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Einfluss der Ätzzeit auf die Oberflächeneigenschaften von verschiedenen CAD/CAM-gefertigten Restaurationsmaterialien auf Siliziumoxid-Basis

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Elena Hristova

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Berichterstatter:	Prof. Dr. med. dent. Daniel Edelhoff
Mitberichterstatter:	Prof. Dr. Dr. Franz-Xaver Reichl
	Prof. Dr. Dr. Heinz Kniha

Mitbetreuung durch die promovierte Mitarbeiterin:

Dr. rer. biol. hum. Dipl. Ing. (FH) Bogna Stawarczyk, MSc

Dekan: Prof. Dr. med. Dr. h.c. M. Reiser, FACR, FRCR

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Eidesstattliche Versicherung

von Elena Hristova

Ich erkläre hiermit an Eides statt,
dass ich die vorliegende Dissertation mit dem Thema

Einfluss der Ätzzeit auf die Oberflächeneigenschaften von verschiedenen CAD/CAM-gefertigten Restaurationsmaterialien auf Siliziumoxid-Basis

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Zusammenfassung

Die vorliegende Dissertation untersuchte den Einfluss der Ätzzeitdauer auf die Oberflächeneigenschaften von verschiedenen CAD/CAM-gefertigten Restaurationsmaterialien auf Siliziumoxid-Basis.

Aus jedem Material wurden fünfundfünfzig Prüfkörper (10×10×1.5 mm) aus CAD/CAM-Blöcken hergestellt: (1) IPS Empress CAD (Ivoclar Vivadent, Schaan, Liechtenstein), (2) VITA Mark II (VITA Zahnfabrik, Bad Säckingen, Deutschland), (3) KLEMA CAD/CAM Glaskeramik (Klema Dentalprodukte, Meiningen, Österreich), (4) VITA ENAMIC (VITA Zahnfabrik, Bad Säckingen, Deutschland) und (5) IPS e.max CAD (Ivoclar Vivadent, Schaan, Liechtenstein). Die Prüfkörper wurden poliert und vor dem Ätzen für fünf Minuten mit destilliertem Wasser im Ultraschallbad gereinigt. Anschließend wurden sie randomisiert in 11 Gruppen (n=5) für folgende Ätzzeiten aufgeteilt: 0s (galt als Kontrollgruppe), 20 s, 30 s, 40 s, 50 s, 60 s, 75 s, 90 s, 105 s, 120 s und 150 s. Für den Ätzvorgang wurde neunprozentige Fluorwasserstoffsäure (Porcelain Etch, Ultradent, Brunnthal, Deutschland) benutzt. Nach dem Ätzen wurden die Prüfkörper sorgfältig mit Alkohol gereinigt und getrocknet.

Die freie Oberflächenenergie wurde durch Kontaktwinkelmessung in einem Gerät zur Benetzungsuntersuchung (Drop Shape Analyzer DSA25, Krüss GmbH, Hamburg, Deutschland) bestimmt. Dafür wurden die Kontaktwinkel gemessen, die sechs unabhängige Flüssigkeitstropfen (drei Tropfen destilliertes Wasser und drei Tropfen Diiodomethan) auf der jeweiligen Keramikoberfläche gebildet haben. Aus diesen Messwerten wurde die Oberflächenenergie jedes Prüfkörpers nach der Owens-Wendt-Rabel-Kaelble-Methode berechnet.

Die Oberflächenrauigkeit der unterschiedlich lang geätzten Keramikprüfkörperoberflächen wurde im Profilometer (MarSurf M400, Mahr GmbH, Göttingen,

Deutschland) mit einer Messkraft von 0,7 mN bestimmt. Es wurden sechs Messungen pro Prüfkörper durchgeführt, drei in der x- und drei in der y-Ebene. Daraus wurde der Rauigkeitsmittelwert ermittelt. Die Oberflächentopographie wurde im Rasterelektronenmikroskop (REM, Carl Zeiss Supra 50 VP FESEM, Carl Zeiss, Oberkochen, Deutschland) aufgenommen. Dafür wurden die zuvor vorbehandelten Prüfkörper mit Gold gesputtert, um die Leitfähigkeit für die Elektronen zu erreichen.

Alle erzielten Resultate wurden statistisch mittels ein- und zweifaktorieller Varianzanalyse mit dem anschließenden Post-hoc Scheffé Test, der linearen Varianzanalyse sowie der linearen Regression analysiert. Dabei wurde das Signifikanzniveau auf p=0.05 gesetzt. Die Analysen wurden mittels dem statistischen Programm SPSS (Version 20, SPSS Inc., Chicago, Illinois) durchgeführt.

Die Ätzzeitdauer zeigte einen signifikanten Einfluss auf die Oberflächeneigenschaften der getesteten Glaskeramiken ($p < 0.001$). Nach dem Ätzen wiesen alle Prüfkörper eine höhere Rauigkeit im Vergleich zur ungeätzten Kontrollgruppe auf. Generell zeigte KLEMA CAD/CAM Glaskeramik die höchste (Ra: 0.63–2.06 µm) und IPS e.max CAD die niedrigste Oberflächenrauigkeit (Ra: 0.02–0.15 µm). Die höchste freie Oberflächenenergie wurde für IPS e.max CAD (55.1–73.1 mN/m) und VITA ENAMIC (43.0–67.9 mN/m) und die niedrigste für KLEMA CAD/CAM Glaskeramik (12.0–41.2 mN/m) gemessen. Längere Ätzzeiten erhöhten die Oberflächenenergie-Werte für IPS e.max CAD und VITA ENAMIC und reduzierten die Werte für VITA Mark II, IPS Empress CAD und KLEMA CAD/CAM Glaskeramik.

Insgesamt zeigten alle geprüften Werkstoffe einen unterschiedlichen Einfluss der Ätzzeitdauer auf ihre Oberflächeneigenschaften. So wurde die Anfangshypothese, nach der alle Glaskeramiken ähnliche Oberflächeneigenschaften in Abhängigkeit von der Ätzzeitdauer besitzen, abgelehnt.

Die getesteten Materialien bestehen hauptsächlich aus Siliziumoxid und verstärkenden Partikeln, wie zum Beispiel Aluminiumoxid, Lithiumdisilikat oder Kunststoffen bei Hybridkeramiken. Darauf basierend kann konstatiert werden, dass sowohl der prozentuale Anteil des Siliziumoxids, als auch die Zusammensetzung der Zusatzpartikel einen signifikanten Einfluss auf die Oberflächeneigenschaften nach dem Ätzvorgang haben.

Fazit: Die Ätzzeitdauer zeigte unterschiedliche Auswirkungen auf die Oberflächeneigenschaften der getesteten Materialien. Ausgehend von den Ergebnissen aus dieser Studie, kann allerdings keine einheitliche Empfehlung für die Ätzzeitdauer gemacht werden.

Klinische Relevanz: Aufgrund der materialspezifischen Änderungen der Oberflächeneigenschaften nach dem Ätzen mit Flusssäure ist eine generelle Aussage zur optimalen Ätzzeitdauer von CAD/CAM-gefertigten Restaurationsmaterialien auf Siliziumoxid-Basis unmöglich. Daher sollten die Empfehlungen des Herstellers zur Ätzzeitdauer des jeweiligen Werkstoffes befolgt werden.

Summary

Objectives: To investigate the effect of etching times on surface properties of different glass-ceramic based CAD/CAM materials.

Methods: Fifty-five specimens (10×10×1.5 mm) were fabricated from each material: (1) IPS Empress CAD (EMP, IvoclarVivadent), (2) VITA Mark II (VMA, VITA Zahnfabrik), (3) KLEMA CAD/CAM glass-ceramic (KLE, KLEMA), (4) VITA ENAMIC (VEN, VITA Zahnfabrik), and (5) IPS e.max CAD (EMC, Ivoclar Vivadent). The specimens were divided into 11 groups (n=5) for different etching times: 0s (control group), 20s, 30s, 40s, 50s, 60s, 75s, 90s, 105s, 120s, and 150s (9% hydrofluoric acid). After etching, surface roughness (SR) and surface free energy (SFE) were measured. The surface topography was determined under scanning electron microscopy (SEM). Data were analyzed using two- and one-way ANOVA with post hoc Scheffé test, linear covariance analysis, and linear regressions (alpha = 0.05).

Results: The interaction between glass-ceramic based materials and etching time showed a significant impact on SR and SFE values (p < 0.001). All etching periods produced rougher surfaces than the control group. Generally, the highest SR values were observed for KLE (Ra: 0.63–2.06 µm) and the lowest for EMC (Ra: 0.02–0.15 µm). The highest SFE values were detected for EMC (55.1–73.1 mN/m) and VEN (43.0–67.9 mN/m) and the lowest for KLE (12.0–41.2 mN/m). Longer etching increased the SFE of EMC and VEN and decreased that of VMA, EMP, and KLE.

Conclusions: Each tested glass-ceramic based material presented different impacts of etching time on the surface properties. General recommendations on the etching time cannot be given.

1. Introduction

Today, ceramics are commonly used in restorative dentistry, especially in the computer-aided design (CAD) / computer-aided manufacturing (CAM) workflow. Dental ceramic restorations are extensively used due to their similar optical properties to natural tooth structure [1], physical and mechanical characteristics [2–4], and biocompatibility [5]. Furthermore, recent trends in aesthetic dentistry include the substitution of metal based restorations by those made of all-ceramics. The increasing demand for metal-free restorations has encouraged the development of all-ceramic materials with improved mechanical properties. As any ceramic surface is inert and does not adhere readily to other materials, it is necessary to achieve surface roughness (SR) for proper bonding. Etching is a reliable procedure to have a dissolving effect on the superficial layer of silicate ceramics [6, 7].

There are different classes of glass-ceramic based materials in dentistry, like ceramics containing crystalline lithium disilicate (IPS e.max CAD, IPS e.max Press), feldspar, and leucite ceramics based on silica and alumina (VITA Mark II, IPS Empress CAD) [8], or recent developments as hybrid ceramics with a dual-network structure (VITA ENAMIC) which includes also an organic matrix. The novel hybrid dental ceramic family includes dental porcelains of a porous consistency infiltrated by a polymer in order to combine ceramic and composite properties in one product, which showed a significant effect of elastic modulus and hardness on the indentation size [9]. Compared with human enamel, hybrid ceramics showed much lower hardness values than standard dental ceramics [9, 10]. In summary, all these glass-ceramic based materials show differences in mechanical and chemical properties dependent on their composition.

Generally, glass-ceramic based materials are the most suitable in mimicking the optical appearance of the natural tooth [10]. The number, the size, and the chemical composition of the particles influence the properties of silicate ceramics, such as opalescence, color, and opacity [2, 10]. A moderate increase of strength can be achieved by adding reinforcement particles, such as aluminum oxide, zirconia oxide, leucite, or lithium silicate [2, 11]. However, glass-ceramic based materials show lower hardness and flexural strength values compared with other dental ceramics, such as glass-infiltrated alumina [12], alumina, or zirconia [11]. Nevertheless, adhesive cementation with resin-based composite cements enhances the clinical efficiency [13] and furthermore increases the stability and fracture resistance of silicate dental ceramics [14–17]. For the adhesive cementation of glass-ceramic based materials, the conditioning of the inner surface of the restoration is needed to accomplish higher surface free energy (SFE) and SR. Chemical conditioning with hydrofluoric acid (HF) is the predominantly used surface treatment process prior to resin bonding [18]. In vitro studies observed a positive effect of HF etching on surface topography by increasing its roughness [19–21]. Applied on glass-ceramic based materials, this method removes the glass matrix selectively and exposes the crystalline structure beneath [6, 7]. This roughly etched surface offers more SFE prior to bonding with resin composite cement [22]. Therefore, glass-ceramic based restorations are generally etched before incorporation (manufacturer's recommendation for EMC, 20 s; for EMP, VMA, KLE, and EMP, 60 s).

Aside from the SR, there are further parameters to determine surface properties, namely, SFE, wettability, and SEM surface topography. SFE is defined as the work required to increase the area of a substance by 1 cm^2. It can be determined by

contact angle measurement. This is the angle formed by a drop of liquid, for example, water and diiodomethane, on a defined surface [23]. The wettability of a solid surface by a liquid is estimated by the dimensions of the contact angle; the lower the contact angle, the higher the wettability of the surface [22–26]. Additionally, the treatment of an etched ceramic surface with a silane agent further increases its wettability [27]. The authors of this study identified limited information to date on the impact of etching time on SR, wettability, SFE, and surface topography of different silicate ceramics.

The aim of this study was to investigate the impact of HF etching duration on surface properties of five different glass-ceramic based materials. The tested null hypothesis was whether all tested glass-ceramic based materials present similar surface properties after HF at the different etching times.

2. Materials and Methods

Five different glass-ceramic based CAD/CAM materials were investigated: (1) IPS Empress CAD (EMP, Ivoclar Vivadent, Schaan, Liechtenstein), (2) VITA Mark II (VMA, Vita Zahnfabrik, Bad Säckingen, Germany), (3) KLEMA CAD/CAM glass-ceramic (KLE, KLEMA Dentalprodukte, Meiningen, Austria), (4) VITA ENAMIC (VEN, Vita Zahnfabrik), and (5) IPS e.max CAD (EMC, Ivoclar Vivadent). Table 1 includes all tested glass-ceramic based materials, their chemical composition, manufacturers, lot numbers, and the abbreviations used in this study.

Table 1. Summary of all tested glass-ceramic based materials, their chemical composition, manufacturers, lot numbers, and the abbreviations used.

Ceramic	**Abbr.**	**Lot No.**	**Manufacturer**	**Composition (Weight, %)**
IPS Empress CAD	EMP	J17565	Ivoclar Vivadent, Schaan, Liechtenstein	SiO_2 > 98%, BaO, Al_2O_3, CaO, CeO_2, Na_2O, K_2O, B_2O_3, < 2% TiO_2, pigments
VITA Mark II	VMA	18090	VITA Zahnfabrik, Bad Säckingen, Germany	SiO_2 56%–64%, Al_2O_3 20%–23%, Na_2O 6%–9%, K_2O 6%–8%, CaO 0.3%–0.6%, TiO_2 0%–0.1%
KLEMA CAD/CAM glass-ceramic	KLE	2008	Klema Dentalprodukte, Meiningen, Austria	SiO_2 55%–65%, K_2O 5%–10%, Na_2O 8%–12%, MgO < 0.1%, CaO 1%–2%, BaO 0.5%, TiO_2, ZrO_2, P_2O_5, CeO_2, CeF_3, SnO_2 < 0.1%, pigments 1%–5%

Ceramic	Abbr.	Lot No.	Manufacturer	Composition (Weight, %)
VITA ENAMIC	VEN	V0155 6/7	VITA Zahnfabrik, Bad Säckingen, Germany	Ceramic 86% SiO_2 58%–63%, Al_2O_3 20%–23%, Na_2O 9%–11%, K_2O 4%–6%, B_2O_3 0.5%–2%, ZrO_2, KaO < 1% Polymer 14% UDMA and TEGDMA
IPS e.max CAD	EMC	P81551	Ivoclar Vivadent, Schaan, Liech-tenstein	SiO_2 57%–80%, Li_2O 11%–19%, K_2O 0%–13%, P_2O_5 0%–11%, ZrO_2 0%–8%, ZnO 0%–8%, Al_2O_3 0%–5%, MgO 0%–5%, pigments 0%–8%

2.1 Specimens preparation

In summary, 55 specimens with a height of 1.5 mm, length of 10 mm, and width of 10 mm were fabricated from each glass-ceramic based material. This resulted in a total number of 275 specimens. The CAD/CAM blocks were sectioned under water cooling on the stated dimensions using Accutom-50 (Struers, Ballerup, Denmark) with a diamond cut-off wheel M0D13 (127 mm [5"] dia. × 0.4 mm × 12.7 mm dia., with a cutting speed of 1000 rpm and a medium force of 40 N).

Subsequently, all specimen surfaces were polished (in the following order: 40 µm diamond pad, 20 µm diamond pad, MD-Largo + DiaPro Allegro/Largo, MD-Largo + DiaPro Largo, MD-Chem + OP-S) with a microprocessor controlled tabletop ma-

chine (Abramin, Struers, Ballerup, Denmark). The EMC specimens were additionally crystallized in a Programat EP 5000 press furnace (Ivoclar Vivadent, Schaan, Liechtenstein) with the following crystallization parameters: closing time: 6 min; stand-by temperature: 403°C; heating rate: 90°C/min; holding time: 10 min; heating rate: 30°C/min; firing temperature: 840°C; holding time: 7min; and long-term cooling: 700°C/min. The polished specimens were cleaned for 5 min using an ultrasonic bath (Sonorex RK102H, BANDELIN electronic, Berlin, Germany) with distilled water. Afterwards, they were air-dried with care. Each glass-ceramic based material group was then randomly divided into 11 subgroups for different etching times: group 1: 0 s (control group), group 2: 20 s, group 3: 30 s, group 4: 40 s, group 5: 50 s, group 6: 60 s, group 7: 75 s, group 8: 90 s, group 9: 105 s, group 10: 120 s, and group 11: 150 s. For the etching process, 9% HF (Ultradent, Brunnthal, Germany, Lot B6X7B) was used. Again, the etched specimens were rinsed with 80% 2-isopropanol (Merck, Darmstadt, Germany). The specimens were then adhered to aluminum SEM carriers for better fixation in the following experiments.

2.2 Surface free energy

To measure the contact angle between a liquid (water/diiodomethane) and a solid (glass-ceramic based specimens), a special device (Drop Shape Analyzer DSA25, Krüss GmbH, Hamburg, Germany) was used. Prior to measurement, the surfaces were again cleansed with 80% 2-isopropanol (Merck) and dried with oil-free air. The contact angle device with a manual double dosing system with two glass syringes, one filled with distilled water and the other one with diiodomethane, was used. Each test drop of water contained 10 µl, and each test drop of diiodomethane contained 5 µl of the respective fluid. Measurement was executed 5 s after the drop made contact

with the ceramic surface. The contact angle was determined for six independent drops of liquid per specimen (three drops of water and three drops of diiodomethane). The tangent-1 method was used for angles above 20 degrees and the circle method for angles under 20 degrees. The SFE was calculated from these results using the Owens-Wendt-Rabel-Kaelble method [28, 29].

2.3 Surface roughness

For the SR measurements, a profilometer (MarSurf M400, Mahr GmbH, Göttingen, Germany) was used. In order to achieve accurate and reproducible results, the specimens were cleaned (2-Propanol, Merck, Darmstadt, Germany) and fixed in a special holding device to retain the surface parallel to the platform of the machine. Its measuring force was approximately 0.7 mN (standard). Six measurements per specimen were performed, three lengthwise and three across each ceramic slide. The distance between the testing points in the x and y planes was approximately 1 mm. SR values were calculated individually as the mean of these six measurements for each specimen.

2.4 SEM surface topography

For scanning electron microscopy (SEM) analyses, two specimens per subgroup were selected. The specimens were ultrasonically cleaned (isopropanol-2, Merck) and then gold-sputtered (layer thickness: 6 nm). Surface topography was evaluated under a SEM (Carl Zeiss Supra 50 VP FESEM, Carl Zeiss, Oberkochen, Germany) operating at 10 kV with a working distance of 7.0–12.4 mm.

2.5 Statistical analysis

Descriptive statistics were calculated. The normality of data distribution was tested using the Kolmogorov-Smirnov and Shapiro-Wilk tests. Two- and one-way ANOVA followed by a post hoc Scheffé test were used to determine the significant differences between groups. In the next step, the data were plotted in scatter diagrams. Linear covariance analysis was computed in order to investigate the differing associations provided by the glass-ceramic based materials between etching time and outcomes (such as SFE and SR). In addition, due to significant interactions ($p < 0.001$), linear regressions for each outcome with respect to each etching time for all tested materials were computed separately. P values smaller than 5% were considered to be statistically significant in all tests. The data were analyzed using SPSS Version 20 (SPSS Inc., Chicago, Illinois).

3. Results

3.1 Surface free energy

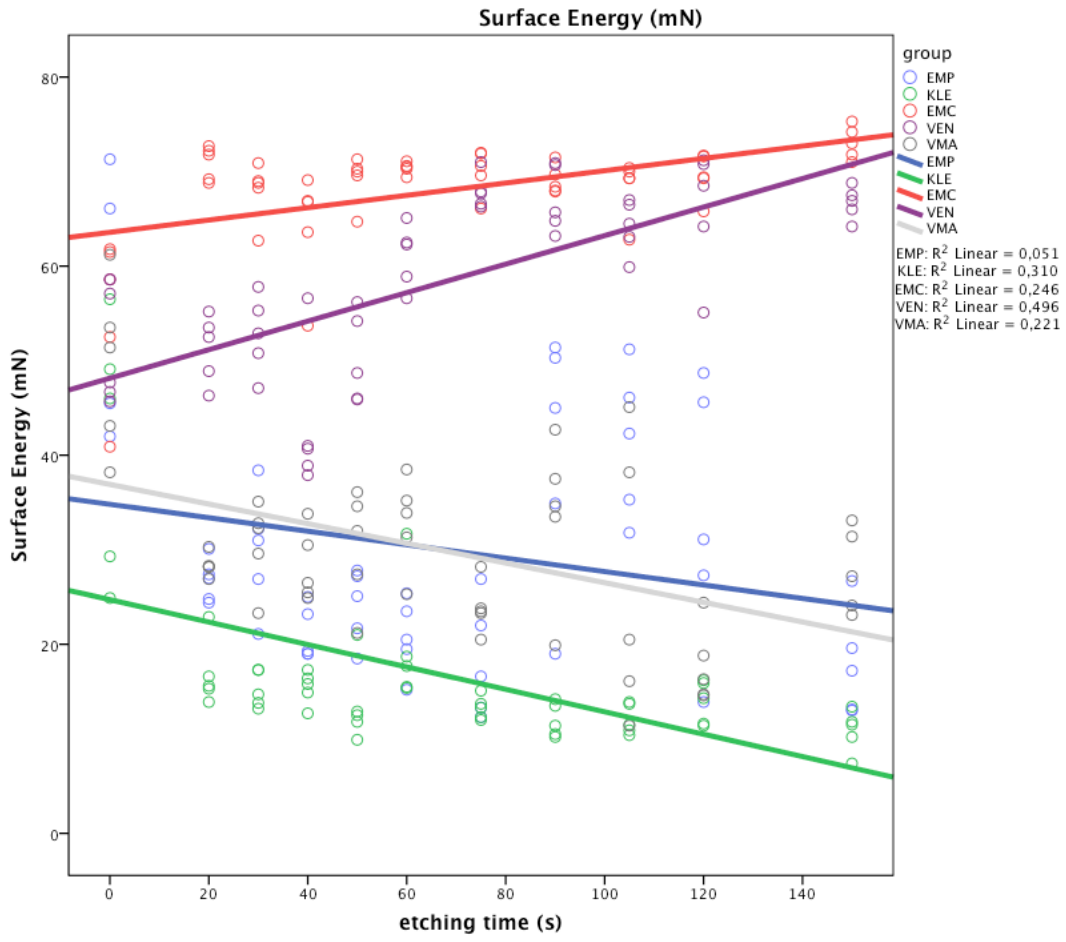
The descriptive statistics for the SFE results are summarized in Table 2. Figure 1 presents the scatter diagram for all five tested glass-ceramic based materials dependent on the etching time. In general, KLE, VMA, and EMP showed a decrease in SFE with an increase of etching time. In contrast, EMC and VEN presented an increase in SFE with increase of etching time. The measured SFE for EMC and VEN was higher than those of KLE, VMA, and EMP.

Table 2. Mean and standard deviation for surface free energy (SFE) values (mN). Differing letters within a row correspond to differing SFE means between treatment groups according to the post hoc Scheffé test.

Etching time	**EMP**	**VMA**	**KLE**	**VEN**	**EMC**
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
0 s	56.7 ± 12.7^{b}	49.5 ± 9^{b}	41.2 ± 13.5^{b}	51.2 ± 6.2^{abc}	55.1 ± 8.8^{a}
20 s	26.7 ± 2.3^{a}	28.4 ± 1.2^{a}	16.9 ± 3.5^{a}	51.3 ± 3.6^{abc}	70.9 ± 1.8^{b}
30 s	29.9 ± 6.4^{a}	30.6 ± 4.5^{ab}	15.3 ± 1.9^{a}	52.8 ± 4.1^{abcd}	67.9 ± 3.1^{b}
40 s	21.1 ± 2.8^{a}	28.2 ± 3.8^{a}	15.4 ± 1.8^{a}	43.0 ± 7.7^{a}	64.0 ± 6.1^{ab}
50 s	24.1 ± 3.9^{a}	30.3 ± 6^{ab}	13.6 ± 4.3^{a}	50.2 ± 4.8^{ab}	69.2 ± 2.6^{b}
60 s	20.8 ± 3.9^{a}	32.8 ± 4.9^{ab}	19.8 ± 6.8^{a}	61.1 ± 3.3^{bcde}	70.4 ± 0.6^{b}
75 s	18.2 ± 6.2^{a}	23.9 ± 2.8^{a}	13.3 ± 1.2^{a}	67.9 ± 1.9^{e}	70.0 ± 2.4^{b}
90 s	40.1 ± 13.5^{ab}	33.6 ± 8.5^{ab}	12.0 ± 1.8^{a}	67.1 ± 3.5^{e}	69.1 ± 1.5^{b}
105 s	41.3 ± 7.9^{ab}	26.3 ± 14.6^{a}	12.1 ± 1.6^{a}	64.2 ± 2.9^{cde}	68.4 ± 3.1^{b}

Etching time	EMP	VMA	KLE	VEN	EMC
120 s	33.3 ± 14.2^{ab}	17.8 ± 4.1^{a}	13.9 ± 2.3^{a}	66.0 ± 6.7^{de}	69.6 ± 2.4^{b}
150 s	17.9 ± 5.7^{a}	27.8 ± 4.4^{a}	10.9 ± 2.2^{a}	66.7 ± 1.7^{e}	73.1 ± 1.7^{b}
Lin. reg. intercept	34.81	36.91	24.72	48.16	63.58
Slope	−0.071	−0.104	−0.119	0.151	0.065

Figure 1: Scatter diagram of surface free energy (SFE) for each tested glass-ceramic based material at each etching time level.



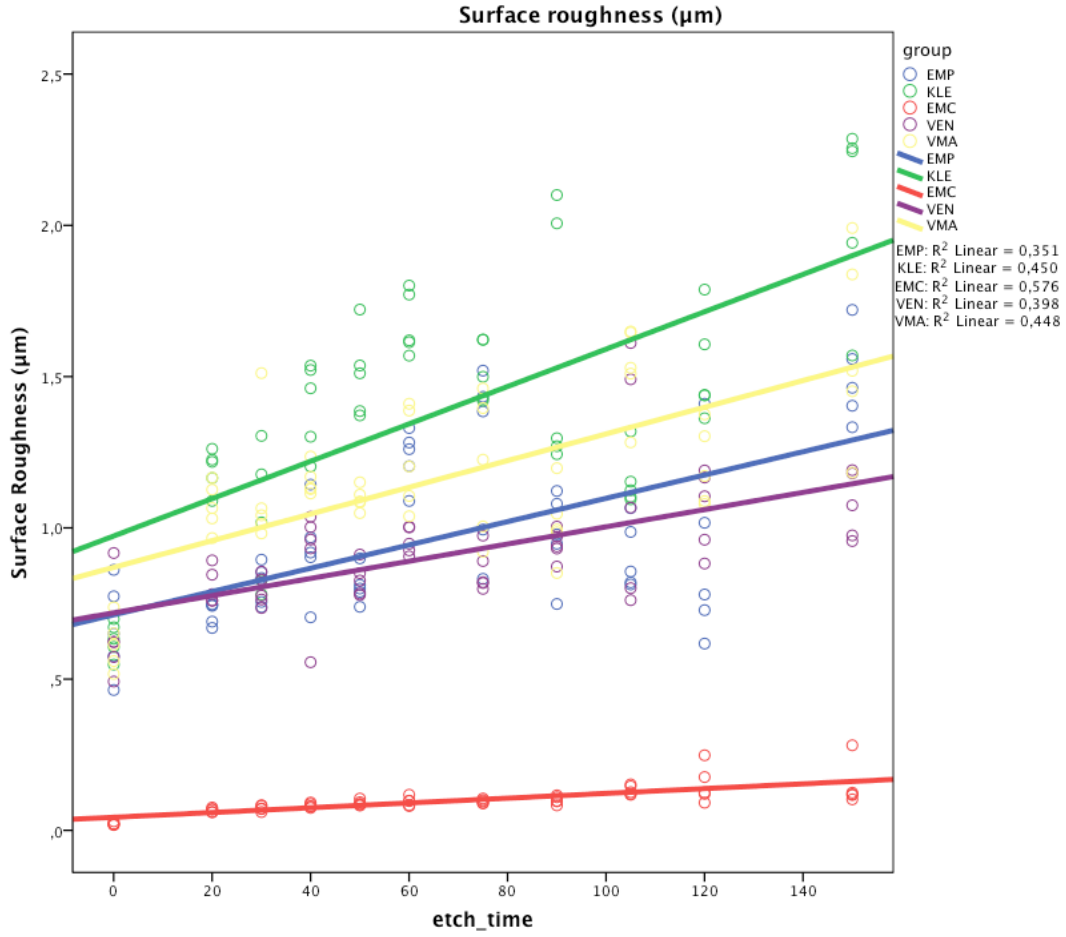
3.2 Surface roughness

Table 3 shows the mean SR with standard deviations (SD) of all tested glass-ceramic based materials. The significantly lowest mean SR was observed for EMC, the highest for KLE. All materials showed an increase of SR dependent on the etching time (Fig. 2).

Table 3. Mean and standard deviation for surface roughness (SR) values (µm). Differing letters within a row correspond to differing SR means between treatment groups according to the post hoc Scheffé test.

Etching time	**EMP**	**VMA**	**KLE**	**VEN**	**EMC**
	Mean ± SD	**Mean ± SD**	**Mean ± SD**	**Mean ± SD**	**Mean ± SD**
0 s	0.67 ± 0.16^{a}	0.62 ± 0.09^{a}	0.63 ± 0.58^{a}	0.65 ± 0.16^{a}	0.02 ± 0.01^{a}
20 s	0.72 ± 0.37^{a}	1.07 ± 0.08^{abc}	1.19 ± 0.67^{abc}	0.81 ± 0.06^{ab}	0.07 ± 0.01^{ab}
30 s	0.82 ± 0.67^{ab}	1.12 ± 0.22^{bcd}	1.02 ± 0.22^{ab}	0.79 ± 0.05^{ab}	0.07 ± 0.01^{ab}
40 s	0.93 ± 0.16^{ab}	1.16 ± 0.05^{bcd}	1.41 ± 0.15^{bc}	0.90 ± 0.20^{ab}	0.08 ± 0.01^{ab}
50 s	0.81 ± 0.58^{ab}	1.10 ± 0.04^{bc}	1.51 ± 0.14^{bcd}	0.83 ± 0.06^{ab}	0.09 ± 0.01^{ab}
60 s	1.23 ± 0.92^{bc}	1.23 ± 0.17^{bcd}	1.68 ± 0.10^{cd}	0.96 ± 0.04^{ab}	0.10 ± 0.02^{ab}
75 s	1.23 ± 0.3^{bc}	1.20 ± 0.24^{bcd}	1.52 ± 1.00^{bcd}	0.86 ± 0.07^{ab}	0.10 ± 0.01^{ab}
90 s	0.98 ± 0.15^{ab}	1.02 ± 0.13^{ab}	1.58 ± 0.43^{bcd}	0.94 ± 0.05^{ab}	0.10 ± 0.01^{ab}
105 s	0.91 ± 0.12^{ab}	1.52 ± 0.15^{cd}	1.16 ± 0.09^{abc}	1.15 ± 0.39^{b}	0.13 ± 0.02^{b}
120 s	0.91 ± 0.32^{ab}	1.20 ± 0.13^{bcd}	1.53 ± 0.17^{bcd}	1.06 ± 0.13^{ab}	0.15 ± 0.06^{b}
150 s	1.50 ± 0.15^{c}	1.60 ± 0.32^{d}	2.06 ± 0.31^{d}	1.08 ± 0.11^{ab}	0.15 ± 0.07^{b}
Lin. reg. intercept	0.713	0.870	0.973	0.719	0.043
Slope	0.004	0.004	0.006	0.003	0.001

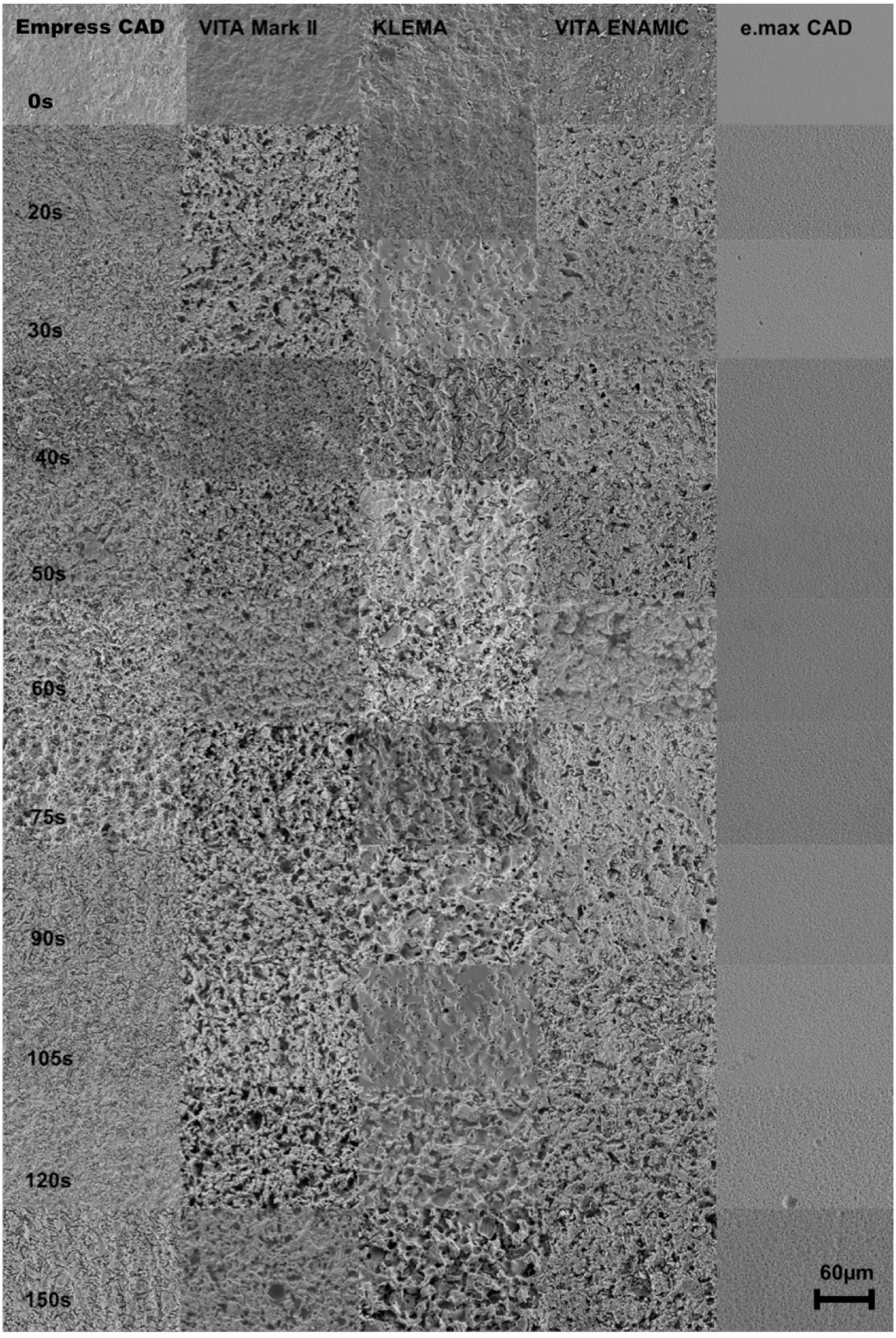
Figure 2: Scatter diagram of SR for each tested glass-ceramic based material at each etching time level.



3.3 SEM surface topography

The SEM pictures are presented in Figure 3. EMP, VMA, KLE, and VEN showed a clear change in surface topography with the increase of etching time. The etching time of EMC caused only minimal changes to its surface.

Figure 3. SEM pictures of etched ceramic surfaces in order of glass-ceramic based materials (horizontal) and etching time (vertical).


Empress CAD
VITA Mark II
KLEMA
VITA ENAMIC
e.max CAD
0s
20s
30s
40s
50s
60s
75s
90s
105s
120s
150s
60µm

4. Discussion

This study investigated the influence of different HF etching durations on the surface properties of five different glass-ceramic based materials. In general, the tested materials showed different impacts of etching times. Therefore, the tested null hypothesis that all tested materials present similar surface properties after HF dependent on the etching time is rejected. All tested materials are based on silica oxide combined with different reinforcement particles. Therefore, it can be stated that the percentage of silica oxide as well as the different particles such as alumina oxide, leucite, and lithium silicate have a significant impact on surface properties in respect of etching duration.

Knowledge of the SFE and especially the interaction between fluids and different dental materials is very important. When adhesion is required, high SFE is favored and, on the contrary, it is undesirable when plaque accumulation should be avoided [30, 31]. SFE defines the surface reactivity and can be determined by contact angle measurement. When an interface exists between a liquid and a solid, the contact angle is the angle between the surface of the liquid and the outline of the contact surface. In literature, numerous approaches to determine SFE are described. According to Owens et al. [28], using the geometric mean approach or the harmonic mean method, SFE can be estimated by measuring contact angles with two liquids. In this study, a two-liquid method was used, making a distinction between dispersive and polar components. Still, there are very controversial opinions on which is the most accurate method for defining SFE. Combe et al. [30] suggested that at least five test liquids are required for precise results and recommended the Zisman method [23], while Carlen et al. [32] and Sipahi et al. [33] favored three liquids. Furthermore,

there is discrepancy in the data for components of the test liquids' surface tension, so the liquid selected for measurements and the interaction between the liquid and the solid also affect the experimental results. Unfortunately, a comparison with other dental materials cannot be made. Other studies dealing with SFE values of glass-ceramic based materials were not identified.

In the present study, the etching time had a significant impact on the SFE of glass-ceramic based materials. In general, SFE decreased with an increase of etching time for KLE, VMA, and EMP and, on the contrary, increased for EMC and VEN. KLE, VMA, and EMP are in contrast with the common expectations that a roughly etched surface helps to provide more surface energy [22].

Furthermore, EMC and VEN showed higher SFE than the remaining specimens. Lithium disilicate (LS_2 in EMC) particles and polymer ingredients (UDMA and TEGDMA in VEN) have a significant impact on etching patterns, creating preconditions for higher SFE. Contact angles on a surface are measured to an assumed horizontal, but on a microscopic level, the liquid might take up an equilibrium value with the gradient of the surface at the edge of the drop: the contact depends on the details of the topography [34]. Newly formed pores due to these non- or less-etched ingredients result into different etching patterns that increase the SFE and the extent of wettability.

Acid etching of porcelain has been widely used in dentistry to increase retention between bonding resins and ceramic restorations. Etching is a dynamic process, and the impact is dependent on the type of etchant and etching time, ceramic microstructure, and composition [20, 35]. It causes preferential dissolution of the weaker

glassy phase of leucite-reinforced ceramics and the introduction of new surface defects or the extension of preexisting ones [18, 20, 36]. HF etching provides the necessary roughness for mechanical interlocking; nevertheless, overetching was described to weaken the porcelain [20, 35, 37]. These considerations have encouraged numerous studies to attempt to determine the adequate HF etching duration prior to micromechanical retention for all kinds of different ceramic products [22, 35, 37].

Jardel et al. [22] concluded that HF gel action combined with a silane coupling agent is the most effective treatment for ceramic surfaces. Zogheib et al. [37] etched a lithium-disilicate-based ceramic using 4.9% HF for four different etching periods: 20 s, 60 s, 90 s, and 180 s. Significantly higher roughness values were measured for all etching periods compared with that of the control group. Roughness increased in unison with etching time. Similar results were achieved by Wolf et al. [21]. They studied the surface properties of a feldspathic ceramic etched with 9.5% HF for 30 s, 60 s, 150 s, and 300 s to find a positive correlation between roughness and etching period, which agreed with further studies [20, 38] and with the present study.

This study investigated the effect of different acid etching times on the SR of five different glass-ceramic based materials. For the etching process, 9% HF was used for 10 different etching times: 20 s, 30 s, 40 s, 50 s, 60 s, 70 s, 90 s, 105 s, 120 s, and 150 s, respectively. HF etching resulted in rougher surfaces of all species. This was highly anticipated since all tested ceramics contain a glassy matrix with a high silicate weight percentage (Table 1). The efficiency of surface treatment is highly dependent on the composition of the ceramics. In comparison, ceramics with high alumina content and no glassy phase remain non-etched [18, 19], as the silicate

phase is the only phase to react with HF. The current study showed that roughening was the least efficient for EMC (highest roughness value for 150 s was 0.15 μm compared with 0.02 μm for the control group); the highest Ra values were measured for KLE (2.06 μm). Therefore, comparing studies is very demanding due to differences in etchants and etchant concentrations, etching time, ceramic composition, and microstructure. Nevertheless, roughness itself is an essential characteristic of surfaces and has to be measured and experimented with, especially for innovative materials such as VEN. Those materials offer limited scientific data and are yet to be established in restorative dentistry.

Microscopic examination is important for the evaluation and characterization of materials. There is an important relationship between microstructure and material properties in dental ceramics [19]. Furthermore, it is vital to analyze new products such as VITA ENAMIC in order to understand their microstructural characteristics and to evaluate their clinical performance [39].

Measured mean Ra values correspond to the SEM images—the longer the etching time, the greater the microscopic irregularities in the images. The SEM micrographs clearly revealed the effect of different etching periods on the microstructure of the ceramic. It is shown that HF etching significantly modified the morphologic surface of groups 1–4. Surface etching almost did not change the morphologic characteristics of IPS e.max CAD, and the same surface irregularities were found in the control group. The EMP specimens showed a “Swiss hole cheese pattern” after etching, VMA produced “honeycomb”-like surfaces, and KLE and VEN had very irregular features, such as big holes, fissures, scratch-like gaps, and areas with grain pullout. The surface of EMC remained almost unchanged, retaining its typical elongated crys-

tal structure. The manufacturer's recommendations were of sufficient duration to produce morphologic change in the tested groups 1–4. For EMC, HF was ineffective in increasing irregularities on the ceramic surface.

The study showed that the efficiency of the surface treatment is highly dependent on the composition of the specimens. Surface irregularities may be considerable in improving the bond strength with resin luting agents. Further studies should investigate the impact of etching duration on flexural strength, fracture toughness, and the dynamic fatigue of the ceramic materials. Whether more roughness results in better adhesion for the tested materials has not been a subject of this study and should be surveyed in the future.

In contrast to the situation in vivo, the specimens were not exposed to a warm humid environment, as it is the case in clinical scenarios. Further studies should look at the impact of SFE and SR on adhesive cementation of ceramic restorations. In addition, important qualities of the natural tooth substance also influence the quality of adhesive bonding. Therefore, future research should consider these aspects when studying SFE and SR values of ceramic restorations dependent on etching duration.

The chosen etchant in this study is 9% HF. There are other acid etchants, such as phosphoric acid, that do not etch ceramics but still have to be considered as they may improve the SFE by cleaning the ceramic surface [40]. One further limitation of this study is that the impact of only one HF concentration was evaluated. Further studies with different etching agents are necessary.

Clinical relevance: The individual manufacturers' recommendations concerning etching time have to be followed to achieve the best possible surface properties of glass-ceramic based materials.

5. Conclusions

Within limitation of this study, the following conclusions can be made:

- Each tested glass-ceramic based material presented a specific surface pattern and specific properties dependent on the etching time.
- General recommendations on the etching time for the tested materials cannot be made.
- The etching time has to be determined individually according to the specific material properties.

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Schlussfolgerung und Zukunftsperspektiven

Ziel Dieser Studie war es, die freie Oberflächenenergie, die Oberflächenrauigkeit und die Topographie von verschiedenen CAD/CAM-gefertigten siliziumoxid-basierten Keramiken in Abhängigkeit von der Ätzzeitdauer zu untersuchen. Jede der getesteten Glaskeramiken zeigte einen unterschiedlichen Einfluss der Ätzzeitdauer auf die Oberflächeneigenschaften. Aufgrund dieser Ergebnisse muss die Ätzzeitdauer für jede Keramik spezifisch ermittelt werden. Eine Pauschalisierung für alle Keramiken ist nicht möglich. Somit muss darauf hingewiesen werden, dass die Empfehlungen des Herstellers bei jeder Keramik getrennt zu befolgen sind.

Dentalkeramiken werden immer mehr als generelle Alternative zu Metalllegierungen angesehen. Der Werkstoff erfüllt nicht nur die gestiegenen Ansprüche der Patienten an die Ästhetik, sondern ist auch unumstritten bezüglich seiner Verträglichkeit gegenüber dem Mundmilieu. Feldspat- und Glaskeramiken eignen sich aufgrund ihrer optischen und ästhetischen Eigenschaften besonders gut für Zahnrestaurationen im Frontzahnbereich. Dies macht die weitergehende Forschung und Vergleich verschiedener Keramikwerkstoffen unentbehrlich für die Zukunft der modernen Zahnmedizin.

Durch das adhäsive Befestigen werden Glaskeramikrestaurationen zusätzlich stabilisiert. Hier ist die klassische Vorbehandlung mit Fluorwasserstoffsäure-Ätzgel Standard in der Praxis. Die dadurch resultierende Oberflächenrauigkeit ist in Bezug auf die Oberflächencharakteristik von großer Bedeutung und sollte für neu eingeführte Materialien gemessen, in Versuchen getestet und mit herkömmlichen Materialien verglichen werden. Bei innovativen Materialien wie VITA ENAMIC handelt es sich um

völlig neue CAD/CAM-Restaurationsmaterialien, über die noch sehr wenige klinische Daten vorliegen. Aufgrund ihrer spezifischen Werkstoffeigenschaften werden sie mit Interesse verfolgt. Bei Hybridkeramiken wird versucht, die Vorteile von Kunststoff und Keramik zu vereinen. Auch eine Individualisierung unter Anwendung von lichthärtenden Kompositmaterialien ist möglich. Dadurch entsteht die Indikation, diese Materialien weiter zu untersuchen und mit herkömmlichen Produkten zu vergleichen, um die optimale Indikationen und Verarbeitungsmechanismen zu identifizieren.

Oberflächenenergie, besonders die Zusammenwirkung von Oberflächen und Flüssigkeiten, ist signifikant für Dentalmaterialien. Wenn ein adhäsiver Verbund angestrebt wird, sind hohe Oberflächenenergie-Werte günstig. Andere Studien zum Thema freie Oberflächenenergie von Dentalkeramiken wurden nicht identifiziert. Dies bietet ein hohes Potential für weitergehende Forschung auf diesem Gebiet. Wie es aus dieser Studie abzulesen ist, bedeutet eine höhere Rauigkeit nicht unbedingt eine höhere Oberflächenenergie. Welche Relevanz dies für die klinische Anwendung von geätzten Keramiken hat, sollten weitere Untersuchungen klären. Dies gilt insbesondere in Bezug auf den Einfluss der Ätzzeitdauer auf die Qualität des adhäsiven Verbundes.

Die Versuche zu dieser In-vitro-Studie wurden im Labor unter ständiger Aufsicht durchgeführt. Die Form, Dimensionen und Zusammensetzung von Dentalrestaurationen sind allerdings ebenso relevante Parameter für den Langzeiterfolg einer prothetischen Versorgung. Um die klinische Relevanz aussagekräftiger zu machen, sollten weitere Untersuchungen zur Oberflächenrauigkeit und Oberflächenenergie unter Bedingungen, die das natürliche Milieu der Mundhöhle simulieren, durchgeführt werden. Nicht nur spezifische Eigenschaften wie Körpertemperatur, Feuchtigkeit und

Speichelzusammensetzung, sondern auch mechanische Aspekte wie zyklische Belastung und Kaukraft müssen beachtet werden. Es wäre interessant, in weiteren Studien zu untersuchen, welchen Einfluss die Ätzzeitdauer bei Bruchlast- und Scherversuchen mit Keramikrestaurationen zeigt.

Zusammenfassend und mit Blick auf die Zukunft kann festgestellt werden, dass die gewonnenen Ergebnisse dieser Studie Potential für weitere akademische Forschung zum Thema Ätzzeitdauer und Oberflächeneigenschaften von Glaskeramiken bieten. Dies gilt insbesondere im Hinblick auf die klinische Relevanz neuer Materialien und auf den Mangel an Studien zum Thema freie Oberflächenenergie von Dentalkeramiken.

Danksagung

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