

BONDING TO CAD-CAM COMPOSITES: AN INTERFACIAL FRACTURE TOUGHNESS APPROACH

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Abstract

The objective of this study was to evaluate the interfacial fracture toughness (IFT) of composite cement with dispersed filler (DF) versus polymer-infiltrated ceramic network (PICN) computer-aided design and computer-aided manufacturing (CAD-CAM) composite blocks after 2 different surface pretreatments using the notchless triangular prism (NTP) test. Two DFs (Cerasmart [CRT] and Lava Ultimate [LVA]), 2 PICNs (Enamic [ENA] and experimental PICN [EXP]), and e.max CAD lithium disilicate glass-ceramic (EMX, control) prism samples were bonded to their counterparts with Variolink Esthetic DC composite cement after either hydrofluoric acid etching (HF) or gritblasting (GR). Both procedures were followed by silanization. All samples ($n = 30$ per group) were thermocycled (10,000 cycles) and tested for their IFT in a water bath at 36°C. Moreover, representative samples from each group were subjected to a developed interfacial area ratio (Sdr) measurement by profilometry and scanning electron microscopy (SEM) characterization. EXP-HF gave the highest IFT ($1.85 \pm 0.39 \text{ MPa}\cdot\text{m}^{1/2}$), followed by EMX-HF and ENA-HF, while CRT-HF gave the lowest ($0.15 \pm 0.22 \text{ MPa}\cdot\text{m}^{1/2}$). PICNs gave significantly better results with HF, and DF showed better results with GR. A 2-way analysis of variance indicated that there were significantly higher IFT and Sdr for PICNs than for DF. A positive correlation ($r^2 = 0.872$) was found between IFT and Sdr. SEM characterization showed the specific microstructure of the surface of etched PICNs, indicating the presence of a retentive polymerbased honeycomb structure. Etching of the typical double-network microstructure of PICNs causes an important increase in the Sdr and IFT, while DF should be gritblasted. DF exhibited significantly lower Sdr and IFT values than PICNs. The present results show the important influence of the material class and surface texture, and consequently the micromechanical bond, on the adhesive interface performance of CAD-CAM composites.

Keywords:

Dental materials, dental prosthesis retention, resin cement, surface properties, ceramics, dental adhesives

Introduction

Computer-aided design and computer-aided manufacturing (CAD-CAM) composites are gaining popularity in the field of restorative materials, competing with glass-ceramics for single-unit restorations. These composites are notable for their better machinability, higher resilience, and lower elastic modulus, hardness, and brittleness (Albero et al. 2015; Coldea et al. 2015). Specifically, their ability to be milled to a very low thickness offers interesting perspectives for use as minimally invasive bonded restorations, such as so-called occlusal tabletops. However, there is still a lack of data regarding their bonding properties compared with the better known glass-ceramic materials (Spitznagel et al. 2014); in particular, the effect of the CAD-CAM composite microstructure on its performance is unknown. Indeed, the CAD-CAM composite blocks can be divided into 2 distinct classes based on their microstructure: dispersed filler (DF) and polymer-infiltrated ceramic network (PICN) materials (Coldea et al. 2013; Mainjot et al. 2016). In DF materials, the fillers are classically incorporated by mixing them in a matrix composed of dimethacrylates, such as urethane dimethacrylate (UDMA) and triethylene glycol dimethacrylate (TEGDMA), which are polymerized under high temperature ($>100^{\circ}\text{C}$). The available products contain varying amounts, sizes, and compositions of filler, according to technical data released by the respective manufacturers. On the other hand, PICNs are composed of a sintered glassceramic block (75% of the solid volume) secondarily infiltrated with UDMA and TEGDMA, which are polymerized under high temperature and high pressure (HT-HP) (180°C , 300 MPa) (Nguyen et al. 2014). The specific polymerization mode of CAD-CAM composite blocks, particularly the patented HT-HP polymerization mode (Sadoun 2011), which has been shown to increase the degree of conversion up to 96% (Phan et al. 2015), may decrease the chemical co-polymerization of any remaining free monomers of the CAD-CAM block with the monomers of the composite cement. In general, manufacturers recommend the same bonding protocol for CAD-CAM composite blocks as for indirect composite filling materials (i.e., the use of alumina air-abrasion or tribochemical silicacoating procedures to roughen the material surface), followed by the application of a silane layer (Spitznagel et al. 2014). For Vita Enamic (ENA; Vita Zahnfabrik), the only PICN on the market, hydrofluoric acid (HF) etching can be used as an alternative to gritblasting (GR), which has also been proposed for Cerasmart (GC), a DF material.

Several previous studies of the bonding properties of composite cement to CAD-CAM composite blocks evaluated the microtensile bond strength (μTBS) or (micro)shear bond strength according to the type of pretreatment, composite cement, or material (Elsaka 2014; Frankenberger et al. 2015; Campos et al. 2016; Cekic-Nagas et al. 2016; Peumans et al. 2016; Schwenter et al. 2016; Lise et al. 2017). However, despite the popularity of the μTBS and its reliability compared with shear bond testing, its use results in inaccuracies in bond strength evaluation, mainly due to the sample preparation after bonding, which leads to an increased number of pretest failures and problems related to nonuniform stress distribution (Scherrer et al. 2010; Van Meerbeek et al. 2010). Therefore,

some authors have recently recommended the introduction of alternative and more reliable methods for evaluating adhesive interfaces, particularly fracture mechanics, which allows the measurement of the interfacial fracture toughness (IFT) (K_{IC}) of the adhesive layer (Armstrong et al. 2010; Scherrer et al. 2010; Soderholm 2010; Van Meerbeek et al. 2010; De Munck et al. 2013; Pongprueksa et al. 2016). The goal is to stably initiate and propagate a crack through the bonded interface and to measure the crack-propagation resistance or peeling resistance from the substrate (Scherrer et al. 2010). The IFT is advantageous because it evaluates the interface properties rather than the mechanical strength of the whole assembly (Pongprueksa et al. 2016). Various types of tests have already been used with dental materials, including the single-edge notched beam (Toparli and Aksoy 1998) and the chevron notch short rod or beam test (Armstrong et al. 1998), which has been modified into various versions adapted to dental samples (Ruse et al. 1996; De Munck et al. 2013; Pongprueksa et al. 2016). One variation is the notchless triangular prism (NTP) test introduced by Ruse et al. (1996), which was reported to be a simple method (Soderholm 2010). This method was previously proposed to evaluate both the fracture toughness of materials and the fracture toughness of bonded interfaces (Ruse et al. 1996; Far and Ruse 2003). The authors validated the stress distribution by a finite element analysis, showing that the maximum tensile stress was concentrated at the tip of the crack (Ruse et al. 1996). A significant advantage of the NTP test is the good level of control and stable crack growth at a low cross-speed (0.05 mm/min), which allows for reliable measurements and the possibility of performing a fatigue process study, controlling crack propagation for a given K_I . Moreover, the NTP test avoids bias related to the creation of a notch, which is particularly challenging due to the low interface thickness.

The objectives of this study were to use the NTP test to evaluate the IFT at mouth temperature of composite cement with 2 classes of CAD-CAM composite blocks, DF and PICN, after 2 different surface pretreatments and upon thermocycling aging.

Materials and Methods

SAMPLES PREPARATION (APPENDIX FIG. 1)

Prism Manufacturing. Two DF composite materials, Lava Ultimate (LVA; 3M ESPE) and Cerasmart (CRT; GC), and 2 PICN materials, ENA and an experimental PICN (EXP; MaJEB), were tested. EXP was composed of 73.8vol.% slip-casted and sintered Vita Mark II glass-ceramic powder (Vita Zahnfabrik, 2.6- μ m D50 grain-size distribution), which was infiltrated by HT-HP (180°C, 300 MPa), UDMA (Esstech), and di-tert-amyl peroxide (Sigma-Aldrich) (initiator), following the procedure described by Nguyen et al. (2014). In addition, a lithium disilicate-reinforced glass-ceramic, IPS e.max CAD (EMX; Ivoclar Vivadent), was used as a positive control.

CAD-CAM blocks were cut using a low-speed saw (IsoMet; Buehler) under continuous water irrigation at an angle of 60° to produce 4 samples per block. The samples ($n = 60$ per material) were then ground into the desired 14.0 ± 0.1 -mm-long triangular prisms with a 6.0 ± 0.1 -mm side width using 220grit silicon carbide (SiC) paper, at 300 rpm under water cooling (Struers) using a custom-built specimen holder. EMX samples were manufactured in the crystalline intermediary stage and then fired in a dedicated furnace (Programat; Ivoclar Vivadent) at 820°C for 10 min (90°C/min),

followed by 840°C for 7 min (30°C/min), according to the manufacturer's recommendations. All prisms were then split into 2 with the NTP test (Ruse et al. 1996) to produce half prisms and to measure material fracture toughness for future research.

Surface Pretreatment. The bonding surfaces were polished with 1,000-grit SiC paper under water cooling to obtain 6.0 ± 0.1 -mm-long prisms. Samples were ultrasonically cleaned in 90% ethanol for 3 min (Vita Sonic II; Vita Zahnfabrik), dried with oil-free air for 10 s, and then randomly distributed to either the HF or GR pretreatment group ($n = 30$ per material in each group). For the HF group, 5% hydrofluoric acid (Vita ceramics etch; Vita Zahnfabrik) was applied and left for 60 s,

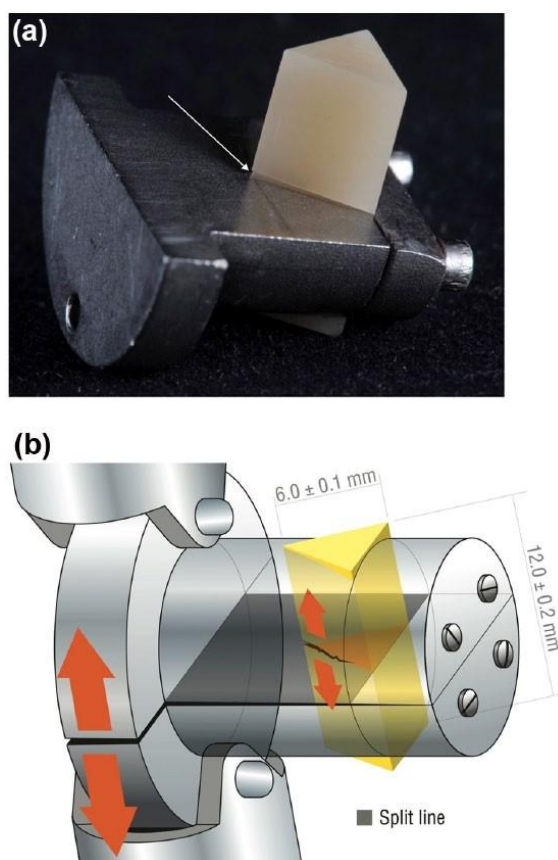


Figure 1. Notchless Triangular Prism (NTP) test. (a) A bonded prism fixed to 1 half of the cylindrical mounting block, with an arrow pointing at the crack initiation point. (b) A schematic illustration of the NTP apparatus in motion, with a bonded prism fixed within. The arrows pointing in opposite directions indicate the application of tensile force on the bonded interface, marked by the split line, with crack propagation starting from the tip of the prism at the crack initiation point until fracture or crack arrest.

and then the samples were washed under running water for another 60 s and air dried, as recommended by the manufacturers of ENA and CRT. The samples were then additionally cleaned ultrasonically in ethanol for 3 min and air dried for 10 s. A silane layer (Monobond Plus; Ivoclar Vivadent) was applied using a microbrush and left for 60 s, and then samples were air dried for 10 s. The positive control (EMX) was treated following the same procedure as the other samples except that the etching was performed with 4.5% hydrofluoric acid (IPS Ceramic; Ivoclar Vivadent) for 20 s, as specified in the manufacturer's recommendations. For the GR group, gritblasting was performed using 50- μ m Al_2O_3 particles (Danville) for 5 s in a perpendicular direction at a distance 1 cm from the sample (Basic Professional 2942; Renfert). The pressure varied according to the manufacturers'

instructions for each material: ENA and EXP were subjected to a 1-bar gritblasting pressure, while 1.5 bars and 2 bars were used for CRT and LVA, respectively. Then, ultrasonic cleaning and silanization were performed in the same way as in the HF group.

Bonding Procedure. Half prisms were bonded to their counterparts using a custom-designed alignment system into which they were fixed (Appendix Fig. 2). A dual-cure composite cement (Variolink Esthetic DC, neutral shade; Ivoclar Vivadent) was applied on each surface with the mixing syringe, and half prisms were put into contact. Three 20-s light applications (Bluephase 20i; Ivoclar Vivadent) were performed at high power ($1,200 \text{ mW/cm}^2$) at close proximity to each side of the alignment apparatus. An extra 40 s of curing was applied at a distance of 2 mm on each side after removal from the alignment apparatus to ensure optimal curing. The samples were left in water for 24 h at 36°C , and then the excess composite cement was removed by polishing the prisms with 1,000-grit SiC paper under water cooling.

Aging. Samples were submitted to thermocycling for 10,000 cycles (5/ 55°C , 30 s in each bath) (Armstrong et al. 2017).

IFT MEASUREMENT WITH THE NTP TEST

The IFT was measured using the NTP test (Fig. 1), following the procedure described by Ruse et al. (1996). Samples ($n = 30$ per group) were fixed into 1 half of the NTP specimen holder, and a crack initiation point ($\sim 0.1 \text{ mm}$) was made at the bond interface under a light microscope (Light Highlight 3001; Olympus) at a magnification of $\times 20$ using a sharp scalpel (size 11 surgical blade; Swann-Morton). After securing the other half of the specimens, the samples were mounted on the computer-controlled (Bluehill; Instron Canada) universal testing machine (Instron model 5565) within a water bath at 36°C , at a cross-head speed of 0.05 mm/min . The strain values were recorded at failure arrest in a tensile mode, and the IFT was calculated using the formula $K_{IC} = P_{\max} / DW^{1/2}$, where $P_{\max}$ is the maximum load at failure, D is the NTP specimen diameter (12.0 mm), W is the NTP specimen length (10.5 mm), and $Y_{\min}$ is the dimensionless stress intensity factor coefficient minimum (28) as given by Ruse et al. (1996).

Each sample was examined under a light microscope following each test to identify the failure mode as adhesive, mixed, or cohesive, as described by Scherrer et al. (2010) and illustrated in Appendix Figure 3.

SURFACE CHARACTERIZATION

Three rectangular samples (dimensions $14.0 \times 12.0 \times 2.0 \text{ mm}^3$) of each material investigated were manufactured by cutting the CAD-CAM blocks using a low-speed IsoMet saw and were polished with 1,000-grit SiC paper. Two of the samples were etched and gritblasted following the previously described procedures. The third sample was used as a control.

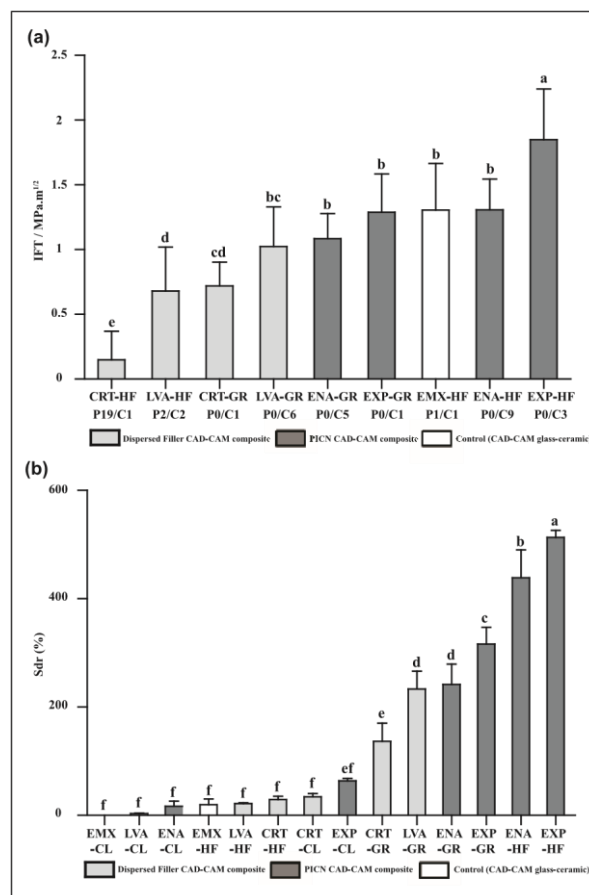


Figure 2. Results of interfacial fracture toughness (IFT) and developed interfacial area ratio (Sdr) measurements. (a) A bar graph of the IFT measurement. The letters P and C under the columns represent pretest failures (P) and cohesive failures (C) among the initial number of tested samples in each group of materials. The (C) samples were not included in the IFT calculation. (b) A bar graph of the Sdr measurement. The results are expressed as the means $\pm$ SD. Superscript letters indicate statistically homogeneous subgroups within a material category (1-way analysis of variance followed by Scheffé test, $\alpha = 0.05$). The same superscript letters demonstrate that there were no significant differences for each factor. CRT-CL, Cerasmart control; CRT-GR, gritblasted Cerasmart; CRT-HF, etched Cerasmart; EMX-CL, IPS e.max CAD control; EMX-HF, etched IPS e.max CAD; ENA-CL, Enamic control; ENA-GR, gritblasted Enamic; ENA-HF, etched Enamic; EXP-CL, experimental polymer-infiltrated ceramic network (PICN) control; EXPGR, gritblasted experimental PICN; EXP-HF, etched experimental PICN; LVA-CL, Lava Ultimate control; LVA-GR, gritblasted Lava Ultimate; LVA-HF, etched Lava Ultimate.

Profilometry. Profilometry was carried out on samples to measure the developed interfacial area ratio (Sdr), which is expressed as the percentage of additional surface area contributed by the texture compared to an ideal plane the size of the measurement region. The Sdr is obtained by calculating the topographical area with respect to this ideal plane and gives the surface enlargement induced by the different pretreatments. Measurements were performed using a 3-dimensional optical microscope (ContourGTi; Bruker) in high-resolution vertical scanning interferometry (VXI) mode at <1 nm, independent of the objective. Five measurements were taken at the center of each sample with a $\times 115$ objective (image size: 0.06×0.04 mm²; optical lateral resolution: 0.33 μ m) with no filtering and removal of the tilt and cylinder terms. The values of the Sdr were obtained by calculating the mean of 5 values measured for each sample.

Scanning Electron Microscopy. The samples were cleaned ultrasonically in 90% ethanol for 3 min and subsequently gold-coated to be analyzed by scanning electron microscopy (SEM) (S-3000N; Hitachi).

STATISTICAL ANALYSIS

The results were analyzed by 1- and 2-way analysis of variance (ANOVA), followed, if warranted, by Scheffé's multiple mean comparisons ($\alpha = 0.05$), using PASW Statistics 18 (SPSS, Inc.). Pearson's tests were used to verify the presence of statistically significant correlations between the IFT and Sdr ($\alpha = 0.05$).

Results

IFT

The means and standard deviations of the IFT measurements for each group of samples, along with the statistical analysis, are provided in Figure 2a and Tables 1 and 2. Some samples experienced debonding prior to IFT testing. The samples showing pretest failures were included as zero values, while samples that fractured in a cohesive mode were excluded from the data analysis. The numbers of pretest and cohesive failures for each group of samples are provided in detail in Figure 2a. EXP-HF had a significantly higher IFT than other samples ($1.85 \pm 0.39 \text{ MPa} \cdot \text{m}^{1/2}$), followed by EMX-HF and ENA-HF, while CRT-HF had the lowest value ($0.15 \pm 0.22 \text{ MPa} \cdot \text{m}^{1/2}$). A 2-way ANOVA revealed that there was a significantly higher IFT for PICNs than for DF, and this finding was independent of the surface pretreatment performed ($P < 0.05$) (Appendix Table). PICNs gave significantly higher results with HF and DF with GR.

DEVELOPED INTERFACIAL AREA RATIO (SDR)

The mean and standard deviations of the Sdr measurements for each group of samples, along with the results of the statistical analysis, are summarized in Figure 2b and Tables 1 and 2. EXP-HF had a significantly higher Sdr than the other groups ($513.0\% \pm 13.1\%$), followed by ENA-HF and EXP-GR, while EMX-CL had the lowest value ($0.2\% \pm 0.1\%$). A 2-way ANOVA revealed that there was a significantly higher Sdr for PICNs than for DF, independent of the surface pretreatment performed ($P < 0.05$) (Appendix Table). PICNs gave significantly higher results with HF and DF with GR.

CORRELATION BETWEEN THE IFT AND SDR

The statistical analysis using Pearson's correlation coefficient revealed that there was a strong ($r^2 = 0.8723$) and significant ($P < 0.05$) correlation between the IFT and Sdr for all groups of CAD-CAM composite blocks. This positive correlation suggests that, under the conditions of this study, over 87% of the variation in the IFT was explained by the Sdr (Appendix Fig. 4). When EMX was included, the correlation was weaker ($r^2 = 0.5697$).

Table 1. Representative Means and Standard Deviations of the Interfacial Fracture Toughness (IFT).

	IFT, MPa·m ^{1/2}	Failure Mode, n				Sdr, %
		Pretest	Adhesive	Mixed	Cohesive	
EMX-CL						0.20 ± 0.10 ^f
EMX-HF	1.31 ± 0.36 ^b	1	26	2	1	19.60 ± 10.80 ^f
CRT-CL						34.30 ± 5.80 ^f
CRT-GR	0.72 ± 0.18 ^{c,d}	0	27	2	1	136.60 ± 33.6 ^e
CRT-HF	0.15 ± 0.22 ^e	19	10	0	1	29.40 ± 5.90 ^f
LVA-CL						3.50 ± 0.60 ^f
LVA-GR	1.02 ± 0.31 ^{b,c}	0	18	6	6	233.10 ± 33.00 ^d
LVA-HF	0.68 ± 0.34 ^d	2	26	0	2	21.70 ± 1.70 ^f
ENA-CL						16.70 ± 9.40 ^f
ENA-GR	1.08 ± 0.19 ^b	0	15	10	5	241.70 ± 37.60 ^d
ENA-HF	1.31 ± 0.24 ^b	0	14	7	9	438.90 ± 51.20 ^b
EXP-CL						63.60 ± 4.50 ^{e,f}
EXP-GR	1.19 ± 0.30 ^b	0	28	1	1	316.20 ± 31.00 ^c
EXP-HF	1.85 ± 0.39 ^a	0	25	2	3	513.00 ± 13.10 ^a

Values are expressed as the MPa·m^{1/2} ± SD, with the number of samples that failed before the test and in an adhesive, mixed, and cohesive mode, respectively (the samples showing pretest failures were included as zero values, while samples that fractured in a cohesive mode were excluded from the data analysis). Also shown are the means and standard deviations of the Sdr (developed interfacial area ratio), expressed as a percentage. Superscript letters indicate statistically homogeneous subgroups within a material category (1-way analysis of variance followed by Scheffé test, $\alpha = 0.05$). The same superscript letters demonstrate that there were no significant differences for each group. CRT-CL, Cerasmart control; CRT-GR, gritblasted Cerasmart; CRT-HF, etched Cerasmart; EMX-CL, IPS e.max CAD control; EMX-HF, etched IPS e.max CAD; ENA-CL, Enamic control; ENA-GR, gritblasted Enamic; ENA-HF, etched Enamic; EXP-CL, experimental polymer-infiltrated ceramic network (PICN) control; EXP-GR, gritblasted experimental PICN; EXP-HF, etched experimental PICN; LVA-CL, Lava Ultimate control; LVA-GR, gritblasted Lava Ultimate; LVA-HF, etched Lava Ultimate.

Table 2. Results of a 1-Way Analysis of Variance for the IFT and Sdr.

	Sum of Squares	Degrees of Freedom	Mean Squares	F Statistic	Significance
IFT					
Between groups	52.678	8	7	77.799	a
Within groups	19.636	232	0.085		
Total	72.314	240			
Sdr					
Between groups	1,944,352.102	13	149,565.392	272.377	a
Within groups	30,750.278	56	549.112		
Total	1,975,100.380	69			

IFT, interfacial fracture toughness; Sdr, developed interfacial area ratio.
^aA significant difference was detected ($P < 0.05$).

SEM

SEM characterization showed the specific microstructure of the surface of etched PICNs, characterized by dissolution of the glass-ceramic network and the presence of a typical polymer-based honeycomb structure, including micro- and nanoporosities. HF had the highest impact on the EXP, with a higher glass-ceramic phase dissolution. For ENA, the impact was slightly lower; the glass-ceramic network was not totally dissolved and the microporosities were larger. With LVA, etching resulted in the partial dissolution of the filler particles and in a significantly smoother surface than PICNs. HF created very minor porosities on the surface of CRT, which appeared to have the smoothest surface among the etched composites. Finally, EMX showed a slight dissolution of glass, with a smoother surface than PICNs. GR created roughness on the surface of all samples, with PICNs showing a finer roughness than DF. CRT showed more roughness when gritblasted than when etched. Finally, gritblasting PICN did not result in the creation of a honeycomb structure, as did etching (Fig. 3).

Discussion

The NTP test was successfully used to evaluate adhesive interfaces, yet the alignment system for half-prism bonding could be improved to accurately control the cement thickness. In the present study, samples were tested in a water bath set at 36°C to eliminate any bias resulting from

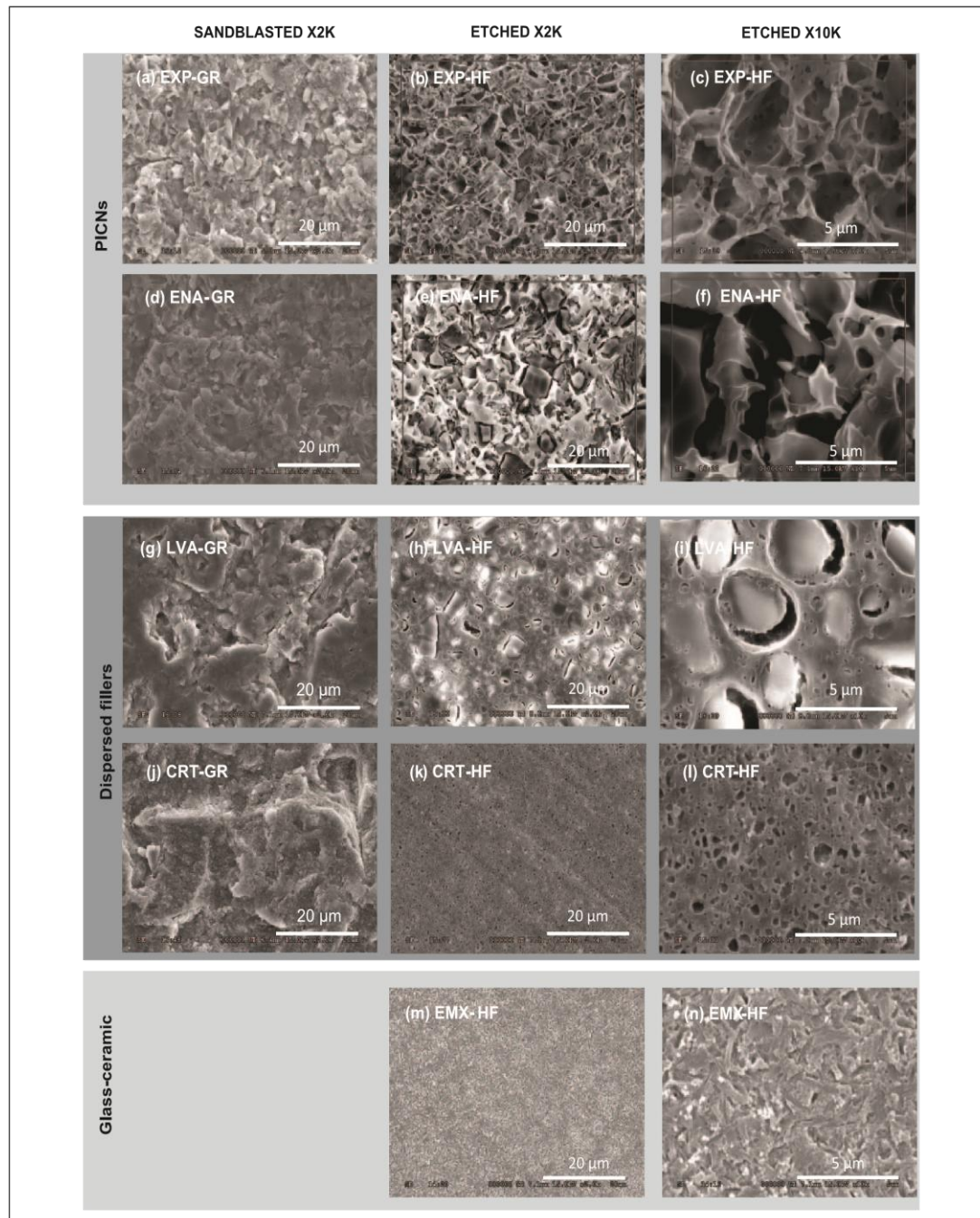


Figure 3. Scanning electron microscopy images of the samples following different surface pretreatments: (a) gritblasted experimental polymerinfiltrated ceramic network (PICN) at $\times 2,000$ magnification (EXP-GR); (b) etched experimental PICN at $\times 2,000$ magnification (EXP-HF); (c) etched experimental PICN at $\times 10,000$ magnification (EXP-HF); (d) gritblasted Enamic at $\times 2,000$ magnification (ENA-GR); (e) etched Enamic at $\times 2,000$ magnification (ENA-HF); (f) etched Enamic at $\times 10,000$ magnification (ENA-HF); (g) gritblasted Lava Ultimate at $\times 2,000$ magnification (LVA-GR); (h) etched Lava Ultimate at $\times 2,000$ magnification (LVA-HF); (i) etched Lava Ultimate at $\times 10,000$ magnification (LVA-HF); (j) gritblasted Cerasmart at $\times 2,000$ magnification (CRT-GR); (k) etched Cerasmart at $\times 2,000$ magnification (CRT-HF); (l) etched Cerasmart at $\times 10,000$ magnification (CRT-HF); (m) etched IPS e.max CAD at $\times 2,000$ magnification (EMX-HF); and (n) etched IPS e.max CAD at $\times 10,000$ magnification (EMX-HF).

differences in temperature (Soderholm 2010) and to provide a close approximation of the conditions in the mouth. Cohesive failures can be explained by the fact that the IFT is close to or higher than the reported fracture toughness of the different CAD-CAM materials (LVA, $0.91 \text{ MPa} \cdot \text{m}^{1/2}$; ENA, $0.88 \text{ MPa} \cdot \text{m}^{1/2}$; EXP, $2.7 \text{ MPa} \cdot \text{m}^{1/2}$; EMX, $1.79 \text{ MPa} \cdot \text{m}^{1/2}$) (Nguyen et al. 2014; Ruse and Sadoun 2014).

Our results indicated that the material class (DF vs. PICN) and its interaction with different surface pretreatment (HF or GR) influence both IFT and Sdr. PICNs showed significantly higher IFT values than DF. In previous studies, etched Enamic gave better results than Lava, regardless of the type of pretreatment (Elsaka 2014; Frankenberger et al. 2015; Cekic-Nagas et al. 2016), while Cerasmart had poorer results when etched (Cekic-Nagas et al. 2016) but similar results when gritblasted, contrary to the present findings (Lise et al. 2017). The difference observed between the 2 classes of materials can be attributed to the surface texture after pretreatment, as shown by the correlation found between the IFT and Sdr, which corresponds to the additional surface area created by acid etching or gritblasting. Indeed, the effectiveness of bonding was suggested to be related to 2 important parameters, the micromechanical bond or interlocking, which is promoted by an increased material surface roughness, and the chemical bond between the composite cement and the specific material, which is promoted by a silane application (Tian et al. 2014). Increasing the surface roughness was previously reported to be more important than chemical conditioning to improve the bonding properties of most indirect composite filling materials (Spitznagel et al. 2014). For those materials, which are all DF, gritblasting was shown to be more effective than etching (Spitznagel et al. 2014), as was shown for DF CAD-CAM composites in the present study. In contrast, for PICNs, etching gave significantly better results than gritblasting, with other studies using μTBS showing also better results with HF (Elsaka 2014; Frankenberger et al. 2015). The influence of micromechanical interlocking on the performance of the adhesive interface of CAD-CAM composites is particularly important, since a high degree of conversion of polymers decreases the potential for chemical co-polymerization of any remaining free monomers with the monomers of the composite cement. This micromechanical interlocking is also influenced by roughness induced by milling, which varies with bur grit size (Lebon et al. 2015).

The significantly higher Sdr and subsequent micromechanical bonding potential of PICNs compared to DF are related to their specific microstructure when etched. As seen in SEM images, surface etching results in the creation of a honeycomb polymerbased structure. The presence of micro- and even nanoporosities for EXP increases the surface texture and consequently promotes interlocking with the composite cement. EXP-HF had a significantly higher IFT than all of the other materials. Indeed, the Sdr of EXP-HF, which was even underestimated due to the lateral resolution of the profilometer (approximately $0.5 \mu\text{m}$), was significantly higher than that of other groups, including ENA-HF, which can be explained by the smaller glass-ceramic grain size of experimental PICN compared to Enamic.

In line with the study by Frankenberger et al. (2015), ENA-HF showed findings similar to those of etched lithiumdisilicate glass-ceramic (EMX-HF), which was used as a positive control due to its good bonding properties (Tian et al. 2014). Moreover, in the present study, EXP-HF gave significantly better results than EMX-HF. Of note, the Sdr values for EMX-HF were low in comparison with PICNs: the absence of a correlation with the IFT suggests that there may be differences in the bonding mechanisms between glass-ceramics and composite materials. While micromechanical interlocking

seems to be fundamental for composites (Spitznagel et al. 2014), the chemical bond seems to be more important for glass-ceramics, as mentioned by Tian et al. (2014) in a recent review.

In the present work, CRT gave the lowest IFT values, and SEM characterization showed the lack of effectiveness of HF on CRT, although the manufacturer recommends this procedure as an alternative to gritblasting.

Conclusion

There is a growing variety of CAD-CAM composite blocks on the market, and recent breakthroughs have led to confusion about their specific properties. Among these properties, the microstructure is a critical factor, which has an important influence on the bonding properties of CAD-CAM composites. Indeed, PICNs, with their typical double-network microstructure resulting in a honeycomb polymer-based structure when etched, were shown to exhibit significantly better IFT values than CAD-CAM composites with dispersed fillers. The correlation found between the IFT and CAD-CAM composite surface enlargement after pretreatment shows the importance of the micromechanical bond on adhesive interface performance. In that view, the present results suggest that PICNs should be etched while DF should be sandblasted. The good results of PICNs compared to a gold standard such as lithium-disilicate glass-ceramic will need to be confirmed by further research, particularly via in vitro fatigue tests of the interface and clinical studies in the framework of partial bonded restorations.

AUTHOR CONTRIBUTIONS

M. Eldafrawy, contributed to design, data acquisition, analysis, and interpretation, drafted and critically revised the manuscript; M.G. Ebroin, P.A. Gailly, contributed to acquisition and analysis, critically revised the manuscript; J.-F. Nguyen, contributed to data analysis and interpretation, drafted the manuscript; M.J. Sadoun, contributed to conception, design, data analysis, and interpretation, critically revised the manuscript; A.K. Mainjot, contributed to conception, design, data analysis, and interpretation, drafted and critically revised the manuscript. All authors gave final approval and agree to be accountable for all aspects of the work.

ACKNOWLEDGMENTS

We express our thanks to Ivoclar Vivadent (Schaan, Liechtenstein) for providing the Variolink Esthetic DC composite cement. M.J. Sadoun has a patent: Composite ceramic block. US patent 8,507,578 B2. The authors received no financial support and declare no other potential conflicts of interest with respect to the authorship and/or publication of this article.

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