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Impact of different pretreatments and aging procedures on the flexural strength and phase structure of zirconia ceramics

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ABSTRACT

Objective. To test the impact of zirconia pretreatment and aging on flexural strength and phase structure.
Methods. For flexural strength measurements, 180 3Y-$TZP_{0.25}$ specimens were fabricated and pretreated: (i) air-abraded (105-μm alumina, 0.25 MPa), (ii) air-abraded (50-μm alumina, 0.25 MPa), (iii) air-abraded (30-μm silica-coated alumina, 0.28 MPa) (iv) non-pretreated. Each pretreated group (n = 15) was aged: (a) hydrothermal (134 °C, 0.23 MPa, 2 h) (b) in a mastication simulator (1,200,000×, 5/55 °C) and (c) not aged. The fractured specimens were stored dry for 5 years (23 °C) for analysis of phase transformation. Additionally, specimens were fabricated from 3Y-$TZP_{0.25}$ (n = 12) and 3Y-$TZP_{0.05}$ (n = 8), pretreated (i, ii, iii, iv), and hydrothermally aged. Each air-abrasion method was alternated using 0.05, 0.25 and 0.4 MPa pressure. The phase transformation was examined by Raman spectroscopy and surface topography by scanning electron microscope. Data were analyzed using univariate ANOVA with the Scheffé post hoc test and partial-eta-squared (η_p^2) ($\alpha = 0.05$).
Results. The highest impact on flexural strength was exerted by the pretreatment ($\eta_P^2 = 0.261$, $p < 0.001$), followed by interactions between pretreatment and aging ($\eta_P^2 = 0.077$, $p = 0.033$). Non-pretreated and non-aged specimens showed the lowest monoclinic percentage. Hydrothermal aging and 5 years of storage at room temperature increased the monolithic percentage of 3Y-$TZP_{0.25}$. The highest phase transformation was observed in groups air-abraded with 105-μm alumina particles. Increasing pressure during the air-abrading process increased the content of the monoclinic phase in zirconia surfaces.
Significance. Air-abrasion with 30-μm silica-coated alumina powder can be recommended for pretreatment of 3Y-$TZP_{0.25}$ and 3Y-$TZP_{0.05}$. For air-abrasion using alumina powder lower pressure should be used.

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1. Introduction

Zirconia ceramic was introduced into dentistry more than 20 years ago and became an important component in contemporary metal-free prosthodontic treatments. Advanced and cost-efficient technologies such as CAD/CAM supported the rapid increase of zirconia restorations avoiding highly skilled handmade fabrication. The suitability of zirconia as a framework material has been demonstrated in vitro and in vivo studies over the last decades. In addition to a simpler fabrication mode and better cost-efficiency, the high fracture rates of veneering ceramic has led to an increasing use of monolithic zirconia restorations in recent years, especially in the posterior region.

3Y-TZP has outstanding biocompatibility [1] and excellent mechanical properties, especially in regard to fracture toughness [2], defined as tolerance until damage occurs. Zirconia shows a unique mechanism for preventing crack advancement: the capability of transformation toughening, which was discovered in the 1970s [3]. Zirconia occurs in three different phases, monoclinic, tetragonal and cubic, depending on the temperature [4]. If not stabilized, the tetragonal phase is theoretically unstable under environmental conditions and may degrade spontaneously. Therefore, additives like yttria are used to stabilize the tetragonal crystals in a metastable configuration at room temperature. The stress field in front of a crack induces the transformation from the tetragonal into the stable monoclinic phase (t -> m) with a 4%–5% volume increase in the crystals. Compressive stresses are generated at the crack tips, which appear to close the cracks and prevent propagation. Additionally crack deflection, which occurs when the propagation direction of a crack is changed after encountering a tetragonal crystal [3,5,6]. At present, four generations of zirconia, with different indications, have been developed. The first (3Y-TZP$_{0.25}$) and second (3Y-TZP$_{0.05}$) zirconia generations have been well investigated both in vitro and in clinical trials. They have a similar yttria content but differ regarding the amount of alumina oxide, which influences flexural strength and translucency. To address esthetic drawbacks such as high opacity, a third (5Y-TZP$_{0.05}$) and fourth (4Y-TZP$_{0.05}$) generation zirconia have been marketed. They are characterized by higher contents of yttria, which stabilizes a cubic phase proportion of up to 53%. These formulations have increased translucency but also decreased flexural strength [4]. Because of their high opacity, the first two generations of zirconia often need to be veneered with ceramic. Additionally, surface treatments are necessary to promote durable bonds to the veneering ceramic and luting resin cement. Air-abrasion seems to be a reliable method of promoting bonding, providing a clean surface with increased roughness and wettability [7–9].

The compressive layer has been reported to protect and strengthen the surface, making it more difficult to generate microcracks and improving mechanical properties [10]. However, other authors have concluded a lack of strengthening effects [11,12] or even the formation of microcracks, leading to the decreased strength of the material [13]. The monoclinic phase content of the surface seems to play an important role in this context, as its value is said to increase or decrease according to the air abrasive type [14,15] or pressure [15–17] used. Controversial observations have been reported by Chintapalli et al. [18], who reported an increase of the monoclinic percentage after air-abrasion, irrespective of the particle size and pressure. Furthermore, monoclinic phase content and flexural strength seem to be influenced by aging, which can provoke a low-temperature degradation (LTD), a slow process starting at the surface and proceeding into the framework, and can be one reason for the failure of the ceramic [19,20]. Humid conditions seem to have a major influence on the degree of LTD [21], influencing surface quality and the development of microcracks with a degradation of aging resistance and mechanical properties [7,8,11].

The objectives of this study were to investigate the impact of different air-abrasion methods and aging procedures on the flexural strength of 3Y-TZP$_{0.25}$ and to evaluate the effect of the possible presence of the monoclinic phase through air-abrasion and aging. Furthermore, the influence of grain size and applied pressure on the occurrence of the monoclinic phase for 3Y-TZP$_{0.25}$ and 3Y-TZP$_{0.05}$ were investigated.

The tested null hypotheses were that pretreatment with air-abrasion or the aging procedure would not affect the flexural strength or phase transformation. In addition, the pressure for air-abrading or the type of zirconia would not affect phase transformation.

2. Material and methods

2.1. *Analysis of flexural strength*

For three-point flexural strength measurements, 180 specimens made of 3Y-TZP$_{0.25}$ (Ceramill Zi, LOT.No. 1206080, AmannGirrbach, Koblach, Austria) were milled (Ceramill Motion 2, AmannGirrbach) in the pre-sintered state. After grinding with SiC abrasive papers P600 and P1,000 (Buehler, Lake Bluff, IL, USA) the specimens were sintered (Ceramill Therm 2, AmannGirrbach) according to the manufacturers' instructions, with the final sintering temperature of 1450 °C. After sintering, the specimens had the final dimensions of length 25 mm, width 4 (±0.2) mm and thickness 1 (±0.2) mm. The resulting sintered layer was removed with a 4000 SiC paper (Buehler), abraded for about 5 s.

In a first step, specimens were randomly divided into four pretreatment groups (n = 45) and pretreated according to the manufacturers' instructions. The air-abraded area of each specimen measured 4 × 4 mm.

- i Air-abrasion using 50-μm alumina powder (Hasenfratz, Assling, Germany) for 20 s with 0.2 MPa from a distance of 10 mm at an angle of 45° (Fig. 1).
- ii Air-abrasion using 105-μm alumina powder (Hasenfratz) for 20 s with 0.2 MPa from a distance of 10 mm at an angle of 45° (Fig. 1).
- iii Air-abrasion using 30-μm silica coated alumina powder (Rocatec soft powder, 3 M, Seefeld, Germany) for 20 s with 0.28 MPa from a distance of 10 mm at an angle of 90°.
- iv Not pretreated.

In a second step the pretreated specimen groups were additionally divided into three aging groups (n = 15)

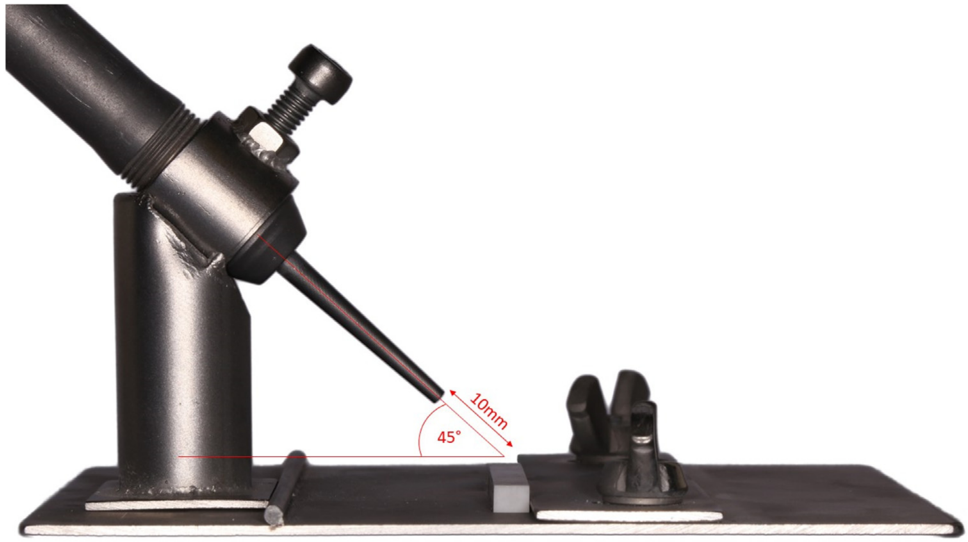

Fig. 1 – Air-abrasion pretreatment device used to ensure consistent conditions with an angle of 45° and a 10 mm distance of the air-abrasion tip.

i Hydrothermal aged at 134 °C and 0.23 MPa for 2 h (Vacuklav 31-B, Melag, Berlin, Germany), which corresponded to about 24 sterilization cycles. The temperature of 134 °C was held for 5.5 min per sterilization procedure.
ii Aged in a mastication simulator (CS-4, SD Mechatronik, Feldkirchen-Westermann, Germany) with a steel antagonist (4 mm diameter) for 1,200,000 mastication and 6000 thermal cycles between 5 °C and 55 °C with 10 N.
iii Not aged.

Before the three-point flexural strength test, the dimensions of the specimens were measured with a digital micrometer (Mitutoyo, Andover, England) to the nearest 0.01 mm. The specimens were tested dry at room temperature. The long side of the specimen was placed in the appropriate sample holder and loaded in a Universal Testing Machine (1445 Zwick/Roell, Zwick) at a crosshead speed of 1 mm/min until failure. The sample holder had a span between the two supports of 12 mm. Supports and both loading pistons were steel knife edges, rounded to a radius of 1 mm (Fig. 2). The flexural strength is calculated according to the following formula: $\sigma = 3Fd/2bh^2$, where σ: flexural strength, F: fracture load (N), d: differences in the distance of the supports (mm), b: width of the specimen (mm), h: height of the specimen (mm).

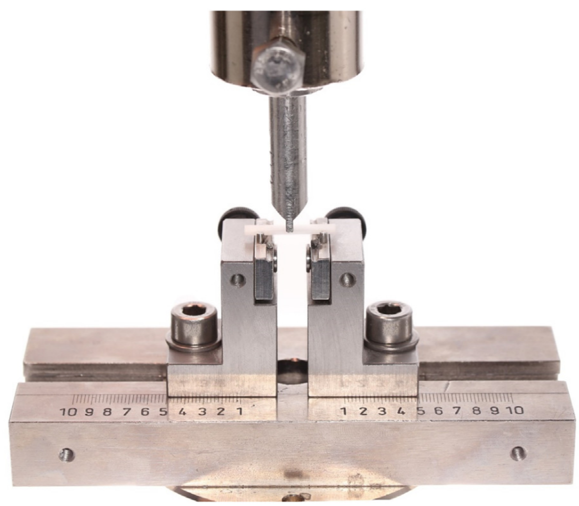

Fig. 2 – Sample holder of three-point flexural strength testing method, with a span between the two supports of 12 mm.

2.2. *Analysis of crystalline structures*

To analyze the crystalline structures, twenty specimens were milled from 3Y-$TZP_{0.25}$ (Ceramill Zi, AmannGirrbach, n = 12) and 3Y-$TZP_{0.05}$ (Ceramill Zolid, LOT.No. 1703001, Amann Girrbach, n = 8). The specimens were pretreated corresponding to the four pretreatment groups and hydrothermally aged as before. To evaluate the influence of the air-abrasion pressure, 50-μm and 105-μm alumina powder was applied with 0.05, 0.25 and 0.4 MPa. The specimens were cleaned for 10 min in an ultrasonic bath (Sonorex, Bandelin electronic, Berlin, Germany) with alcohol (Ethanol 96%, Otto Fischer GmbH & Co. KG, Saarbrücken, Germany) and air dried. To evaluate changes concerning the phase structure of 3Y-$TZP_{0.25}$ after a dry aging period of 5 years at room temperature (23 °C), the fractured specimens used for the flexural strength test were analyzed as follows. The phase transformation was detected with a Raman spectroscope (inVia Qontor, Renishaw plc, New Mills, Wotton-under-Edge, Gloucestershire, United Kingdom). The measurements of the hydrothermally aged and non-aged specimens were recorded initially and after a period of 5 years. For this purpose, the specimens were fixed onto glass carrier plates and inserted into its measuring chamber. The single mode laser (RL532C50, Renishaw plc) operated with a wavelength of 532 nm and 45 W of output power. After calibration of the system the specimens were mapped, and a measuring field of 25 × 400 spectra was set which corresponded to an area of 0.024 × 0.399 mm. The measurements ran under live track control to ensure precise focus even in irregular surfaces. An

Table 1 – Study design.

Material	Air-abrasion	Pressure	Aging procedure	Flexural strength measurement	Phase transformation measurement	5 years storage at room temperature	Phase transformation measurement
Material	**Air-abrasion**	**Pressure**	**Aging procedure**	**Flexural strength measurement**	**Phase transformatio n measurement**	**5 years storage at room temperature**	**Phase transformatio n measurement**
3Y-TZP 0.25 w% Al_2O_3 (N=184)	Alumina 50 µm (n=47)	0.05 MPa (n=1)	no	no	yes	no	no
		0.25 MPa (n=45)	autoclave	yes (n=15)	yes (n=1)	yes	yes
			mastication	yes (n=15)	no	no	no
			no aging	yes (n=15)	yes (n=1)	yes	yes
		0.4 MPa (n=1)	no	no	yes	no	no
	Alumina 105 µm (n=47)	0.05 MPa (n=1)	no	no	yes	no	no
		0.25 MPa (n=45)	autoclave	yes (n=15)	yes (n=1)	yes	yes
			mastication	yes (n=15)	no	no	no
			no aging	yes (n=15)	yes (n=1)	yes	yes
		0.4 MPa (n=1)	no	no	yes (n=1)	no	no
	Silica-coated alumina 30 µm (n=45)	0.28 MPa (n=45)	autoclave	yes (n=15)	yes (n=1)	yes	yes
			mastication	yes (n=15)	no	no	no
			no aging	yes (n=15)	yes (n=1)	yes	yes
	No air-abrasion (n=45)		autoclave	yes (n=15)	yes (n=1)	yes	yes
			mastication	yes (n=15)	no	no	no
			no aging	yes (n=15)	yes (n=1)	yes	yes
3Y-TZP 0.05 w% Al_2O_3 (N=8)	Alumina 50 µm (n=3)	0.05 MPa (n=1)	no	no	yes	no	no
		0.25 MPa (n=1)	no	no	yes	no	no
		0.4 MPa (n=1)	no	no	yes	no	no
	Alumina 105 µm (n=3)	0.05 MPa (n=1)	no	no	yes	no	no
		0.25 MPa (n=1)	no	no	yes	no	no
		0.4 MPa (n=1)	no	no	yes	no	no
	Silica-coated alumina 30 µm (n=1)	0.28 MPa	no	no	yes	no	no
	No air-abrasion (n=1)		no	no	yes	no	no
3Y-TZP 0.25 w% Al_2O_3 (N = 184)	Alumina 50 µm (n = 47)	0.05 MPa (n = 1)	No	No	Yes	No	No
		0.25 MPa (n = 45)	Autoclave	Yes (n = 15)	Yes (n = 1)	Yes	Yes
			Mastication	Yes (n = 15)	No	No	No
			No aging	Yes (n = 15)	Yes (n = 1)	Yes	Yes
		0.4 MPa (n = 1)	No	No	Yes	No	No
	Alumina 105 µm (n = 47)	0.05 MPa (n = 1)	No	No	Yes	No	No
		0.25 MPa (n = 45)	Autoclave	Yes (n = 15)	Yes (n = 1)	Yes	Yes
			Mastication	Yes (n = 15)	No	No	No
			No aging	Yes (n = 15)	Yes (n = 1)	Yes	Yes
		0.4 MPa (n = 1)	No	No	Yes (n = 1)	No	No
	Silica-coated alumina 30 µm (n = 45)	0.28 MPa (n = 45)	Autoclave	Yes (n = 15)	Yes (n = 1)	Yes	Yes
			Mastication	Yes (n = 15)	No	No	No
			No aging	Yes (n = 15)	Yes (n = 1)	Yes	Yes

– **Table 1 (Continued)**

Material	Air-abrasion	Pressure	Aging procedure	Flexural strength measurement	Phase transformation measurement	5 years storage at room temperature	Phase transformation measurement
3Y-TZP 0.05 w% Al_2O_3(N = 8)	No air-abrasion (n = 45)		Autoclave	Yes (n = 15)	Yes (n = 1)	Yes	Yes
			Mastication	Yes (n = 15)	No	No	No
			No aging	Yes (n = 15)	Yes (n = 1)	Yes	Yes
	Alumina 50 μm (n = 3)	0.05 MPa (n = 1)	No	No	Yes	No	No
		0.25 MPa (n = 1)	No	No	Yes	No	No
		0.4 MPa (n = 1)	No	No	Yes	No	No
	Alumina 105 μm(n = 3)	0.05 MPa (n = 1)	No	No	Yes	No	No
		0.25 MPa (n = 1)	No	No	Yes	No	No
		0.4 MPa (n = 1)	No	No	Yes	No	No
	Silica-coated alumina 30 μm (n = 1)	0.28 MPa	No	No	Yes	No	No
	No air-abrasion (n = 1)		No	No	Yes	No	No

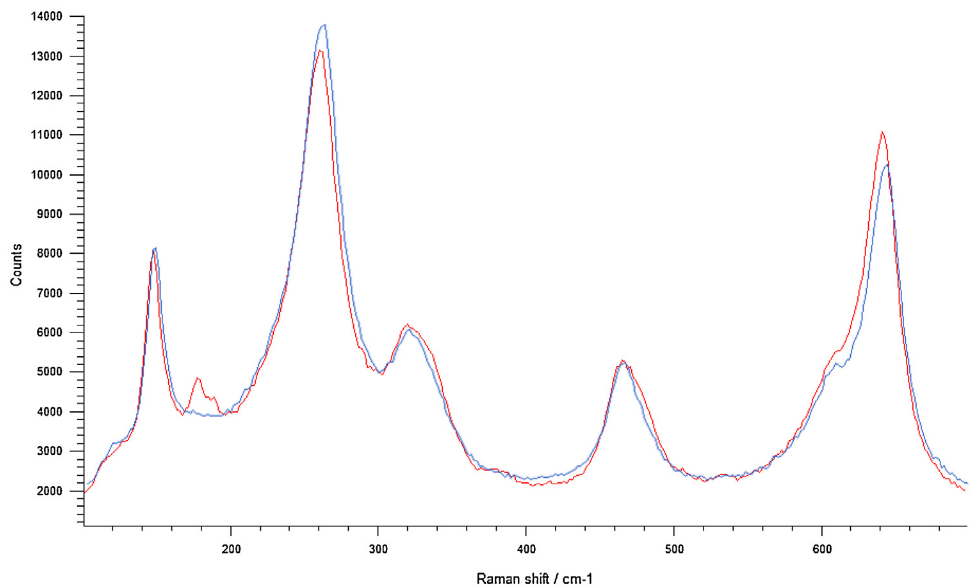

Fig. 3 – Tetragonal spectrum (blue curve) and characteristic peaks at 178 and 190 cm-1 of a monoclinic spectrum (red curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

overview of the study design is given in Table 1. The obtained data were processed using WiRE 4.4 software. The spectra were first truncated at the 100 and 700 Raman shift to obtain a smaller spectrum range. In a second step, the recorded cosmic rays were removed in order to minimize false outcome. For detection of monoclinic phase transformation, the spectrum peaks at the 178 and 190 Raman shift were analyzed (Fig. 3). The range for detecting a peak was set to ±3 Raman shift.

2.3. *Analysis of surface topography*

For the surface topography examination, 3Y-$TZP_{0.25}$ specimens were pretreated using 50-μm and 105-μm alumina powder at a pressure of 0.05, 0.25 and 0.4 MPa and 30-μm silica-coated alumina. One specimen was untreated. Then, the specimens were ultrasonically cleaned in ethanol and sputtered with 2 nm tungsten using a vacuum coater (CCU-010, Safamatic GmbH, Bad Ragaz, Switzerland). The zirconia surface was evaluated under a scanning electron microscope (Carl Zeiss Supra 50 V P FESEM, Carl Zeiss, Oberkochen, Germany) operating at 5 kV with a working distance of 6.7–9.2 mm (Fig. 5) For a deeper understanding, a quantitative analysis of the surface roughness was carried out using MarSurf SD 26 (Mahr, Göttingen, Germany). The horizontal position of the specimens was verified with a spirit level. The measuring length was defined 5.6 mm with an applied force of 5 N of the measurement sensor.

2.4. *Statistical methods*

Descriptive statistics were computed. For quantitative variables, the assumption of normality was tested with the Kolmogorov-Smirnov test. For global analysis, univariate ANOVAs followed by Scheffé post hoc test and partial eta squared (η_p^2) were made (IBM SPSS Statistics, v25; IBM Corp).

For parametric analysis, one-way ANOVA was performed ($\alpha = 0.05$ for all tests).

3. Results

No violation of the assumption of normality was observed. The highest impact on the flexural strength was exerted by the pretreatment ($\eta_P^2 = 0.261$, $p < 0.001$), followed by interactions between pretreatment and aging ($\eta_P^2 = 0.077$, $p = 0.033$). In contrast, aging showed no significant impact on the flexural strength results ($\eta_P^2 = 0.024$, $p = 0.134$) (Fig. 4). Therefore, the fixed effects of pretreatment and aging cannot be compared directly as the higher order interactions were found to be significant. Consequently, different analyses were computed and divided by levels of pretreatment and aging depending on the hypothesis of interest.

Within non-aged specimens, air-abrasion using 105-μm alumina powder led to significantly higher flexural strength values compared with non-pretreated groups or groups pretreated using 30-μm silica coated alumina ($p < 0.001$).

Within non-pretreated groups ($p = 0.719$) as well as groups air-abraded using 30-μm silica coated alumina powder ($p = 0.618$), no impact of aging was found. Within groups air-abraded using 50-μm alumina, specimens aged in the mastication simulator showed significantly higher flexural strength than specimens hydrothermal or non-aged ($p = 0.017$). After air-abrasion using 105-μm alumina powder, hydrothermal aging showed lower flexural strength than aging in the mastication simulator or non-aged specimens ($p = 0.001$).

After hydrothermal aging, 50-μm alumina powder air-abraded specimens showed higher flexural strength than non-pretreated specimens ($p = 0.012$).

After aging using the mastication simulator, non-pretreated specimens showed significantly lower flexural strength than air-abraded ones using 50-μm and 105-μm alumina powder ($p < 0.001$).

Non-pretreated and non-aged specimens showed the lowest monoclinic percentage (0.35-0.36%), regardless of the zirconia material (Table 2). Hydrothermal aging and 5 years of storage at room temperature increased the monolithic percentage of 3Y-TZP$_{0.25}$. The highest phase transformation was observed in groups air-abraded with 105-μm alumina particles. After 5 years of storage, non-pretreated and specimens air-abraded with silica-coated alumina powder showed lower monoclinic percentage compared with air-abraded specimens using uncoated alumina powder. 3Y-TZP$_{0.25}$ and 3Y-TZP$_{0.05}$ showed comparable results with respect to phase transformation, regardless of the pretreatment. As the pressure during air-abrasion increased, the monoclinic proportions of zirconia also increased.

The SEM images of pretreated zirconia surfaces are presented in Fig. 5. Corresponding results of the surface roughness are listed in Table 3. Air-abrasion using 30-μm silica-coated alumina particles showed significant differences in comparison with 50-μm ($p = 0.001$) and 105-μm ($p = 0.011$) alumina powder.

4. Discussion

4.1. *Part 1: Influence of air-abrasion parameters and aging procedures on the flexural strength*

The influence of air-abrasion on the flexural strength of 3Y-TZP$_{0.25}$ has been the subject of many investigations [9,14,15,22–25]. In this study, the pretreatment had the highest effect on the flexural strength of 3Y-TZP$_{0.25}$; therefore, the first null hypothesis was rejected. Air-abrasion using 50-μm and 105-μm led to a significant increase in the flexural strength, compared with the untreated and 30-μm silica-coated alumina group. The increase in the flexural strength of air-abraded specimens compared with untreated ones has also been reported by other authors [22–24]. These studies used similar test arrangements, but different abrasive materials were used [24], and the specimens were initially cyclic loaded in water [23]. In contrast, other studies [11,12] did not report any improvement in the mechanical properties of zirconia after air-abrasion. This may be because the specimens were air abraded for only 5 s, and different testing methods and material compositions were used. A decrease in the flexural strength was reported by Passos et al. [22] when air-abrading before sintering and by Garcia et al. [14] when air-abrading with 250-μm alumina powder. The effect of the abrasive particle size has been controversial. In contrast with the present study, Passos et al. [22] and Souza et al. [15] did not find a correlation between particle size or applied pressure and flexural strength, even though similar pretreatment methods were used. These studies used different testing methods, with four-point- [22] and biaxial flexural strength testing [15] being used. A trend towards higher absolute values with four-point flexural strength testing and lower absolute values using biaxial flexural strength test has been reported [26]; however, the results were consistent. Garcia et al. [14] reported increased flexural strength with increasing particle size, except after air-abrasion with 250-μm alumina powder. While the results of the present study are supported by the theory of transformation toughening [3], they may be interpreted critically to mean that severe destruction of the surface will lead to a decrease in mechanical properties. From the results of Garcia et al. [14], the critical particle size causing severe destruction was between 105 and 250-μm. In order to avoid damage of the surface, the use of smaller [15] or smaller silica-coated [23] particles is recommended. As reported in different studies, the use of 25-μm alumina or 30-μm silica-coated alumina powder does not increase the flexural strength compared with that of untreated groups [9,14,25]. In this regard, the findings of Qeblawi et al. [25] may be related to the specimen design. A thick specimen-configuration of 4 mm could hide a possible effect of phase transformation on the flexural strength of zirconia, which is why authors have used thin specimens ranging from 0.6 to 1.3 mm [11,12], especially when it comes to aging [27]. A thickness of 1 mm was chosen for the present study, as a further reduction of the specimen thickness does not seem to show additional effects [28].

Previous studies used varying pretreatment setups, where duration, distance and angle of alumina abrasive took place in an uncontrolled manner. In order to achieve reliable results,

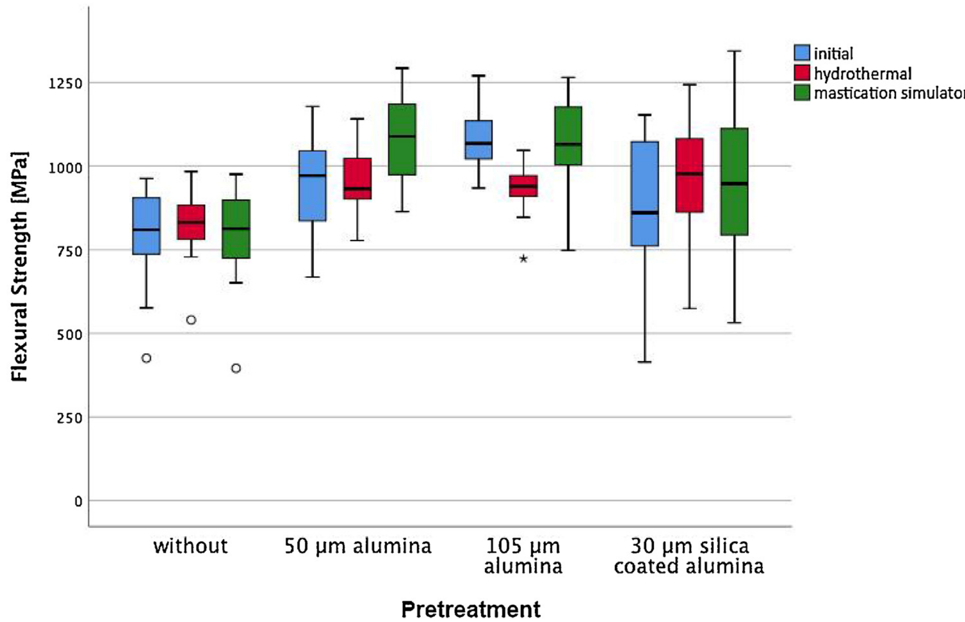

Fig. 4 – Flexural strength values in MPa of 3Y-TZP$_{0.25}$ according to the different pretreatments and aging groups.

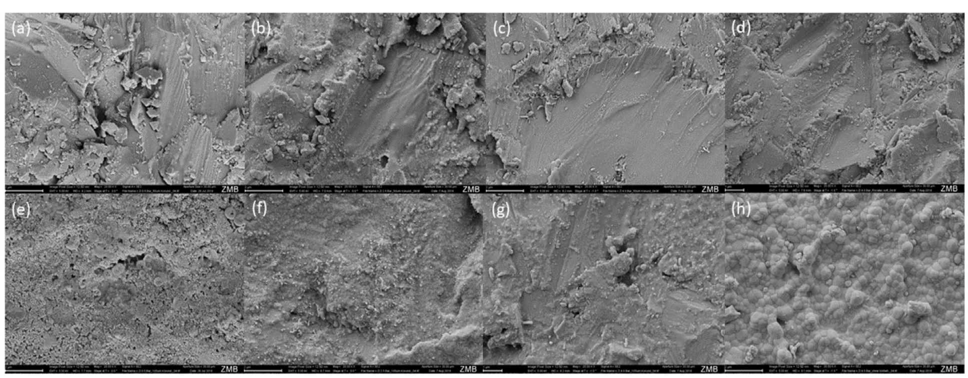

Fig. 5 – Scanning electron microscopy images of air-abraded zirconia surfaces. Magnification 20.00 KX. (a) Alumina 50 μm, 0.05 MPa (b) Alumina 50 μm, 0.25 MPa (c) Alumina 50 μm, 0.4 MPa (d) Silica-coated 30 μm (e) Alumina 105 μm, 0.05 MPa (f) Alumina 105 μm, 2.5 MPa (g) Alumina 105 μm, 0.4 MPa (h) No air-abrasion.

Table 3 – Surface roughness of air-abraded zirconia specimens.

Air-abrasion method	Mean ± standard deviation [μm]	95% confidence interval
Alumina 50 μm, 0.25 MPa	0.392 ± 0.039^{a}	(0.363; 0.421)
Alumina 105 μm, 0.25 MPa	0.369 ± 0.057^{a}	(0.327; 0.410)
Silica-coated 30 μm	0.281 ± 0.047^{b}	(0.246; 0.315)
No air-abrasion	0.334 ± 0.073^{ab}	(0.281; 0.387)

[abc]Shows significant differences in the air-abrasion methods.

a custom-made standardized device was used in the present study. Although some previous studies have only focused on pretreatment methods without taking into consideration the influence of aging procedures [7,14,22,24,29] or lacked a control group [23], the specimens of this study underwent mastication simulation and hydrothermal aging to simulate clinically relevant conditions. Aging of untreated and air-abraded specimens using 30-μm silica coated alumina powder did not have any impact on the flexural strength of 3Y-TZP$_{0.25}$, while it had a partial impact in the groups pretreated with 50-μm and 105-μm alumina powder. Therefore, this null hypothesis was only partially accepted. Aging is affected by relevant changes in the surface structure after pretreatment through air-abrasion, which did not occur without pretreatment or with the use of 30-μm coated alumina powder. SEM revealed a disordered surface of all air-abraded specimens without lateral cracks, which has been reported by other authors [29,30]. The analysis of the surface roughness demonstrated different changes after pretreatment using 30-μm coated alumina powder, compared to pretreatment with 50-μm and 105-μm alumina powder. Severe surface destruction during air-abrasion deeper than the compressive stress layer can cause a decrease in strength [18].

Table 2 – Monoclinic percentage for all tested groups after different pretreatment and different aging methods.

	Air-abrasion method	Air-abrasion pressure [MPa]	F_M – no aging [%]	F_M - no aging + 5a storage RT [%]	F_M – Autoclave [%]	F_M - Autoclave + 5a storage RT [%]
3Y-TZP$_{0.25}$	Alumina 50 µm	0.05	7			
		0.25	11	24	31	31
		0.4	15			
	Alumina 105 µm	0.05	5			
		0.25	30	42	38	45
		0.4	30			
	Silica-coated alumina 30 µm	0.28	21	16	38	23
	No air-abrasion	–	0	10	46	67
3Y-TZP$_{0.05}$	Alumina 50 µm	0.05	4			
		0.25	8			
		0.4	12			
	Alumina 105 µm	0.05	6			
		0.25	19			
		0.4	24			
	Silica-coated alumina 30 µm	0.28	17			
	No air-abrasion	–	0			

Regarding hydrothermal aging, the use of 105-µm alumina powder led to reduced flexural strength, consistent with the analysis of the phase structure which revealed the highest amount of monoclinic phase after air-abrasion with 105-µm alumina powder. LTD with a decrease in the flexural strength and an increase in monoclinic phase after hydrothermal aging has been reported by other authors [27,31]; however, the impact of air-abrasion prior to aging was not analyzed. The opposing behavior of the other pretreatment groups could be explained by the shorter autoclaving duration of 2 h at 134 °C and 0.23 MPa compared with these earlier studies, where autoclaving parameters ranged from 5 to 200 h at 134 to 180 °C and 0.1 to 0.2 MPa. A systematic review of Pereira et al. [32] concludes that an aging time higher than 20 h at 134 °C and 0.2 MPa should promote an LTD effect. It is therefore not surprising that hydrothermal aging for 0, 30, 60 and 90 min will not affect the flexural strength [33]. From the results of the present study, it seems that air-abrasion using 105-µm alumina powder could provide a greater increase of LTD, even if autoclaving parameters are substantially lower than recommended. Significantly higher flexural strength values were found after mastication simulation and air-abrasion with 50-µm alumina powder. Mastication simulation without pretreatment did not affect the flexural strength, which is consistent with other studies [34,15]. Cotes et al. [35] even reported a decrease in the flexural strength after mechanical and thermomechanical cycling. It could be concluded that air-abrasion with 50-µm alumina led to transformation of the surface structure into the monoclinic phase, which was intensified through mastication simulation with a resulting increase in the flexural strength. The lack of flexural strength change after air-abrasion with 105-µm alumina powder could be explained by a large increase in the monoclinic phase content before mastication simulation so that no further changes in the phase structure took place. As the monoclinic phase content was not determined after mastication simulation, this statement remains conjecture. In contrast, Souza et al. [15] reported that neither particle type and pressure nor mastication simulation influenced flexural strength. Further studies are needed to clarify these issues.

4.2. *Part 2: Influence of air-abrasion parameters, aging procedures and material composition on the monoclinic phase content*

All but one null hypothesis concerning the occurrence of monoclinic phase were rejected. Except for the type of zirconia used, the different parameters did affect the phase structure. Monoclinic phase content increased after air-abrasion. This increase was also reported by other authors using X-ray diffractometry (XRD) [7,9,14,15] or Raman spectroscopy in combination with XRD [15,18,23]. XRD would have been a useful addition to the present study, as the X-rays penetrate a few micrometers into the surface of the specimens [36,37]. In addition, a second method of evaluating tetragonal to monoclinic phase transformation would have supported the reliability of the measurements. The F_M-values after air-abrasion using 30-µm silica-coated alumina powder should be considered with caution, as they appear relatively high. However, 2 studies [38,39] also reported higher monoclinic phase content when using silica-coated alumina particles, even though they used XRD to detect the F_M.

The monoclinic peaks were identified at 178 and 190 cm^{-1}, locations where the t->m phase transformation is most apparent [40]. Additional characteristic monoclinic peaks could have been considered to refine the results. According to a systematic review [41], an increasing amount of monoclinic phase transformation occurring with an increasing particle size has been reported in several studies. Garcia et al. [14] reported the highest values after abrasion with 250-µm alumina powder. Souza et al. [15] reported a similar percentage of monoclinic phase content to the present study, with the highest values after air-abrasion with 110-µm alumina powder, ranging from 0% to 27.21%, whether or not the particles were silica-coated.

Lower relative monoclinic phase content in the range of 9.5% to 15.7% has been reported after air-abrasion with 110-

μm alumina powder at 0.4 MPa [7] or even 0.5 MPa [29]. These findings may be related to a greater distance from the air-abrasion tip, specimens fabricated from 3Y-TZP powders [7], where material defects cannot be excluded or where a different zirconia composition contains 5 wt% of yttrium oxide [29]. Chintapalli et al. [18] reported that the impact of grain size was minimal, concluding that erosion while air-abrading leads to a constant amount of phase transformation. These findings should be interpreted critically, as the working distance of 25 mm is higher than recommended.

Souza et al. [15] reported higher monoclinic phase percentages with increasing air-abrasion pressures of 0.25 and 0.35 MPa. Increased monoclinic phase content was also reported with 0.4 MPa instead of 0.2 MPa [16,17]. Hydrothermal aging affects monoclinic phase content and surface topography [33], which manifests as an increase in monoclinic phase. This has been reported by different authors, who analyzed the influence of hydrothermal aging on zirconia [27,31,42].

Lower F_M-values were found after air-abrasion followed by hydrothermal aging compared with hydrothermal aging of non-pretreated specimens. This protective capacity has also been reported by other authors [43,44] and could be because of the compression layer which results after air-abrasion [43,45]. Mastication simulation may be expected to affect phase transformation [34], which should be evaluated in further studies.

Previous studies have not used a storage period of more than 2 years. However, the 5-year results appear consistent with the 2-year storage reported by Dapieve et al. [46], where the m-phase content of unpretreated specimens increased by 13%. Prior hydrothermal aging led to the highest monoclinic value of 75.27%, which is consistent with the present study. The slightly higher value could be due to the longer aging period in the autoclave of 20 h. A 1-year water storage at 37 °C used by Guilardi et al. [47] showed 17.6% of monoclinic phase occurrence. This higher value could give an indication of the influence of water on aging. The protective effect of mechanical pretreatment was not apparent after storage at room temperature, where the lowest values were found for non-air-abraded and 30-μm silica-coated alumina pretreated specimens. However, after additional hydrothermal aging 67% of monoclinic phase content of non-air-abraded specimens and approximately half of the value for air-abraded ones were found. Similar results have been reported by Silvestri et al. [48], who combined different common aging methods in order to promote LTD. Specimens ground with a diamond rotary instrument before aging showed 30.75% of monoclinic phase content.

Interestingly, the monoclinic volume fraction of non-aged, air-abraded specimens using 30-μm silica-coated alumina decreased after 5 years of storage. An additional examination was performed in order to confirm this finding. The surfaces of two different specimens of the same group were measured using Raman spectroscopy, both showing lower monoclinic phase proportions (20% and 18%). This supports the use of air-abrasion with 30-μm silica-coated alumina as a beneficial pretreatment. Further studies are needed to analyze this specific characteristic.

The type of zirconia used in this study differed in the percentage of aluminum oxide and zirconia with higher aluminum oxide concentrations have been reported to resist the occurrence of monoclinic phase after aging [31]. However, the results of the present study showed comparable values for both zirconia generations, leading to acceptance of the null hypothesis and not supporting the previous study. Effects concerning LTD resistance have been reported with the use of different stabilizers [49] or manufacturers [42]. The exact composition of the material is usually unknown; therefore, more studies to identify protective or damaging factors could lead to a more reliable clinical performance.

The present study was limited as the in vitro testing did not fully replicate the in vivo oral environment. Clinical studies should be carried out in order to determine the clinical relevance of the different parameters tested in this study.

5. Conclusions

Mechanical pretreatment through air-abrasion increased the flexural strength of non-aged 3Y-$TZP_{0.25}$ with increasing alumina particle-size. Hydrothermal aging and mastication simulation of 50-μm and 105-μm air-abraded specimens had more influence on flexural strength compared with prior pretreatment using 30-μm silica-coated alumina powder. Increasing particle size and pressure led to increased monoclinic phase content. All pretreatment groups showed higher monoclinic phase content after hydrothermal aging and/or 5 years of dry storage at room temperature with the exception of the specimens air-abraded with 30-μm silica-coated alumina powder. Therefore, this pretreatment method can be recommended regardless of whether a first or second generation zirconia is used.

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