

A FUNCTIONALLY GRADED PICN MATERIAL FOR BIOMIMETIC CAD-CAM BLOCKS

M. Eldafrawy¹, J.F. Nguyen^{2,3}, A.K. Mainjot^{1,4,*}, and M.J. Sadoun⁵

¹Dental Biomaterials Research Unit (d-BRU), Institute of Dentistry, University of Liège (ULiège), Liège, Belgium

²UFR d'Odontologie, Université Paris Diderot, Paris, France

³PSL Research University, Chimie ParisTech-CNRS, Institut de Recherche de Chimie Paris, Paris, France

⁴Department of Fixed Prosthodontics, Institute of Dentistry, University of Liège Hospital (CHU), Liège, Belgium

⁵MaJEB sprl, Liège, Belgium

*Corresponding Author: A.K. Mainjot, Email: a.mainjot@chuliege.be

A supplemental appendix to this article is available online.

Abstract

The objective of this study was to introduce a functionally graded (FG) polymer-infiltrated ceramic network (PICN) block, characterized by a gradient of mechanical properties, as a biomimetic material for computer-aided design and manufacturing (CAD-CAM) prostheses. FG-PICN blocks were manufactured from a slurry of glass-ceramic powder, which was subsequently centrifuged and sintered. The ceramic network was infiltrated with urethane dimethacrylate and polymerized under high temperature-pressure. Blocks were sectioned into 9 layers, and each layer was subsequently cut into 3 samples. Samples were loaded into a 3-point bending device and tested for flexural strength, flexural load energy, and flexural modulus. The volume percentage of glass-ceramic, hardness, and brittleness index were also measured and scanning electron microscopy (SEM) observations were performed. Katana translucent zirconia (HT-ZIR) and e.max-CAD (EMX) were tested for comparison. Flexural strength, flexural load energy, and Weibull modulus of FG-PICN were shown to increase from the first (enamel-like zone) to the ninth layer (dentin-like zone), while, on the contrary, flexural modulus, hardness, brittleness index, and ceramic volume percentage decreased. SEM characterization highlighted a higher porosity in layer 9 than in layer 1. Flexural strength of the dentin-like zone (372.7 ± 27.8 MPa) was similar to EMX and lower than HT-ZIR. Flexural modulus was shown to vary from 41.9 ± 5.1 to 28.6 ± 2.0 GPa from surface to depth. Flexural load energy in the dentin-like zone (27.1 ± 4.9 mJ) was significantly superior to EMX and HT-ZIR. Hardness gradient was shown to be close to tooth tissues. This work introduces FG-PICN blocks, with a gradient of mechanical and optical properties through the entire thickness of the block designed to mimic dental tissues. FG-PICN demonstrated a favorable gradient of flexural strength, elastic modulus, and, most of all, flexural load energy and hardness compared to other CAD-CAM materials, which can promote the biomechanical behavior of single-unit restorations on teeth and implants.

Keywords

prosthetic dentistry/prosthodontics, composite materials, bioengineering, ceramics, biomaterial(s), materials science(s)

Introduction

Biomimetics aims to use artificial processes to synthesize materials that are similar in structure to those that are biologically produced by natural processes. Ideally, materials used for dental prostheses should imitate the tissues to be replaced (i.e., enamel and dentin). Like many other biological structures, enamel and dentin are graded materials. The structure of human enamel is nonhomogeneous in composition and microstructure with a decrease in mechanical properties from the surface (cusp tip or incisal edge) toward the dentin-enamel junction (DEJ). The modulus of elasticity (E) and hardness of enamel at the occlusal surface were reported to be ~ 94 GPa and ~ 3.6 GPa (Xu et al. 1998), and in a more recent publication ~ 108 GPa and ~ 5.8 GPa (Elfallah et al. 2015), and decrease to ~ 64 GPa and ~ 3.5 GPa near the DEJ, respectively (Marshall et al. 2001). Those values drop substantially in the less brittle structure of dentin (~ 20 GPa for E and ~ 0.8 GPa for hardness) (Xu et al. 1998; Marshall et al. 2001).

One of the main causes of failure of materials that interface with one another is at the contact between them, particularly if the transition is sharp, as this creates stresses at the interface, which leads to failure (Mahamood et al. 2012; Madfa and Yue 2016). However, the DEJ creates a buffer zone between the enamel and dentin, delivering a gradual decrease in elastic modulus, thus avoiding the creation of subsurface cracks that may lead to fracture of the tooth under long-term masticatory forces (Marshall et al. 2001; Mahamood et al. 2012; Madfa and Yue 2016).

Unfortunately, most dental restorations offer no gradual transition within the tooth restoration assembly. In bilayered prostheses, the E of the restoration is ~ 70 GPa at the ceramic veneer, fused, for example, to a stiff zirconia or metal core with a higher E of ~ 200 GPa, then dropping to 2 to 13 GPa at the composite cement interface, which is bonded to dentin with an E of ~ 20 GPa (Niu et al. 2009; Rahbar and Soboyejo 2011; Madfa and Yue 2016). This mismatch in E leads to stress concentration and promotes crack initiation (Rahbar and Soboyejo 2011; Zhang et al. 2012) and fracture, which constitutes a major clinical complication of all-ceramic restorations (Conrad et al. 2007).

Nowadays, recent advances, especially in computer-aided design and manufacturing (CAD-CAM) processes, have shifted the tendency toward monolithic restorations, either ceramics or composites, with uniform mechanical properties, showing either higher values than enamel (ceramics) or lower than dentin (composites), except for polymer-infiltrated ceramic network (PICN) CAD-CAM composites, which were shown to exhibit intermediary values (Awada and Nathanson 2015; Lawson et al. 2016; Mainjot et al. 2016; Swain et al. 2016). Monolithic ceramics include glass-ceramics and polycrystalline ceramics. IPS e.max CAD (Ivoclar Vivadent) is a popular lithium disilicate-reinforced glass-ceramic, with E and hardness values close to those of enamel (flexural strength ~ 340 to 380 MPa, $E \sim 60$ to 80 GPa, hardness ~ 4.5 to 6.0 GPa) (Stawarczyk et al. 2015; Elsaka and Elnaghy 2016; Lawson et al. 2016; Swain et al. 2016), while 3 mol% yttria-stabilized dental zirconia (3Y-TZP) is a polycrystalline ceramic known for its high strength (flexural strength ~ 900 to $1,500$ MPa, $E \sim 200$ to 210 GPa), hardness (~ 12.9 GPa), and toughness (~ 3.5 to 4.5 MPa.m^{1/2}) due to the phase transformation it can exhibit, but at the same time, its optical properties limit its use as monolithic restorations (Tong et al. 2016; Zhang and Lawn 2018). Second and third generations of zirconia have progressively led to translucency improvement but at the expense of strength and toughness (dropping to ~ 400 to 900 MPa and ~ 2.2 MPa.m^{1/2}, respectively), without affecting E , while hardness was increased (~ 13.1 GPa) (Tong et al. 2016; Zhang and Lawn 2018). CAD-CAM composites are also used as monolithic restorations and can be divided into 2 subclasses according to their microstructure:

dispersed fillers and PICNs (Mainjot et al. 2016). Dispersed fillers are composed of inorganic fillers of different sizes, amounts, and compositions according to each manufacturer; dispersed in a matrix of urethane dimethacrylate (UDMA), either with or without triethylene glycol dimethacrylate (TEGDMA); and polymerized under high temperature (HT). Their E is lower, while their hardness is similar to dentin (~ 8 to 16 GPa and ~ 0.6 to 1 GPa, respectively) (Awada and Nathanson 2015; Lawson et al. 2016). PICNs, on the other hand, are composed of a presintered glass-ceramic scaffold (86 wt.%) infiltrated with urethane dimethacrylate (UDMA), which is secondarily polymerized under high temperature and pressure (HT-HP), offering a high degree of conversion of monomers ($\sim 95\%$). The unique microstructure of PICNs increases the E and hardness to values ranging between those of dentin and enamel (~ 22 to 32 GPa and ~ 1.5 to 2.4 GPa, respectively) (Awada and Nathanson 2015; Lawson et al. 2016; Mainjot et al. 2016; Swain et al. 2016). Flexural strength of commercially available PICNs (Vita Enamic; Vita Zahnfabrik) was shown to be similar to dispersed filler CAD-CAM composites (~ 137 to 248 MPa) (Albero et al. 2015; Awada and Nathanson 2015; Stawarczyk et al. 2015; Lawson et al. 2016; Swain et al. 2016), while some experimental PICNs demonstrated higher values (305 MPa), close to that of lithium- disilicate glass-ceramic (Nguyen et al. 2014). Regarding bonding properties with resin cements, PICNs exhibited high performance when etched with 5% hydrofluoric acid (Eldafrawy et al. 2018).

On the other hand, engineers in materials science have been developing functionally graded materials (FGMs) since the 1980s. These form a class of advanced materials that are characterized by engineered gradients in composition and structure over volume, resulting in corresponding changes in the properties of the material, which are overall unique and different from any of the individual materials that they are formed from (Mahamood et al. 2012; Madfa and Yue 2016). There is a wide range of manufacturing processes and applications for FGMs, including the centrifugal method, which leads to the creation of a gradient from powders of materials with different densities (Mahamood et al. 2012). In the dental field, some researchers have developed experimental FGMs for prosthodontics, but none of them have reproduced the properties of enamel and dentin combined (Madfa and Yue 2016). Zhang and Kim (2009) infiltrated silicate glass on the top and bottom surfaces of 3Y-TZP to produce a glass-zirconia-glass restoration with graded E to improve esthetics, reduce radial cracking at the cementation surface, and promote bond strength (Zhang and Lawn 2018). The graded material showed an increase in E from the surface toward the core from 125 to 240 GPa (Zhang et al. 2010). Dorthe and Zhang (2012) also infiltrated alumina with silicate glass in the same way to manufacture graded glass-alumina-glass, with a resulting E gradient from 110 to 419 GPa. In an attempt to mimic the gradual decrease in E from enamel to dentin via the DEJ, Huang et al. (2007) synthesized an experimental functionally graded layer (FGL) on the micro-scale to offer a smooth transition between the tooth and the restoration, in the same way as the DEJ, and to reduce stresses induced by the E mismatch, as demonstrated by finite element simulation. FGL is a composite material composed of layers with varying amounts of alumina and zirconia to control the E (from ~ 190 GPa to ~ 35 GPa) toward dentin (Huang et al. 2007; Niu et al. 2009; Rahbar and Soboyejo 2011; Du et al. 2013).

The objective of this work is to introduce a functionally graded PICN block characterized by a gradient of mechanical and optical properties throughout the entire thickness, as a biomimetic material for CAD-CAM prostheses.

Materials and methods

Manufacturing of CAD-CAM blocks

Functionally graded PICN (FG-PICN) blocks were produced by preparing a slurry by mixing 2 albite glass-ceramic powders: enamel powder (25 vol.%, 2.6 μm D50 grain size, incisal optical properties) and D2M2 (25 vol.%, 4.5 μm D50 grain size, dentin optical properties) (Vita Zahnfabrik) with deionized water (50 vol.%) for 20 min in a planetary mixer (ARE-250; Thinky). The slurry was then centrifuged at 200 g for 15 min in a 20 mm square-shaped container, dried, and sintered at 860°C for 2 h to form the glass-ceramic porous network. Silanization was done using prehydrolyzed 3-(Trimethoxysilyl) propyl methacrylate (Sigma-Aldrich); then, after drying under vacuum at 130°C for 1 h, infiltration with UDMA (Esstech) monomer with (0.5 wt.%) di-tert-amyl peroxide (Sigma-Aldrich) initiator was done under vacuum. Blocks were polymerized under HT-HP (180°C– 300 MPa) following the procedure described by Nguyen et al. (2014), resulting in FG-PICN blocks with dimensions of $(13.2 \pm 0.1) \text{ mm} \times (14.6 \pm 0.1) \text{ mm} \times (18 \pm 0.1) \text{ mm}$.

Commercial blocks ($n = 4$) of IPS e.max CAD lithium disilicate glass ceramic (EMX) (Ivoclar Vivadent) as well as a disc of high translucent zirconia (HT-ZIR) (Katana Zirconia; Kuraray Noritake) were also used in this study for comparison.

Flexural strength, flexural load energy, and flexural modulus

For each block, 9 layers of $(1.2 \pm 0.1) \text{ mm}$ thickness were cut using a low-speed saw (thickness 0.3 mm) (Isomet; Buehler) under continuous water irrigation starting from the surface (enamel zone) to the bottom (dentin zone) (Fig. 1). The layers were then cut to the desired $(1.2 \pm 0.1) \text{ mm} \times (4.0 \pm 0.1) \text{ mm} \times (18 \pm 0.1) \text{ mm}$ bars ($n = 30$ per layer), then polished with a diamond pad (10 μm) on one side, at 150 rpm under water (Struers).



Figure 1. A functionally graded polymer-infiltrated ceramic network (FG-PICN) block with, on the left part, a schematic illustration of the cutting into 9 layers from the top (enamel zone) to the bottom (dentin zone). The black spaces between the layers represent the 0.3 mm of material lost during cutting (saw thickness). The thickness of each layer is $(1.2 \pm 0.1) \text{ mm}$; measurements refer to the center of each layer (dashed line).

EMX samples ($n = 30$) were manufactured in the crystalline intermediary stage with the same dimensions and were polished with 320-, 600-, and 1,000-grit silicon carbide (SiC) paper, then with the diamond pad. Crystallization firing of EMX was performed 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. HT-ZIR samples ($n = 30$) were prepared with larger dimensions, $(1.6 \pm 0.1) \text{ mm} \times (5.5 \pm 0.1) \text{ mm} \times (22 \pm 0.1) \text{ mm}$, to compensate for shrinkage after sintering, and then were polished carefully on the diamond pad. HT-ZIR samples were sintered following the manufacturer's recommendations by heating at 1,550°C for 2 h (10°C/min) and subsequent cooling at the same rate to room temperature (Zyrcomat furnace; Vita Zahnfabrik).

Bars were tested in a 3-point bending device (15 mm span width), with the polished surface in tension, on a computer-controlled (Bluehill; Instron) universal testing machine (Instron model 4301, with an extensometer) at a cross-head speed of 1 mm/min.

Flexural strength, σ_f , was calculated according to the following formula:

$$\sigma_f = \frac{3FL}{2hc^2},$$

where F is the load at fracture, L the span, h the specimen width, and c the specimen height. The values of h and c were measured immediately prior to testing of each sample using a digital caliper (Mitutoyo).

Flexural load energy, Ur , was calculated according to the following formula:

$$Ur = \frac{F\Delta}{2},$$

where Δ is the maximum deflection.

The flexural modulus (modulus of elasticity), E , was calculated according to the following formula:

$$E = \frac{FL^3}{4hc^3d},$$

where d is the deflection corresponding to load F at a point in the straight-line portion of the trace.

Hardness

The microhardness gradient was measured using the Vickers indenter (Zwick-Rowell) with integrated software (Indentec) on 5 additional FG-PICN blocks with surfaces polished in the same manner, using a 25-N loading and 10-s dwell time. On each block, 3 indentations were made every 0.25 mm following straight lines parallel to the surface (gradient lines, $n = 15$ per gradient line group); starting from the enamel zone to the dentin zone, each indentation was separated from the next by 2 mm to avoid overlap. For HT-ZIR, a representative sample $(12 \pm 0.1) \text{ mm} \times (4 \pm 0.1) \text{ mm} \times (20 \pm 0.1) \text{ mm}$ was used, in which 15 indentations were made using a 10-N load and 10-s dwell time.

Brittleness index

Brittleness index (B) was measured on 2 additional FG-PICN blocks, as described in the Appendix.

Volume percentage glass-ceramic

The volume percentage of ceramic of each layer was measured from all fractured samples by weighing the samples (Mettler Toledo) before and after firing at 900°C for 2 h until all the polymer was burned and calculating the vol.% of glass-ceramic, assuming that the densities of the glass ceramic and UDMA are 2.42 and 1.206, respectively.

Scanning electron microscopy

Samples of the first and the last layers (from the volumetric percentage glass-ceramic experimentation) were gold-coated and examined by scanning electron microscopy (SEM) (S-3000N; Hitachi).

Statistical analysis

The results were analyzed by 1-way analysis of variance (ANOVA), followed, if warranted, by Scheffé's multiple mean comparisons ($\alpha = 0.05$), using PASW Statistics 18 (SPSS, Inc.). Weibull statistical parameters were calculated for the flexural strength of each layer using the Weibull statistics option in Excel (Microsoft).

Results

Results for flexural strength, flexural load energy, flexural modulus, Weibull modulus, brittleness index, and volume percentage of glass-ceramic are presented in the Table, along with the associated statistical analysis. Hardness results are summarized in Figure 2. Flexural strength, flexural load energy, and Weibull modulus were shown to increase from the first (enamel-like zone) to the ninth layer (dentin-like zone), while, on the contrary, flexural modulus, hardness, brittleness index, and volume percentage of glass-ceramic decreased (Figs. 2 and 3, Appendix Fig.).

SEM porous network characterization highlighted a higher porosity in layer 9 than in layer 1 (Fig. 4).

Table. Mechanical Properties and Weibull Modulus of the 9 Layers of the Functionally Graded Polymer-Infiltrated Ceramic Network (FG-PICN) Blocks, HT-ZIR and EMX, and the Brittleness Index and the Glass-Ceramic Vol.% of the 9 Layers of the FG-PICN Blocks.

Layer	Flexural Strength, <i>σ_f</i> (MPa)	Flexural Load Energy, <i>U_r</i> (mJ)	Elastic Modulus, <i>E</i> (GPa)	Weibull Modulus	Brittleness Index, <i>B</i> ($\mu\text{m}^{-1/2}$)	Vol.% Glass-Ceramic
1	175.8 ± 30.8 ^f	2.9 ± 1.3 ^g	41.9 ± 5.1 ^a	6.4	1.8 ± 0.4 ^a	82.4
2	198.8 ± 26.3 ^{ef}	4.2 ± 1.2 ^{fg}	40.0 ± 3.5 ^a	7.8	1.4 ± 0.1 ^b	80.2
3	210.6 ± 25.8 ^{de}	5.1 ± 1.6 ^{efg}	36.8 ± 3.8 ^b	8.9	1.2 ± 0.1 ^{bc}	78.2
4	217.2 ± 22.6 ^{de}	6.0 ± 1.7 ^{ef}	33.9 ± 2.5 ^b	10.7	1.1 ± 0.1 ^{bcd}	77.0
5	231.7 ± 26.5 ^d	7.3 ± 1.7 ^{de}	30.9 ± 2.1 ^c	9.4	1.0 ± 0.1 ^{cd}	74.7
6	263.3 ± 20.8 ^c	10.1 ± 2.4 ^d	29.8 ± 1.6 ^{cd}	13.2	0.8 ± 0.1 ^{de}	73.5
7	301.0 ± 25.2 ^b	14.0 ± 2.6 ^c	28.8 ± 1.2 ^{cd}	13.1	0.6 ± 0.3 ^{ef}	72.6
8	327.9 ± 34.0 ^b	20.5 ± 4.9 ^b	27.2 ± 2.1 ^d	10.2	0.4 ± 0.4 ^{fg}	72.4
9	372.7 ± 27.8 ^a	27.1 ± 4.9 ^a	28.6 ± 2.0 ^{cd}	14.6	0.1 ± 0.3 ^g	72.4
EMX	369.0 ± 55.6	6.5 ± 2.0	92.5 ± 14.0	7.1		
HT-ZIR	673.77 ± 170.0	12.0 ± 4.9	214.8 ± 19.8	4.1		

EMX, IPS e.max CAD; HT-ZIR, translucent zirconia.

The results are expressed as the means ± SD. Materials with similar letters in each column were not statistically different (1-way analysis of variance followed by Scheffé test, $\alpha = 0.05$).

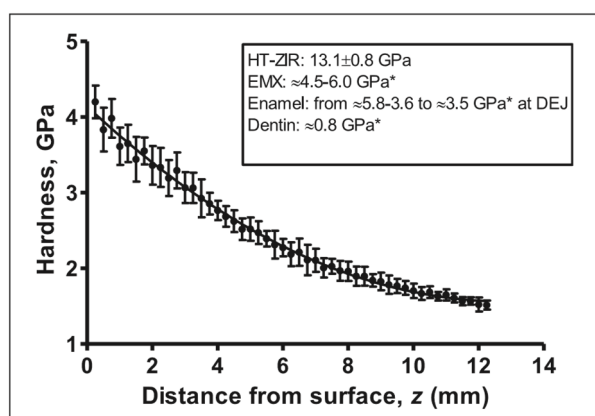


Figure 2. Gradient of Vicker's microhardness in GPa across the functionally graded polymer-infiltrated ceramic network (FG-PICN) blocks. Indentations were done every 0.25 mm following straight lines parallel to the surface, starting from the enamel zone to the dentin zone. For each gradient line, 15 indentations were taken. The results are expressed as the means $\pm$ SD of 15 indentations per gradient line. Hardness value of translucent zirconia (HT-ZIR) is noted separately on the upper right corner of the graph ($n = 15$). Average values of microhardness of IPS e.max CAD (EMX), enamel, and dentin are also presented for comparison. *Data from Xu et al. (1998), Marshall et al. (2001), Elfallah et al. (2015), Elsaka and Elnaghy (2016), Lawson et al. (2016), Swain et al. (2016), and Madfa and Yue (2016).

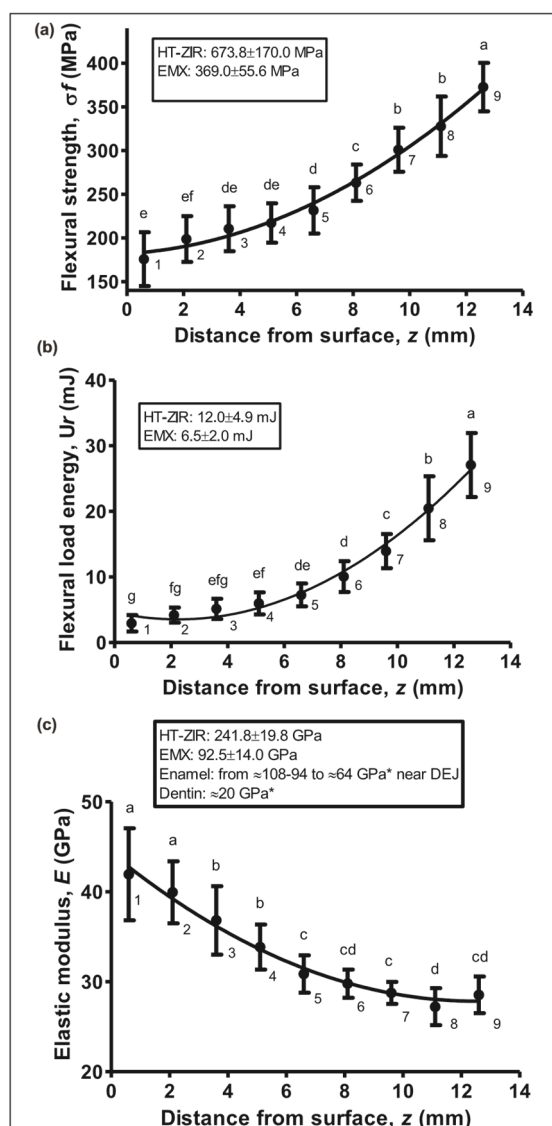


Figure 3. Flexural properties. (a) Flexural strength (σ_f) in MPa of the 9 layers of the functionally graded polymer-infiltrated ceramic network (FG-PICN) blocks ($n = 30$ per layer). Values of translucent zirconia (HTZIR) and IPS e.max CAD (EMX) are noted separately on the upper left corner of the graph ($n = 30$ per material). (b) Flexural load energy (U_r) in mJ of the 9 layers of the FG-PICN blocks ($n = 30$ per layer). Values of HT-ZIR and EMX are noted separately on the upper left corner of the graph ($n = 30$ per material). (c) Modulus of elasticity (E) in GPa of the 9 layers of the FG-PICN blocks ($n = 30$ per layer). Values of HT-ZIR and EMX are noted separately on the upper right corner of the graph ($n = 30$ per material). Average values of E of enamel and dentin are also presented for comparison. *Data from Xu et al. (1998), Marshall et al. (2001), Elfallah et al. (2015), and Madfa and Yue (2016). The numbers (1 to 9) underneath the data points represent the corresponding layer within the FG-PICN blocks. 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.

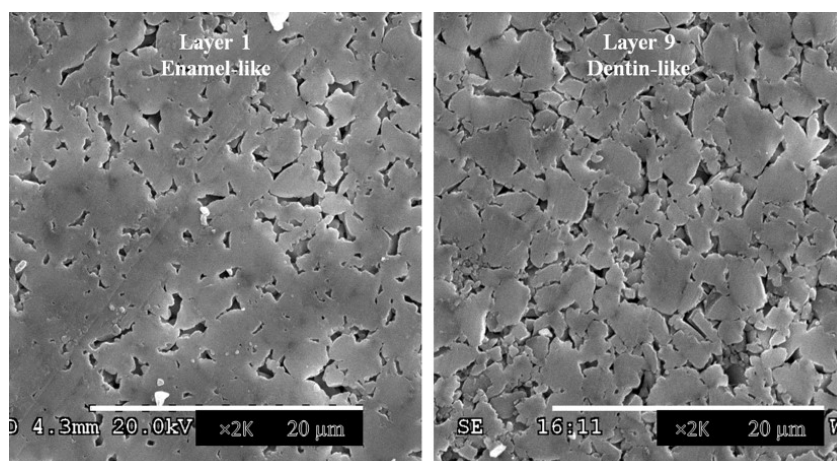


Figure 4. Scanning electron microscopy images of the first (enamel-like) layer (to the left) and the last (dentin-like) layer (to the right) at x2,000 magnification.

Discussion

Composite materials exhibit several advantages in regard to producing CAD-CAM monolithic restorations. They show better machinability than ceramics, characterized by a faster milling process, less edge chipping, and the possibility to be milled to a very low thickness to produce minimally invasive restorations (Coldea et al. 2015; Lebon et al. 2015; Chavali et al. 2017). They are particularly adapted to chair-side systems since they do not require any firing procedures, as is the case with many ceramic materials. They are also easy to adjust and repair intraorally, and their optical properties allow for the manufacturing of restorations with various degrees of translucency. Among CAD-CAM composites, PICNs, due to their specific microstructure and manufacturing process, also showed bonding properties better than lithium-disilicate glass-ceramics (Eldafrawy et al. 2018) and good biocompatibility properties toward human gingival fibroblasts and keratinocytes, with the absence of monomer release (Phan et al. 2014; Grenade et al. 2016; Grenade et al. 2017). The larger elastic modulus of PICNs with a glass-ceramic network infiltrated by polymer, compared to dispersed filler composites, can be explained by its underlying microstructure (Awada and Nathanson 2015; Lawson et al. 2016; Mainjot et al. 2016; Swain et al. 2016). The wet manufacturing process of the glass-ceramic network used in experimental PICNs, associated with the HT-HP polymerization process of polymer, was previously shown to increase material flexural strength up to ~305 MPa (Nguyen et al. 2014). In the present work, the addition of a centrifugation processing of the glass-ceramic powder before the sintering procedure allowed the obtaining, after sintering, of a gradient of glass-ceramic powder density, as demonstrated by the decrease of glass-ceramic volume percentage with depth (around 10 vol.%). The centrifugation of 2 different glass-ceramic powders with respective grain sizes (enamel powder, 2.6 μm D50 grain size, incisal optical properties, and D2M2, 4.5 μm D50 grain size, dentin optical properties) allowed for the creation of a gradient in the distribution of the different grains: large grains will concentrate in the external part of the centrifuged block and the smaller ones inside. Due to their respective grain size, the partial sintering of the enamel powder will give rise to higher shrinkage and a reduced ratio of open porosities for monomer infiltration than dentin powder, as shown in the SEM images. Consequently, the resulting FG-PICN is characterized by a gradient in microstructure over the thickness of the sample,

resulting in progressive and significant variations in the material optical properties, on one hand, and in the mechanical properties, on the other hand, as demonstrated by flexural strength, E , flexural load energy, and hardness measurements.

Regarding flexural strength, the results cannot be compared to enamel and dentin values due to the absence of data in the literature related to the difficulty in measurement (Coldea et al. 2013). Compared to other CAD-CAM materials, the flexural strength of FG-PICN in the dentin-like zone (372.7 ± 27.8 MPa) was shown to be significantly higher than commercial PICN or other CAD-CAM composites (~ 137 to 248 MPa) (Albero et al. 2015; Awada and Nathanson 2015; Stawarczyk et al. 2015; Lawson et al. 2016; Swain et al. 2016) and similar to lithium-disilicate glass-ceramic, while HT-ZIR showed much higher flexural strength (673.8 ± 170.0 MPa). The dentin-like zone was shown to be more resistant than the enamel-like zone, with the flexural strength increasing from 175.8 ± 30.8 to 372.7 ± 27.8 MPa with increasing polymer fraction (from 17.6 to 27.6 vol.%). In fact, the polymer fraction promotes material viscoelastic behavior, which hinders crack initiation and propagation, similar to dentin (while enamel is brittle, with only 10 vol.% polymer fraction compared to 30 vol.% for dentin) (Berkovitz et al. 2009), as confirmed by the Weibull modulus increase from layer 1 to 9. The brittleness of ceramic materials is an inconvenience compared to composites due to edge chipping during the manufacturing process (Chavali et al. 2017).

The FG-PICN elastic modulus was shown to be, within the surface, around 20 GPa lower than deeper layers of natural enamel and similar to dentin in depth, while EMX is similar to the in-surface layers of natural enamel and HT-ZIR is much too rigid. Actually, glass-ceramics are similar to enamel in terms of stiffness: the more glass-ceramic phase in the FG-PICN, the closer to enamel the E value is, while experimental graded zirconia exhibited a value close to enamel only on the material surface, which was infiltrated with glass (~ 75 GPa) (Zhang and Ma 2009). In fact, FG-PICN mimics the gradient found in dentin and deeper layers of enamel in terms of stiffness variations. However, it must be noticed that the reported data of the E of enamel and dentin (Xu et al. 1998; Marshall et al. 2001; Elfallah et al. 2015), as well as graded zirconia (Zhang and Ma 2009; Zhang et al. 2010; Dorthe and Zhang 2012), were obtained via indentation, while those of EMX were obtained via flexion (Awada and Nathanson 2015; Elsaka and Elnaghy 2016; Lawson et al. 2016), as in the present study, which could result in some differences. The gradual transition in E , in a similar manner to tooth tissues, suggests that fatigue stresses and restoration failure can be decreased (Rahbar and Soboyejo 2011; Du et al. 2013). Moreover, compared to metal or ceramics, restorative materials with low E , such as composites, are reputed to better distribute stresses around implants (Maminskas et al. 2016) and to show a damping effect (Magne et al. 2013), which can promote implant osseointegration and survival (Lambert and Mainjot 2017).

The most interesting finding are the results of the flexural load energy, which were shown to reach 27.1 ± 4.9 mJ in the dentin-like zone, while EMX and HT-ZIR exhibited only 6.5 ± 2.0 mJ and 12.0 ± 4.9 mJ, respectively. Flexural load energy is the amount of stresses a material can absorb before fracture. This capacity also improves the material's damping effect, which is particularly important in the case of high stress, such as in the presence of bruxism, or with implants.

The enamel-like zone showed significantly higher brittleness compared to the dentine-like zone, as observed with tooth tissues. Hardness showed a biomimetic tendency with values nearly matching those of enamel and dentin. This property is particularly important not only to the wearing processes of the material itself but to antagonistic teeth, as well. Actually, materials should wear at the same rate as tooth tissues: not more, not less, to allow for favorable evolution of occlusion. From that point of view, ceramic

materials are not well adapted, with zirconia being not susceptible to self-wear and glass-ceramics causing excessive wear of the opposing teeth (Swain et al. 2016). If commercial PICN was shown to be submitted to more self-wearing than enamel, due to their higher in-surface hardness, it could be expected that the behavior of FG-PICN would be more favorable (hardness ~1.5 to 2.4 GPa for Vita Enamic compared to 4.2 for enamel-like zone of FG-PICN) (Lawson et al. 2016; Swain et al. 2016; Xu et al. 2017). In addition, increasing hardness decreases the machinability of CAD-CAM blocks, with composite materials being more advantageous than zirconia from that point of view.

Finally, the manufacturing process allowed for the creation of a shade gradient through the block. The presence of a higher volume percentage of glass-ceramic in the surface is susceptible to improving material polishing and gloss compared to commercial PICN.

The limitation of FG-PICN is that the gradient is 1-dimensional, while it is 3-dimensional in natural teeth, which should not cause a problem in manufacturing inlays, onlays, tabletops, and palatal and buccal veneers, but is not ideal for crowns.

Conclusion

This work introduces, for the first time, a functionally graded biomimetic material for CAD-CAM prostheses, with a gradient of mechanical and optical properties throughout the entire thickness of the block. The FG-PICN material demonstrated a favorable gradient of 1) flexural strength similar to lithiumdisilicate glass-ceramic (EMX), associated with a high Weibull modulus; 2) elastic modulus close to tooth tissues; 3) flexural load energy superior to EMX and translucent zirconia; and 4) hardness similar to enamel and dentin. The graded character of this material can improve the biomechanical behavior of single-unit restorations on teeth and implants. Due to its innovative microstructure, FG-PICN combines the advantages of both CAD-CAM composite and glass-ceramic materials, without their limits or those of zirconia, in terms of mechanical properties, but also in terms of machinability, absence of firing procedure, and optical and bonding properties.

Future perspectives include the study of the fatigue behavior of this innovative material and clinical studies.

Author contributions

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

Acknowledgments

The authors received no financial support for this work. M.J. Sadoun has a US patent 8,507,578 B2 with royalties paid by Vita Zahnfabrik. The authors declare no other potential conflicts of interest with respect to the authorship and/or publication of this article.

References

- Albero A, Pascual A, Camps I, Grau-Benitez M. 2015. Comparative characterization of a novel CAD-CAM polymer-infiltrated-ceramic-network. *J Clin Exp Dent*. 7(4):e495–e500.
- Awada A, Nathanson D. 2015. Mechanical properties of resin-ceramic CAD/ CAM restorative materials. *J Prosthet Dent*. 114(4):587–593.
- Berkovitz BKB, Holland GR, Moxham BJ. 2009. *Oral anatomy, histology and embryology*. 4th ed. New York: Mosby/Elsevier.
- Chavali R, Nejat AH, Lawson NC. 2017. Machinability of CAD-CAM materials. *J Prosthet Dent*. 118(2):194–199.
- Coldea A, Fischer J, Swain MV, Thiel N. 2015. Damage tolerance of indirect restorative materials (including PICN) after simulated bur adjustments. *Dent Mater*. 31(6):684–694.
- Coldea A, Swain MV, Thiel N. 2013. Mechanical properties of polymer- infiltrated-ceramic-network materials. *Dent Mater*. 29(4):419–426.
- Conrad HJ, Seong WJ, Pesun IJ. 2007. Current ceramic materials and systems with clinical recommendations: a systematic review. *J Prosthet Dent*. 98(5):389–404.
- Dorthe E, Zhang Y. 2012. Load-bearing increase in alumina evoked by introduction of a functional glass gradient. *J Eur Ceram Soc*. 32(6):1213–1220.
- Du J, Niu X, Rahbar N, Soboyejo W. 2013. Bio-inspired dental multilayers: effects of layer architecture on the contact-induced deformation. *Acta Biomater*. 9(2):5273–5279.
- Eldafrawy M, Ebroin MG, Gailly PA, Nguyen JF, Sadoun MJ, Mainjot AK. 2018. Bonding to CAD-CAM composites: an interfacial fracture toughness approach. *J Dent Res*. 97(1):60–67.
- Elfallah HM, Bertassoni LE, Charadram N, Rathsam C, Swain MV. 2015. Effect of tooth bleaching agents on protein content and mechanical properties of dental enamel. *Acta Biomater*. 20:120–128.
- Elsaka SE, Elnaghy AM. 2016. Mechanical properties of zirconia reinforced lithium silicate glass-ceramic. *Dent Mater*. 32(7):908–914.
- Grenade C, De Pauw-Gillet MC, Gailly P, Vanheusden A, Mainjot A. 2016. Biocompatibility of polymer-infiltrated-ceramic-network (PICN) materials with human gingival fibroblasts (HGFs). *Dent Mater*. 32(9):1152–1164.
- Grenade C, De Pauw-Gillet MC, Pirard C, Bertrand V, Charlier C, Vanheusden A, Mainjot A. 2017. Biocompatibility of polymer-infiltrated-ceramic- network (PICN) materials with human gingival keratinocytes (HGKs). *Dent Mater*. 33(3):333–343.
- Huang M, Wang R, Thompson V, Rekow D, Soboyejo WO. 2007. Bioinspired design of dental multilayers. *J Mater Sci Mater Med*. 18(1):57–64.
- Lambert F, Mainjot A. 2017. One-tooth one-time (1T1T): a straightforward approach to replace missing teeth in the posterior region. *J Oral Implantol*. 43(5):371–377.
- Lawson NC, Bansal R, Burgess JO. 2016. Wear, strength, modulus and hardness of CAD/CAM restorative materials. *Dent Mater*. 32(11):e275–e283.
- Lebon N, Tapie L, Vennat E, Mawussi B. 2015. Influence of CAD/CAM tool and material on tool wear and roughness of dental prostheses after milling. *J Prosthet Dent*. 114(2):236–247.
- Madfa AA, Yue XG. 2016. Dental prostheses mimic the natural enamel behavior under functional loading: a review article. *Jpn Dent Sci Rev*. 52(1):2–13.

- Magne P, Silva M, Oderich E, Boff LL, Enciso R. 2013. Damping behavior of implant-supported restorations. *Clin Oral Implants Res.* 24(2):143–148.
- Mahamood RM, Akinlabi ET, Shukla M, Pityana S. 2012. Functionally graded material: an overview. *Proc World Cong Eng.* 3:2078–0958. [accessed 2018 June 6] http://www.iaeng.org/publication/WCE2012/WCE2012_pp1593-1597.pdf
- Mainjot AK, Dupont NM, Oudkerk JC, Dewael TY, Sadoun MJ. 2016. From artisanal to CAD-CAM blocks: state of the art of indirect composites. *J Dent Res.* 95(5):487–495.
- Maminskas J, Puisys A, Kuoppala R, Raustia A, Juodzbalsys G. 2016. The prosthetic influence and biomechanics on peri-implant strain: a systematic literature review of finite element studies. *J Oral Maxillofac Res.* 7(3):e4.
- Marshall GW Jr, Balooch M, Gallagher RR, Gansky SA, Marshall SJ. 2001. Mechanical properties of the dentinoenamel junction: AFM studies of nanohardness, elastic modulus, and fracture. *J Biomed Mater Res.* 54(1):87–95.
- Nguyen JF, Ruse D, Phan AC, Sadoun MJ. 2014. High-temperature-pressure polymerized resin-infiltrated ceramic networks. *J Dent Res.* 93(1):62–67.
- Niu X, Rahbar N, Farias S, Soboyejo W. 2009. Bio-inspired design of dental multilayers: experiments and model. *J Mech Behav Biomed Mater.* 2(6):596–602.
- Phan AC, Tang ML, Nguyen JF, Ruse ND, Sadoun M. 2014. High-temperature high-pressure polymerized urethane dimethacrylate-mechanical properties and monomer release. *Dent Mater.* 30(3):350–356.
- Rahbar N, Soboyejo WO. 2011. Design of functionally graded dental multilayers. *Fatigue Fract Eng Mater Struct.* 34(11):887–897.
- Sehgal J, Ito S. 1998. A new low-brittleness glass in the soda-lime-silica glass family. *J Am Ceram Soc.* 81(9):2485–2488.
- Stawarczyk B, Liebermann A, Eichberger M, Guth JF. 2015. Evaluation of mechanical and optical behavior of current esthetic dental restorative CAD/ CAM composites. *J Mech Behav Biomed Mater.* 55:1–11.
- Swain MV, Coldea A, Bilkhair A, Guess PC. 2016. Interpenetrating network ceramic-resin composite dental restorative materials. *Dent Mater.* 32(1):34–42.
- Tong H, Tanaka CB, Kaizer MR, Zhang Y. 2016. Characterization of three commercial Y-TZP ceramics produced for their high-translucency, highstrength and high-surface area. *Ceram Int.* 42(1 Pt B):1077–1085.
- Xu HH, Smith DT, Jahanmir S, Romberg E, Kelly JR, Thompson VP, Rekow ED. 1998. Indentation damage and mechanical properties of human enamel and dentin. *J Dent Res.* 77(3):472–480.
- Xu Z, Yu P, Arola DD, Min J, Gao S. 2017. A comparative study on the wear behavior of a polymer infiltrated ceramic network (PICN) material and tooth enamel. *Dent Mater.* 33(12):1351–1361.
- Zhang Y, Chai H, Lawn BR. 2010. Graded structures for all-ceramic restorations. *J Dent Res.* 89(4):417–421.
- Zhang Y, Chai H, Lee JJ, Lawn BR. 2012. Chipping resistance of graded zirconia ceramics for dental crowns. *J Dent Res.* 91(3):311–315.
- Zhang Y, Kim JW. 2009. Graded structures for damage resistant and aesthetic all-ceramic restorations. *Dent Mater.* 25(6):781–790.
- Zhang Y, Lawn BR. 2018. Novel zirconia materials in dentistry. *J Dent Res.* 97(2):140–147.
- Zhang Y, Ma L. 2009. Optimization of ceramic strength using elastic gradients. *Acta Mater.* 57(9):2721–2729.