Dental ceramics: a review of new materials and processing methods

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Abstract: The evolution of computerized systems for the production of dental restorations associated to the development of novel microstructures for ceramic materials has caused an important change in the clinical workflow for dentists and technicians, as well as in the treatment options offered to patients. New microstructures have also been developed by the industry in order to offer ceramic and composite materials with optimized properties, *i.e.*, good mechanical properties, appropriate wear behavior and acceptable aesthetic characteristics. The objective of this literature review is to discuss the main advantages and disadvantages of the new ceramic systems and processing methods. The manuscript is divided in five parts: I) monolithic zirconia restorations; II) multilayered dental prostheses; III) new glass-ceramics; IV) polymer infiltrated ceramics; and V) novel processing technologies. Dental ceramics and processing technologies have evolved significantly in the past ten years, with most of the evolution being related to new microstructures and CAD-CAM methods. In addition, a trend towards the use of monolithic restorations has changed the way clinicians produce all-ceramic dental prostheses, since the more aesthetic multilayered restorations unfortunately are more prone to chipping or delamination. Composite materials processed via CAD-CAM have become an interesting option, as they have intermediate properties between ceramics and polymers and are more easily milled and polished.

Keywords: Ceramics; Dental Materials; Dental Porcelain; Computer-Aided Design; Composite Resins.

Introduction

The evolution of computerized systems for the production of dental restorations associated to the development of novel microstructures for ceramic materials has caused an important change in the clinical workflow for dentists and technicians, as well as in the treatment options offered to patients. One of the most important changes in this scenario was the introduction of monolithic restorations produced from high-strength ceramics, like zirconia. This concept *per se* is not new, since ceramic materials have been used for a relatively long time for the production of monolithic restorations, but it was only when zirconia started to be used to produce full-contour crowns that dentists and technicians became more confident to indicate a ceramic material for crowns and bridges in the posterior region.

In fact, by offering monolithic prostheses, clinicians are able to overcome one of the major problems associated to multilayered restorations, which is the fracture of the low-strength veneering layer, usually made of a feldspathic dental ceramic. However, when using a monolithic zirconia restoration, other clinical problems may arise and need to be taken care of, such as wear of the antagonist dentition and matching the aesthetic characteristics of the natural dentition.

Due to the problem of chipping of the veneering layer, multilayered restorations have also evolved significantly in the past ten years. Most of the evolution of this system is associated to new processing techniques that aim at improving the final quality of the veneering material. Injection of the porcelain over the zirconia framework is an example of a new processing method that eliminates the porosity within the veneering layer and therefore improves its mechanical reliability. Other solutions have also been proposed, such as CAD-on and rapid layer techniques. The CAD-on technique involves the production of a stronger veneering layer based on lithium disilicate glass-ceramics sintered onto the zirconia framework using a fusion glass solder, and the rapid layer uses CAD-CAM (computer-aided design and computer-aided manufacturing) technology to mill the veneering layer that is afterwards cemented onto the zirconia framework. These new processing methods are relatively new and still need more clinical trials to prove their efficacy in relation to the traditional processing routes.

New microstructures have also been developed by the industry in order to offer ceramic and composite materials with optimized properties, *i.e.*, good mechanical properties, appropriate wear behavior and acceptable aesthetic characteristics. Examples of these novel microstructures are lithium silicate glass-ceramics reinforced with zirconia and a composite constituted of a polymer-infiltrated ceramic. The latter uses an innovative processing technique in which a porous ceramic block is infiltrated with a UDMA-based polymer, as opposed to traditional resin composites produced by means of adding ceramic fillers to a polymer matrix. The main advantage of this material is that it is easier (faster) to be machined by CAD-CAM techniques, and its elastic modulus is closer to that of tooth tissues.

The objective of this literature review is to discuss the main advantages and disadvantages of the above mentioned new ceramic systems and processing methods. Clinical and laboratorial findings are thoroughly discussed in order to help clinicians and technicians to use these new technologies. The manuscript is divided in five parts: 1) monolithic zirconia restorations; 2) multilayered dental prostheses; 3) new glass-ceramics; 4) polymer infiltrated ceramics; and 5) novel processing technologies.

Monolithic zirconia restorations

Among polycrystalline ceramics, yttria stabilized tetragonal zirconia polycrystal (Y-TZP) for monolithic (full-contour) restorations has been developed more recently to overcome problems related to chipping of porcelain layers applied over zirconia.[1,2] Zirconia exists in three different crystallographic forms: cubic, tetragonal and monoclinic phases. Y-TZP shows superior performance among dental ceramics due the high strength level of more than 1000 MPa and its superior fracture toughness of 4 to 5 $MPa.m^{0.5}$. Especially the high fracture toughness is a consequence of a toughening mechanism related to the transformation of tetragonal grains into the monoclinic phase, which generates compression stresses around defects, hindering their catastrophic propagation. The microstructure of Y-TZPs for monolithic prostheses has been tailored to improve their translucency in comparison with conventional Y-TZP.

The better translucency of the new zirconia materials has been achieved by means of microstructural modifications, like decrease in alumina content, increase in density, decrease in grain size, addition of cubic zirconia and decrease in the amount of impurities and structural defects.[3,4] The size of the crystalline grain is the microstructural feature that is more closely related to the adjustment of the translucency of polycrystalline ceramics. The creation of ceramic materials with high translucency has been done in the past by means of increasing the grain size during sintering.[5] Lager grains lead to a smaller number of grain boundaries, therefore reducing light scattering. For Y-TZP, it has been shown that larger grains are detrimental for both the mechanical properties and

the stability of the tetragonal phase. Therefore, the translucency of zirconia cannot be achieved by means of increasing its grain size.

Another approach to produce a more translucent Y-TZP is to decrease significantly the grain size. However, the grain size needs to be decreased until reaching a critical value that results in mitigation of the so-called birefringence phenomenon.[4] Birefringence occurs in Y-TZP due to the large amount of tetragonal crystal phase (> 90%), which is a crystal that has different refractive indexes according to its crystallographic orientation in the microstructure. Such anisotropic behavior related to the variation in the refractive index causes significant light scattering.[4,6] Another way to overcome these scattering effects is the use of cubic zirconia, which offers optical isotropic behavior, increasing the translucency.

For clinicians and dental technicians, monolithic zirconia restorations have become a very promising alternative, since the processing methods are simplified in comparison to traditional multilayered restorations, and therefore are less time consuming. From the biological standpoint, monolithic restorations made with zirconia allow clinicians to make much less invasive preparations, since this ceramic material has relatively high mechanical properties, especially when compared to veneering porcelains. In fact, important microstructural mechanisms, such as transformation toughening, hinder crack propagation through the restorations, and therefore, thinner structures can be constructed, preserving tooth tissues.

Although novel zirconia microstructures have higher translucency, the color of the final restoration is still limited to a whitish shade. Therefore, an important technological development for these materials is the coloring process that allows for a larger range of aesthetic possibilities.[7] Laboratory studies indicated that the addition of coloring pigments to monolithic zirconia does not affect its flexural strength and translucency, however these results are related to specific coloring methodologies and cannot be generalized.[8,9] Different techniques can be used to add color to zirconia restorations. One of them involves immersion of the material (dip coating) when it is at the pre-sintered state in a solution containing different types of coloring dyes. This method has the disadvantage

of resulting in a non-homogeneous final shade, since the pigments may penetrate only to a certain depth.[10] Another coloring technique allows for the production of pre-colored zirconia pre-sintered blocks with a much more homogeneous shade. Pre-colored blocks of monolithic zirconia can be manufactured from a powder that is synthesized together with pigments or a powder which has been mixed with pigments.[7]

One factor that affects the translucency of dental ceramics is the restoration thickness. In general, the lower the thickness, the higher the translucency of a ceramic restoration,[11,12] therefore, it is mandatory that translucency data is always reported accompanied by the material thickness. Considering the thickness of 0.5 mm, traditional Y-TZP shows contrast ratio (CR) values that are higher (0.77) than those of monolithic Y-TZPs (0.57 to 0.62).[13]

In addition to the mechanical and optical properties, another important characteristic for the long-term success of a restoration is the wear of the antagonist enamel and the marginal adaptation. Fortunately, laboratory studies have shown that monolithic zirconia usually causes a rather comparable wear of the antagonists in comparison to other restorative ceramics, and this wear rate is within the physiological range reported in the literature. Some of these studies compared different surface finishing techniques for monolithic zirconia restorations, such as polishing versus glazing, and found that polished surfaces resulted in less enamel wear of the antagonist.[13,14,15,16]

It is needless to say that the high surface hardness of zirconia has a major influence on the antagonist wear and a perfect polish of any monolithic zirconia restoration is therefore very important. A clinical study evaluated the occlusal surface wear of monolithic zirconia crowns placed in premolars and molars. Impressions of the restorations were taken at the beginning of the trial and then 24 months later. Epoxy replicas were produced and both a qualitative (scanning electron microscopy) and a quantitative (optical profilometry) surface analyses were performed. The results showed that monolithic zirconia promoted an acceptable surface wear rate of the antagonist surface (natural enamel or ceramic material) after two years.[17] Therefore, monolithic Y-TZP restorations with good surface finishing are not likely to wear significantly

the antagonist element. However, following up these Y-TZP restorations is important because if there is a decrease in the surface quality, their wear potential will increase significantly.

The marginal adaptation of the monolithic restorations of Y-TZP improved over the years due to the evolution of CAD-CAM systems. Several of these systems and different materials had their adaptation evaluated: TZI, TZ Incoris (Dentsply-Sirona, Bensheim, Germany), CZ, Ceramill Zolid White (Amann Girrbach, Koblach, Austria), ZZ, Zenostar Zirconia (Wieland, Pforzheim, Germany), PZ, Prettau Zirconia (Zirkonzahn) and BZ, Bruxzir Solid Zirconia (Glidewell, Gais, Germany). Fortunately, all brands showed acceptable marginal discrepancy n, with the most advanced five-axis milling systems being superior to others.[18]

Another important issue regarding the use of monolithic zirconia for dental restorations is the ageing phenomenon, since these restorations are loaded in direct contact with the oral environment. Laboratory studies have evaluated the formation of the monoclinic crystalline phase and the flexural strength of different monolithic zirconia after ageing. Their results indicated that some brands are not susceptible to aging while others are more prone to tretragonal-to-monoclinic (t-m) transformation.[19,20] However, more studies are needed to evaluate this ageing phenomenon, since to date there is no scientific evidence from clinical studies linking the clinical failure of dental Y-TZP with this type of ageing.

The higher translucency of monolithic Y-TZPs expanded their indication for rehabilitations in aesthetic regions. However, extra caution is necessary before using this type of restoration indiscriminately, as there are only a few clinical follow-ups that evaluated monolithic zirconia crowns. One of these studies showed that out of 82 monolithic zirconia crowns installed in 60 patients, 6 (7.3%) had complications after 3 years. The study showed that problems that affect this type of restoration are mostly related to loss of crown retention (2.4%) and endodontic complications (4.9%). Thus, this type of treatment is considered as promising, but clinical studies with longer follow-up times are still desirable.[21]

Another study collected data over five years from two United States laboratories. The laboratories provided insurance for restorations of monolithic zirconia that had problems, making new restorations without additional costs to the clinicians. The study included 39,827 restorations (all cemented in the natural dentition), which were classified into: anterior single crown (1,952); posterior single crown (29,808); anterior fixed dental prostheses (1,779) and posterior fixed dental prostheses (6,288). Only the restorations that returned to laboratories to be replaced due to catastrophic fracture were considered as failures. The fracture rate (%) was 0.97 for anterior single crowns; 0.71 for posterior single crowns; 3.26 for the anterior fixed dental prostheses and 2.42 for the posterior fixed dental prostheses. The study concluded that restorations made with monolithic zirconia showed relatively low fracture rates. However, possibly some failed restorations may not have been counted, since the patient may have returned to another dentist or the dentist may have chosen another material to replace the restoration.[22]

Multilayered dental prostheses

Traditionally, fixed partial dentures (FPDs) produced with a metallic infrastructure and a ceramic veneering layer have excellent clinical performance, with studies showing an annual failure rate around 1% and a survival rate of 94% after 5 years of clinical follow-ups.[23] Although these metal/ceramic bilayers are still considered the gold standard for FPDs, many studies have been carried out in order to achieve the same level of excellence using all-ceramic systems.

The lower biocompatibility[24] and lower translucency of metals, when compared to ceramic materials, are the factors responsible for the use of ceramics as infrastructure materials in multilayered restorations. On the other hand, the relatively low fracture toughness of ceramic materials is a major limitation for their unrestricted use for prosthodontics solutions. This problem led to the development of a series of ceramic materials with high crystalline content, which are able to withstand the mechanical stresses generated during the application of chewing forces. Examples of such materials are alumina-based zirconia-reinforced glass infiltrated ceramic, polycrystalline alumina and Y-TZP.

Among these ceramic materials, Y-TZP has gained remarkable popularity because of its excellent mechanical properties.[25] However, materials with a high crystalline content still require a veneering layer constructed with a compatible porcelain in order to achieve a more favorable aesthetic result.

With respect to all-ceramic multilayered restorations, clinical follow-ups have reported little or no damage to the Y-TZP infrastructure during clinical use, however, chipping fractures of the veneering ceramic have been frequently reported.[26] These failures compromise the restoration both functionally and aesthetically, requiring the replacement of the prosthetic piece when the fractured area is too large. The fracture of the veneering layer applied over Y-TZP frameworks has been associated with different factors, such as: a) design of the Y-TZP infrastructure, which should give support to the veneering layer;[27] b) relation between the thicknesses of the restoration layers (infrastructure and veneering ceramic, anatomical design);[28] c) thermal residual stresses within the restoration, which are generated either during the cooling step at the sintering furnace[29] or due to a certain mismatch of the coefficients of thermal expansion (CTE) of both layers and d) mechanical properties of the veneering ceramic.

Several methodologies for the application of the veneering layer on the ceramic infrastructure are available in the market and all of them aim at optimizing the resistance of this layer and, in some cases, to reduce the generation of residual thermal stresses. In the traditional or stratified processing technique, the manufacturer provides a ceramic powder and a modeling liquid (distilled water mixed with rheological modifiers). In order to produce the restoration, the Y-TZP framework receives the application of a mixture containing the veneering ceramic powder and the modeling liquid with the use of a brush. Several layers need to be applied in order to construct the desired dental element anatomy. This technique generates veneering layers susceptible to processing porosities and a series of intrinsic defects that can act as stress concentration areas, favoring the fracture of the restoration during chewing.

Another technique for the application of the veering layer is the so-called press-on method, in which the veneering material is applied on the ceramic infrastructure (made of Y-TZP) by means of a lost-wax in combination with a hot-pressing technique, resulting in a veneering layer with less pores and better mechanical behavior when compared to a veneering layer applied by the traditional technique. In this case, the veneering ceramic is provided in the form of pellets which are injected into a refractory mold (generated from the lost wax technique) containing the previously sintered Y-TZP framework. Stawarczyk et al.[30] evaluated the load-bearing capacity of bilayered all-ceramic crowns as a function of different techniques for application of the veneering layer (injection of the Y-TZP versus the stratified technique) and concluded that crowns produced by means of injection of the veneering layer exhibited comparable and under certain configurations even superior fracture loads when compared to those made with the stratified technique.

Advances in CAD-CAM systems (computer aided design-computer aided manufacturing) in addition to an attempt to decrease the generation of residual thermal stresses in bilayered all-ceramic restorations have led to the development of new processing methods that involve milling of CAD-CAM blocks for both the framework and the veneering layer. In a further step, these layers are bonded with a resin cement or a fusion glass-ceramic. One of these systems is called the Rapid Layer Technique (Vita) and involves milling of both the Y-TZP infrastructure and the veneering layer, including a posterior cementation step using dual-cure resin-based luting agents. The other technique is called CAD-on (Ivoclar Vivadent, Schaan, Liechtenstein) and involves milling of the veneering layer from a lithium disilicate glass-ceramic CAD-CAM block. Lithium disilicate is a ceramic material that has much higher crystalline content compared to feldsphatic veneering ceramics and therefore presents higher mechanical properties. In the end of the process, both layers are bonded by means of a firing cycle that is carried out after the application of a fusion glass-ceramic (glass solder) between both layers.

One great advantage of restorations produced via CAD-CAM systems is the fact that the blocks used for production of the veneering layer are originated from optimized sintering procedures carried out by the manufacturer under ideal industrial conditions,

which results in mechanically stronger blocks with less defects when compared to the veneering layers obtained by the previously described methodologies.

In 2012, one study[31] evaluated the load-bearing capacity of all-ceramic crowns composed of Y-TZP veneered using the traditional technique, and crowns produced with the Cad-on system. The fracture load values were significantly different between these two groups, with mean values of 1,575 N for the crowns produced by the CAD-on system and 1,166 N for the crowns that received the veneering layer by the traditional technique. Another study[32] used the CAD-on system to evaluate the effect of the bonding technique on the fracture resistance of molar crowns. In this study, specimens that had their layers bonded by a resin cement (Multilink Implant; Ivoclar Vivadent) showed a mean fracture resistance value lower than the value obtained for the group in which the components were bonded by means of the fusion glass-ceramic (IPS e.max Crystall Connect; Ivoclar Vivadent, Schaan, Liechtenstein). The mean values obtained in this study were 1,388 ± 190 N for the fusion glass ceramic group versus 1,211 ± 158 N of the cemented group; however, this difference was not statistically significant.

Another in vitro study[33] compared the fracture resistance of all-ceramic first molar crowns with Y-TZP infrastructures veneered with different techniques: layering (VM9; Vita, Bad Sachingen, Germany), press-on (IPS e.max ZirPress; Ivoclar vivadent, Schaan, Liechtenstein), and milling from CAD-CAM blocks (Lava™ DVS; 3M, Seefield, Germany) with posterior bonding using a fusion glass-ceramic. Multilayered restorations made from CAD-CAM blocks showed significantly higher fracture strength values (6,242 N) when compared to crowns made with the layering (4,264 N) and press-on (5,071 N) techniques.

New glass-ceramics

Nowadays, glass-ceramics are broadly used in prosthetic dentistry due to the continuous improvements of their mechanical properties associated to better microstructures and new processing methods. The adequate mechanical properties of these materials reflect in the good longevity of such dental restorations.[34] The good aesthetic quality is another factor that greatly contributes to the attractiveness of glass-ceramics to clinicians[35,36,37].

Since glass-ceramics started to be used in dentistry,[38] materials with varied compositions have been developed; however, this class of materials gained popularity after the launching of lithium disilicate glass-ceramic in 1998 (IPS Empress® 2, Ivoclar Vivadent Ltda, Schaan, Liechtenstein, later on marketed as e.max®). In comparison with leucite glass-ceramics,[39] lithium disilicate-based materials have superior mechanical properties (Table 1), what expands their indication to the production of all-ceramic fixed partial dentures up to 3 elements.[43]

The first lithium disilicate glass-ceramic (based on the system $Li_2O:2SiO_2$) was produced by melting a glass, which was then ground to form a powder that was used to make the so-called "blue" blocks or ingots with composition according to Table 2.[44] Depending on the type of piece produced, whether it was a "blue" block for CAD-CAM system or the ingot for hot-pressed technique, the crystallization technique of this glass-ceramic changed. However, the crystallization process was similar in all situations.

Table 1. Mechanical properties for the traditional glass-ceramics in the market.[40,41,42]

Material	Flexural strength (MPa)	Fracture toughness ($MPa.m^{1/2}$)	Hardness (GPa)
Leucite glass-ceramic	164	1.03	6.5
Lithium disilicate glass-ceramic	365	2.80	5.3

Table 2. Composition of the glass-ceramic lithium disilicate IPS Empress® 2 raw powder.[44]

Constituent	Weight %
SiO_2	57–80
Al_2O_3	0–5
La_2O_3	0.1–6
MgO	0–5
ZnO	0–8
K_2O	0–13
Li_2O	11–19
P_2O_5	0–11
Additives	~ 8

Briefly, the crystallization of the lithium disilicate is controlled by a heating cycle, in which lithium metasilicate (Li_2SiO_3) reacts with the glassy phase (SiO_2) to originate lithium disilicate ($Li_2Si_2O_5$).[45] Lithium metasilicate is nucleated from the base glass (Li_3PO_4, amorphous) at the initial temperatures of the cycle. Later on, lithium disilicate glass-ceramics underwent some changes and gave rise to IPS e.max Lithium Disilicate (Ivoclar Vivadent Ltda., Barueri, Brazil), which has better mechanical properties, mostly due to the decrease in the size of the platelet-shaped crystals (length varying from 2.0 to 3.0 μm) and the increase in interlocking among crystals.[46,47]

Despite the great acceptance and broad use of lithium disilicate glass-ceramics, the evolution of dental materials has attempted to suppress the remaining disadvantages of this ceramic system by means of the development of glass-ceramics reinforced with polycrystalline ceramics. These new glass-ceramics were designed to contain lithium silicate as the main crystalline phase in a vitreous matrix reinforced with zirconium dioxide crystals (~10%).[48] When this material goes through the crystallization process, the nucleated lithium silicate crystals achieve a mean size (0.5 to 1 μm) that is up to 6 times smaller than that observed for lithium disilicate crystals present in lithium disilicate glass-ceramics.[49] The formation of a smaller and finer crystalline phase occurs due to the presence of zirconia particles in the material, which acts as an additive influencing the crystallization by hindering crystal growth.[50] A microstructure containing smaller crystals guarantees to this material mechanical properties similar to those observed for lithium disilicate ceramics.[47] Additionally, as observed for traditional glass-ceramics, these new zirconium-reinforced lithium silicate materials maintain good optical properties, are easily milled in CAD-CAM machines and attain good surface finishing, as they still have a high amount of glass matrix.[51]

The two existing commercial examples of lithium silicate glass-ceramics are: a) Suprinity (Vita Zahnfabrik, Bad Sachingen, Germany), a material marketed in a partially crystallized state and that requires an additional thermal cycle in a furnace; and b) CELTRA Duo (Dentisply-Sirona, Bensheim, Germany), a material that is already in its final crystallization stage. Both materials have similar composition as shown in Table 3.[52]

These novel zirconia-reinforced lithium silicate glass-ceramics have good mechanical properties associated with an excellent esthetic quality, thus being a valid alterative to lithium disilicate materials for prosthetic rehabilitations with high aesthetic demand. The main advantage of these materials is their timesaving ability for the production of dental restorations, since they are faster to be milled in CAD-CAM machines than lithium disilicate glass-ceramics[53] and are already offered in their fully crystallized state (CELTRA Duo, Dentisply-Sirona, Bensheim, Germany) no furnace need) or need a very short crystallization cycle (Suprinity, Bad Sachingen, Germany). A particular advantage of the lithium silicate ceramic over the lithium disilicate version is the superior polishability due to the smaller crystal sizes in the microstructure.

Polymer infiltrated ceramic networks (PICNs)

In the last decades, the use of CAD-CAM systems in dentistry has increased exponentially, especially because of the general trends towards high productivity and aesthetics.[54,55] Although CAD-CAM systems were developed initially for the production of ceramic restorations, pre-polymerized resin composites blocks have also been developed to be used with these systems. One of the first resin composites developed as a CAD-CAM block was Paradigm™ (3M™, St Paul, USA), which was considered a fast-milling and wear-friendly alternative to the use of ceramics. However, problems commonly related to resin composite systems still need to be overcome, such as the reduced mechanical properties and poor wear resistance.[54]

Recently, a new material has been developed by Vita (VITA Zahnfabrik, Bad Säckingen, Germany) which is marketed as a polymer infiltrated in a porous ceramic,

Table 3. Composition of lithium silicate-based glass-ceramics.[52]

Constituent	Weight %
SiO_2	56–64
Al_2O_3	1–4
CeO_2	0–4
ZrO_2	8–12
K_2O	1–4
Li_2O	15–21
P_2O_5	3–8

generating an interpenetrating network (polymer infiltrated ceramic network, PICN). This new material was developed based on the glass infiltrated ceramic technology (In-Ceram System, Vita, Bad Sachingen, Germany), which was originally released by Vita in the 90's.[54] The infiltration of a resin into a porous ceramic preform is significantly different from the infiltration of a glass, since the final shrinkage of the polymer after infiltration is almost 5%, *i.e.*, much greater than the shrinkage experienced upon cooling of the infiltration glass, which is in the order of 1%.[56]

PICNs have the advantage of presenting an elastic modulus that is approximately 50% lower compared to feldspathic ceramics and hence closer to that of dentin, they are easier to mill and adjust, and also can be more easily repaired by composite resins.[56] In comparison to dental porcelains, this new material has been proven to have lower elastic modulus and higher damage tolerance.[57] In 2013, the product Enamic (Vita, Bad Sachingen, Germany) was introduced for dental restorations. This PICN is based on initial sintering of a porcelain powder to approximately 70% of its full density, followed by infiltration with a monomer mixture.[54,58,59] The material is considered a resin-ceramic composite material, composed of two interconnected networks: a dominant ceramic and a polymer. Recent publications showed that the polymeric part of this material is composed of urethane dimethacrylate (UDMA) and triethylene glycol dimethacrylate (TEGDMA) cross-linked polymers.[60] Compositional analyses of the dominant ceramic network revealed a major ceramic phase, composed (by weight) of SiO_2 (58–63%), Al_2O_3 (20–23%), Na_2O (9–11%), K_2O (4–6%), B_2O3 (0.5–2%), CaO (<1%) and TiO_2(<1%).[61] Although being marketed as a polymer infiltrated ceramic, scientific analysis has shown that the inorganic matrix is rather an amorphous glass.

A recent publication[62] reported that Enamic showed elastic modulus values similar to that reported by the manufacturer (around 30 GPa), however, the fracture toughness values measured in this investigation (0.86 MPa.m$^{1/2}$) were lower than that reported by the manufacturer (1.5 MPa.m$^{1/2}$). The fracture toughness value obtained for PICN was similar to that of the feldspathic ceramic evaluated. Therefore, the authors rejected the hypothesis that the presence of a polymer network would create toughening mechanisms in the microstructure of the material. In addition, this study showed that PICN had increased susceptibility to SCG compared to a feldsphatic ceramic. This raised the question if the polymer is susceptible to water permeation and degradation.

PICNs have positive properties related to both the ceramic and composites, with an interesting balance between elasticity and strength, being indicated for single crowns, inlays, onlays and veneers. The polymeric part has a strength below 30 MPa and the ceramic network has a strength around 160 MPa, whereas the final PICN has strength of 135 MPa. As expected for a composite material, the properties are intermediate between those of ceramics and particle-filled resins.[60,61,63]

The elastic modulus of these materials is in the range of 30 GPa, which is half of that reported for conventional veneering ceramics but closer to what is usually reported for dentin (15–20 GPa).[58,63] Typical ceramic materials have a higher elastic modulus values than PICN[64]. The Vickers hardness of human enamel (3.43 ± 0.16 GPa) and PICN (3.31 ± 0.11 GPa) are similar,[54,65,66,67] and both are higher than the hardness reported for resin composites (0.73 GPa to 1.60 GPa),[68,69] and lower than the hardness of zirconia (13.94 GPa)[70] and lithium disilicate glass ceramics (10.0 GPa to 11.31 GPa).[71] The flexural strength of Enamic (130 MPa)[56] is lower than that of a reference lithium disilicate glass-ceramic material, IPS e.max (342 MPa).[72] PICN has a higher tolerance to diamond bur grinding damage than other CAD/CAM and pressed materials.[54,60,73] A study evaluated the damage tolerance of different dental materials and showed that the damage tolerance of PICN was higher when compared to other ceramics for CAD-CAM, like veneering ceramics.[55,73]

With respect to optical properties, the shrinkage of the curing resin results in interfacial stresses occurring between the ceramic framework and the polymer resulting in debonding and leading to a higher opacity because of the gaps developed at the interface. The selection of resin, the application of high pressure during the curing phase, and the silanization process enhanced bonding and helped overcoming the aesthetic problems by increasing the translucency of the material.[64] However, Enamic has been shown to be less translucent than IPS e.max or Lava Ultimate (3M ESPE, St Paul, USA).[74] Previous

works have also shown that the surface of PICN is not as glossy as those obtained for IPS e.max or Lava Ultimate. Nevertheless, the stain resistance of PICN was superior than that measured for Lava Ultimate and inferior than that reported for IPS e.max.[56,75]

Clinical simulations show promising lifetime results for PICN. A chewing simulation of five years demonstrated that none of the Enamic crowns failed, while six IPS e.max CAD had minor cracking and twelve Vita Mark II restorations revealed significant crack failures.[64] In a cyclic fatigue experiment of 500,000 cycles, Enamic performed as well as a lithium disilicate glass-ceramic.[58,76] Based on the reduced elastic modulus of Enamic, this material is especially indicated for prosthetic treatments on stiff implants. Due to the inferior optical properties, PICNs are more suitable in the molar than in the anterior region.

Novel processing technologies

CAD-CAM refers to a computer system that is used to both design and manufacture a dental restoration. CAD technology uses a software to define the shape and dimensions of the restoration, while CAM technology takes the designed model to a computer numeric control (CNC) machine to manufacture the restoration, usually from a block made of a dental material (subtractive manufacturing).

Currently, the production of metal-free restorations using polycrystalline ceramic infrastructures (*e.g.*, Y-TZP) depends on the use of the CAD-CAM systems.[77] The introduction of CAD-CAM milling systems for the production of restorations with these polycrystalline ceramics allowed their use in prosthetic restorations with greater reliability, since the only manufacturing technique available in the past was slip-casting, which resulted in a greater number of defects and cracks in the microstructure of the final restorations.[78]

CAD-CAM systems have been used in Dentistry for almost 30 years,[79] and during this period different machines have been launched, as these systems are constantly evolving and producing restorations with much better adaptation.[80,81] Moreover, the evolution of CAD-CAM system have allowed their use to produce restorations with other materials such as veneering ceramics, resin composites and metal alloys.[77,82]

Among dental CAD-CAM systems, there are two types of techniques for producing restorations. The first one is the machining of the prosthetic restoration from a block of the sintered material, while the second consists of machining a block in a partially sintered state with subsequent final sintering in a specific furnace. Both techniques are used in dentistry and each of them have their advantages and disadvantages.

Machining a block of sintered material provides the restoration with a greater precision of its contours and shape in addition to saving clinical time, since the restoration does not require an additional heat treatment. However, when machining a material with high strength like polycrystalline ceramics, both the wear of the machining unit tools and the machining time are very high. Also, machining brittle materials such as dental ceramics can lead to the formation of microcracks and surface defects.[83] On the other hand, when the restoration is produced from a partially sintered block, there is the advantage of promoting healing of machining microcracks during the subsequent sintering process.[84] This processing technique is expected to have a shorter machining time for a less dense material, but one must keep in mind that the final sintering will promote dimensional changes due to shrinkage, which may lead to prosthetic restoration misfit.[85]

Although the CAD-CAM systems described above are already well established in the dental market, they present a major drawback related to the great waste of material upon machining. The waste corresponds to approximately 90% of the prefabricated block for a typical restoration[86] and leftovers from these dental restorations are not reusable. Therefore, new technologies have been developed to overcome this problem. Some of them produce the restoration by means of adding layers instead of grinding pre-fabricated blocks (additive manufacturing).

Addition CAD-CAM systems, also called "solid free-form fabrication", are still a focus of research and development for polycrystalline ceramic materials and there are three techniques that have stood out recently.[86,87,88,89,90] These techniques are: 1) Selective Laser Sintering or Melting, 2) Direct 3D Printing and 3) Stereolithography.

The Selective Laser Sintering or Melting is an already well-established technique for metal alloys,

but is still in development for polycrystalline ceramics (BEGO Medifacturing® System, BEGO Medical GmbH, Bremen, Germany). In this technique, the laser beam sinters thin layers of a ceramic from a container filled with powder to create a single coping or framework, in which each layer represents a cross section of the CAD model.[86] Direct 3D Printing is similar to a traditional inkjet printer, performing the direct printing of a ceramic suspension, allowing the generation of dense green bodies with high resolution, and producing complex shapes.[90,91]

Stereolithography is frequently used nowadays, and has already evolved enough to allow production of more complex ceramic pieces, whereas the previously mentioned techniques are in the early development stage for dental applications. Stereolithography is similar to 3D printing, however it makes use of a suspension containing ceramic particles mixed with a resin components (acrylates or epoxy monomers).[87,88] This resin part is polymerized during printing to shape the solid object and is subsequently removed during the ceramic sintering process. The great advantage associated with all additive techniques is that they provide minimal or no material waste. One still existing disadvantage of all additive methods to date is the rough surface quality and the poor fit or marginal precision.

Considering the mentioned additive methods, Direct 3D Printing is the technique that stands out,

as the equipment is relatively more accessible and allows for the production of a dense green body ready for sintering. In 2009,[91] using a modified inkjet printer, a zirconia crown was manufactured with sufficient mechanical properties to be used in the oral cavity. The impression of the posterior dental crown was performed using a cartridge filled with a 27 vol% solid content of zirconia-based ceramic suspension. Variations of the Direct 3D Printing technique have also been studied, the so-called "Robocasting".[89] Both techniques are very similar, differing only in the way the deposition of the ceramic suspension is made. Robocasting uses extruded filaments instead of ejected droplets to produce the object.

Conclusion

Dental ceramics and processing technologies have evolved significantly in the past ten years, with most of the evolution being related to new microstructures and CAD-CAM methods. Also, a trend towards the use of monolithic restorations has changed the way clinicians produce all-ceramic dental prostheses, since the more aesthetic multilayered restorations unfortunately are more prone to chipping or delamination. Composite materials processed via CAD-CAM have become an interesting option, as they have intermediate properties between ceramics and polymers and are more easily milled and polished.

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