to the hybrid CAD–CAM material; H_02 was also rejected since both bleaching procedures influenced the elution of monomers from the materials; and H_03 was accepted since Er,Cr:YSGG laser irradiation did not influence surface roughness or monomer elution in comparison with the conventional bleaching technique.

There has been thorough research concerning the elution of monomers from composite materials after storage,[26-28] or after conventional[17] or laser-assisted tooth bleaching treatments.[3,29] However, there are few studies that have evaluated the leaching pattern from CAD–CAM materials,[30-32] and, to the authors' knowledge, there are no studies that evaluated the leaching of monomers from CAD–CAM materials after an Er,Cr:YSGG laser-assisted bleaching treatment.

It has been demonstrated that tooth bleaching agents may affect the three-dimensional polymer network of resin composites.[7] The aftereffect of the above concern is the potential for release of unpolymerized monomers, additives, filler components, or degradation products and impurities of monomers in the oral environment.[33] The release of unpolymerized monomers into the oral environment causes concerns regarding toxic effects, which may irritate the surrounding soft tissues and promote allergic reactions.[34] Furthermore, some studies reported that the eluted monomers or (co)monomers and the additives released from composite materials have estrogenic and genotoxic effects.[35]

In the present study, a hybrid CAD–CAM material and a composite resin were investigated regarding the leaching of monomers after an Er,Cr:YSGG tooth bleaching treatment. The main finding of the study was that there was no monomer elution from the hybrid CAD–CAM restorative material, and that the Er,Cr:YSGG laser bleaching treatment did not have an effect on the elution of monomers from the composite resin. Studies have demonstrated that the main disadvantage of conventional resin composite materials

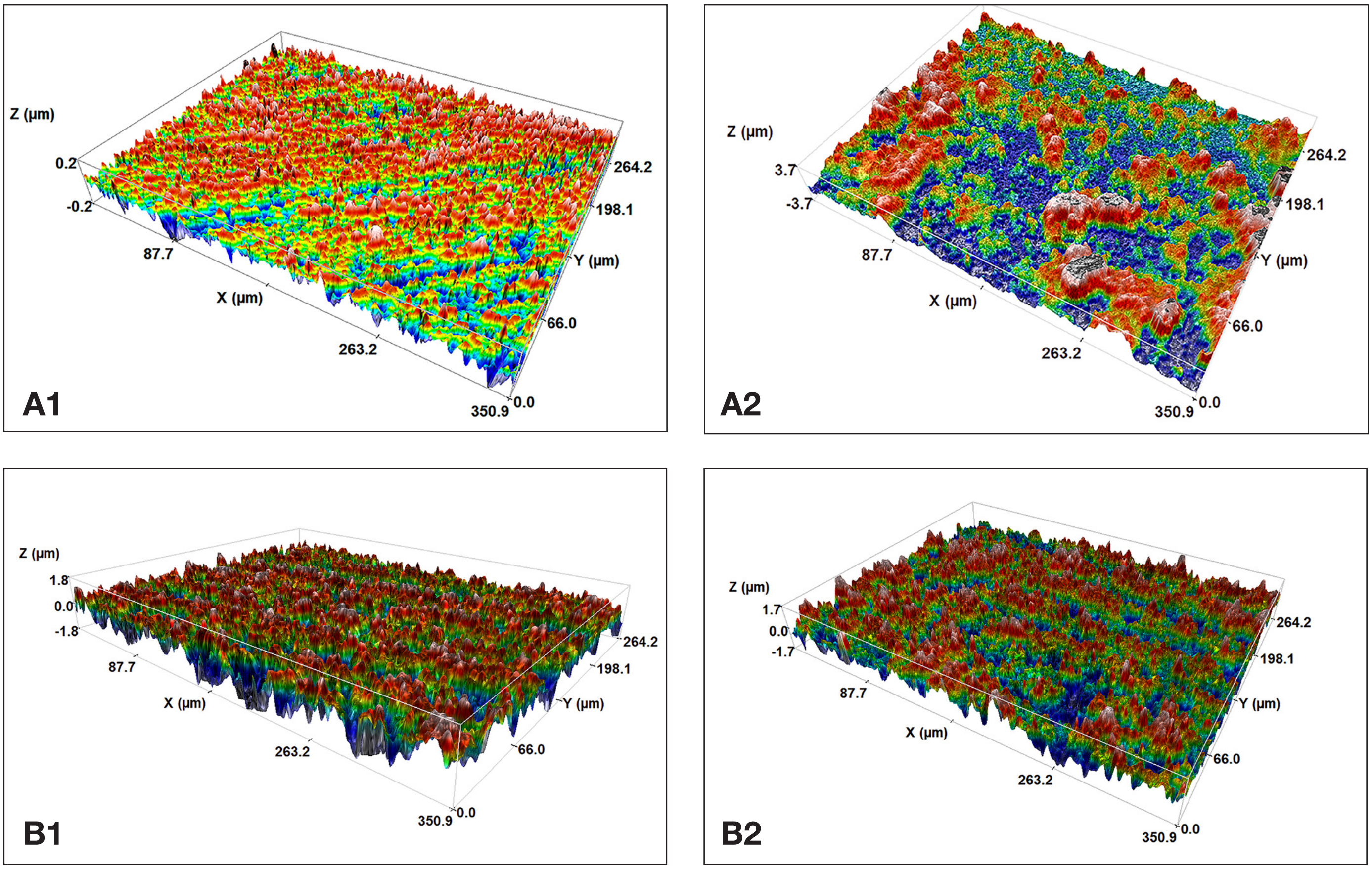

Figure 4. *Representative topographic images (20x magnification) of the surface of the specimens before (1) and after (2) the Er,Cr:YSGG laser bleaching treatment. A: Conventional resin composite and B: hybrid CAD–CAM material.*

is the incomplete polymerization.[36] In particular, the lower degree of conversion that they exhibit, results in increased release of unreacted monomers—a phenomenon that is determined by their chemical structure.[27] Furthermore, the hydrolytic degradation that follows may result in chain scission and release of polymeric breakdown products in the form of monomeric or oligomeric molecules.[37]

A previous study has reported that the amount of the eluted monomers is dependent on the medium used for extraction.[37] The solvent can penetrate the matrix of the resin composite and may enlarge the space between the polymer chains, resulting in dimensional change in the mass of the material. The latter may cause elution of unreacted monomers into the medium.[27] Most of the studies have examined the leaching of monomers in distilled water for a short time period extending between 7 and 14 days, in order to mimic the oral conditions.[37] Other studies have used organic solvents like ethanol 75%, methanol, or acetone, because, according to the Food and Drug Administration guidelines, those solutions are food simulators able to induce artificial aging of the restorations.[38] In the present study, artificial saliva was used in order to simulate the oral conditions, while distilled water was used as a control storage medium.[39] Moreover, before the experimental period, the specimens from both materials were stored in artificial saliva for 3 days to simulate the aging of the composite materials and allow for a sufficient polymerization.[17]

In the current study, the evaluation of monomer elution was implemented in artificial saliva that did not contain proteins and enzymes. As it was found in previous studies, the concentration of the eluted monomers released into the human saliva was significantly lower than the concentration released into protein-free artificial saliva. This may be because the eluted monomers are bound to proteins in both the oral cavity and in the plasma.[28]

No monomers were eluted from the hybrid CAD–CAM material after the bleaching treatments. This could be attributed to the different method

Table 6: *Means and Standard Deviations of Surface Roughness Parameters (S_a, S_q, S_z, and S_{dr}) of the Specimens after Incubation in Artificial Saliva Before and after the Bleaching Treatments*[a]

Artificial Saliva	**Surface Parameter**	**Er,Cr:YSGG Laser Bleaching Treatment**		**Conventional Bleaching Treatment**	
		Before treatment	After treatment	Before treatment	After treatment
Enamic	S_a (μm)	0.93 ± 0.13 a	1.04 ± 0.17 a	1.46 ± 0.29 a	1.09 ± 0.05 a
Tetric	S_a (μm)	0.50 ± 0.22 a	0.87 ± 0.24 a	0.78 ± 0.15 a	0.65 ± 0.19 a
Enamic	S_q (μm)	1.17 ± 0.15 a	1.29 ± 0.19 a	1.81 ± 0.35 a	1.43 ± 0.03 a
Tetric	S_q (μm)	0.66 ± 0.38 a	1.14 ± 0.29 a	1.01 ± 0.20 a	0.84 ± 0.26 a
Enamic	S_z (μm)	7.30 ± 0.83 a	8.09 ± 1.05 a	8.79 ± 0.26 a	8.61 ± 0.13 a
Tetric	S_z (μm)	4.40 ± 2.59 a	7.71 ± 1.42 b	6.29 ± 0.50 a	5.46 ± 1.85 a
Enamic	S_{dr} (%)	7.30 ± 3.79 a	8.09 ± 4.02 a	10.07 ± 0.71 a	8.67 ± 0.57 a
Tetric	S_{dr} (%)	3.32 ± 1.39 a	4.34 ± 3.38 a	5.13 ± 1.96 a	3.46 ± 1.29 a
Vita Enamic	S_a (μm)	1.14 ± 0.02 a	1.18 ± 0.01 a	1.29 ± 0.40 a	1.98 ± 0.47 a
Tetric	S_a (μm)	0.67 ± 0.09 a	0.45 ± 0.07 a	0.44 ± 0.09 a	0.51 ± 0.08 a
Vita Enamic	S_q (μm)	1.42 ± 0.02 a	1.49 ± 0.01 a	1.61 ± 0.05 a	1.89 ± 0.31 a
Tetric	S_q (μm)	0.87 ± 0.10 a	0.60 ± 0.10 a	0.59 ± 0.12 a	0.66 ± 0.10 a
Vita Enamic	S_z (μm)	8.72 ± 0.06 a	8.96 ± 0.19 a	9.55 ± 0.28 a	9.44 ± 0.22 a
Tetric	S_z (μm)	5.62 ± 0.50 a	4.04 ± 0.74 a	3.60 ± 0.70 a	4.30 ± 0.53 a
Vita Enamic	S_{dr} (%)	9.91 ± 0.43 a	10.05 ± 0.47 a	11.30 ± 0.45 a	10.97 ± 0.35 a
Tetric	S_{dr} (%)	3.00 ± 1.19 a	1.94 ± 0.74 a	1.89 ± 0.78 a	2.48 ± 0.75 a

of fabrication of the hybrid CAD–CAM material (high pressure and high temperature), which provide increased polymerization. This method of fabrication is responsible for improved matrix formation of the material and the advanced interaction between fillers and matrix, contributing to a more uniform cross-linked network of monomers.[32]

Another significant finding of this study was that the Er,Cr:YSGG laser did not have an effect on the leaching of monomers from either material tested, suggesting that the bleaching treatment with a Er,Cr:YSGG laser is a safe clinical procedure to accelerate and improve in-office bleaching treatments regarding this property.

In the present investigation, a release of BPA from the conventional composite resin was detected before and after the Er,Cr:YSGG laser bleaching treatment and in both the materials tested. Pure BPA is not a component of composite resins, but derivatives of BPA are widely used as Bis-GMA. Therefore, BPA is present in composite resins as an impurity of the production process of these monomers, which can potentially be released.[40] This is one of the reasons why manufacturers prefer not to use *Bis*-GMA, and instead include UDMA and TEGDMA as the main monomers of the hybrid CAD–CAM materials or some conventional composite materials.[41]

The results of the present study coincide with those of other studies indicating that TEGDMA was the main released monomer from composite materials.[41,42] The reason of the absence of UDMA and *Bis*-GMA in the tested solutions may be the fact that bleaching agents induce a degradation procedure of those high molecular weight molecules, and thus a decrease of their concentration in the storage media. This may explain the decomposition of those monomers that possibly lead to the regeneration of other substances with other molecular weight and retention time.[17] This is in agreement with the current study, where an unknown peak appeared in the representative high-performance liquid chromatograms at 16 minutes for the laser-assisted bleaching group of the composite resin (Fig. 3). Therefore, additional research is necessary to investigate the additional substances that may be released after the Er,Cr:YSGG laser bleaching treatment that may influence the clinical behaviour of the materials.

The increased surface roughness of dental restorative materials is an important factor that may jeopardize the health of hard dental tissues, because it increases the risk of secondary caries formation.[43,44] Restorations that are manufactured with CAD–CAM technology are milled with rotary instruments coated with diamond abrasive particles of 64-mm grit size.[45] The above instruments produce a rather high initial surface roughness, which may lead to the increased wear of adjacent teeth and the discoloration of the restoration.[46,47] In addition, there is a constraint for the crystallization of the hybrid CAD–CAM materials, and, therefore, these materials can only be hand polished. Additionally, bleaching treatment and high-energy free radicals produced by peroxides may increase the surface roughness of resin composites and CAD–CAM restorations, since they may cause matrix softening and complete or partial detachment of the fillers and increased water uptake leading to a more porous and rougher surface of the materials.[48,49]

The ideal threshold value for the roughness of restorations in terms of bacterial retention has yet to be established.[50] However, the higher values of roughness in dental restorations, the higher the risk of plaque accumulation and caries development.47 The tested hybrid CAD–CAM material is a PICN material, and it contains a porous sintered ceramic network filled with plastic. Thus, it consists of two different interlocking networks—a ceramic and a polymer network, which is called double network hybrid. The main monomer of this material is UDMA, which, in general, achieves a lower degree of conversion and cross-link density; as a consequence, the material could wear relatively easy and leave exposed inorganic fillers on the surface.[50] However, Vita Enamic is fabricated under conditions of high temperature and high pressure during polymerization. This different approach of polymerization contributes to an improved polymeric matrix and better matrix–filler interaction, leading to a higher degree of cure and to a more homogeneously cross-linked network of monomers.[32]

There are numerous studies that have evaluated the surface roughness of resin composites after bleaching treatments,[51,52] studies that have evaluated the surface roughness of resin composites after Er,Cr:YSGG laser bleaching treatment,[3,6] or studies that have evaluated the effect of bleaching treatments on the enamel surface.[53,54] There are also studies that have evaluated the bleaching treatment on CAD–CAM materials,[49,55] but, except for the present study, there are no studies that have evaluated the surface roughness of composite resins or hybrid CAD–CAM materials after Er,Cr:YSGG laser in-office tooth bleaching.

The outcomes of the current study are in accordance with Varanda and others[56] who did not find significant alteration of surface roughness of nanofilled and microhybrid resin composites after the application of 35% bleaching agents and also in accordance with Rodrigues and others[48] where bleaching treatments did not promote alterations in the surface roughness of resin composites. Similarly, the same pattern refers to the CAD–CAM material, where the results of this study coincide with those of Karakava and others,[49] who found that bleaching application did not have any significant effect on the surface roughness and the surface topography of CAD–CAM materials. According to the results of this study, the laser irradiation did not have an effect on the surface roughness of the specimens, thus the Er,Cr:YSGG laser would not affect the bonding interface of the restorations and the resin composite does not need repolishing after the bleaching treatment.

In this study it was found that the roughness parameter S_z, for the composite resin specimens in artificial saliva, presented a statistically significant increase after the 7-day experimental period. This evidence may be attributed to the precipitation of artificial saliva ingredients on the specimen surfaces combined with the Er,Cr:YSGG laser irradiation of the surface.

CONCLUSIONS

Within the limitations of this study, it could be concluded that (1) the tested hybrid CAD–CAM material is potentially safer for tooth restoration than the tested conventional composite resin regarding the elution of residual monomers; (2) tooth bleaching treatments may influence the elution of the monomers from the tested composite resin; (3) the surface roughness of the tested materials is not affected by the tooth bleaching treatments; (4) Er,Cr:YSGG laser-assisted tooth bleaching treatment is as safe as the conventional technique in regards to changes in monomer elution and surface roughness; and (5) monomer elution was higher in distilled water compared to artificial saliva in both materials tested.

Conflict of Interest

The authors of this manuscript certify that they have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this manuscript.

Regulatory Statement

Author represents that the study was performed in compliance with author's institution's appropriate policies related to the use of animal and/or human subjects and human-derived material/s.

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