The Effects of Acid Etching on the Morphology and Properties of Medical Grade Alumina and Zirconia Surfaces for Prosthetics

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Abstract

In this study we modify and functionalize the surface of alumina and zirconia ceramics for medical applications using chemical etching with mixtures of sulfuric, nitric, hydrofluoric acids and peroxide. After etching, the impact of processes on surface development, chemical composition, and topography is studied to select the most effective process of surface development. Medical grade alumina and zirconia ceramic powders have been chemically etched with selected three kinds of acidic solutions : 1.sulfuric and nitric acid, 2.sulfuric acid and peroxide, 3.fluoric acid various diluted aqueous solution during the selected time periods. Following heat treatment was performed and the samples characterization were undertaken: morphology and chemical composition , phase composition, functional group determination, and the specific surface area and porosity evaluation.. Comparing the results raised from acidic etching, it was noticed that the use of $\text{H}_2\text{SO}_4\text{:HNO}_3$ solutions causes sulphur residues in ceramic in the form of sulphates. The application of HF negatively affects the structure of the material and cause agglomeration. The most advantageous modification of ceramic powders was application of piranha solution, the obtaining surface development was achieved, satisfactory degree of agglomeration and post-process pollution.

Introduction

Ceramic biomaterials are widely used in medicine, mainly in orthopaedic and dentistry applications [1, 2]. This is due to their high hardness, resistance to tribological wear, chemical inertness, lack of inflammatory reaction for the host organisms, their ability to form complex shapes, and aesthetic effects of prostheses, these are important for dental prosthetics [2–4]. Ceramics such as alumina and cubic zirconia are used for acetabulum joints, auditory ossicles, bone scaffolds, dental prostheses (such as crowns), bridges and prosthetic implants, and abutments [5, 6]. Ceramics are popular in biomedical applications and allows for the elimination of problems with the use of metal implants such as metallosis and corrosion which can cause inflammation, colonization by pathogenic microorganisms, rejection of the implants by the human body, and in extreme cases can lead to cancer [7, 8]. The adverse effects of metallic implants is associated with the accumulation of harmful metallic ions in detoxification organs [7, 9]. Particularly important problems are associated with inflammation caused by pathogenic microorganisms, which are the main cause of inflammation and rejection of the implants [7]. The main pathogens, which cause implant rejection, are from the fungal family *Candida albicans*, while within bacteria, the main culprits include bacteria from the *Typhlococcus aureus* group [10]. Various other organisms also can cause complications, these include; *Aggregatibacter actinomycetemcomitans*, *Eikenella corrodens*, *fusobacterium nucleatum*, and *Tannerella Fforsythia* [11]. These pathogens are well-known symbiotes that are frequently isolated in oral diseases, and because of their nature, varying antimicrobial treatments are required to treat them [11 – 3]. Based on the published data, it is assumed that over 65% of all human infections have been estimated to be biofilm-related [14]. Bacterial and fungal inflammations, and their related issues, are the most prominent in metal biomaterials such as 316 LVM

SS and Ti6Al4V alloy [14–16]. Inflammations, bone loss, are problems that can be avoided with the use of ceramic biomaterials.

Despite the numerous advantages, the application of ceramics brings some issues that arise from the physicochemical nature of this group of materials. This is analogous to the zirconium drawbacks connected with the metastable nature of these materials, which a significant amount of work has been dedicated to, such as the work of Guo, Gremillard and Chevalier [17, 18]. In the work of Chevalier and Gremillard, the problem of the influence of the body environment on the structure is addressed, *i.e.* the structural changes caused by the interaction between the zirconium material with saliva and moisture [19]. These structural changes are described with the term low thermal degradation (LTD) and are a well-known mechanism that destructively affects dentures and prostheses made from ZrO_2 [19, 20]. The main problem that results from LTD is swelling of zirconia grains, falling out of the structure and, as a result, the formation of critical fractures of the dentures and prostheses [17]. The mechanisms associated with the formation of these adverse phenomena have been described by Guo, who presents kinetic models which are confirmed experimentally by other authors [21, 22]. Other disadvantages of ceramics are their high fragility and a relatively time-consuming and expensive production process [23, 24]. The proper selection of process parameters when milling dental crowns and bridges creates many problems, for the case of zirconia, special attention needs to be paid to the cooling of the material during milling to prevent overheating of the structure, which negatively affects the durability of the dentures [23, 25]. Besides, to the best of our knowledge, there is no clear position as to whether water or oils used during cooling initiate the uncontrolled phase transformation and in consequence LTD which cause premature ageing and destruction of dentures [17, 18]. These and other problems *i.e.* metastable phases stabilisation, dopant selection have been previously addressed in the literature [26–28]. In summary, biomedical ceramics are an interesting class of materials but require a lot of attention and further development to aforementioned deficiencies.

Polymer-ceramic composites *i.e.* ZrO_2 -PEEK (polyether ether ketone), SiO_2 -PMMA (poly(methyl methacrylate)) as biomaterials are an interesting alternative to ceramics and metals. These materials aim to combine the required properties of the ceramic and polymer groups and minimize occurrence of structural defects, as much as possible. Particular interesting to this type of composite is connected with durability and tribological resistance of ceramics, and low costs and the resistance to brittle fracture of polymers. Previous literature has focused on oxide ceramics combined with PMMA and PEEK [29, 30]. The main problem associated with obtaining valuable polymer-ceramic composites is achieving a secure connection between the ceramic and the polymer [31, 32]. Depending on the surface treatment of the ceramic grains, a chemical or mechanical bond can be formed which is the adhesive between the ceramic grains and the polymer resin. Therefore, surface modification of ceramics is one of the most important issues in these composites. An important way to improve the bond between the ceramic and the polymer is to obtain a chemical bond between the chemically inert ceramic and the polymer. It is possible through the functionalization of the ceramic surface with functional groups and coupling agents *i.e.* -OH, - CH_2HNH_2 , - NH_2 , - CF_3 , -COOH, H_3PO_4 , aminosilanes and fluorosilanes [33, 34]. The main reason of

application of coupling agents is to prevent the high differences between the surface energy of the hydrophilic ceramic and that of the hydrophobic polymer matrix, which leads to agglomeration and poor dispersion of the ceramic filler particles and in the results preventing in the formation of voids and interfacial defects [34]. There are many ways to create a sufficiently large surface area development on the ceramic surface: oxidation, application of characteristic functional groups, silanization, thermal treatment in a gas atmosphere, melt infiltration, ionic liquid etching, sol-gel process, and co-precipitation [35–39]. For example, the chemical etching processes have a large amount of literature focused on chemical etching concerns the preparation of the ZrO_2 surface in a way that enables permanent bonding to hard dental tissues or composite materials [39]. One of the important aspects required for the success of ZrO_2 ceramics is the establishment of proper adhesion between substrate and adherent [39, 40]. The gold-standard protocol for resin bonding to glass-ceramics is etching with hydrofluoric acid followed by the application of a silane coupling agent (chemical and mechanical adhesion) [39, 40]. Acid etching (various concentration and times) has been shown to change the surface micro-morphology of glass and oxide ceramics (many surface defects) [39], the resin adhesion, the increase in HF acid concentration, and the etching time associated with an increase of the surface area available to adhesion with resin [39].

Here, we report a simple and low-cost surface modification process for medical-grade ZrO_2 and Al_2O_3 ceramics using chemical acid in the form of an acid-perchlorate bath. This treatment was carried out in order to prepare ceramic fillers for mixing with selected polymers in future, and in consequence preparation of polymer-ceramic composites for biomedical applications. For etching process we use sulphuric acid, nitric acid, perchlorate, and hydrofluoric acid, for comparison, baths. This performed research concerns the assessment of the impact of the prepared baths on surface development, chemical and phase composition, as well as the occurrence of characteristic functional groups, *i.e.* hydroxyl, which positively affect the chemical connection with the polymer species in composite.

Materials And Methods

2.1. Samples Preparation

The test samples were prepared from ceramic powders of alumina (Sigma Aldrich) and zirconia (Acros Organics) with 99.9% submicron powder. The samples were prepared in 3-gram batches. Powder samples without any additional treatment were chemically etched in the following solutions: (I) hot, fresh Piranha solution, (II) sulfuric and nitrogen acid mixture, and (III) hydrofluoric acid. The etching solution concentrations and ratios are shown in Table 1. All reagents were purchased from Avantor Chemicals. The following were selected as process variables: concentration and volume ratios of the individual reagents and the etching times. The times were set to 30, 60 and 120 seconds. The ceramic powder samples were placed in a beaker with an etching solution and mixed with a magnetic stirrer. The sample names, process times, and etching baths are given in Table 1. After etching, the samples were quantitatively transferred to a paper filter and washed with deionized water and filtered under pressure. After etching, the samples were quantitatively transferred to a paper filter and washed with deionized

water ($3 \times 200 \text{ cm}^3$) and filtered under pressure through filter with a ceramic membrane to remove the remaining etching solution. The samples were then transferred to a dryer and dried without any forced airflow at 80°C for 24 hrs. After cooling the sample to disintegrate the agglomerates, they were added to a beaker with 2-propanol (Acros Orgnics) and placed in an ultrasonic bath to homogenize them for 15 minutes. The samples prepared in this way were then used for materials characterization. The samples were then again transferred to a dryer and dried without any forced airflow at 80°C for 24 hrs The figure Fig. 1. shows the entire sample preparation process.

Table 1
Sample description and experimental conditions for zirconia and alumina samples.

Etching agent, Cp%	Etching time, (s)	Etching agent concentration in water, Cp%	Sample name ZIRCONIA	Sample name ALUMINA
98% H ₂ SO ₄ :	30	100	ZrO ₂ _PS1_30	Al ₂ O ₃ _PS1_30
	60		ZrO₂_PS1_60	Al₂O₃_PS1_60
	120		ZrO₂_PS1_120	Al₂O₃_PS1_120
35% H ₂ O ₂ (Piranha solution) Volume ratio	30	50	ZrO ₂ _PS0.5_30	Al ₂ O ₃ _PS0.5_30
	60		ZrO ₂ _PS0.5_60	Al ₂ O ₃ _PS0.5_60
	120		ZrO ₂ _PS0.5_120	Al ₂ O ₃ _PS0.5_120
3:1	30	25	ZrO ₂ _PS0.25_30	Al ₂ O ₃ _PS0.25_30
	60		ZrO ₂ _PS0.25_60	Al ₂ O ₃ _PS0.25_60
	120		ZrO ₂ _PS0.25_120	Al ₂ O ₃ _PS0.25_120
98% H ₂ SO ₄ : 65% HNO ₃ Volume ratio 1:3	30	100	ZrO ₂ _SN1_30	Al ₂ O ₃ _SN1_30
	60		ZrO₂_SN1_60	Al₂O₃_SN1_60
	120		ZrO ₂ _SN1_120	Al ₂ O ₃ _SN1_120
	30	50	ZrO ₂ _SN0.5_30	Al ₂ O ₃ _SN0.5_30
	60		ZrO ₂ _SN0.5_60	Al ₂ O ₃ _SN0.5_60
	120		ZrO ₂ _SN0.5_120	Al ₂ O ₃ _SN0.5_120
	30	25	ZrO ₂ _SN0.25_30	Al ₂ O ₃ _SN0.25_30
	60		ZrO ₂ _SN0.25_60	Al ₂ O ₃ _SN0.25_60
	120		ZrO ₂ _SN0.25_120	Al ₂ O ₃ _SN0.25_120
45% HF	30	15	ZrO ₂ _HF0.15_30	Al ₂ O ₃ _HF0.15_30
	60		ZrO₂_HF0.15_60	Al₂O₃_HF0.15_60
	120		ZrO₂_HF0.15_120	Al₂O₃_HF0.15_120
	30	10	ZrO ₂ _HF0.1_30	Al ₂ O ₃ _HF0.1_30
	60		ZrO ₂ _HF0.1_60	Al ₂ O ₃ _HF0.1_60

Note: in **bold** highlighted samples taken for further analytical evaluation

Etching agent, Cp%	Etching time, (s)	Etching agent concentration in water, Cp%	Sample name ZIRCONIA	Sample name ALUMINA
	120		ZrO2_ HF0.1_120	Al2O3_HF0.1_120
	30	5	ZrO2_HF0.05_30	Al2O3_HF0.05_30
	60		ZrO2_ HF0.05_60	Al2O3_HF0.05_60
	120		ZrO2_ HF0.05_120	Al2O3_HF0.05_120
Note: in bold highlighted samples taken for further analytical evaluation				

2.2. Characterisation

The prepared samples were tested in terms of their morphology, characteristic functional group content, phase composition, and specific surface development. The morphology and initial elemental composition analysis were performed using scanning electron microscopy equipped with energy-dispersive X-ray detector (SEM/EDX). A high resolution scanning electron microscopes FEI INSPECT f50 (ThermoFisher Scientific, USA) and JEOL JSM-7610F+ (JEOL, Japan) with Schottky cathode and microanalyser Aztec Ultima Max 65 (Oxford Instruments, UK) were used for these measurements. Both secondary and back scattered electrons were detected for imaging, mapping, and analysing the selected areas. Samples were prepared on stubs covered with carbon tape and coated with gold to optimise resolution and avoid possible charging.

The analysis of characteristic functional groups was performed using Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra of all samples were measured using the attenuated total reflectance (ATR) technique. The samples were pressed by a pressure device on the single-reflection diamond ATR crystal, and spectra were collected using an FT-IR Nicolet iS50 (Thermo Scientific, USA) spectrometer with a Smart Orbit ATR accessory and a deuterated triglycine sulphate (DTGS) detector. The measurement parameters were as follows: spectral region = $4000 - 400 \text{ cm}^{-1}$; spectral resolution = 4 cm^{-1} ; 64 scans; Happ-Genzel apodisation.

The X-ray powder diffraction (XRD) analysis was performed using a RIGAKU Ultima IV diffractometer, with a scintillation detector, CuK α radiation source, NiK β filter, and Bragg-Brentano arrangement. Samples were measured in ambient atmosphere using reflexion mode (conditions: 40 kV, 40 mA, 2°/min, 0.05 step). The database used for qualitative phase analysis was ICDD PDF-2/Release 2011 RDB.

Specific surface development was determined by constructing nitrogen adsorption/desorption isotherms, which were measured using Autosorb (Quantachrome Instruments iQ2). Prior to the analysis, all samples were degassed for 3.6 h at 300 °C. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. Porosity and pore size distribution was determined using the Barrett–

Joyner–Halenda (BJH) method, applying the software from the producer of the apparatus. Approximate pore shapes were specified based on de Boer adsorption hysteresis classification.

Results And Discussion

3.1. Morphology evaluation and elements mapping of the surface

Microscopic observations allowed to determine structural changes, aggregation, and agglomeration of ceramic grains caused by acidic etching. In addition, EDX measurements confirmed the chemical composition in the selected areas of interest. Initial microscopic observations followed the criteria such as high levels of surface development, low levels of agglomeration and aggregation, and high uniformity of chemical composition without etching agent residues. On the base of these input measurements the most suitable samples were chosen for further optimisation works. The initial powders of alumina and zirconia are shown in Fig. 2. Based on the SEM/EDX observations, twelve samples were selected for the next tests: for zirconia and alumina at equal conditions (1) ZrO₂_PS1_60 & Al₂O₃_PS1_60 ; (2) ZrO₂_PS1_120 & Al₂O₃_PS1_120; (3) ZrO₂_PS0.5_60 & Al₂O₃_PS0.5_60 (4) ZrO₂_SN1_60 & Al₂O₃_SN1_60; (5) ZrO₂_HF0.15_60 & Al₂O₃_HF0.15_60; (6)- ZrO₂_HF0.15_120 & Al₂O₃_HF0.15_120. Samples with relatively high degrees of agglomeration or aggregation, and those containing residues from etching agents were eliminated from further study.

The zirconia samples displayed a general tendency to agglomerate independently of the etching agent. Among all etching agents, the largest degrees of agglomeration and aggregation were observed when using a mixture of sulphuric and nitric acids; less agglomeration was noted following the use of hydrofluoric acid. The smallest degree of agglomeration was observed in powders that were etched with Piranha solution. In general, less agglomeration was observed in alumina samples, because these powders were more dispersed and therefore less susceptible to agglomeration. However, the dependence of alumina agglomeration on the etching agent was similar to that observed for the zirconia samples. Specifically, most alumina agglomerates and aggregates were observed following treatments with a mixture of sulphuric acid and nitric acid, less were observed for hydrofluoric acid, and the least for Piranha solution. Figure 3 presents a comparison of the degree of agglomeration in zirconia and alumina samples for all etching agents.

The second important factor that was assessed using microscopic observations was the presence of impurities/residues from the etching process. After analysing all sample variants, it was discovered that only samples that had been etched with a sulphuric and nitric acid mixture contained some residue, and these samples contained only sulphur residue after etching. Depending on the type of ceramic, sulphur was found in various forms. In the case of zirconia, sulphur-containing impurities took the form of layer-like precipitates on grains, whereas, in the case of alumina, sulphur impurities exhibited more diverse geometries. Figures 4 display examples showing sulphur contamination for zirconia and alumina, and

the weight percentage of sulphur detected using EDS semi-quantitative analysis in samples ZrO₂_SN1_60 and Al₂O₃_SN1_60 were 0.5 and 2.3, respectively.

The effect of etching agent on the development of zirconia and alumina surfaces was examined under electrons. For zirconia, the most visible impact of etching on the material's morphology occurred using Piranha solution, which also caused the least agglomeration. Additionally, there was a significant degree of surface structural changes following etching using a mixture of sulphuric acid and nitric acid, while surprisingly, the least-altered zirconia structure was observed upon hydrofluoric acid etching. The situation was different in the alumina samples, which showed the least structural change after etching with Piranha solution, partial etching of the structure caused by a mixture of sulphuric and nitric acid, and the largest changes in the structure were observed after etching with hydrofluoric acid.

Based on the observations for zirconia powders, it was determined that the Piranha solution at a concentration of Cp = 100% and an etching time of 120 s etched the surface the most, causing the largest surface structural changes. As the concentration of the etching agent decreased or the time was reduced, the zirconia was less etched. In the case of a mixture of nitric and sulphuric acid, the zirconia surface was generally disrupted poorly, regardless of time and concentration. After etching with hydrofluoric acid, the samples exhibited greater surface changes with increasing concentration and time. As mentioned above more developed surface was obtained for Piranha solution. For alumina, the Piranha solution caused a similar degree of change to the surface of the samples, regardless of time and concentration; the morphology of alumina samples was changed, but no trend is clear.

The situation was similar after etching alumina samples with a mixture of sulphuric and nitric acid, although these surfaces were etched to a lesser degree than those subjected to Piranha solution. The best results were obtained applying treatment with hydrofluoric acid at a concentration of Cp = 15% and an exposure time of 120 s. In general, longer times and higher HF concentrations caused the grain surface to change more, and the original spatial structure became distorted. Figure 6 shows the most etched structures that were obtained in these experiments. In these images, the degree of structural change after etching is clear in both the zirconia and alumina samples. Both images display etched and non-etched structures, the latter of which is especially visible in the alumina photo, where flat hexagonal crystals can be observed (Fig. 5b). In contrast, the ball-like grains in the zirconia sample have changed to a sponge-like form after etching (Fig. 5a).

3.2. Structural characterization

The FTIR spectra for all ten samples are shown in Fig. 6. For zirconia samples etched in Piranha solution ZrO₂_PS1_120 and ZrO₂_PS1_60, several characteristic bands were identified. The absorption bands that appear at 1633, 1031, and 1030 cm⁻¹ are related to the vibration, stretching, and deformation of the O–H bonds present due to absorption and coordination of water in the samples. The peaks at 1088 (1089) cm⁻¹ result from the bending vibrations of hydroxyl groups bound to zirconium oxide. However, the absorption bands at 724(725), 485, 482, 447, and 444 cm⁻¹ correspond to Zr–O bond vibrations in both zirconia samples [39–43]. Zirconia sample ZrO₂_PS1_60 FTIR spectrum contains characteristic

absorption bands at 722 and 483 cm^{-1} , which are associated with the Zr-O bending vibration [41–43]. In addition, it was determined that the bands at $450\text{--}550\text{ cm}^{-1}$ and $750\text{--}950\text{ cm}^{-1}$ correspond to tetragonal zirconia. The monoclinic phase cannot be determined decisively from the FTIR spectrum [40]. Samples etched in hydrofluoric acid exhibited bands at 721 , 485 (486), and 447 cm^{-1} , which all originate from bending vibrations of Zr-O [41–43]. The band at 666 cm^{-1} is due to fluoride adsorption. For alumina etched in Piranha solution, the bands at 2984 and 2979 cm^{-1} were identified as being associated with Al_2O_3 stretching vibrations, along with those in the region of $2950\text{--}2850\text{ cm}^{-1}$ (which are not shown in the spectra in Fig. 6) [44]. This is likely due to so-called “bulk-like” droplets in the pores, or a thin film adsorbed on the surface of the alumina. Other bands observed at 634 , 555 , 551 , 494 , and 406 cm^{-1} are associated with the bending vibrations of Al-O and Al-O-Al in the $\gamma\text{-Al}_2\text{O}_3$ and Al-O-H moieties [45, 46]. The alumina sample etched with a mixture of sulphuric and nitric acid had characteristic absorption bands at 589 , 416 , and 412 cm^{-1} , corresponding approximately to the range previously determined to contain Al-O and Al-O-Al bending motions within $\gamma\text{-Al}_2\text{O}_3$ and Al-OH [45, 46]. The FTIR spectra for alumina samples etched with hydrofluoric acid were interpreted similarly to the alumina sample etched in the mixture of sulphuric and nitric acid spectrum.

Evaluation of the structure and changes at the etching process was performed using XRD measurements, and a summary of samples diffractograms is presented in Figs. 7 and 8.

No significant effect on the phase composition was observed in samples of zirconium oxide. The original samples possess typical reflexes for the monoclinic phase ZrO_2 (PDF card No. 01-083-0942) and the tetragonal phase ZrO_2 (PDF card No. 01-079-1764), which overlap with the HfO_2 (PDF card No. 00-053-0560) peaks that usually accompanies ZrO_2 in a small amount. Differences were noted after using different etching agents, especially in the Piranha solution case. For example, a new crystalline phase with the formula $\text{Zr}(\text{SO}_2)_4\cdot\text{H}_2\text{O}$ (PDF card No.01-085-0703), was observed in sample $\text{ZrO}_2\text{-PS0.5}_{120}$; however, other sample $\text{ZrO}_2\text{-PS1}_{60}$ did not contain this compound. The reason for phenomenon can be, that the content of this crystalline phase increases as time of etching solution increases. A similar result was observed in the case of Al_2O_3 (PDF card No. 01-075-6776), where the use of Piranha solution in the sample $\text{Al}_2\text{O}_3\text{-PS1}_{120}$ the crystalline phase of $\text{Al}(\text{HSO}_4)_3\cdot 6\text{H}_2\text{O}$ (PDF card No. 00-028-0104)was detected.

3.3. Surface size and porosity properties

Figure 9 shows the adsorption and desorption isotherms, as well as the multi-point BET for chosen samples. In addition, Table 2 presents the data from measuring specific surface area, porosity, and pore shapes of selected samples. Samples etched in mixture of sulfuric acid and nitric acid were excluded because they contained impurities in the form of residual sulphur from sulphuric acid, which could not be removed from the ceramic grains. In general, the zirconia samples underwent greater surface development than alumina after etching with any of the respective acids tested herein, although the results show a large range of values. As for zirconia, the samples' pore volumes tended to be greater than

0.4 cm³g⁻¹. Overall, the observations regarding surface developments indicated that the etching agents have fulfilled their task. However, it is difficult to compare the obtained results with published data from other researchers, because limited information could be found related to the effects of any pickling baths on the development of the specific surfaces and/or the formation of functional groups. Only one report from Aida et al. refers to surface treatment of zirconia in a similar way, but the results are only relevant for ceramic blocks [47]. The alumina samples in this study exhibited a lesser degree of surface development in each case. This can be explained by the fact that the initial zirconia has a lower susceptibility to etching and greater fineness than the original alumina. In the case of sample ZrO₂-HF0.15_120 (Table 2), no reliable pore data was obtained to allow comparison to other samples.

Table 2
Surface area development, pore volumes, and pore diameters.

Powder	Sample	Specific surface area, [m ² g ⁻¹]	Pore volume, [cm ³ g ⁻¹]	Pore diameter, [nm]
Zirconia	ZrO ₂ -PS1_60	11.842	0.437	214.681
	ZrO ₂ -PS1_120	7.369	0.072	17.658
	ZrO ₂ -HF0.15_60	13.455	0.425	183.673
	ZrO ₂ -HF0.15_120	12.745	0.431	206.289
Alumina	Al ₂ O ₃ -PS1_60	3.543	0.165	186.250
	Al ₂ O ₃ -PS1_120	0.220	0.006	3.069
	Al ₂ O ₃ -HF0.15_60	0.316	0.008	3.817
	Al ₂ O ₃ -HF0.15_120	0.610	n. d.	n. d.

n. d. – even after grinding the samples with an agate mortar and pestle, and conducting the BET analysis, it was difficult to obtain valuable results

Conclusions

The main objective of this study was to use etching processes to achieve the surface development of medical grade zirconia and alumina for use as fillers in polymer-ceramic composites. Such development of the ceramic surfaces is intended to allow for a permanent mechanical connection with polymer resins, which is a current challenge in the field. For this purpose, three etching agents were used; (I) fresh and hot Piranha solution, (II) a mixture of 98% H₂SO₄ and 65 Cp% HNO₃ acids, and (III) 45 Cp% hydrofluoric acid. The first two acidic etching solutions were diluted in water to ratios of 100, 50, and 25, and HF was diluted in water to ratios of 15, 10, and 5 to provide various experimental conditions. For each acid solution, etching times of 30, 60, and 120 seconds were selected. These experimental durations were chosen because, based on available literature data, it was concluded that they should be sufficient to

modify the surface of the ceramic grains to an extent that they can make connections with polymers [49]. Based on the observed morphologies, and the chemical and phase composition studies, the following relationships were elucidated:

- **Impact on morphology and surface development.** SEM images of zirconia and alumina revealed that the most beneficial surface structural effects are obtained after using Piranha solution, whereas the $\text{H}_2\text{SO}_4/\text{HNO}_3$ solutions had the least influence on surface development. In the case of HF, the effect is indirect. However, the acid type clearly has a strong impact on ceramic grain agglomeration. Depending on the acid's oxidation power, different degrees of agglomeration are introduced, and as the oxidation power decreases, the least agglomeration was observed (using HF in both zirconia and alumina samples). Regardless of the acid used, a larger extent of agglomeration was always observed in zirconia, most likely due to a higher degree of short-range weak van der Waals-type interactions, relative to alumina. Based on BET specific surface development measurements and their correlation with SEM results, the highest specific surface development was observed for zirconia etched in HF. Slightly lower values were obtained after using Piranha solution, while samples etched in H_2SO_4 and HNO_3 were not considered at all due to sulphur impurities that could not be removed with the available methods. For alumina, the BET results revealed a more complicated relationship. Since these ceramic powders were already larger than zirconia, the alumina tiles were broken down into agglomerates, and it was difficult to disintegrate them. Therefore, even after grinding the samples with an agate mortar and pestle, and conducting the BET analysis, it was difficult to obtain a concrete conclusion.
- **Effects on chemical composition and content of characteristic functional groups.** After etching and EDX testing, sulphur impurities were detected in samples etched with a mixture of H_2SO_4 and HNO_3 . Etched ceramics took different forms (Fig. 4) depending on the type and conditions. The compounds formed on the surface of zirconia and alumina (i.e., inorganic salts sulphate), may have been formed by reactions with dissociated nitric acid. FTIR analysis was carried out in order to verify the presence of characteristic functional groups on the ceramic surface, which can positively influence the chemical interaction between ceramics and polymers in a future composite. It was possible to identify hydroxyl groups in some of the samples, especially those that were etched in Piranha solution. The occurrence of hydroxyl groups permanently bound to the surface of ceramics positively influences their abilities to chemically interact with phenolic and polyphenolic formaldehyde resins, and after dehydration (i.e., losing water), they favour formation of carbonyl bonds.
- **Impact on phase composition.** After acid etching, no major changes to the samples' phase compositions were observed that would prevent the use of modified alumina and zirconia in medical applications. The phase composition was only slightly altered after etching samples with Piranha solution for 120 seconds. Content of new sulphur-containing crystalline phases on these samples was small but it was detected by SEM/EDX.

Declarations

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Figures

Figure 1

Sample preparation process.

Figure 2

Starting powders of (a) zirconia and (b) alumina.

Figure 3

SEM images comparing the degree of agglomeration of zirconia and alumina powders after etching with different acids. (a) zirconia: a-1 Piranha Solution, a-2 sulphuric and nitric acid mixture, a-3 hydrofluoric

acid; (b) alumina: b-1 Piranha Solution, b-2 sulphuric and nitric acid mixture, b-3 hydrofluoric acid.

Figure 4

Mapping of residual elements from acid treatment of (a) alumina and (b) zirconia samples using SEM/EDS.

Figure 5

Powders with the most significantly altered surface structures a) $\text{ZrO}_2\text{_PS1_120}$, (b) $\text{Al}_2\text{O}_3\text{_PS1_120}$

Figure 6

FTIR spectra of modified samples with denoted most intensive bands

Figure 7

XRD patterns for zirconia: as received sample (top) and modified samples (bottom): A) $\text{ZrO}_2\text{-HF0.15}_{120}$; B) $\text{ZrO}_2\text{-HF0.15}_{60}$; C) $\text{ZrO}_2\text{-SN1}_{60}$; D) $\text{ZrO}_2\text{-PS0.5}_{120}$; E) $\text{ZrO}_2\text{-PS1}_{60}$; where peaks of evaluated phases are mentioned in the pattern.

Figure 8

XRD patterns for alumina: as received sample (top) and modified samples (bottom). A) $\text{Al}_2\text{O}_3\text{-HF0.15}_{120}$; B) $\text{Al}_2\text{O}_3\text{-HF0.15}_{60}$; C) $\text{Al}_2\text{O}_3\text{-SN1}_{60}$; D) $\text{Al}_2\text{O}_3\text{-PS0.5}_{120}$; E) $\text{Al}_2\text{O}_3\text{-PS1}_{60}$; where peaks of evaluated phases are mentioned in the pattern.

Figure 9

Adsorption/desorption isotherms and BJH plots for zirconia sample ZrO₂_PS1_60