Ceramics International 48 (2022) 4604–4613

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Wear of zirconia/leucite glass-ceramics composites: A chewing simulator study

A.C. Branco [a,b,c], T. Santos [d], M. Polido [c], R. Colaço [e], A.P. Serro [a,c,*], C.G. Figueiredo-Pina [b,c,f]

[a] CQE, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal
[b] CDP2T, Escola Superior de Tecnologia de Setúbal, Instituto Politécnico de Setúbal, Setúbal, Portugal
[c] CiiEM, Instituto Universitário Egas Moniz, Monte de Caparica, Portugal
[d] HiTEC, Porto Salvo, Portugal
[e] IDMEC e Departamento de Engenharia Mecânica, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal
[f] CeFEMA, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal

ARTICLE INFO

Keywords:
Leucite
Zirconia
Composites
Chewing simulator
Tribological behaviour
Wear

ABSTRACT

Leucite and zirconia are commonly used in the production of prosthetic dental materials. Leucite presents attractive optical properties but low toughness and wear resistance, which limits its use. Zirconia has much higher toughness, but due to aesthetic reasons and ageing issues, needs to be glass veneered. Chipping of such veneer is usually responsible for the abnormal wear induced on the antagonist teeth. Leucite reinforced with 25% of nano-zirconia is a promising alternative to overcome these issues, allowing the production of dental restorations without veneer. This study aims to investigate if leucite-zirconia composites have suitable optical, mechanical and tribological properties to be used in dental restoration. Samples with different compositions of leucite and/or nano-zirconia were produced by unidirectional compression and characterized concerning density, surface morphology, roughness, hardness, toughness, and translucency. Wear tests were performed in a chewing simulator using human cusps as counterbodies. Tests were also performed in glazed zirconia for comparison. 25% ZrO_2 leads to the lowest wear of the tribological pair among the studied systems, except 100% ZrO_2. This can be attributed to the toughening effect of zirconia and reduced size of third body particles. Abrasion was the main wear mechanism observed in this pair. In addition, this was the composite that presented the highest translucency.

1. Introduction

Due to the aesthetic similarity with natural teeth, ceramic materials are the ultimate choice to repair/replace damaged/lost dental tissues. Among them, zirconia is one of the most used for dental restorations, mainly due to its toughness [1,2]. However, zirconia frameworks need to be coated with a glass veneer (glaze) to improve their optical properties [3]. One of the major issues of these type of coatings arises from their inability to support the high loads during biting and mastication processes, suffering chipping [4]. An alternative to overcome this problem is to use monolithic structures produced with vitroceramics, like leucite and lithium disilicate, which present excellent optical properties [5–7]. However, their use in crowns is usually limited to restorations applied to the anterior part of the dental arcade where the mechanical requirements are lower [8]. In fact, both leucite and lithium disilicate materials can experience brittle fracture and chipping wear mechanisms that lead to the formation of third body particles, dramatically increasing the antagonist natural teeth wear [9–11].

In order to improve the mechanical resistance of vitroceramics for dental applications, several strategies have been followed to delay or suppress the propagation of cracks towards the interface [12,13]. One of the approaches that has been widely investigated is the reinforcement of vitroceramics with high toughness ceramic particles (e.g., zirconia and alumina), resulting in a composite material with enhanced properties. Huang et al. [14] observed that the flexural strength and fracture toughness of a lithium disilicate glass-ceramic reinforced with 15% wt. zirconia increased from 310 MPa to 340 MPa and from 2.2 MPa $m^{1/2}$ to 3.5 MPa $m^{1/2}$, respectively, relatively to lithium disilicate glass-ceramic. Santos et al. [13] evaluated the mechanical properties of porcelain before and after the addition of zirconia particles and observed that the

* Corresponding author. CQE, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal.
E-mail address: anapaula.serro@tecnico.ulisboa.pt (A.P. Serro).

https://doi.org/10.1016/j.ceramint.2021.10.247
Received 10 September 2021; Received in revised form 26 October 2021; Accepted 30 October 2021
Available online 5 November 2021

material containing 30% of zirconia particles led to the highest flexural strength (218 MPa) and fracture toughness (2.1 MPa $m^{1/2}$) values, which were significantly higher than those obtained for porcelain without reinforcement particles (98 MPa and 0.9 MPa $m^{1/2}$, respectively). In another study, Elsaka et al. [15] investigated the mechanical performance of two types of CAD/CAM glass-ceramics: zirconia reinforced lithium silicate glass-ceramic (Vita Suprinity) and monolithic lithium disilicate (IPS e.max CAD). The first one showed higher fracture toughness (2.3 MPa $m^{1/2}$), flexural strength (444 MPa), elastic modulus (70.4 GPa), and hardness (6.5 GPa) compared with lithium disilicate glass-ceramic (2.1 MPa $m^{1/2}$, 348 MPa, 60.6 MPa and 5.5 GPa, respectively).

Concerning the tribological behaviour of reinforced vitroceramics, it has been poorly addressed and only simple configuration wear tests have been used. Santos et al. [16] carried out pin-on-plate tests with dental glass–ceramics reinforced with different contents of zirconia particles against alumina, and concluded that 30% wt. zirconia content led to the lowest specific wear rate. In another work, the same authors studied the tribological behaviour of a dental glass-ceramic reinforced with zirconia agglomerates (ZA) and pre-sintered zirconia particles (ZP) [17] and observed that the wear of the glass-ceramic reinforced with ZP was much lower. They attributed it to the uniform dispersion of zirconia particles within the glass matrix, which leads to a load transfer reinforcing mechanism from the matrix to the reinforcement. Yilmaz et al. [18] studied the wear behaviour of two types of glass-ceramics, lithium disilicate (IPS e.max CAD) and zirconia-reinforced lithium silicate (Vita Suprinity), against alumina and observed that Vita Suprinity presented a higher wear resistance than IPS e.max CAD. This was explained by the fact that Vita Suprinity has a homogeneous distribution of zirconia particles into the ceramic material. In contrast, IPS e.max CAD presents a structure with needle-shaped fine-grained crystals embedded in a glassy matrix and after the wear tests, deep microcracks were observed, which suggested fatigue wear.

The works reported above refer to the mechanical and tribological behavior of zirconia-reinforced lithium silicate materials. As far as the authors know, there are no studies regarding leucite reinforced materials. Thus, the aim of this work is to evaluate the effect of the addition of different contents of zirconia nanoparticles to leucite on the wear performance of the pair tooth/prosthesis. A wide characterization was performed to identify the composite that minimizes the wear and understand the associated wear mechanisms.

Leucite-reinforced glass-ceramics (in the SiO_2–Al_2O_3–K_2O system) contains up to 45% by volume of tetragonal leucite ($KAlSi_2O_6$) within a glass matrix made of feldspathic porcelain. The introduction of leucite crystals in the feldspar glass improves the mechanical properties of the glass ceramic for dental applications, since the presence of a crystalline phase delays or suppresses the propagation of cracks through the absorption of the fracture energy, thus enhancing the toughness and strength of the material [19,20]. Leucite glass-ceramics are mainly used in veneers, inlays and onlays, and in anterior crowns. Although they present more than the double of the strength of porcelains, they are still not suitable to be used in posterior fixed dental prosthesis (bridges) [21]. For this application, reinforced leucite glass-ceramics could be used as a cheaper alternative to zirconia-reinforced lithium disilicate.

2. Materials and methods

2.1. Teeth preparation

Ten permanent healthy human molars/wisdom teeth without caries, damages or fillers/sealants were provided by the Human Teeth BioBank from University Dental Clinic Egas Moniz and used in the present study (Teeth donated with informed consent of patients. Research work approved by the Ethical Commission Egas Moniz, from Instituto Universitário Egas Moniz, with the Ref nº 1001/2021). Before extraction, patients signed informed consents regarding the collection of the teeth for research purposes. The teeth were immersed in 1% chloramine-T trihydrate solution (VWR, ≥98%) at 4 °C during one week for disinfection. After, they were brushed with toothpaste to remove the bacterial plaque and food scraps and were stored in distilled and deionized (DD) water at 4 °C to avoid dehydration, till further use. Before the chewing simulation tests, teeth were equally cut into 4 parts to isolate the cusps and then each cusp was fixed in a thermosetting phenol formaldehyde resin (Bakelite, Vertex Castapress).

2.2. Ceramic prosthetic samples production

Leucite-based samples were produced with different amounts of zirconia reinforcement: 25% ZrO_2, 50% ZrO_2 and 75% ZrO_2 (wt%), using leucite glass-ceramic powder (IPS Empress Esthetic Veneer Incisal Opal MT, Ivoclar Vivadent) and yttria (3% mol) partially stabilized tetragonal zirconia powder (SF YSZ-1011, Zircomet). Samples containing only leucite (100% Leu) and only zirconia (100% ZrO_2) were also produced for comparison purposes. To produce the samples, firstly a polyvinyl alcohol (PVA) solution (4.5 wt%) was prepared by dissolution of the PVA (Kuraray Poval, Frankfurt, Germany) in DD water, at 95 °C. Then, a paste of zirconia and a paste of leucite were prepared by dispersing the respective ceramic powders (60 wt%) in this solution. The obtained pastes, which contain 3% (w/w) of the binder PVA relatively to the solid loading weight, were left to homogenize in a magnetic stirrer for 30 min. Composites were produced by mixing the previous prepared pastes in the required proportions, in a magnetic stirrer for 30 min. The pastes were poured in cylindrical silicon moulds (13 mm diameter) and left for 2 days at room temperature to evaporate most of the water. The obtained discs were taken from the moulds and submitted to unidirectional compression in an evacuable pellet die set, applying a constant load of 3 tons for 1 min (220 MPa). The 100% ZrO2 samples were sintered at 1500 °C, 100% Leu at 850 °C, and 25% ZrO_2, 50% ZrO_2 and 75% ZrO_2 at 1000 °C, for 2 h, with a heating rate of 10 °C/min in all cases, being the cooling done inside of the furnace until reaching room temperature. All samples were polished using silicon carbide sandpapers with granulometries up to 4000 mesh, followed by polishing until diamond paste 3 μm. Finally, samples were washed with DD water and then dried with nitrogen gas.

Some 100% ZrO_2 samples were manually coated with a ceramic glaze (IPS e.max Ceram Glaze Paste 3 g, Ivoclar Vivadent) layer (thickness ≈ 50 μm) and submitted to 430 °C for 30 min.

2.3. Samples characterization

2.3.1. Density

Samples' density (ρ_{sample}) was determined based on the Archimedes method, from their weight in air (m_{air}) and immersed in water (m_{water}) (AND GR-200 balance), considering the density of water at room temperature (ρ_{water}):

$$\rho_{sample} = \frac{m_{air}}{m_{air} - m_{water}} \rho_{water} \quad (1)$$

Four samples of each type were used for measurements.

2.3.2. Morphology

The leucite and zirconia powders, prosthetic materials and dental surfaces' morphology was observed by scanning electron microscopy (SEM, JSM-7001F) using a voltage of 15 kV and a vacuum of ~8×10^{-4} Pa. Chemical analysis was performed by energy dispersive spectroscopy (EDS). Prior to SEM observation, all samples were previously coated with a thin film of Au/Pd.

2.3.3. Surface roughness

The surface roughness of samples was estimated using a profilometer (Profilm, Filmetrics) with an objective of 20X, in envelop peak mode, using 0.07 mm and 0.15 mm for backscan and scan length, respectively.

Values were obtained from linear profiles with a length range 0.85–1.5 mm in areas free of pores.

2.3.4. Hardness and toughness

Vickers hardness was measured using a microdurometer (HSV-30 Shimadzu). A load of 5 N and a dwell time of 15 s was applied for all samples except 100% Leu which only resisted to a load of 1 N. Five indentations in different zones were performed on four samples of each type.

Fracture toughness was determined from the indentations' cracks observed by SEM. The crack's length was measured using ImageJ software and the following equation was used to estimate the fracture toughness (K_{IC}) [22,23]:

$$K_{IC} = 0.0726 \times \frac{P}{c^{3/2}} \tag{2}$$

P is the indentation load and *c* is the length of the most severe produced crack in each indentation mark.

2.3.5. Translucency

The translucency parameter (TP) of the samples was evaluated using a spectrophotometer (VITA EasyShade 2.0). Measurements were performed over white ($_W$) and black ($_B$) backgrounds to obtain the color coordinates of the CIE system: L*, a* and b*. L* is the lightness, a* corresponds to the shade and saturation in the red–green axis and b* to the saturation in the blue–yellow axis [ref]. TP can be calculated from the following equation [24]:

$$TP = \left[(L_B{}^* - L_W{}^*)^2 + (a_B{}^* - a_W{}^*)^2 + (b_B{}^* - b_W{}^*)^2\right]^{1/2} \tag{3}$$

The translucency of dental commercial zirconia (yttria (3% mol) stabilized zirconia blocks Ice Zirkon Translucent from Zirkonzahn) and of natural human tooth was also measured, for comparison purposes.

2.3.6. Tribological behaviour

Wear studies were performed in a chewing simulator (CS-4.2 SD Mechatronik), with artificial saliva at room temperature, using dental cusps against the produced ceramic samples. Artificial saliva (pH 6.9–7.0) was prepared by dissolving the following reagents (all from Sigma-Aldrich) [25] in DD water: sodium sulphide nonahydrate ($Na_2S•9H_2O$, 0.005 g/L), sodium chloride (NaCl, 0.4 g/L), potassium chloride (KCl, 0.4 g/L), sodium phosphate monobasic dihydrate ($NaH_2PO_4•2H_2O$, 0.69 g/L), urea (NH_2CONH_2, 1 g/L), sodium phosphate dibasic (Na_2HPO_4, 0.8 g/L), calcium chloride ($CaCl_2$, 0.2 g/L). Each test consisted of 360,000 chewing cycles (correspondent to approximately 1.5 year of human mastication [26]). A vertical load of 50 N was applied, since it falls in the range of the typical masticatory loads observed *in vivo* [27–30] and has been used in some *in vitro* studies as a reference load during chewing simulation tests [18,31,32]). The tests were carried out with a vertical speed 40 mm/s, horizontal speed 20 mm/s, vertical movement 2 mm, horizontal movement 0.7 mm and frequency ~1 Hz. Eight tests were carried out per system.

The wear volume of the ceramic prosthetic samples was estimated from profilometer images (Profilm, Filmetrics). For that, several images (1×0.85 mm^2) of the wear track were obtained in envelop peak mode, using 0.1–0.3 mm and 0.15–0.5 mm for backscan and scan length, respectively, and stitched with the Profilm online software. In order to determine the cusps' wear, a 3D scanner (Scanner S300 Arti – Zirkonzahn, Fig. 1) was used. The wear volume was estimated by overlapping the 3D scans of the cusps obtained before and after the wear tests, using the Autodesk Netfabb Premium 2021 software. The wear coefficients (*K*) for both prosthetic samples and dental cusps were estimated through:

$$K = \frac{V}{SxL} \tag{4}$$

where *V* corresponds to the volume loss, *S* to the sliding distance and *L* the applied load.

SEM and EDS analysis were performed on the worn surfaces to infer about the wear mechanisms.

2.4. Statistical analysis

Statistical analysis was performed using Excel statistical tools. Shapiro-Wilk test was carried out to verify the normality of the results. ANOVA (one-way analysis of variance) was done to compare three or more groups, while t-Student test was applied to compare two independent groups. The level of significance chosen was 0.05.

3. Results

3.1. Leucite and zirconia powder characterization

The powders' particle morphology is depicted in Fig. 1. It can be observed that leucite particles (Fig. 1A) present mostly an angular shape, with sizes that range from 500 nm to 70 μm. On the other hand, zirconia particles (Fig. 1B) are round and much smaller than leucite particles (~160 nm).

3.2. Prosthetic materials density

The density of the ceramic samples is shown in Fig. 2. Statistically significant differences were observed among the different systems ($p < 0.001$). It is observed a tendency of increase in the density as the amount of reinforcement increases. However, 25% ZrO_2 and 50% ZrO_2 present similar densities ($p = 0.87$).

3.3. Prosthetic materials surface morphology

Fig. 3 shows the morphology of the ceramic samples surface. Leucite presents a glass matrix reinforced with leucite crystals (darker sites), which are randomly distributed. 25% ZrO_2, 50% ZrO_2 and 75% ZrO_2

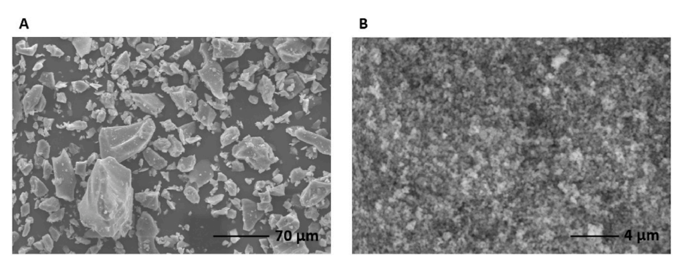

Fig. 1. SEM images of leucite (A) and zirconia (B) powder.

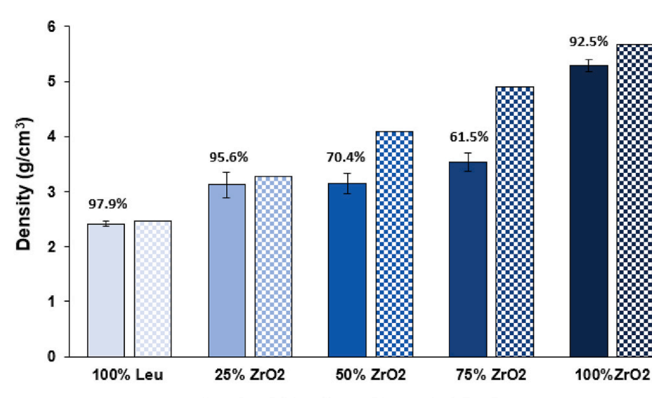

Fig. 2. Theoretical and experimental density of the ceramic samples. The values presented over the bars quantify in percentual terms the experimental densities relative to the correspondent theoretical ones.

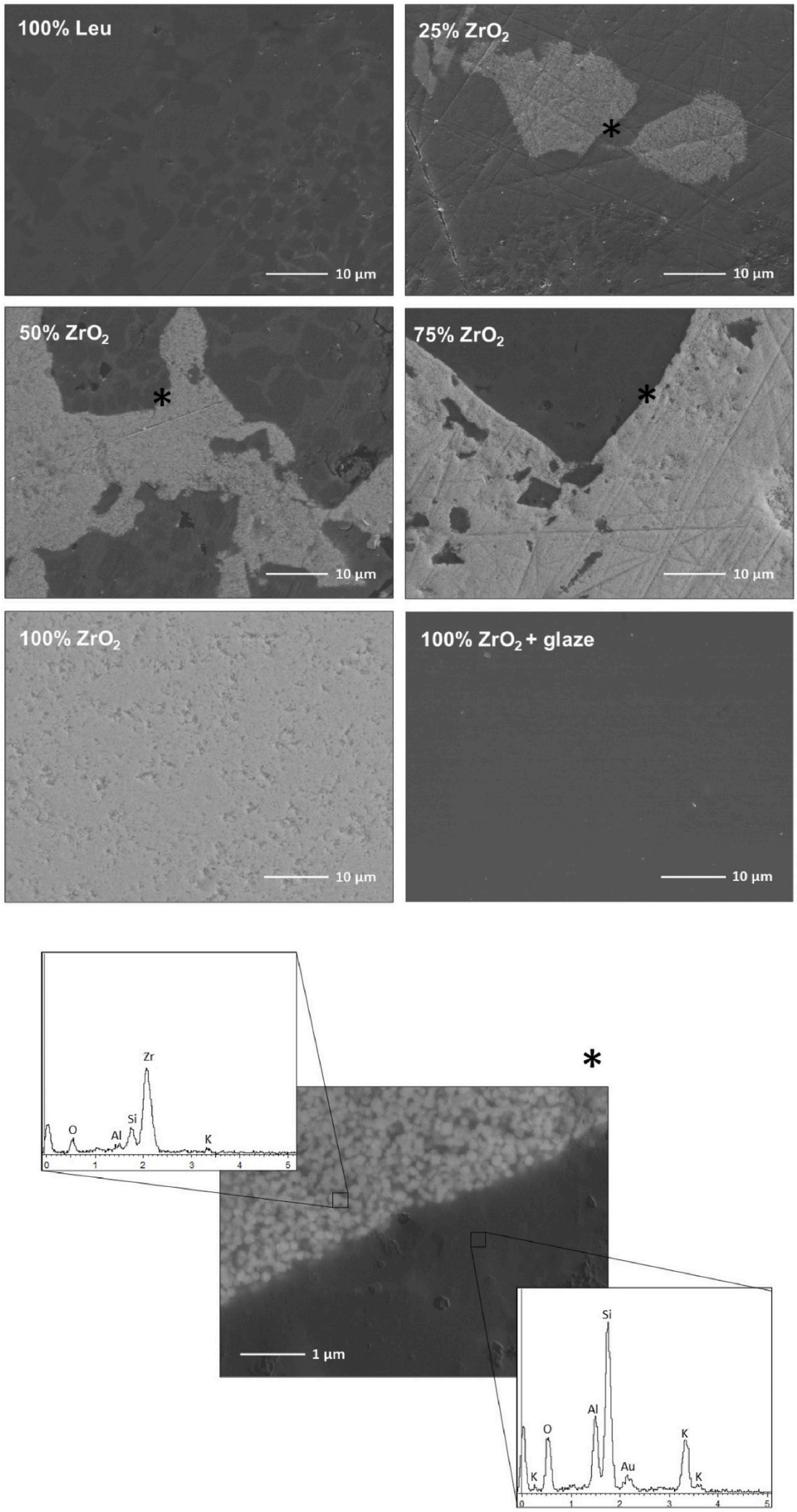

Fig. 3. SEM images of the ceramic samples surface. * represents a typical magnification of the interface between zirconia rich zone and leucite with the respective EDS spectra showing the respective elemental composition.

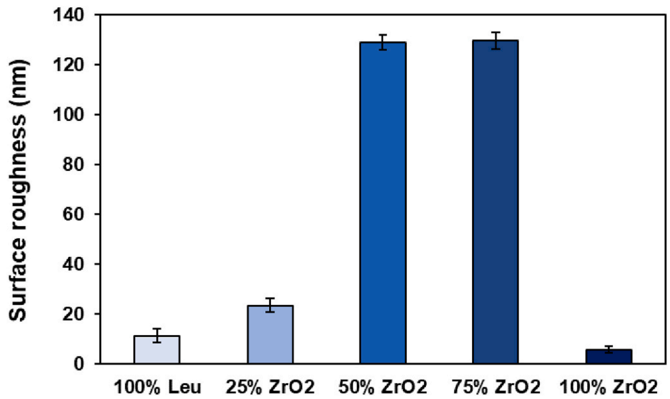

Fig. 4. Surface roughness of ceramic samples.

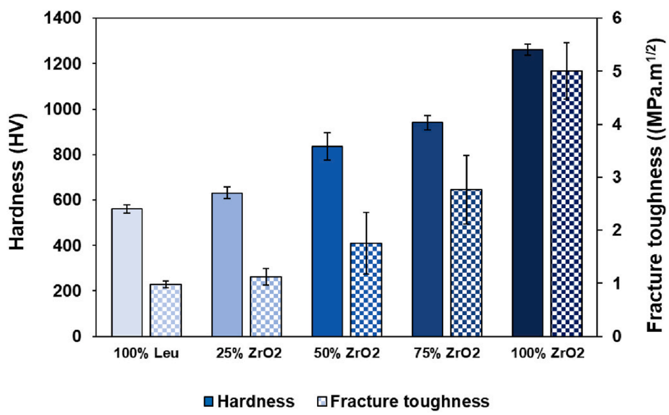

Fig. 5. Hardness and fracture toughness of the ceramic samples.

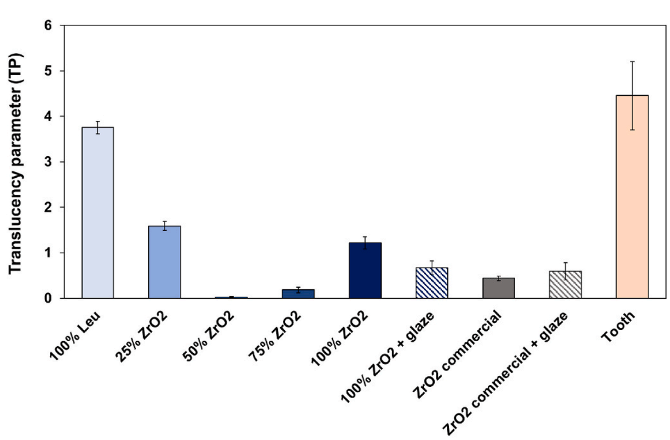

Fig. 6. Translucency parameter of the prosthetic samples and human tooth.

present two main areas: zirconia agglomerates (lighter areas) roundly dispersed in a leucite glass matrix (darker areas), with a highly continuous interface between the two zones. In the composite samples, within the zirconia agglomerates there is a tiny amount of leucite glass ceramic surrounding most of the zirconia nanoparticles (see insert). 100% ZrO_2 presents an irregular surface with small defects randomly distributed. Concerning the coating of zirconia with glaze, it presents a homogeneous polished appearance without porosity signs.

3.4. Prosthetic materials surface roughness

Regarding surface roughness (Fig. 4), 100% ZrO_2 presents the lowest average value among the studied systems, while 50% ZrO_2 and 75% ZrO_2 have the highest roughness, being similar between them ($p = 0.815$). 25% ZrO_2 presents slightly higher roughness than 100% Leu ($p = 0.044$).

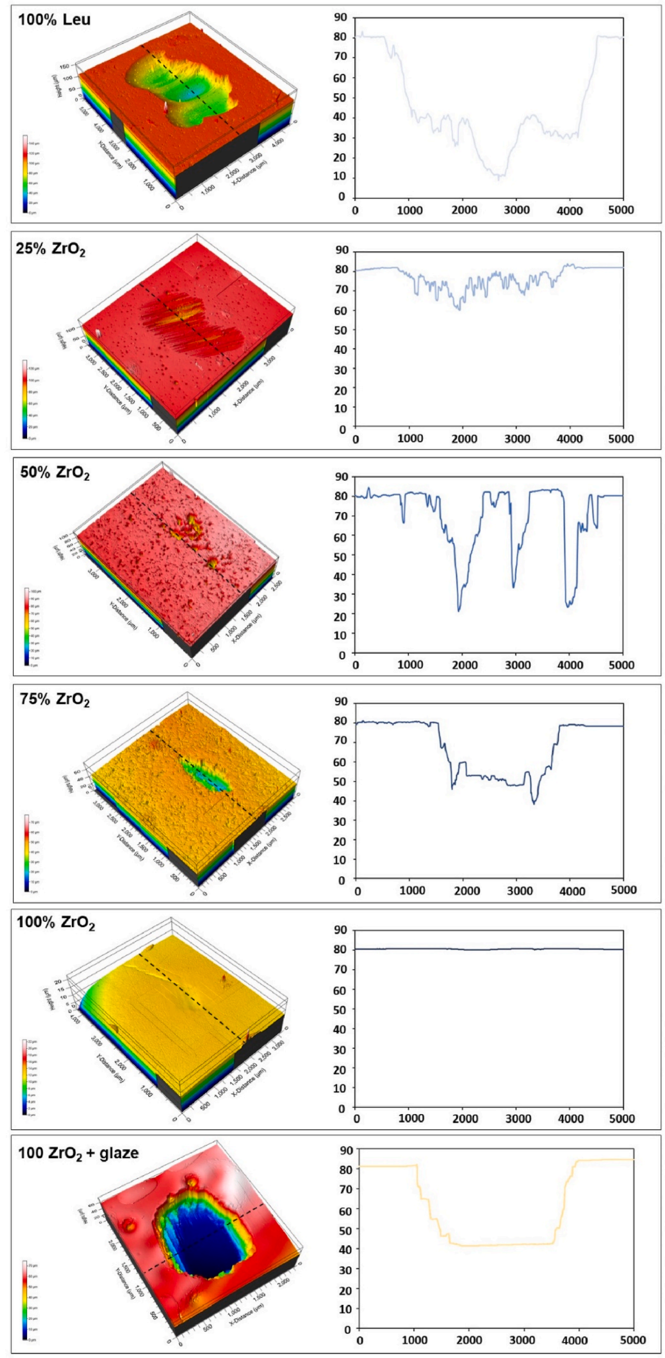

Fig. 7. Profilometer images and 2D profiles of the ceramic materials' wear scars obtained after chewing simulation tests.

3.5. Prosthetic materials hardness and toughness

The samples hardness and fracture toughness are depicted in Fig. 5. It can be observed that these two properties are highly determined by the content of the reinforcing agent in the composite's composition: the higher the zirconia amount, the higher the hardness and fracture toughness.

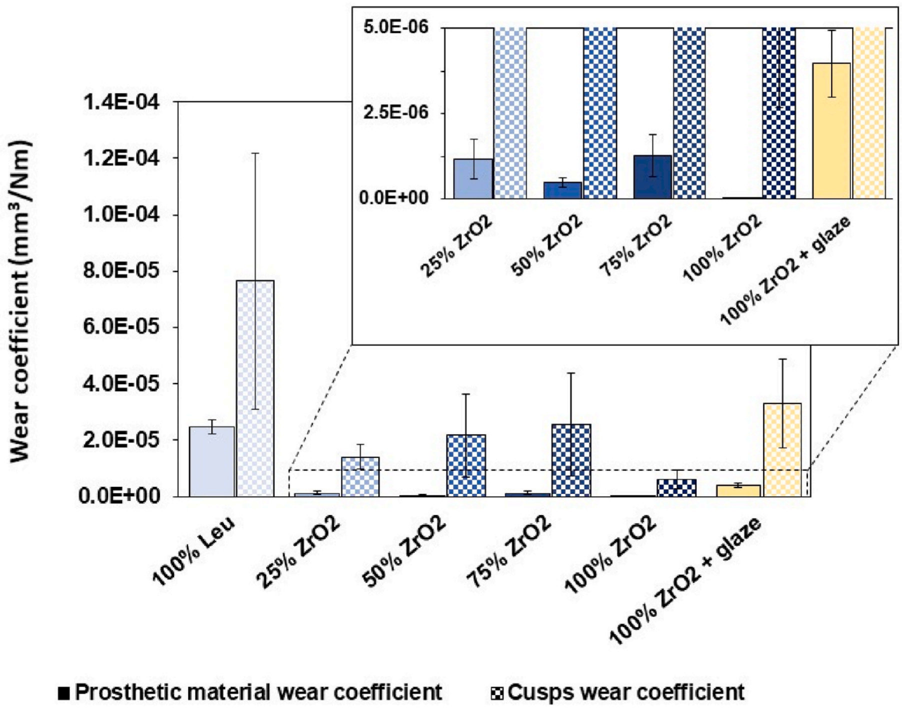

Fig. 8. Prosthetic material and cusps wear coefficients.

3.6. Prosthetic and dental materials translucency

The translucency parameter (TP) of the materials is presented in Fig. 6. Leucite samples (100% Leu) presented the highest translucency degree among the prosthetic materials, comparable to the natural tooth ($p = 0.07$), followed by 25% ZrO_2 which led to a value slightly higher than 25% ZrO_2 ($p = 0.001$). In turn, 50% ZrO_2 were the less translucent material. Commercial ZrO_2 presented a translucency 2.8 times lower than 100% ZrO_2. The glaze coating led to similar translucency values ($p = 0.61$), independently of the underlying substrate, giving rise to intermedium values between commercial ZrO_2 or 100% ZrO_2.

3.7. Tribological behaviour

3.7.1. Wear coefficient

Fig. 7 depicts profilometer images and the corresponding 2D profiles of the wear scars obtained after chewing simulation tests for each system. It can be observed that all systems present irregular and different wear scar shapes. 100% Leu show the highest wear depth (≈70 μm) and 100% ZrO_2 presents neglectable wear depth (≈0.8 μm). 75% ZrO_2 and 50% ZrO_2 show wear scars of intermediate depth, higher to that observed on 25% ZrO_2. The wear tests against the glazed zirconia showed that in the contact area with the cusp, the coating (with a thickness ≈ 40 μm) was removed in large extent, exposing the underlying zirconia.

Concerning the ceramic materials wear coefficient (Fig. 8), 100% Leu presents the highest wear while 100% ZrO_2 presents minimal wear. No statistical differences were found among the different composite system ($p = 0.12$).

The cusps wear coefficient is shown in Fig. 8. The results obtained with the cusps tested against 100% Leu present a high dispersion, but its average is much higher than those observed for the remaining systems. Contrarily, 100% ZrO_2 led to the lowest cusps wear coefficient. It was found that, for the composite materials, the wear of the antagonist cusps increased with the reinforcement content. Zirconia glazed samples led to a wear coefficient similar to those induced by 50% ZrO_2 and 75% ZrO_2 ($p = 0.48$) and higher than for 25% ZrO_2 ($p = 0.03$).

3.7.2. Worn surfaces analysis

SEM images of the ceramic samples (Fig. 9) show that 100% Leu presents mainly parallel scratches and accumulation of dental debris (see EDS spectra in the insert, rich in Ca and P). In 25% ZrO_2, agglomerates' zirconia particles became protruded and scratches in the sliding direction are visible close to the interface between the agglomerates and leucite zones. Features associated to full agglomerate pull out are also noted. Both 50% ZrO_2 and 75% ZrO_2 samples present a high adhesion of dental material and signs of fracture. The surface of 100% ZrO_2 has essentially a polished appearance without signs of abrasion, being clearly visible the adhesion of dental material (see EDS). Regarding the glaze coating, since it was widely removed from the contact zone, only the transition area in the wear track was analyzed. Some pores can be identified in the internal structure of the glaze as well as adhered dental particles (see insert and EDS).

The SEM images of the dental cusps after wear testing (Fig. 10) shows that the cusps tested against both 100% Leu and 25% ZrO_2 samples present parallel grooves. A detailed analysis reveals that 100% Leu induces in the cusps' surface the formation of a large number of craters which extend through the sliding direction and adhesion of dental and leucite particles (see EDS spectra in the insert). In contrast, 25% ZrO_2 leads to the appearance of aligned scratches and some dental wear particles (see EDS spectra in the insert) are also visible on the surface. The cusps tested against 50% ZrO_2, 75% ZrO_2 and 100% ZrO_2 show polished surfaces. However, while in the former two cases the surfaces present scratches confined to a specific area and some material detachment, in the last case fractures are visible on the cusps' edges.

The wear tests against glazed zirconia led to the appearance of scratches and deep fractures, mainly in the periphery of the cusps. Besides, adhesion of dental material and glaze is also observed (see inserts).

4. Discussion

Leucite glass-ceramics have been used in dentistry mainly due to their ability to mimic the optical properties of dental tissues. However, in the literature, cases of failure due to fracture of the prosthetic material

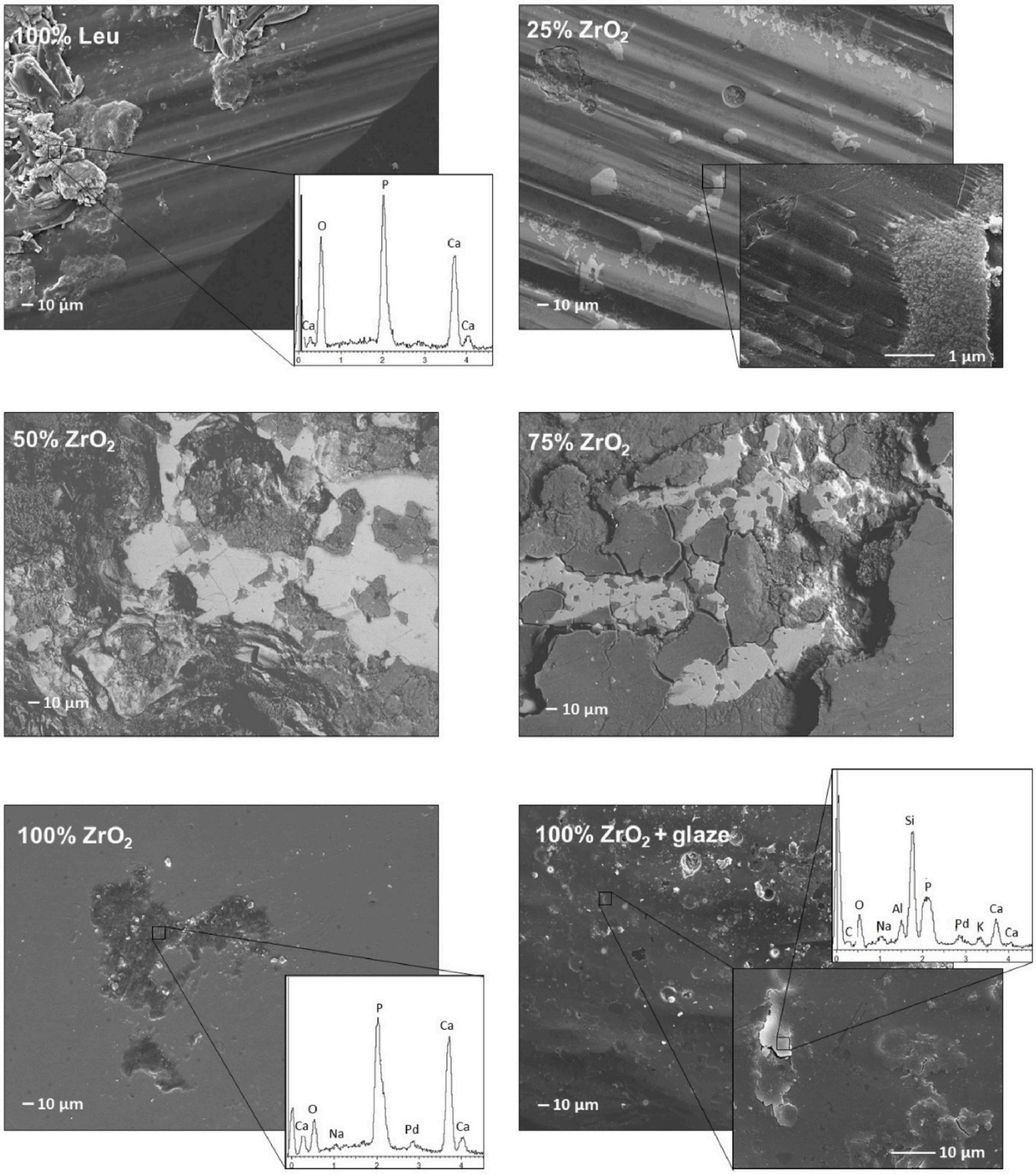

Fig. 9. SEM images of the ceramic samples and glaze surfaces after wear testing. EDS spectra show the elemental composition of the marked areas.

are often reported [9,33–35]. Moreover, tribological tests show that these materials may lead to abnormal wear of the antagonist dental surfaces [9,35,36]. In order to improve the tribomechanical performance of vitroceramics, zirconia particles can be added as reinforcement agents. In this study, different amounts of zirconia were incorporated in leucite glass-ceramics, and the effect on the tribological behaviour of the prosthetic material/tooth pair was investigated.

Density measurements of the produced materials show that 100% Leu and 100% ZrO_2 present similar densities to those reported in the literature: 2.47 g/cm^3 for leucite and 5.68 g/cm^3 for zirconia [4]. 25% ZrO_2 shows a density quite similar to the theoretical density (≈96%, Fig. 2). However, the other composites (50% ZrO_2 and 75% ZrO_2) show densities much lower than the theorical values, which can be explained by the high observed porosity (Fig. 7). Due to the asymmetry in the size and shape of the constituent powders (Fig. 1B), during the ceramic pastes preparation, the zirconia nanoparticles form clusters in the voids left by the larger and angular leucite particles. The sintering process leads to leucite partial melting (liquid phase sintering), which due to capillary forces wets the zirconia nanoparticles, keeping them agglomerated in a vitreous matrix (Fig. 3). Samples' porosity results from compaction issues, which are determined by factors such as size and shape of the particles, amount of each component, load and time of compression and humidity. The last, not only increases the friction between the particles during the compression process impairing the material densification, but also leads to the formation of pores during the sintering cycle due to vapor formation. The presence of pores increases surface roughness at a macro scale. It was also found that the composites, specially 50% ZrO_2 and 75% ZrO_2, present a higher interpore roughness (Fig. 4). The presence of hard and soft phases shall lead to differential wear between them during the sample surface's preparation (polishing), being the hard phase protruded.

Concerning the mechanical properties (Fig. 5), the results show that there is an increase of hardness and fracture toughness with the increase in zirconia content, which shall be related to the toughening effect of zirconia. In fact, it was observed that 100% ZrO_2 samples' hardness is approximately two-fold the hardness of 100% Leu, while the toughness is almost 5 times higher. Several studies report a similar behavior when lithium disilicate is reinforced with increasing amounts of zirconia [14,

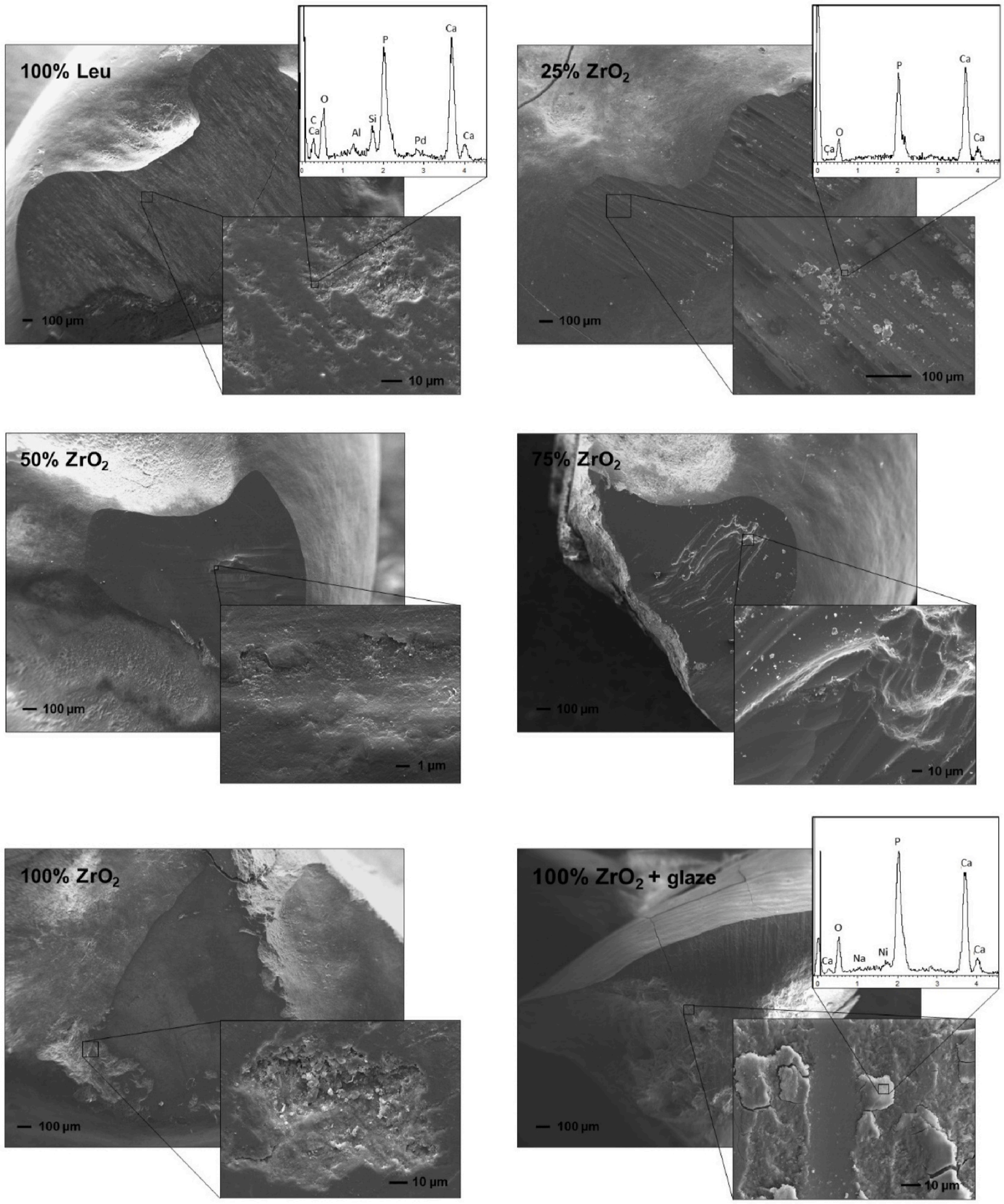

Fig. 10. SEM images of the cusps surface after wear testing. EDS spectra show the elemental composition of the marked areas.

15]. The obtained results show that 100% Leu and 25% ZrO_2 show the lowest hardness among the produced materials, with values that are close to the upper limit of those found in the literature for enamel (306–612 HV [4]). Both 100% Leu and 25% ZrO_2 presented a fracture toughness values that fall in the range found for enamel (0.7–1.5 MPa. $m^{1/2}$ [37]).

The analysis of the wear performance of the tribological pairs ceramic material/tooth shows that after the wear tests, leucite (100% Leu surfaces) present features associated with abrasion and dental wear debris accumulation (Fig. 9). In the opposite dental cusps, a change from abrasion to adhesion, followed by delamination and material transfer, shall have occurred during wear testing (Fig. 10). In the initial stages of wear, the asperity contact between the surfaces might lead to micro-fracture of leucite, due to its low toughness, producing three body particles that are able to plough/cut both contacting surfaces and origin the release of the debris. The continuous sliding results into adhesion of the dental debris onto both surfaces with leucite incorporation. Simultaneously, the adhesion between the two surfaces and the consequent detachment of material through delamination leads to the formation of craters on the cusp's counterface. Hutchings [38] states that in aqueous environments, some local plastic flow can occur due to the formation of softer oxide hydration layers, as well as tribochemical reactions, enhancing the materials' wear. This may explain the occurrence of some plough in the prosthetic worn surface.

The addition of zirconia to leucite led to a dramatic decrease of the wear of the prosthetic material and of the antagonist dental cusps (Fig. 8). This may result from the toughening effect of zirconia referred above, that prevents fracture and consequently reduces the formation of wear debris from the prosthetic material. However, no significant differences were found in the wear coefficients of the three composite materials (Fig. 8), which shall be related with the wear mechanisms that occur in each system. In the presence of 25% ZrO_2, the wear of the leucite matrix (which presents a lower hardness) origins the pull out of the zirconia nanoparticles and small agglomerates that cut/plough the surrounding leucite surface, leading to the abrasion not only of the prosthetic material but also of the dental surface (Figs. 9 and 10). The remaining agglomerates deflect the trajectory of the third body particles, protecting the area behind them. In 50% ZrO_2 and 75% ZrO_2, the zirconia patches present some fractures, leading to a higher tendency to the release of bigger particles from the worn surface. Therefore, the ploughing action on the dental surface will be higher than that of the smaller zirconia hard particles of 25% ZrO_2, being probably this the main reason for the higher average values of the wear coefficient obtained for dental cusps (Fig. 8). Besides, the higher hardness (Fig. 5) and roughness (Fig. 4) of 50% ZrO_2 and 75% ZrO_2 composites also contribute to the higher wear of the antagonist dental surfaces.

Regarding 100% ZrO_2, it suffered neglectable wear and induced the lowest wear on dental cusps, in agreement with what was found in previous works [1,9]. This is mainly due to the high toughness of zirconia that prevents surface microcracking and the formation of hard three body particles. SEM observation confirmed the absence of fractures on the surface of zirconia with some adhesion of dental material from the cusps wear (identified by EDS, Fig. 9). The antagonist cusps show a smooth surface suggesting that polishing wear shall prevail.

Even though the 100% ZrO_2tooth tribological pair presents the lowest wear, zirconia ageing in humid environment at physiological temperatures or higher may lead to the transformation from tetragonal to monoclinic phase, resulting in lower tribomechanical resistance [39, 40]. In order to protect zirconia and also due to aesthetic reasons, zirconia prostheses are usually coated with glaze. The obtained results show that the glaze coating leads to considerable wear of the antagonist dental surfaces, in agreement with what was found in other studies [1,3, 9]. The observed wear is in average higher than that induced by the three composite materials. Regarding the glazed material, it suffered the highest wear among all prosthetic materials, except from 100% Leu: glaze was extensively worn in the contact area with the cusp, leaving the underneath zirconia exposed.

Overall, 25% ZrO_2 is the material that presents the best tribological performance among the three composites, leucite and 100% ZrO_2 + glaze, since it led to lower wear of the prosthetic material and of the antagonist dental surfaces. In addition, its translucency is higher than the ZrO_2 commercial + glaze (Fig. 6), which is usually the ultimate choice in dental practice. Thus, 25% ZrO_2 material can be considered a potential candidate for dental restorations.

5. Conclusion

The suitability for dental application in terms of wear resistance of the leucite-nano zirconia composites was investigated. For that, samples with 0%, 25%, 50%, 75% and 100% of zirconia were produced and characterized concerning density, surface morphology, roughness, hardness, toughness, and translucency. Wear tests were performed in a chewing simulator using human cusps as counterbodies. Tests were also performed in glazed zirconia for comparison reasons. It was found that the density, hardness and toughness of the produced materials increase with the amount of zirconia. Concerning translucency, the highest values were found for leucite (100% Leu) followed by 25% ZrO_2. The value for the composite was 2.4 times higher than the one obtained for glazed zirconia. The tribological pair (ceramic material/tooth) that presented the lowest wear involved 100% ZrO_2 while the highest was found for leucite. Among the composites 25% ZrO_2 was the one that showed the lowest total wear. Leucite presented abrasion and dental wear debris accumulation and the opposite dental cusps showed features associated to delamination and material transfer. In 25% ZrO_2 the pull out of zirconia nanoparticles and small agglomerates led to abrasion of the two sliding counterfaces. The increase in the zirconia amount in the composites (50% ZrO_2 and 75% ZrO_2) resulted in higher dental wear, probably due to the release of larger prosthetic third body particles. 100% ZrO_2 almost did not suffer wear. Dental material transfer was observed on zirconia surface, while polishing wear was identified as the main wear mechanism in the cusps. The glaze was totally worn from the zirconia substrate during wear testing exposing the underlying material. The obtained results confirmed that glazing zirconia dental frameworks is not a suitable practice due to its low wear resistance. Besides, the reinforcement of leucite with 25% of zirconia is a good option, since it reduces the wear of both prosthetic material and antagonist teeth.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

To Fundação para a Ciência e a Tecnologia (FCT) for funding through the unit projects UIDB/00100/2020 (CQE), UIDB/04585/2020 (CiiEM), UID/CTM/04540/2020 (CeFEMA) and UIDB/50022/2020 (IDMEC/ LAETA), and for the PhD grant of A.C. Branco (SFRH/BD/145423/ 2019).

References

[1] A.C. Branco, R. Silva, T. Santos, H. Jorge, A.R. Rodrigues, R. Fernandes, S. Bandarra, I. Barahona, A.P.A. Matos, K. Lorenz, M. Polido, R. Colaço, A.P. Serro, C.G. Figueiredo-Pina, Suitability of 3D printed pieces of nanocrystalline zirconia for dental applications, Dent. Mater. 6 (2020) 442–455, https://doi.org/10.1016/j.dental.2020.01.006.

[2] A.C. Branco, R. Silva, H. Jorge, T. Santos, K. Lorenz, M. Polido, R. Colaço, A. P. Serro, C.G. Figueiredo-Pina, Tribological performance of the pair human teeth vs 3D printed zirconia: an in vitro chewing simulation study, Submitt. to J. Mech. Behav. Biomed. Mater. 110 (2020), 103900.

[3] C.G. Figueiredo-Pina, A. Monteiro, M. Guedes, A. Maurício, A.P. Serro, A. Ramalho, C. Santos, Effect of feldspar porcelain coating upon the wear behavior of zirconia dental crowns, Wear 297 (2013) 872–877, https://doi.org/10.1016/j.wear.2012.10.016.

[4] A.C. Branco, R. Colaço, C.G. Figueiredo-Pina, A.P. Serro, A state-of-the-art review on the wear of the occlusal surfaces of natural teeth and prosthetic crowns, Materials 13 (2020), https://doi.org/10.3390/MA13163525.

[5] K. Ledić, I. Majnarić, S.M. Ortolan, S. Špalj, S. Štefančić, K. Mehulić, Analysis of translucency parameter of glass-ceramics fabricated by different techniques, Acta Stomatol. Croat. 49 (2015) 27–35, https://doi.org/10.15644/asc49/1/4.

[6] M.-M. Manziuc, C. Gasparik, M. Negucioiu, M. Constantiniuc, A. Burde, I. Vlas, D. Dudea, Optical properties of translucent zirconia: a review of the literature, EuroBiotech J 3 (2019) 45–51, https://doi.org/10.2478/ebtj-2019-0005.

[7] Q. Zhang, S. Gao, C. Liu, Y. Lu, X. Chen, H. Yu, Evaluation of wear resistance of dental chairside CAD/CAM glass ceramics reinforced by different crystalline phases, J. Tribol. 141 (2019), https://doi.org/10.1115/1.4041536.

[8] I. Denry, J.A. Holloway, Ceramics for dental applications: a review, Materials 3 (2010) 351–368, https://doi.org/10.3390/ma3010351.

[9] F. Santos, A. Branco, M. Polido, A.P. Serro, Comparative study of the wear of the pair human teeth/Vita Enamic® vs commonly used dental ceramics through chewing simulation, J. Mech. Behav. Biomed. Mater. 88 (2018) 251–260, https://doi.org/10.1016/j.jmbbm.2018.08.029.

[10] C.G. Figueiredo-Pina, N. Patas, J. Canhoto, R. Cláudio, S.M. Olhero, A.P. Serro, A. C. Ferro, M. Guedes, Tribological behaviour of unveneered and veneered lithium disilicate dental material, J. Mech. Behav. Biomed. Mater. 53 (2016) 226–238, https://doi.org/10.1016/j.jmbbm.2015.08.007.

[11] L. Wang, Y. Liu, W. Si, H. Feng, Y. Tao, Z. Ma, Friction and wear behaviors of dental ceramics against natural tooth enamel, J. Eur. Ceram. Soc. 32 (32) (2012) 2599–2606, https://doi.org/10.1016/j.jeurceramsoc.2012.03.021.

[12] F.C. Serbena, I. Mathias, C.E. Foerster, E.D. Zanotto, Crystallization toughening of a model glass-ceramic, Acta Mater. 86 (2015) 216–228, https://doi.org/10.1016/j.actamat.2014.12.007.

[13] R.L.P. Santos, F.S. Silva, R.M. Nascimento, F.V. Motta, J.C.M. Souza, B. Henriques, On the mechanical properties and microstructure of zirconia-reinforced feldspar-based porcelain, Ceram. Int. 42 (2016) 14214–14221, https://doi.org/10.1016/j.ceramint.2016.05.195.

[14] X. Huang, X. Zheng, G. Zhao, B. Zhong, X. Zhang, G. Wen, Microstructure and mechanical properties of zirconia-toughened lithium disilicate glass–ceramic composites, Mater. Chem. Phys. 143 (2014) 845–852, https://doi.org/10.1016/j.matchemphys.2013.10.023.

[15] S.E. Elsaka, A.M. Elnaghy, Mechanical properties of zirconia reinforced lithium silicate glass-ceramic, Dent. Mater. 32 (2016) 908–914, https://doi.org/10.1016/j.dental.2016.03.013.

[16] R.L.P. Santos, M. Buciumeanu, F.S. Silva, J.C.M. Souza, R.M. Nascimento, F. V. Motta, B. Henriques, Tribological behavior of zirconia-reinforced glass–ceramic composites in artificial saliva, Tribol. Int. 103 (2016) 379–387, https://doi.org/10.1016/j.triboint.2016.07.019.

[17] R.L.P. Santos, M. Buciumeanu, F.S. Silva, J.C.M. Souza, R.M. Nascimento, F. V. Motta, O. Carvalho, B. Henriques, Tribological behaviour of glass-ceramics reinforced by yttria stabilized zirconia, Tribol. Int. 102 (2016) 361–370, https://doi.org/10.1016/j.triboint.2016.05.047.

[18] E.Ç. Yilmaz, Investigation of two-body wear behavior of zirconia-reinforced lithium silicate glass-ceramic for biomedical applications; in vitro chewing simulation, Comput. Methods Biomech. Biomed. Eng. (2020) 1–19, https://doi.org/10.1080/10255842.2020.1852555, 0.

[19] S. JegouSaint-Jean, Dental glasses and glass-ceramics, Adv. Ceram. Dent. (2014) 255–277.

[20] R.G. Craig, Chapter 11 - restorative materials: ceramics, in: Craig's Restor. Dent. Mater., 2019, pp. 209–227.

[21] S. JegouSaint-Jean, Chapter 12 - dental glasses and glass-ceramics, in: Adv. Ceram. Dent., 2014, pp. 255–277.

[22] F. Sergejev, M. Antonov, Comparative study on indentation fracture toughness measurements of cemented carbides, Proc. Est. Acad. Sci. Eng. 12 (2006) 388–398, https://doi.org/10.1179/096797899680381.

[23] H.H.K. Xul, D.T. Smith, S. Jahanmir, E. Romberg, J.R. Kelly, V.P. Thompson, E. D. Rekow, Indentation damage and mechanical properties of human enamel and dentin, J. Dent. Res. 77 (1998) 472–480, https://doi.org/10.1177/00220345980770030601.

[24] M. Salas, C. Lucena, L.J. Herrera, A. Yebra, A. Della Bona, M.M. Pérez, Translucency thresholds for dental materials, Dent. Mater. 34 (2018) 1168–1174, https://doi.org/10.1016/j.dental.2018.05.001.

[25] T. Fusayama, T. Katayori, S. Nomoto, Corrosion of gold and amalgam placed in contact with each other, J. Dent. Res. 42 (1963) 1183–1197, https://doi.org/10.1177/00220345630420051301.

[26] R. DeLong, R.L. Sakaguchi, W.H. Douglas, M.R. Pintado, The wear of dental amalgam in an artificial mouth: a clinical correlation, Dent. Mater. 1 (1985) 238–242, https://doi.org/10.1016/S0109-5641(85)80050-6.

[27] Y.-S. Jung, J.-W. Lee, Y.-J. Choi, J.-S. Ahn, S.-W. Shin, J.-B. Huh, A study on the in-vitro wear of the natural tooth structure by opposing zirconia or dental porcelain, J. Adv. Prosthodont. 2 (2010) 111–115, https://doi.org/10.4047/jap.2010.2.3.111.

[28] J.-W. Choi, I.-H. Bae, T.-H. Noh, S.-W. Ju, T.-K. Lee, J.-S. Ahn, T.-S. Jeong, J.-B. Huh, Wear of primary teeth caused by opposed all-ceramic or stainless steel crowns, J. Adv. Prosthodont. 438 (2016) 43–52, https://doi.org/10.4047/jap.2016.8.1.43.

[29] C. Mehl, S. Scheibner, K. Ludwig, M. Kern, Wear of composite resin veneering materials and enamel in a chewing simulator, Dent. Mater. 23 (2007) 1382–1389, https://doi.org/10.1016/j.dental.2006.11.026.

[30] M. Steiner, M.E. Mitsias, K. Ludwig, M. Kern, In vitro evaluation of a mechanical testing chewing simulator, Dent. Mater. 25 (2009) 494–499, https://doi.org/10.1016/j.dental.2008.09.010.

[31] D. Lazaridou, R. Belli, A. Petschelt, U. Lohbauer, Are resin composites suitable replacements for amalgam? A study of two-body wear, Clin. Oral Invest. 19 (2015) 1485–1492, https://doi.org/10.1007/s00784-014-1373-4.

[32] N. Koottathape, H. Takahashi, N. Iwasaki, M. Kanehira, W.J. Finger, Two- and three-body wear of composite resins, Dent. Mater. 28 (2012) 1261–1270, https://doi.org/10.1016/j.dental.2012.09.008.

[33] S.A. Santander, A.P. Vargas, J.S. Escobar, F.J. Monteiro, L.F.R. Tamayo, Ceramics for dental restorations - an introduction, Dyna 77 (2010) 26–36.

[34] J.A. Arsecularatne, J.P. Dingeldein, M. Hoffman, An in vitro study of the wear mechanism of a leucite glass dental ceramic, Biosurface and Biotribology 1 (2015) 50–61, https://doi.org/10.1016/j.bsbt.2015.02.004.

[35] A. Theocharopoulos, X. Chen, R. Hill, M.J. Cattell, Reduced wear of enamel with novel fine and nano-scale leucite glass-ceramics, J. Dent. 41 (2013) 561–568, https://doi.org/10.1016/j.jdent.2013.02.006.

[36] J. Nakashima, Y. Taira, S.T. In, In vitro wear of four ceramic materials and human enamel on enamel antagonist, Eur. J. Oral Sci. 124 (2016) 295–300, https://doi.org/10.1111/eos.12272.

[37] S. Bechtle, S. Habelitz, A. Klocke, T. Fett, G.A. Schneider, The fracture behaviour of dental enamel, Biomaterials 31 (2010) 375–384, https://doi.org/10.1016/j.biomaterials.2009.09.050.

[38] I.M. Hutchings, Tribology: Friction and Wear of Engeneering Materials, 1992.

[39] S.M. Kurtz, K. Ong, 7 - contemporary total hip arthroplasty: alternative bearings, in: UHMWPE Biomater. Handb., third ed., 2016, pp. 72–105.

[40] J. Chevalier, L. Gremillard, A.V. Virkar, D.R. Clarke, The tetragonal-monoclinic transformation in zirconia: lessons learned and future trends, J. Am. Ceram. Soc. 1920 (2009) 1901–1920, https://doi.org/10.1111/j.1551-2916.2009.03278.x.