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In Vitro Evaluation of the Shading Effect of Various Zirconia Surface Stains on Porcelain Crowns

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Abstract: Human teeth display various colors under natural light. Dental restorations, such as zirconia crowns, are generally used to rehabilitate the oral function of patients with tooth loss due to trauma or natural tooth falls. However, significant improvements in the color and translucency of zirconia are required to meet the clinical needs for dental restoration. In the past, a large amount of ceramic powder has been used to improve the appearance of zirconia. However, the interface between the ceramic powder and zirconia makes them prone to falling off. Therefore, the aesthetics of zirconia crowns remains a major challenge. Recently, substantial advances have been made in the field of dental materials, as special staining agents for zirconia have been introduced as alternatives to ceramic powders. Therefore, this study tested zirconia-specific staining agents that were used to produce zirconia samples with A1 and A3 colors. A dental colorimetric plate was used as the control group to assess the staining effects of the different brands of staining agents. Meanwhile, two hypotheses were proposed: that the staining effects of these special staining agents for zirconia met the criteria for clinical application and that there was no significant difference between the different staining agents for zirconia. The results showed that the coatings of different brands of staining agents were ultrathin, with a thickness of approximately 27–78 μm. In addition, the coloring effects of the zirconia staining agents were not significantly different from those of the colorimetric plates. After staining, the zirconia samples had decreased surface roughness and contact angle values, which improved surface smoothness and cleanliness. In summary, the results support the hypothesis of this study that zirconia stains can be used as an alternative to the current fabrication methods for clinical dental restorations. We sought to identify the clinical techniques that are easier to perform and to overcome the current problem of dental technicians requiring considerable dentin space for staining. It is expected that the results of this study will be useful in clinical dental restorations.

Keywords: zirconia; digital dentistry; dental aesthetics; dental stains; dental technician

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1. Introduction

Dental restoration technology innovations in dental clinical practice are currently on the rise. Hence, when faced with tooth damage, patients no longer expect their dentist or dental technician to simply fabricate a dental restoration with chewing functions and normal occlusion [1]. Restoring the appearance, occlusion, and color of the patient's teeth with a bionic design has become essential [2,3], as aesthetics must be considered in dental restoration [4–6]. The characteristic of being aesthetically pleasing is based on subjective opinion; with personal standards and perception of colors, there is a reciprocal relationship between aesthetic consciousness and the aesthetic object [7]. Therefore, a sense of harmony and aesthetics are important indicators of dental restorations and the appearance of teeth in the oral cavity [5].

In the past, most clinical dental restoration techniques produced dental restorations with good occlusion, color, and appearance, similar to those of real teeth. Generally, the traditional method is to replace natural teeth with porcelain fused to metal (PFM) crowns [8]. Traditional PFM crown fabrication is divided into two steps: wax-up and sintering. In this context, dental technicians must dedicate a large amount of time practicing to perform dental restorations independently and skillfully. However, the process of porcelain layering is prone to instability because of the long duration of the operation procedure and the dental technician's technical skills. In addition, the ceramic layer is prone to bubbles, which increases the chance of failure [9,10]. Traditional PFM crowns consist of a two-layer structure, in which a layer of porcelain is sintered on the outside of a metal inner crown. Because PFM crowns are not one piece, the interface of the two different materials, namely, the metal and porcelain, is a fragile region that can easily lead to the breakage of porcelain [11–14]. In the past, the traditional porcelain layering technique required the layering of a large amount of porcelain powder in the order of dentin, enamel, and stained enamel paste to produce an appearance similar to that of natural teeth. This creates important challenges related to operational difficulties and color expression [15,16]. In addition, if color changes are needed, it is necessary to remake the crown, which is expensive and time-consuming.

Therefore, traditional porcelain layering in clinical dentistry has been gradually replaced through digital fabrication. Only a few steps are required in digital dental technology: scanning using an oral scanner → model design → CAD/CAM or 3D printing → finished product [17,18]. The transfer of dental restoration techniques to digital technology has been shown to shorten the fabrication process and control the restoration shape for clinical application [19,20]. In addition, to reduce the tendency for failure in the binding between the metal and ceramics, full ceramic crowns are now used for dental restorations in clinical practice [21]. These full-ceramic crowns have replaced the metal part of PFM crowns, improving the crown's appearance by reducing the shadow caused by the metal part [22]. The materials currently used for full-ceramic crowns in dental clinical practice are zirconia and glass-ceramics (disilicate glass) [23,24].

Zirconia is a commonly used material in dental crown restorations and is widely used clinically because of its high strength, good biocompatibility, and ease of fabrication [25,26]. However, the color of zirconia may change with the addition of yttrium oxide (also known as yttria), which decreases its translucency and optical properties [27,28]. Therefore, fine-tuning the color of zirconia is currently the main challenge. The current approach is to enhance translucency by increasing the concentration of yttrium oxide. However, literature reports that adding too much yttria (5–6%) will reduce the strength of zirconia [28,29]. Therefore, zirconia has mostly been used for molars [30]. For the anterior teeth, where the appearance is important, much porcelain layering must be utilized on the labial side to improve the appearance, similar to PFM crowns. Significant progress has been made in dental materials, and staining agents for zirconia that are both aesthetically pleasant and easy to use have been developed [31]. In clinical practice, dental restorations can be made using 3D printing or CAD/CAM, followed by staining [32]. In this process, the crown or veneer is made using digital molding, and the color of the zirconia surface is directly changed by applying staining agents, which addresses the aesthetic issues of the opaque white zirconium materials.

Therefore, this study mainly investigated and assessed the staining effects of various zirconia surface-staining agents on dental restorations. The surface properties, optical properties, and surface roughness of the stained layer were assessed after staining with zirconia. In addition, the clinical application of the staining agents was assessed during the preparation of zirconia crown restorations. Meanwhile, two hypotheses were proposed: the staining effects of the special staining agents for zirconia met the criteria for clinical application, and there was no significant difference between the different zirconia staining agents. We sought to identify the clinical techniques that are easier to perform. Overcoming the current problem of dental technicians requiring considerable dentin space for staining. These zirconia staining agents are expected to solve the current color modification issues associated with zirconia restorations and can be used as a novel technique for clinical dental restoration.

2. Materials and Methods

2.1. Preparation of Zirconia

Dental zirconia discs (ST-Color, Upcera, Shenzhen, China) were used as the main sample, which were cut into two sizes. To analyze the properties of zirconia, zirconia materials were cut into $10 \times 14 \times 1$ mm^3 samples, and waterproof abrasive paper was used for polishing (#800, #1200, and #2000). Zirconia was assessed using a dental desktop scanner (Medit, T5100, Seoul, Korea) to first establish a dental cast. Dental restorations were then designed and fabricated using an inLab 16 CAD/CAM (Cerec, Dentspy Sirona, Bensheim, Germany). After all the zirconia prints were cut, sintering and strengthening of the zirconia (1530 °C, 8 h) was performed according to the product instruction manuals to obtain the final zirconia samples.

2.2. Staining of Zirconia

In this study, different staining agents were used to stain the zirconia samples. In dental clinical practice, the natural tooth colors A1 (bright) and A3 (dark) are commonly observed. Therefore, A1 and A3 were used for the experimental groups, and the VITA standard 16-color colorimetric plate (Classical, VITA, Bad Säckingen, Germany) was used as the control. Each group of samples was tested five times and the mean values were calculated. However, zirconia stains usually use only a single color. Appropriate colors must be prepared based on the experience of the dental technician and preferably as a mixture of individual colors to achieve a natural result. Therefore, we adjusted the appropriate color in accordance with different color ratios before staining (Table 1). Subsequently, all samples were stained by the dental technician. The sample was placed in vertical contact with a stain pen (Figure 1). Sintering was performed according to the manufacturer's instructions (Table 1), which included AKZENT Plus (VITA, Bad Säckingen, Germany), Biomic (Aidite, Qinhuangdao, China), Miyo (JENSEN, Panama City, FL, USA), and Crystall (Ivoclar Vivadent, Zurich, Switzerland). Finally, all the samples were analyzed using a dental spectrometer (EASYSHADE V, VITA, Bad Säckingen, Germany) to ensure color performance consistency.

Table 1. Staining agent name, brand, and temperature.

Name	Brand	Type	Sintering Temperature (°C)	Colors Used	Proportion (%)	
AKZENT Plus	Vita	Powder/liquid	780	BS03	15.4	100
				BS05	30.8	
				ES07	53.8	
Biomic	Aidite	Paste	730	ShadeA	62.5	100
				ShadeB	31.3	
				Black	6.3	
Miyo	JENSEN	Paste	720	TRANS SHADE A	33.3	100
				TRANS SHADE B	44.4	
				TRANS SMOKE	11.1	
				TRANS STORM	11.1	
Crystall	Ivoclar Vivadent	Paste	830	Shade 2	25.0	100
				Shade I2	70.0	
				Shade I1	5.0	

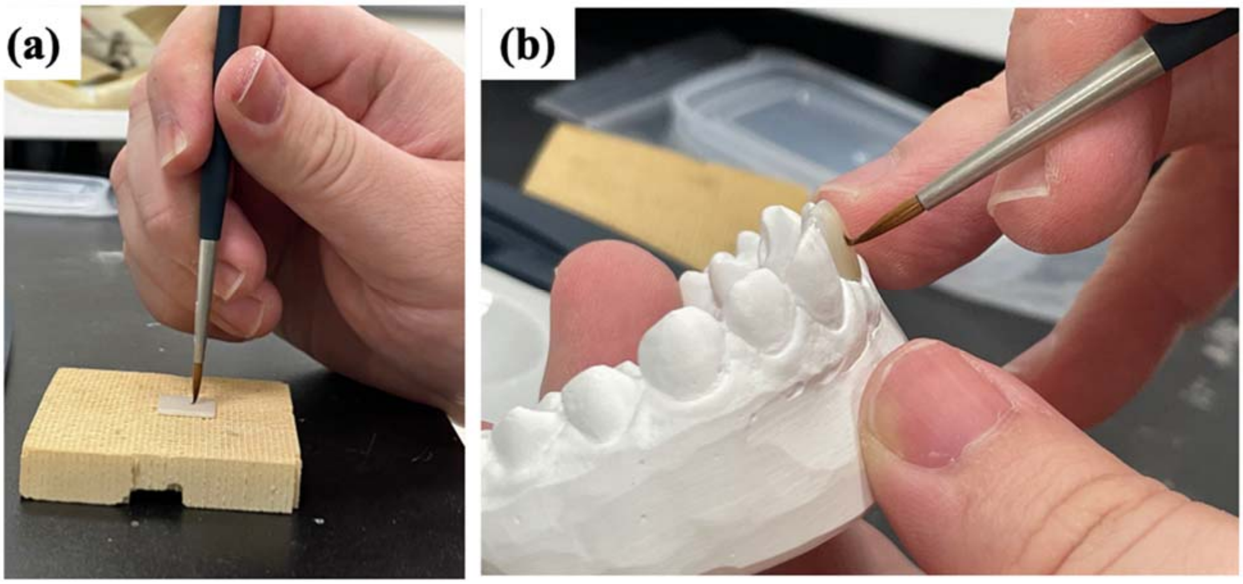

Figure 1. A dental technician performs zirconia surface staining: (**a**) piece and (**b**) crow.

2.3. Optical Properties of Zirconia

In this study, the optical properties of zirconia samples stained with A1 and A3 were analyzed using a dental spectrometer (EASYSHADE V, VITA, Germany). Spectrometer measurements were performed for each group of samples in three environments: a white background (W), a black background (B), and B1 and A3 color plates of the traditional 16-color VITA shade guide plate. The L^*, a^*, and b^* values of each tooth color group were recorded. In addition, different optical properties of the zirconia samples, such as the translucency parameter (TP), opalescence parameter (OP), and color difference (ΔE), were calculated using the following formulae [33,34]:

$$\text{Translucency Parameter (TP)} := \sqrt{\left(L_B^* - L_W^*\right)^2 + \left(a_B^* - a_W^*\right)^2 + \left(b_B^* - b_W^*\right)^2} \quad (1)$$

$$\text{Opalescence Parameter (OP)} := \sqrt{\left(a_B^* - a_W^*\right)^2 + \left(b_B^* - b_W^*\right)^2} \quad (2)$$

$$\text{Color difference } (\Delta\text{E}) := \sqrt{\left(L^{*1} - L^{*2}\right)^2 + \left(a^{*1} - a^{*2}\right)^2 + \left(b^{*1} - b^{*2}\right)^2} \quad (3)$$

2.4. Surface Modification of Zirconia

A field-emission scanning electron microscope (JSM-7610F, JEOL, Tokyo, Japan) was used to observe the microstructure of the stained layer on the surface of zirconia. The surface of the test piece was plated with gold at 30 KV for 30 s to increase the conductivity and to make it easier to observe the surface of the zirconia sample and crown.

2.5. Contact Angle Test

The contact angle is a common indicator for assessing the hydrophilicity and hydrophobicity of a material's surface. Contact angle testing of the hydrophilicity and hydrophobicity of the materials was performed by titrating deionized water at 25 °C and 70% relative humidity (RH). Subsequently, the contact angle was calculated using the angle tool function in ImageJ software [35].

2.6. Thickness of the Staining Layer

In this study, a clamp was applied to the zirconia samples to produce fractured cross-sections. Subsequently, the thickness of the staining layer on the surface of each zirconia sample was observed using an optical microscope (LEICA S9; Leica, Germany). Finally, digital analysis software (LEICA S9, Leica, Munich, Germany) was used for measurements and recordings.

2.7. Surface Roughness Test

Atomic force microscopy (AFM, Benyuan Nanometer Instrument Co., Ltd., CSPM5500, Beijing, China) uses a special tiny probe to detect the interactions between the probe and the sample surface. The probe scans left and right on the sample surface to convert the signals to images, and the scanner is used to analyze the roughness average (Ra), the maximum height of the profile (Rz), root mean square (RMS), and the maximum height of the sample surface. This study adopted a measurement size of 30 μm $\times$ 30 μm. Measurements were performed at five points on each sample to calculate the mean values.

2.8. Applied Assessment

Human teeth are rich in surface features and structures [36]. To assess the performance of staining agents in clinical crown restorations more vividly, crown samples were prepared according to the clinical preparation steps for zirconia crowns (Section 2.1) in this study. Oxidized crowns were used for staining and analysis of the optical properties and color differences. In addition, a dental desktop scanner (Medit, T5100, Seoul, Korea) was used to create digital files for the crowns, and the coating thicknesses before and after staining were analyzed using a software (Medit compare, T5100, Seoul, Korea). Finally, the thickness of the stained layer was assessed by weighing the crown before and after staining. The sample was placed on an electronic scale (ATX224, Shimadzu, Tokyo, Japan) with a precision of two digits after the decimal point.

The above analytical methods were used to assess the clinical applicability of the staining agents for zirconia crowns.

2.9. Statistical Analysis

All data are expressed as mean $\pm$ standard deviation (SD) of four samples. The data were analyzed using JMP 14 software (SAS Institute, Cary, NC, USA). A one-way ANOVA followed by Tukey's HSD post-hoc test was used to determine the level of significance, where $p < 0.05$ was considered significant.

3. Results and Discussion

3.1. Staining of Zirconia

Currently, more focus is being placed on restorations in dental clinical practice. Significant progress has been made in the development of new dental materials. In the past, dental technicians could only express the color using a large number of ceramic layers, while we are currently attempting to modify the color of a crown's surface by staining. In this study, staining agents were applied to zirconia surfaces to change the original color and assess the differences between different brands. The results showed that both B1 and A3 could be produced on pure white zirconia surfaces using staining agents (Figure 2). Furthermore, the black background resembled a dark environment inside the mouth, whereas the white background represented a bright environment outside the mouth. The original zirconia samples appeared white against both backgrounds. However, the color changed after staining the samples with different staining agents. This indicates that the staining agents improved the color of the zirconia surface when observed with the naked eye.

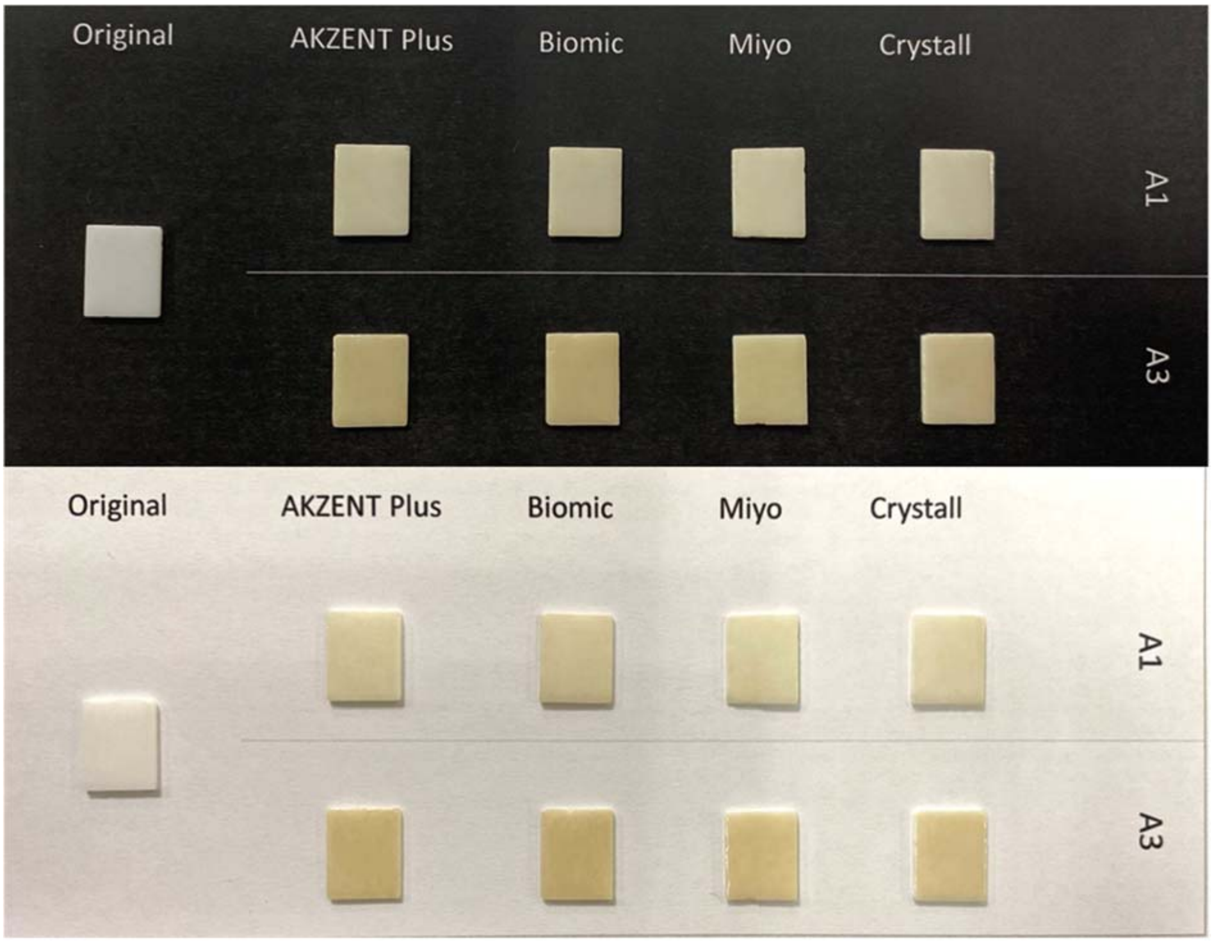

Figure 2. Visual appearance of zirconia samples after staining on black and white backgrounds.

3.2. Optical Properties of Zirconia

As the human eye has certain limitations in terms of color perception, it is necessary to convert such colors to relative numbers using a colorimetric instrument. In this study, a dental spectrometer was used to record the optical values of zirconia samples after staining and to obtain the TP, OP, and ΔE values of the surfaces. The results showed that the surface TP of the original zirconia was 11.28 [37], which was similar to the values reported in the literature. However, the translucency of the stained zirconia samples all improved by 20–40%, with AKZENT Plus and Crystall being the highest and showing a significant difference ($p < 0.05$) (Figure 3a). Interestingly, TP appeared to correlate with color brightness. The brighter A1 of all the stained samples had a higher translucency than the darker A3 color, especially with AKZENT Plus, Biomic, and Miyo, which showed significant differences. The ceramic was more translucent with higher TP values. The outermost layer of human teeth is composed of enamel, which is relatively translucent, whereas the dentin inside is opaque. Therefore, fabrication of dental restorations must meet these aesthetic requirements. The results of this study show that zirconia samples may be stained to improve their translucency.

Human teeth are composed of hydroxyapatite and a small amount of collagen. Therefore, teeth are sometimes fluorescent (colored) when exposed to light. Previous studies have shown that opalescence can be calculated using a formula [34]. Therefore, in this study, the opalescence values before and after staining of the zirconia samples were calculated using the formula for assessment. The results showed that the opalescence values of the zirconia samples coated with different staining agents increased 2–5.5 times, with significant differences ($p < 0.05$) (Figure 3b). Miyo had the highest opalescence values for A1 staining (approximately three times higher). There were almost no significant differences between the different brands in A3 staining. However, similar to the translucency results, this study found that darker A3 staining was associated with higher opalescence. This seemed to be caused by the thicker layer of the staining agent required for the staining of the A3 color system. However, the true thickness of the stained layer must be determined to confirm this hypothesis.

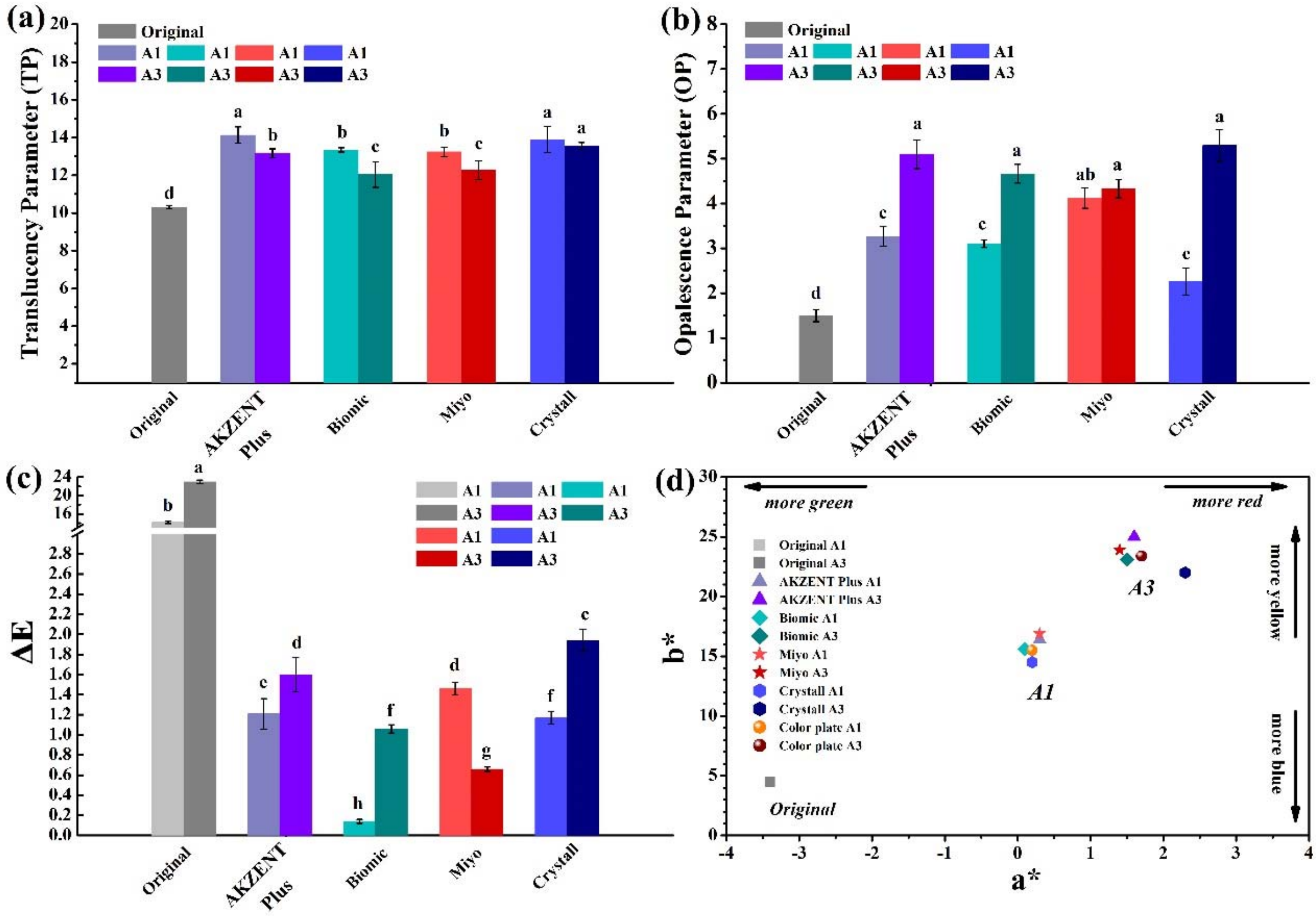

Figure 3. Optical properties of zirconia. (**a**) Translucency parameter (TP), (**b**) opalescence parameter (OP), (**c**) ΔE, and (**d**) coordinate distance. Means with different letters were significantly different ($p < 0.05$, mean ± SD, $n = 5$).

During the fabrication of dental restorations, dental technicians attempt to match the color of the dentures to that of the patient's natural teeth. The purpose of this study was to assess whether staining agents could improve the color performance of the zirconia. According to the Munsell color system, all colors have three-dimensional coordinates consisting of value, hue, and chroma [38]. Therefore, the optical values of the zirconia samples after staining and those of the standard colorimetric plate were calculated, and the coordinate differences between the two were determined to analyze the staining effect, which was expressed as ΔE [31]. A lower ΔE indicates less error between the two, which suggests a consistent color performance. The results showed that the original zirconia samples differed the most from the colorimetric plate (Figure 3c), reinforcing the conclusion that zirconia samples must be modified to meet clinical requirements. The ΔE values of all the zirconia sample groups after staining were between 0.2 and 2.0 (Figure 3c). The A1 color staining effects showed that samples stained with Biomic were the most similar to the colorimetric plate, followed by those stained with Crystal, AKZENT Plus, and Miyo. The A3 staining effect was the best in samples stained with Miyo, followed by those stained with Biomic, Crystall, and AKZENT Plus. The literature reports a ΔE of 2.6 is the lowest limit of color differentiation by human eyes [39]. The staining results of this study showed that although there were significant differences in the A1 and A3 performances between the different staining agents, all the ΔE values were below 2.6. This indicates that the colors of the stained zirconia samples were not significantly different from those of the colorimetric plate.

In addition, this study found that the main factors affecting the coordinates were the a^* and b^* values of the optical parameters. Therefore, the a^* and b^* values of the standard colorimetric plate and all samples were analyzed. The results showed that the original zirconia samples differed the most from the colorimetric plate (Figure 3d). The results for the remaining stained zirconia samples mainly focused on A1 and A3 of the colorimetric plate. This result was consistent with the ΔE results, showing that the zirconia samples were not significantly different from the standard colorimetric plate after staining.

3.3. Surface Modification of Zirconia

The topography of a material's surface may affect its properties, such as light refraction, roughness, and biocompatibility [40,41]. In this study, the zirconia surface before and after staining was observed using scanning electron microscopy to assess the impact of staining on the microstructure of the zirconia surface. The microstructure of the zirconia particles could be clearly observed on the zirconia surface before the staining, which is in accordance with the literature (Figure 4a). Conversely, the stained zirconia samples exhibited smooth surfaces (Figure 4a). This showed that the stained layers on the zirconia surface had improved smoothness, regardless of the brand. In addition, the microstructures showed that the stain was smoothly and uniformly coated on the surface of the zirconia samples.

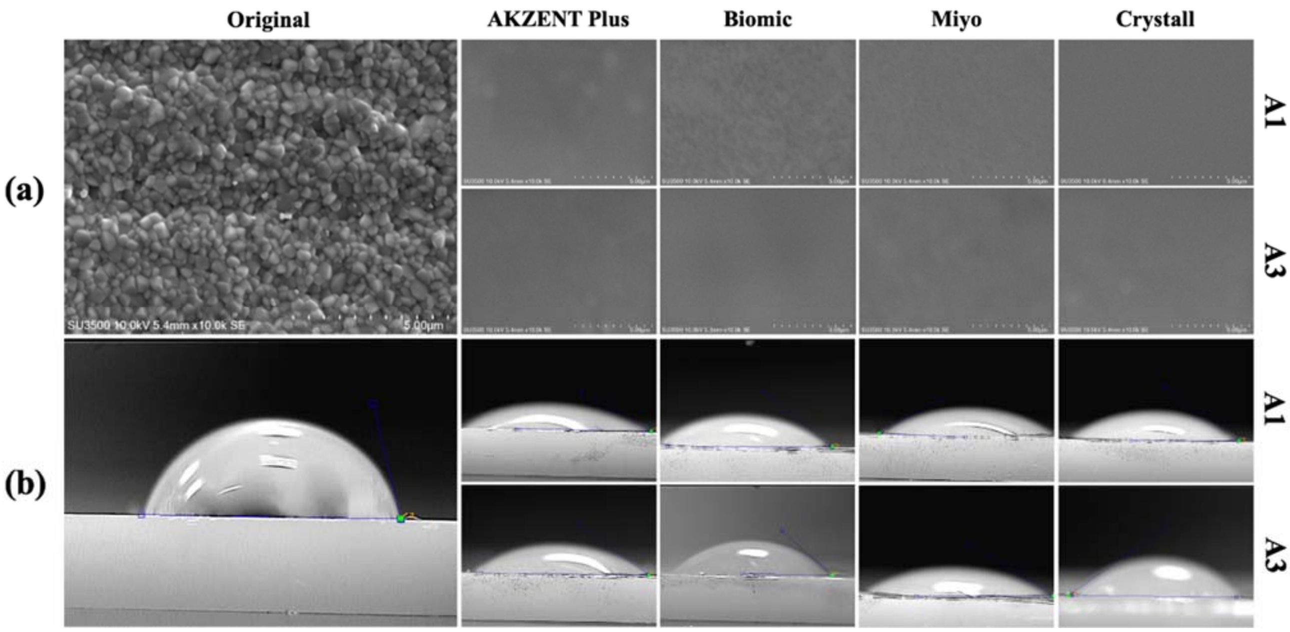

Figure 4. Surface modification of zirconia. (**a**) Microscopic image and (**b**) contact angle.

3.4. Contact Angle Test

The contact angle is generally used to assess the hydrophilicity and hydrophobicity of a material surface [42]. In this study, pure water was used to test the zirconia surfaces (Figure 4b). The results showed that the surface contact angle of the original zirconia sample was 75°, which is similar to the findings of previous studies (Figure 5) [43]. After staining, the contact angle of the surface was greatly reduced, and the hydrophilicity of the zirconia surface was improved (reduced by approximately 64–40%). The largest decrease was observed for sample surfaces stained with Miyo in both the A1 and A3 color groups, with significant differences ($p < 0.05$). It is worth noting that the contact angle of A3 was higher than that of A1 as the color deepened. It was speculated that an increase in the thickness of the staining layer could increase the contact angle. Nonetheless, the hydrophilicity and hydrophobicity results indicated that staining helped increase the hydrophilicity of the zirconia surface.

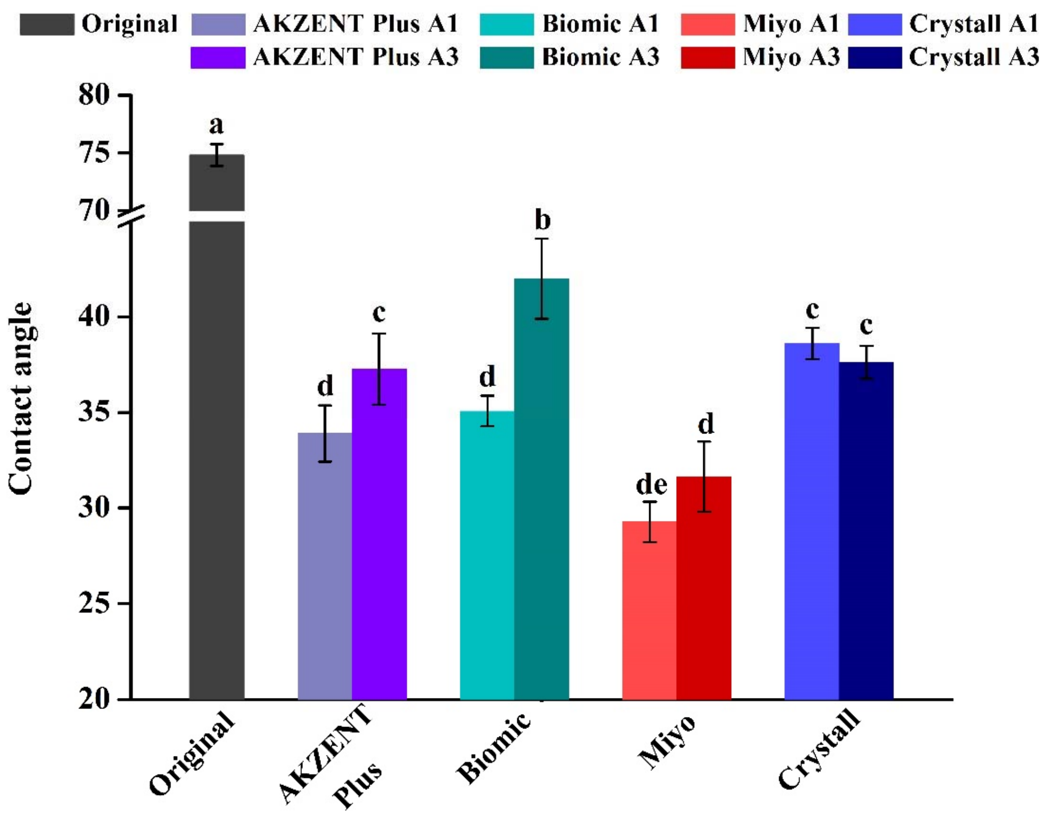

Figure 5. Comparison of the contact angle values of the zirconia samples after staining. Means with different letters were significantly different ($p < 0.05$, mean ± SD, $n = 5$).

3.5. Thickness of the Staining Layer

Human teeth are quite special, in that there are only permanent teeth after the deciduous teeth have fallen on their own. Dental restorations are required when there is decay or a defect in one or more permanent teeth [44]. However, natural dentin is precious, and excessive grinding must be avoided as much as possible. Therefore, dental restorations must produce an appropriate color with a limited thickness. In previous clinical practice, large amounts of different types of ceramic powder had to be layered to produce color changes within a thickness of 1–1.5 mm [45]. Currently, to reduce the porcelain layering steps and save space, improved solutions have emerged to replace the layering of large amounts of porcelain with staining agents. To analyze the layer thickness, a clamp was used to break the stained zirconia samples. The cross-sections of the zirconia and stain coatings were then observed using an optical microscope (Figure 6). Finally, the coating thickness was measured using a software, and the differences between the diverse colors and brands were analyzed (Figure 7a). The results showed that the layer of the staining agent Biomic for color A1 was the thinnest (28 μm) and there was no difference in the thicknesses of the stains between the other groups (35 μm). However, the stain thickness of A3 was greater than that of A1. Among them, Biomic (47 μm) was the thinnest, followed by AKZENT Plus (50 μm), Miyo (74 μm), and Crystall (77 μm). Color differences between the different brands were observed, resulting in differences in coating thickness. Nonetheless, the thickness of all the staining agents was less than 0.1 mm, which was 15 times smaller than that produced using the traditional method of porcelain layering. It was demonstrated that only a very thin layer of staining agent is required to change the color. However, in addition to assessing the thickness of the stain for clinical applications, it is more important to consider the optical properties and surface properties. In addition, this study found colored crystalline particles on the surface after using these staining agents. The size was calculated to be approximately 15–23 μm, with almost no significant difference (Figure 7b). These colored particles were speculated to be the main source of color expression. However, the shade was not adjusted by a change in the particle size but was caused by an increase in the thickness of these particles and the coating.

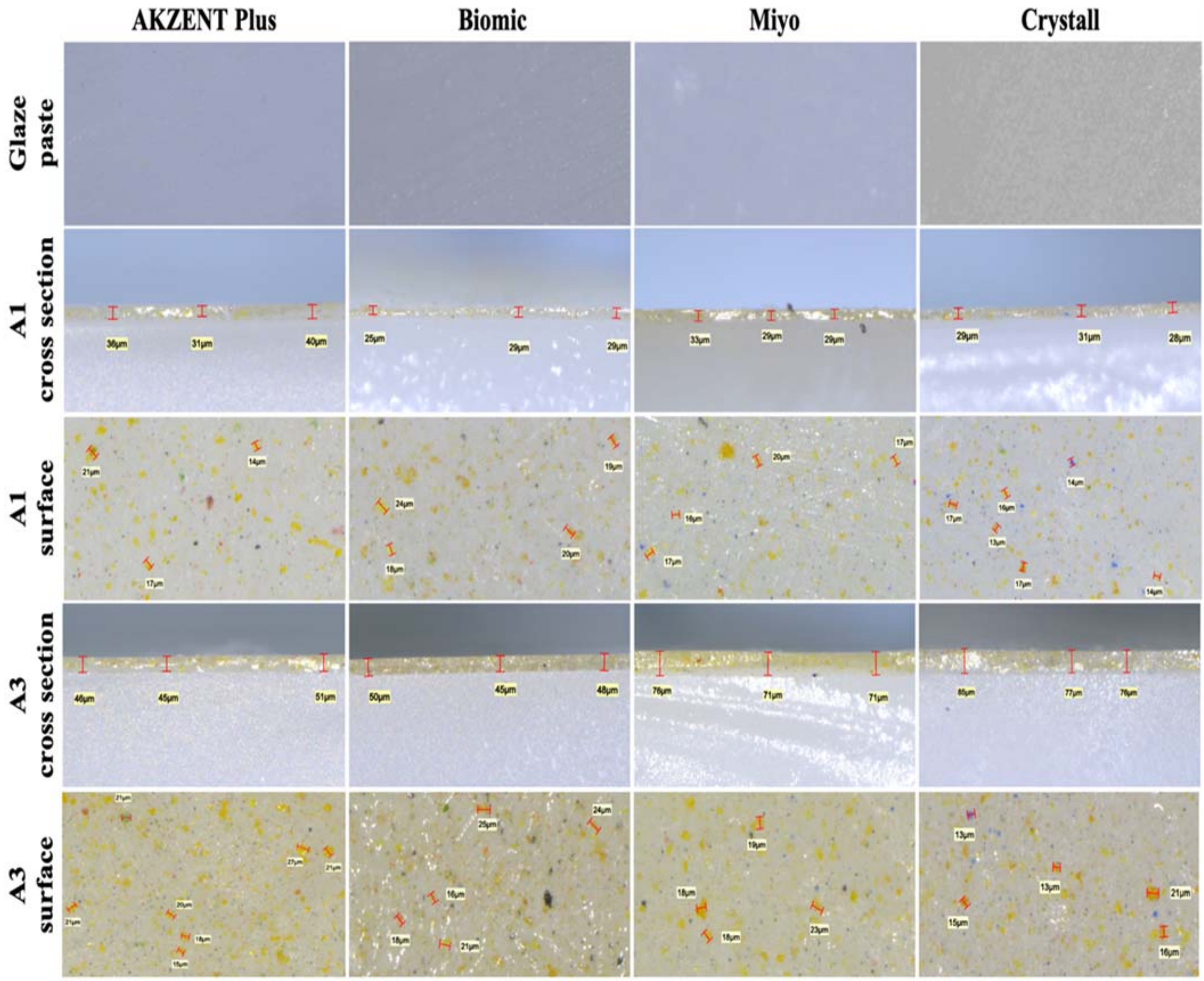

Figure 6. Thickness of the staining layer.

3.6. Surface Roughness Test

Many microorganisms are present in the human oral environment [46]. Therefore, the surface roughness of dental restorations is important as a mean to prevent excess accumulation of such microorganisms. A smooth surface may reduce the adhesion of food and bacteria as well as prevent oral diseases. In this study, the surface roughness values of the zirconia samples were observed using AFM (Figure 8), and the Ra, Rz, RMS, and maximum height values of the sample surfaces were analyzed. The results showed that all roughness indices decreased after staining and smooth surfaces were produced (Figure 9). The differences in the surface roughness values between the zirconia and stained samples were 5.6–7.9 times (Ra), 1.5–2.1 times (Rz), 6.2–9.3 times (RMS), and 4.9–10.2 times (max height). However, the roughness results for different brands of staining agents were very similar. The results showed that the surface fineness was improved, and the surface roughness was reduced after staining the zirconia samples.

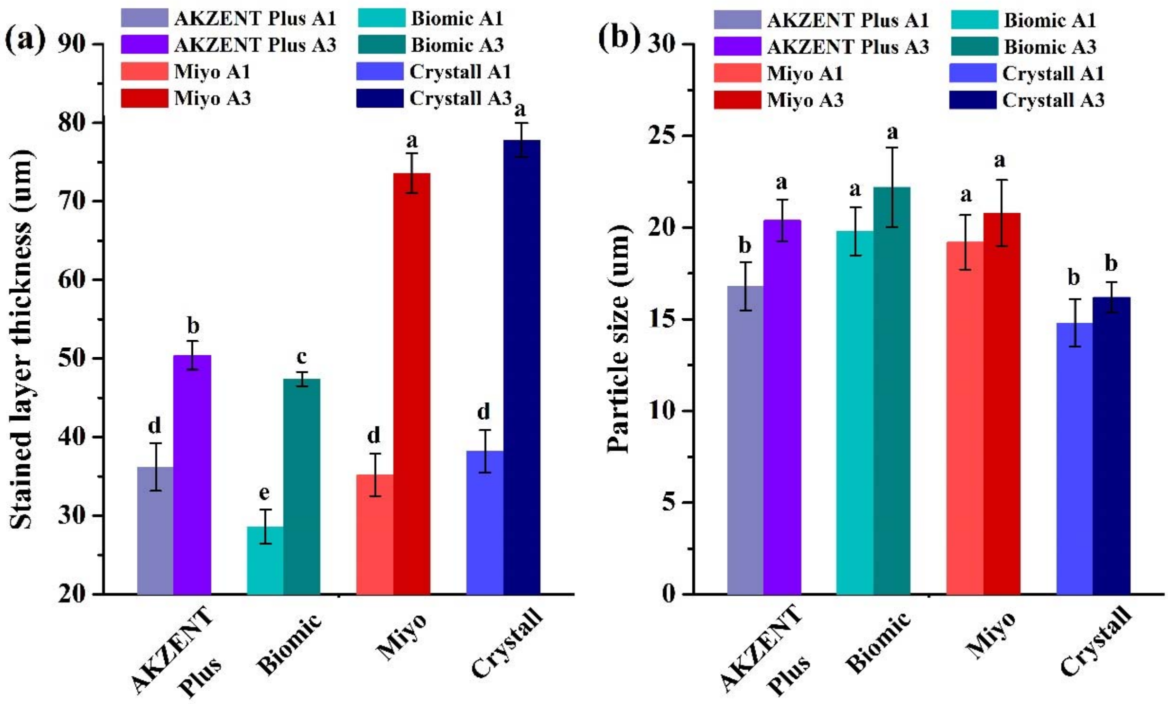

Figure 7. Comparison of the thickness of the zirconia samples after staining. (**a**) Thickness and (**b**) particle size. Means with different letters were significantly different ($p < 0.05$, mean ± SD, $n = 5$).

3.7. Applied Assessment

In dental clinical practice, teeth are composed of complex surface structures and angles [47]. In this study, to meet the requirements for clinical applications, zirconia crowns consistent with those used in clinical practice were fabricated, and different stains were used for surface staining. The thickness of these zirconia crowns in this study was set to 1 mm. The results showed that the surface of the original zirconia crowns was white (Figure 10). However, it could be clearly observed that all the crowns had a standard A3 color after staining. According to the literature, there is a limit to the color discrimination of the human eye [39]. Therefore, in this study, the optical properties were measured using a dental spectrometer, and the color difference (ΔE) was calculated and compared to the A3 results for the control group. The results showed that the original zirconia crown had the largest difference (22.2 ± 0.3). The ΔE values of the crowns treated with staining were all lower than the lowest limit of color differentiation for human eyes, which were 2.1 ± 0.1 (AKZENT Plus), 2.5 ± 0.2 (Biomic), 2.1 ± 0.1 (Miyo), and 1.6 ± 0.1 (Crystall) (Figure 9). This showed that different brands of staining agents met the color requirements of clinical dental restorations.

Meanwhile, this study established digital archives to overlap zirconia crowns before and after staining and calculate the thickness of the stained layer. The results showed that the thickness of the stained layer on the crown surface was uniform, which is consistent with the results obtained for the zirconia samples (Figure 11). The thicknesses of the stained layers were higher when using Miyo and Crystall, followed by those with AKZENT Plus and Biomics (Figure 11b). In addition, weight changes before and after staining were calculated. The results show that the weight was positively correlated with the thickness of the coating (Figure 11c). The weights of all the stains were less than 11.5 mg, which posed a little extra burden on crown restoration. Based on the above assessment results for clinical applicability, it can be observed that the staining agents may be used as an alternative for the color modification of zirconia crowns.

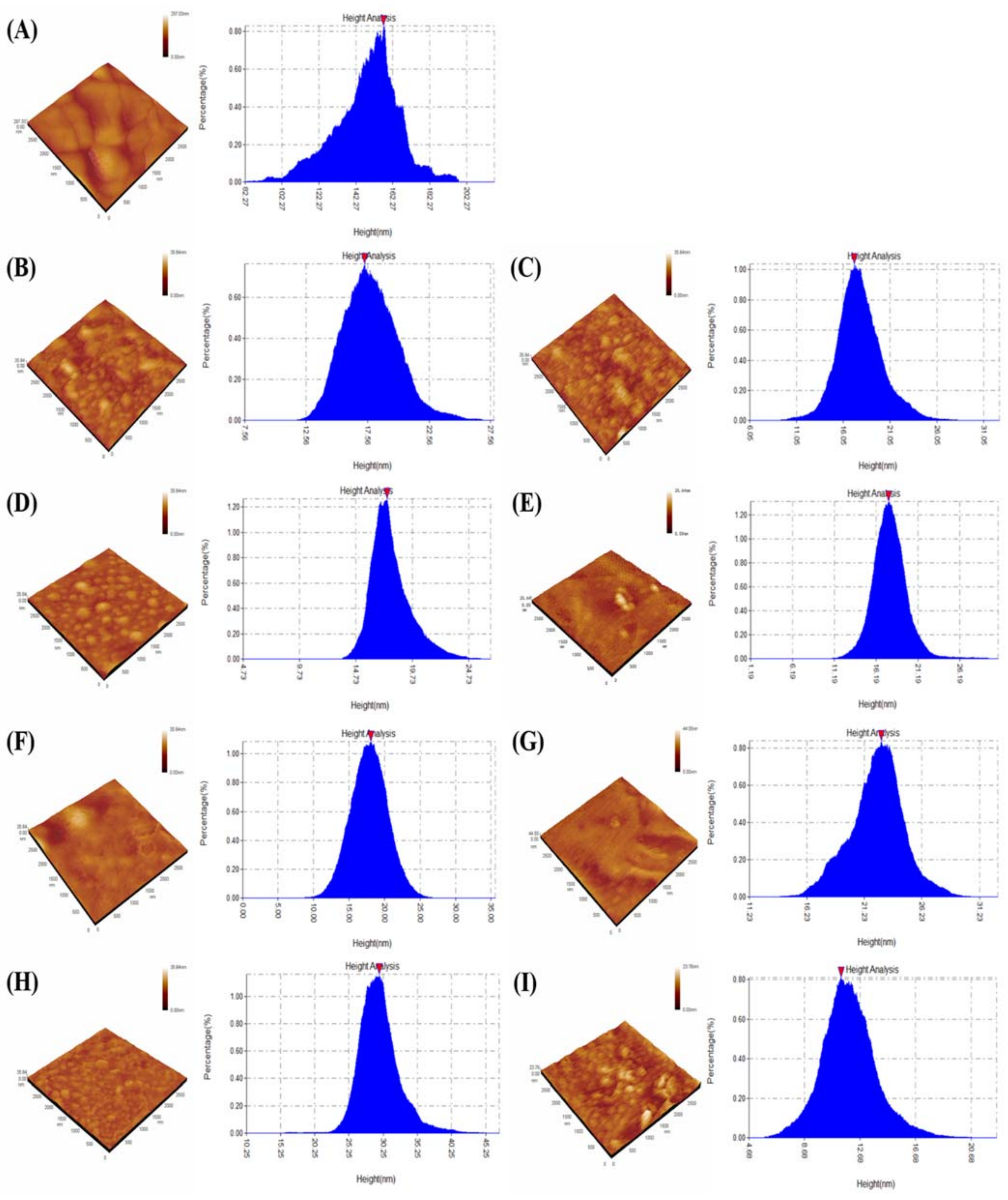

Figure 8. Surface roughness images (AFM) of the zirconia samples after dyeing. (**A**) Original, (**B**) AKZENT Plus A1, (**C**) AKZENT Plus A3, (**D**) Biomic A1, (**E**) Biomic A3, (**F**) Miyo A1, (**G**) Miyo A3, (**H**) Crystall A1 and (**I**) Crystall A3.

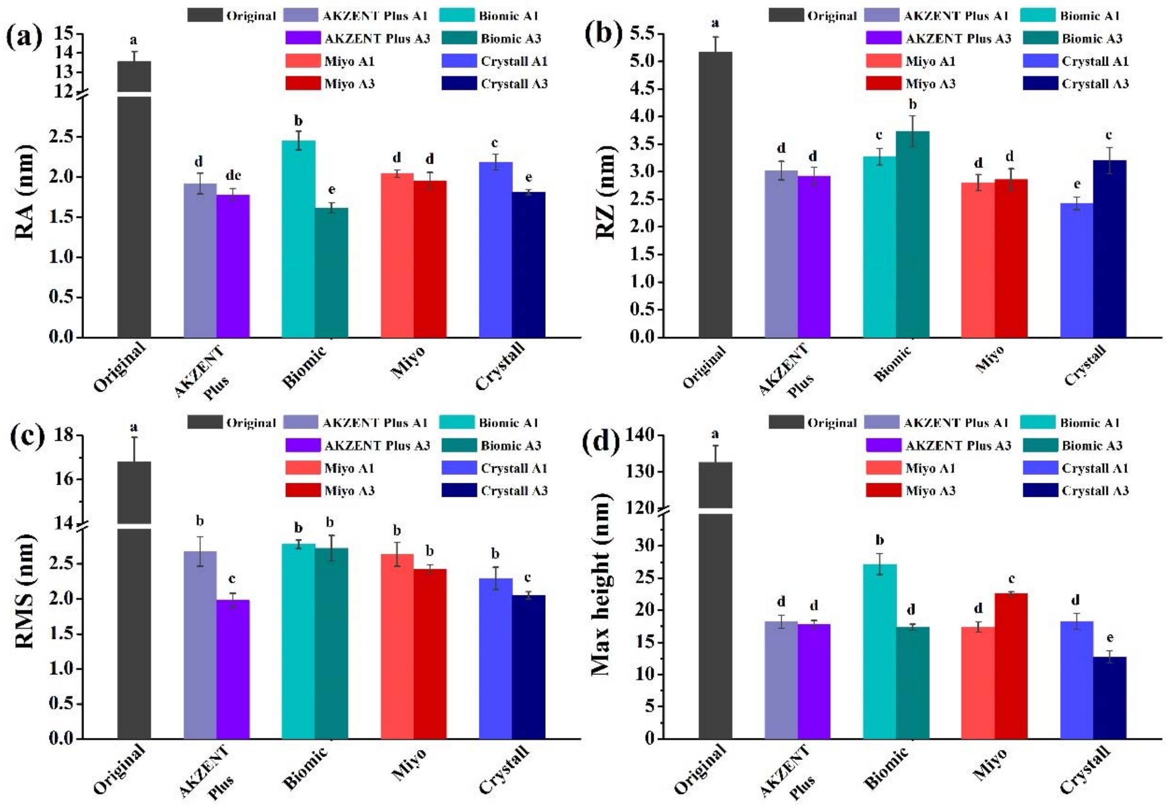

Figure 9. Surface roughness test of the zirconia samples. (**a**) Roughness Average, (**b**) root mean square, (**c**) maximum height of profile, and (**d**) maximum height. Means with different letters were significantly different ($p < 0.05$, mean $\pm$ SD, $n = 5$).

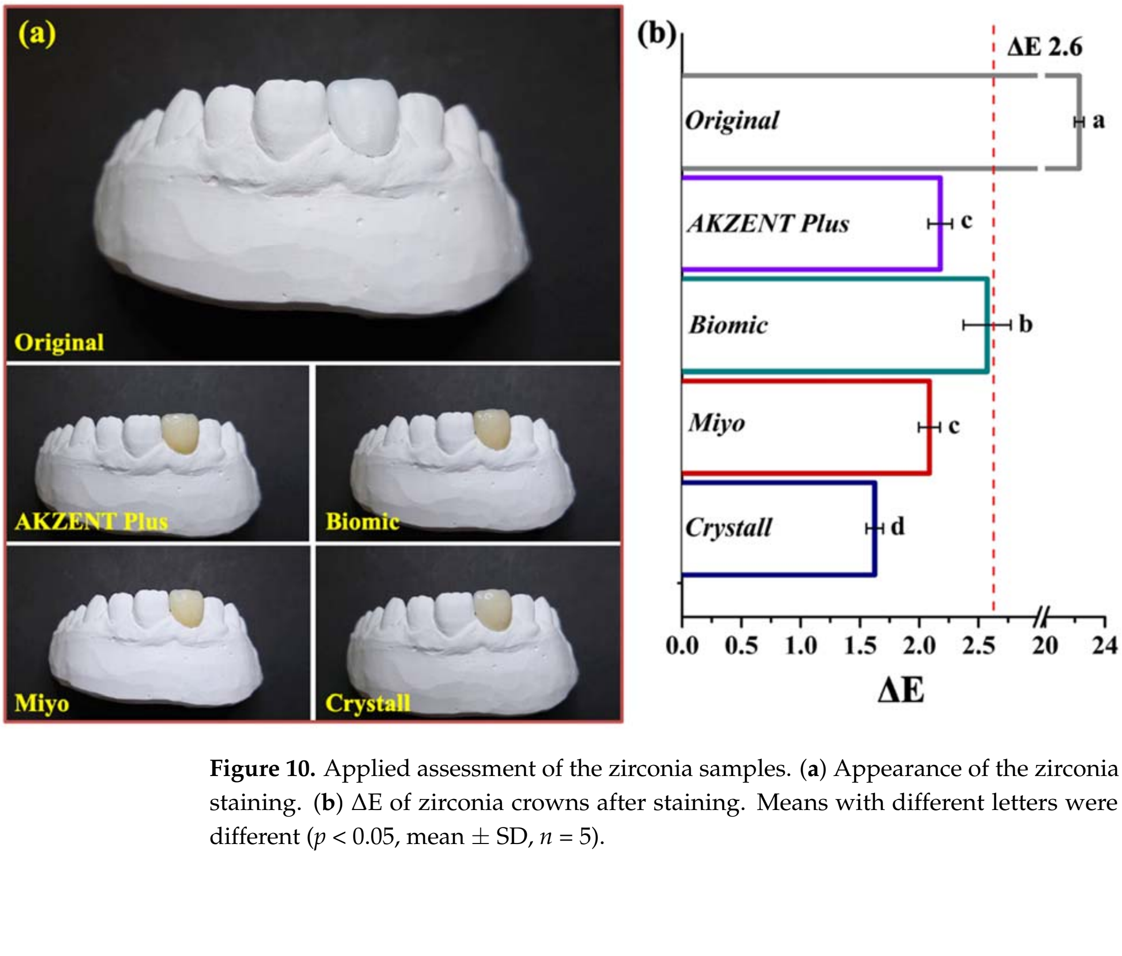

Figure 10. Applied assessment of the zirconia samples. (**a**) Appearance of the zirconia crowns after staining. (**b**) ΔE of zirconia crowns after staining. Means with different letters were significantly different ($p < 0.05$, mean $\pm$ SD, $n = 5$).

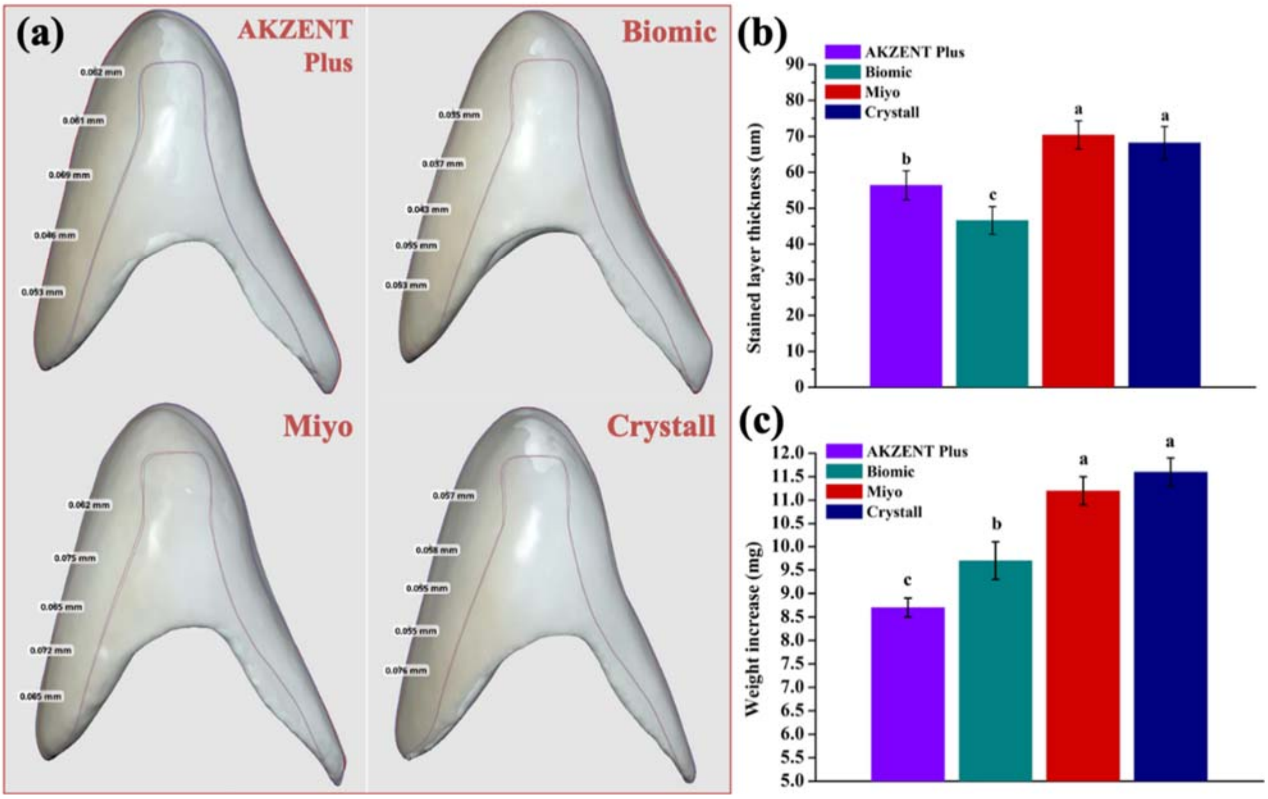

Figure 11. Thickness and weight of stained layers after the staining of zirconia crowns. (**a**) Digital comparison, (**b**) thickness of stained layers, and (**c**) weight of stained layers. Means with different letters were significantly different ($p < 0.05$, mean ± SD, $n = 5$).

4. Conclusions

This study assessed the effects of novel dental zirconia stains in clinical dental practice. The results indicate that the zirconia stain layer requires only a small amount (less than 80 μm) of thickness to meet the effect of dental clinical staining. Different brands of stains can improve the surface fineness and help keep the crown surface clean. The results supported our hypothesis that the staining effects of the special staining agents for zirconia met the criteria for clinical application and there was no significant difference between the different zirconia staining agents. The zirconia stains described in this study may serve as a potential option for staining zirconia restorations and provide a novel dental technology approach for all-ceramic restorative procedures. In the future, the behavior of zirconia strains in the oral environment will be explored.

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References

1. Lee, J.-H.; Kim, D.H.; Park, Y.-G.; Lee, S.Y. Chewing discomfort according to dental prosthesis type in 12,802 adults: A cross-sectional study. *Int. J. Environ. Res. Public Health* **2020**, *18*, 71. [CrossRef] [PubMed]
2. Mount, G.J.; Hume, W.R.; Ngo, H.C.; Wolff, M.S. *Preservation and Restoration of Tooth Structure*; John Wiley & Sons: Hoboken, NJ, USA, 2016.
3. Venâncio, G.N.; Júnior, R.R.G.; Dias, S.T. Conservative esthetic solution with ceramic laminates: Literature review. *RSBO Rev. Sul-Bras. Odontol.* **2014**, *11*, 185–191.
4. Gracis, S.; Fradeani, M.; Celletti, R.; Bracchetti, G. Biological integration of aesthetic restorations: Factors influencing appearance and long-term success. *Periodontology 2000* **2001**, *27*, 29–44. [CrossRef] [PubMed]
5. Blatz, M.; Chiche, G.; Bahat, O.; Roblee, R.; Coachman, C.; Heymann, H. Evolution of aesthetic dentistry. *J. Dent. Res.* **2019**, *98*, 1294–1304. [CrossRef]
6. Spear, F.; Holloway, J. Which all-ceramic system is optimal for anterior esthetics? *J. Am. Dent. Assoc.* **2008**, *139*, S19–S24. [CrossRef]
7. Ahmad, I. Anterior dental aesthetics: Dental perspective. *Br. Dent. J.* **2005**, *199*, 135–141. [CrossRef]
8. Paul, N.; Raghavendra Swamy, K.N.; Dhakshaini, M.R.; Sowmya, S.; Meravini, M. Marginal and internal fit evaluation of conventional metal-ceramic versus zirconia cad/cam crowns. *J. Clin. Exp. Dent.* **2020**, *12*, e31–e37. [CrossRef]
9. McLaren, E.; Giordano, R. Ceramics overview: Classification by microstructure and processing methods. *Compend. Contin. Educ. Dent* **2010**, *31*, 682–684.
10. Trunec, M.; Maca, K. Advanced ceramic processes. In *Advanced Ceramics for Dentistry*; Elsevier: Amsterdam, The Netherlands, 2014; pp. 123–150.
11. Krug, K.-P.; Knauber, A.W.; Nothdurft, F.P. Fracture behavior of metal-ceramic fixed dental prostheses with frameworks from cast or a newly developed sintered cobalt-chromium alloy. *Clin. Oral Investig.* **2014**, *19*, 401–411. [CrossRef]
12. Graham, J.D.; Johnson, A.; Wildgoose, D.G.; Shared, M.Y.; Cannavina, G. The effect of surface treatments on the bond strength of a nonprecious alloy-ceramic interface. *Int. J. Prosthodont.* **1999**, *12*, 330–334.
13. Çökeliler, D.; Erkut, S.; Shard, A.G.; Akdoğan, E.; Özden, N.; İmirzalıoğlu, P.; Mutlu, M. A novel approach for improvement of the interfacial binding of ceramics for dental materials: Chemical treatment and oxygen plasma etching. *J. Appl. Polym. Sci.* **2008**, *110*, 2656–2664. [CrossRef]
14. Sailer, I.; Makarov, N.A.; Thoma, D.S.; Zwahlen, M.; Pjetursson, B.E. All-ceramic or metal-ceramic tooth-supported fixed dental prostheses (fdps)? A systematic review of the survival and complication rates. Part I: Single crowns (scs). *Dent. Mater.* **2015**, *31*, 603–623. [CrossRef] [PubMed]
15. Sharkey, S. Metal ceramic versus all ceramic restorations: Part 1. *J. Ir. Dent. Assoc.* **2010**, *56*, 196–199. [PubMed]
16. Warreth, A.; Elkareimi, Y. All-ceramic restorations: A review of the literature. *Saudi Dent. J.* **2020**, *32*, 365–372. [CrossRef] [PubMed]
17. Sierra, J.A.; Cho, S.-H.; Maroulakos, G. Accuracy of anterior denture tooth arrangements of cad-cam complete removable dental prostheses made with a tooth mold template. *J. Prosthet. Dent.* **2021**. [CrossRef]
18. Kollmuss, M.; Kist, S.; Goeke, J.E.; Hickel, R.; Huth, K.C. Comparison of chairside and laboratory cad/cam to conventional produced all-ceramic crowns regarding morphology, occlusion, and aesthetics. *Clin. Oral Investig.* **2015**, *20*, 791–797. [CrossRef]
19. Yoon, H.I.; Bae, J.W.; Park, J.M.; Chun, Y.S.; Kim, M.A.; Kim, M. A study on possibility of clinical application for color measurements of shade guides using an intraoral digital scanner. *J. Prosthodont.* **2018**, *27*, 670–675. [CrossRef]
20. Aslan, Y.; Coskun, E.; Ozkan, Y.; Dard, M. Clinical evaluation of three types of cad/cam inlay/onlay materials after 1-year clinical follow up. *Eur. J. Prosthodont. Restor. Dent.* **2019**, *27*, 131–140.
21. Bahadır, H.S.; Karadağ, G.; Bayraktar, Y. Minimally invasive approach for improving anterior dental aesthetics: Case report with 1-year follow-up. *Case Rep. Dent.* **2018**, *2018*, 4601795. [CrossRef]
22. Zarone, F.; Di Mauro, M.I.; Ausiello, P.; Ruggiero, G.; Sorrentino, R. Current status on lithium disilicate and zirconia: A narrative review. *BMC Oral Health* **2019**, *19*, 134. [CrossRef]
23. Bajraktarova-Valjakova, E.; Korunoska-Stevkovska, V.; Kapusevska, B.; Gigovski, N.; Bajraktarova-Misevska, C.; Grozdanov, A. Contemporary dental ceramic materials, a review: Chemical composition, physical and mechanical properties, indications for use. *Open Access Maced. J. Med. Sci.* **2018**, *6*, 1742–1755. [CrossRef] [PubMed]
24. Skorulska, A.; Piszko, P.; Rybak, Z.; Szymonowicz, M.; Dobrzyński, M. Review on polymer, ceramic and composite materials for cad/cam indirect restorations in dentistry—Application, mechanical characteristics and comparison. *Materials* **2021**, *14*, 1592. [CrossRef] [PubMed]
25. Zhang, Y.; Lawn, B.R. Novel zirconia materials in dentistry. *J. Dent. Res.* **2017**, *97*, 140–147. [CrossRef] [PubMed]
26. Mikeli, A.; Walter, M.H.; Rau, S.A.; Raedel, M.; Raedel, M. Three-year clinical performance of posterior monolithic zirconia single crowns. *J. Prosthet. Dent.* **2021**. [CrossRef] [PubMed]
27. Zhang, F.; Reveron, H.; Spies, B.C.; Van Meerbeek, B.; Chevalier, J. Trade-off between fracture resistance and translucency of zirconia and lithium-disilicate glass ceramics for monolithic restorations. *Acta Biomat.* **2019**, *91*, 24–34. [CrossRef] [PubMed]
28. Camposilvan, E.; Leone, R.; Gremillard, L.; Sorrentino, R.; Zarone, F.; Ferrari, M.; Chevalier, J. Aging resistance, mechanical properties and translucency of different yttria-stabilized zirconia ceramics for monolithic dental crown applications. *Dent. Mater.* **2018**, *34*, 879–890. [CrossRef]

29. Sulaiman, T.A.; Abdulmajeed, A.A.; Donovan, T.E.; Cooper, L.F.; Walter, R. Fracture rate of monolithic zirconia restorations up to 5 years: A dental laboratory survey. *J. Prosthet. Dent.* **2016**, *116*, 436–439. [CrossRef]
30. Tang, Z.; Zhao, X.; Wang, H.; Liu, B. Clinical evaluation of monolithic zirconia crowns for posterior teeth restorations. *Medicine* **2019**, *98*, e17385. [CrossRef]
31. Farzin, M.; Ansarifard, E.; Taghva, M.; Imanpour, R. Effect of external staining on the optical properties and surface roughness of monolithic zirconia of different thicknesses. *J. Prosthet. Dent.* **2021**, *126*, e681–e687. [CrossRef]
32. Dai, Y.; Li, W.; Zhong, M.; Chen, J.; Liu, Y.; Cheng, Q.; Li, T. Preconditioning and post-treatment with cobalt chloride in rat model of perinatal hypoxic-ischemic encephalopathy. *Brain Dev.* **2014**, *36*, 228–240. [CrossRef]
33. Gunal, B.; Ulusoy, M.M. Optical properties of contemporary monolithic cad-cam restorative materials at different thicknesses. *J. Esthet. Restor. Dent.* **2018**, *30*, 434–441. [CrossRef] [PubMed]
34. Schmeling, M.; Maia, H.P.; Baratieri, L.N. Opalescence of bleached teeth. *J. Dent.* **2012**, *40*, e35–e39. [CrossRef] [PubMed]
35. Tang, C.-M.; Fan, F.-Y.; Ke, Y.-C.; Lin, W.-C. Effects of electrode plate annealing treatment and the addition of hydrogen peroxide on improving the degradation of cobalt hydroxyapatite for bone repair. *Mater. Chem. Phys.* **2021**, *259*, 123962. [CrossRef]
36. Joiner, A. Tooth colour: A review of the literature. *J. Dent.* **2004**, *32*, 3–12. [CrossRef] [PubMed]
37. Kwon, S.J.; Lawson, N.C.; McLaren, E.E.; Nejat, A.H.; Burgess, J.O. Comparison of the mechanical properties of translucent zirconia and lithium disilicate. *J. Prosthet. Dent.* **2018**, *120*, 132–137. [CrossRef] [PubMed]
38. Della Bona, A.; Pecho, O.E.; Ghinea, R.; Cardona, J.C.; Perez, M.M. Colour parameters and shade correspondence of cad-cam ceramic systems. *J. Dent.* **2015**, *43*, 726–734. [CrossRef]
39. Oh, S.-H.; Kim, S.-G. Effect of abutment shade, ceramic thickness, and coping type on the final shade of zirconia all-ceramic restorations:In vitrostudy of color masking ability. *J. Adv. Prosthodont.* **2015**, *7*, 368. [CrossRef]
40. Schünemann, F.H.; Galárraga-Vinueza, M.E.; Magini, R.; Fredel, M.; Silva, F.; Souza, J.C.; Zhang, Y.; Henriques, B. Zirconia surface modifications for implant dentistry. *Mater. Sci. Eng. C* **2019**, *98*, 1294–1305. [CrossRef]
41. Karthigeyan, S.; Ravindran, A.J.; Bhat, R.T.; Nageshwarao, M.N.; Murugesan, S.V.; Angamuthu, V. Surface modification techniques for zirconia-based bioceramics: A review. *J. Pharm. Bioallied Scie.* **2019**, *11*, S131.
42. Komalsingsakul, A.; Senawongse, P. Effect of the surface roughness of composite resins on the water contact angle and biofilm formation. *M. Dent. J.* **2019**, *39*, 75–84.
43. Kniha, K.; Heussen, N.; Modabber, A.; Hölzle, F.; Möhlhenrich, S.C. The effect of zirconia and titanium surfaces on biofilm formation and on host-derived immunological parameters. *Int. J. Oral Maxillof. Surg.* **2021**, *50*, 1361–1374. [CrossRef] [PubMed]
44. Warreth, A.; Abuhijleh, E.; Almaghribi, M.A.; Mahwal, G.; Ashawish, A. Tooth surface loss: A review of literature. *Saudi Dent. J.* **2020**, *32*, 53–60. [CrossRef] [PubMed]
45. Dal Piva, A.M.d.O.; Tribst, J.P.M.; Benalcázar Jalkh, E.B.; Anami, L.C.; Bonfante, E.A.; Bottino, M.A. Minimal tooth preparation for posterior monolithic ceramic crowns: Effect on the mechanical behavior, reliability and translucency. *Dent. Mater.* **2021**, *37*, e140–e150. [CrossRef] [PubMed]
46. Razdolsky Michalczyk, E.; Senderak, A.R.; Melfyn Jones, R.; Coulter, W.H.; Goudy, S.L. Changes in the microbiome during oral wound healing. *Dent. Rev.* **2022**, *2*, 100040. [CrossRef]
47. Dobrzynski, M.; Pajaczkowska, M.; Nowicka, J.; Jaworski, A.; Kosior, P.; Szymonowicz, M.; Kuropka, P.; Rybak, Z.; Bogucki, Z.A.; Filipiak, J. Study of surface structure changes for selected ceramics used in the cad/cam system on the degree of microbial colonization, in vitro tests. *BioMed Res. Int.* **2019**, *2019*, 9130806. [CrossRef] [PubMed]