A focus on zirconia: an in-vitro lifetime prediction of zirconia dental restorations
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CHAPTER 2

Influence of heat treatment and veneering on the storage modulus and surface of zirconia.

Keywords: zirconia, veneering, storage modulus, CAD/CAM
2.1 Abstract

Objective. The aim of this investigation was to evaluate whether heat treatment during glass-ceramic veneering, the application of glass-ceramic for veneering or long term storage have an influence on the storage modulus of zirconia.

Materials and Methods. Zirconia bars were fabricated and treated according to veneering conditions. Heating regimes between 680°C and 1000°C (liner bake and annealing), sandblasting and steam cleaning were used. The bars were investigated after 90 days of storage in water and acid. To investigate the influence of veneering, the bars were veneered by press or layer technique. Dynamic mechanical analysis was performed to determine the storage modulus. All specimens were loaded on top and bottom (treatment on pressure or tensile stress side). Scanning electron microscopy was used for evaluating the zirconia surface.

Results. Sintered zirconia provided a storage modulus E’ of 215 (203/219) GPa. Sandblasting reduced E’ to 213 GPa, while heating modulated E’ between 205GPa (liner) and 222 GPa (dentin). Steam cleaning, annealing and storage changed E’ by between 4 and 22 GPa, depending on the side of loading. After veneering, a strong E’ reduction was found down to 84 -125 GPa.

Conclusion. The veneering of zirconia with glass-ceramic, in contrast to heat treating during the veneering procedure, had a strong influence on the storage modulus.
2.2 Introduction

Zirconia fixed partial dentures (FPDs) are used as alternatives for metal-supported dental restorations. For protection and aesthetic aspects, the zirconia core is veneered with glass ceramics that were adjusted in their thermal expansion coefficient (TEC) and firing temperature (FT), e.g. Insufficient tuning of these aspects may lead to fracture of the veneering under clinical conditions [1-3].

During baking of the veneering, small differences in the TEC generally cause tensile stress on the ceramic, improving the bond between glass-ceramic and the zirconia core. Veneering with “weaker” glass ceramics (E<100GPa), in comparison to zirconia (E≈200GPa), may result in reduced stability of the FPD [4], but contradicting opinions have been published [5]. The location, i.e. whether the veneering is placed under pressure (on top) or tensile stress (bottom), is reported to have a significant influence on the strength of the restoration [6]. Stress in the veneering may cause manifold failures: cracks that evolve in the glass ceramic may run at the border between veneering and core (interfacial chipping), in a superficial layer of the veneering (chipping) or even may jump into the core (fracture). Tensile or compressive stress may develop due to different visco-elastic relaxation mechanisms in two-layer systems [7]. The application of an opaquer as a stress-brake improved the bonding between zirconia and layering glass ceramic, but the combination of opaquer and press veneering reduced bonding results [4].

As the application of veneering material may cause weakening of a restoration, heat or superficial treatments may influence the zirconia ceramic. Temperature loadings up to 250°C [8] are regarded as not having any influence on the structure of zirconia, but the question arises, whether heat treatment during veneering causes variations. According to the manufacturers’ instruction the zirconia restoration is baked for applying the liner, shoulder, dentin, glaze/stain, correction or final shoulder with decreasing temperature. During the veneering process, the zirconia framework is subjected to a graduated thermal treatment between 1000°C and 680°C.

Sandblasting of the surface is recommended before veneering or cementation of the FPDs. This procedure modifies the surface after milling and reduces superficial defects or milling traces, but it is also assumed to be responsible for both damaging the surface and causing microcracks. Superficially induced damage is presumed to be the origin of tetragonal (t) to monoclinic (m) transformations , which may spread into the bulk material [9]. Annealing at 1000°C/1h is supposed to repair this damage and for improve the strength and Weibull modulus of zirconia [10].

These techniques may modify the zirconia surface, but it is not determined whether the described treatments during veneering modify zirconia strength and brittle / elastic behaviour.
The application of veneer ceramic, which results in the formation of a bi-layer system, may have a strong influence on the elasticity of the whole restoration. The modulus of elasticity was shown to be an important factor for the strength evaluation of a multi-layer system [11, 12]. Dynamic mechanical analysis (DMA) is used for evaluating the changes in visco-elastic properties, subjecting the specimens to a defined, forced sinusoidal oscillation and measuring the reduced and deferred output. The differences in phase angle and force amplitude between input and output were used for calculating the storage modulus, which correlates with the modulus of elasticity. DMA is a complex analytical method, which allows for determining even small differences in the modulus. The aim of this study was to investigate the influence of firing, sandblasting and storage on the storage modulus of zirconia. The influence of glass-ceramic press or layering veneering on the storage modulus should also be investigated.

2.3 Materials and Methods

Rectangular bars of the zirconia core material Cercon base (DeguDent, Hanau, Germany) were milled with a water-cooled cutter (Leica SP1600, Bensheim, Germany) and sintered (Cercon Heat, DeguDent, Hanau, Germany) to the final dimensions (height: 0.5 mm, width: 2 mm, length: 20 mm). The height of 0.5 mm was used as representative for a standard thickness of the coping.

All specimens were divided into groups of three specimens each (Table 2.2). Blank zirconia cores (#C) were subjected to a standard veneering temperature program without applying veneering ceramic. Temperatures and times are provided in the Table 2.2.

Groups C_{acid}, C_{water}, C_{anneal} were formed for investigating the influence of heat treatment and storage on a core without veneering. Group C_{anneal} provides annealing of the sandblasted core. Group C_{water} investigates the samples after 90d of storage in water and group C_{acid} in acetic acid (25%). In all these groups no veneering material was applied.

In group LT, zirconia specimens were investigated with additional veneering ceramic (Cercon Kiss, DeguDent, Hanau, Germany) using the layering technique (=LT). Group PT was designed for investigating the influence of a ceramic veneering that was applied by press technique (=PT) (Cercon Xpress, surface treatment 50 μm/0.2 MPa glass pearls; DeguDent, Hanau, Germany). Measurements in both groups PT and LT were performed using a core thickness of 0.5 mm (although the specimens were thicker with additional veneering) and the real thickness core with veneering (thickness 0.5 mm + veneering) as a direct comparison.

For investigating the superficial influence of each treatment, scanning electron micrographs (Field emission -SEM Quanta, FEI Phillips; Eindhoven, Netherlands, magnification: 30 000x) were made. The surface roughness was examined (Perthometer SP6; Perthen-Mahr,
Influence of heat treatment and veneering on the storage modulus and surface of zirconia.

Göttingen, Germany), and energy dispersive X-ray spectroscopy (EDX/SEM; 30KV) was performed for analysing the ceramic composition.

**Table 2.2:** Study overview and classification of the different treatments (X indicates the performed treatments)

<table>
<thead>
<tr>
<th>Group</th>
<th>C</th>
<th>LT</th>
<th>PT</th>
<th>C_{\text{Anneal}}</th>
<th>C_{\text{acid}}</th>
<th>C_{\text{water}}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp [°C]/Time [min]</td>
<td>Layering technique</td>
<td>Press technique</td>
<td>Annealing 90d</td>
<td>acid 90d</td>
<td>water 90d</td>
</tr>
<tr>
<td>Material</td>
<td>Core</td>
<td>Core + veneering</td>
<td>Core</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bar thickness [mm]</td>
<td>0.5</td>
<td>0.5 and 0.5+veneering</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>After treatment:</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sintering</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Al_{2}O_{3} (110μm/0.25MPa)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<tr>
<td>Steam cleaned</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
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<tr>
<td>Liner 1</td>
<td>970/1</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
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<tr>
<td>Liner 2</td>
<td>960/1</td>
<td>X</td>
<td></td>
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<tr>
<td>Shoulder bake</td>
<td>850/1</td>
<td>X</td>
<td></td>
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<tr>
<td>Dentin first bake</td>
<td>830/1.5</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
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<tr>
<td>Dentin second bake</td>
<td>820/1.5</td>
<td>X</td>
<td></td>
<td></td>
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<tr>
<td>Glaze/Stain</td>
<td>800/1</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<tr>
<td>Correction</td>
<td>680/1</td>
<td>X</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Final Shoulder</td>
<td>680/1</td>
<td>X</td>
<td></td>
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<tr>
<td>Annealing</td>
<td>1000/60</td>
<td>X</td>
<td></td>
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<tr>
<td>90days Water</td>
<td></td>
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<td></td>
<td>X</td>
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<tr>
<td>90days Acid</td>
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<td>X</td>
</tr>
</tbody>
</table>

All groups were investigated in a three-point bending test design where the specimen is supported on two edges and the end of the push rod applies load centrally from the top (amplitude: 20 μm, dynamic load: 6 N, static load: 0.2 N, Frequency: 1.66 Hz). The distance between the two edges was 10 mm. Before testing, dimensions of the bars were determined with accuracy up to 0.01 mm (micrometer gauge). All samples were subjected to a temperature program between 25°C and 180°C in an air atmosphere with a heating rate of
10K/min (Dynamic mechanical testing device DMA 242, Netzsch, Selb, Germany). All measurements were repeated twice from each side. This procedure was performed to investigate differences, when the surface treatment/veneering was located on top (pressure zone) or bottom (tensile zone) of the bar. E’ was determined at a clinical relevant mouth temperature of 37°C.

The complex modulus of elasticity ($E^* = E' + iE''$) in three-point-bending configuration is calculated as follows:

$$E^* = \frac{l^3 \times F}{(4 \times w \times h^3 \times a^*)} \quad \{1\}$$

where:

- $E^*$ = complex elasticity modulus [Pa]
- $E'$ = storage modulus [Pa]
- $E''$ = loss modulus [Pa]
- $a^*$ = complex dynamic displacement [mm]
- $F$ = dynamic load [N]
- $h$ = sample height [mm]
- $l$ = bending length [mm]
- $w$ = sample width [mm]

$\tan \delta$ is calculated as the ratio of $E'$ and $E''$. The application of veneering (groups PT and LT) on the zirconia core changed the mono-layer system to a bi-layer where the influence of the thickness of both layers had to be regarded in the calculation of $E'$. According to formula \(\{1\}\), the height of the specimen had to be considered with the power of three. Coherent, $E'$ of the bi-layer system is further labelled $E'_{bi}$. For estimating the influence of the veneering glass-ceramic on $E'_{bi}$, we investigated the bars in relation to the real core thickness (0.5mm + height of veneering ceramic) as well as on the original core height (0.5mm, $E'_{bi}$ "effective”). Specimens were excluded from further evaluation, when defects due to fabrication (inclusions, air) or insufficient bonding between the two ceramic layers caused a significant reduction of $E'_{bi}$ below $E'$ of the veneering ceramic.

Zirconia may show strong variations due to the Weibull strength distribution according to fabrication, treatment or surface conditions. Therefore, the influence of the treatment was investigated on every single bar by calculating $E'$ or the difference, $\Delta E'$, after relevant treatment in relation to the situation after sintering.

Median and 25-75-percentiles were calculated and pairwise tests for statistics were carried out using the Mann-Whitney-U-Test at a level of significance $\alpha \leq 0.05$. 

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2.4 Results

The results and figures show the storage modulus (E’) at a temperature of 37°C. After sintering, the median E’ was 215 GPa and the 25%/75% values were 203/219 GPa, respectively. The storage modulus decreased about 10% with increasing temperature (from 30°C to 180°C). For sintered zirconia a tan δ of 0.04 was found at about 110°C (Fig. 2.1). In further treatments, no shift of tan δ was found. The thickness of the tested specimens was 0.49±0.03 mm.

Fig. 2.1: Storage modulus E’ [GPa] and tan δ of zirconia after sintering (Cercon Base).

The zirconia surface changed with sintering, milling, sandblasting, liner application, shoulder bake, dentin bake and glaze/stain (Fig. 2.2).
Sandblasting with Al₂O₃ caused a small reduction of median E’ to 213 GPa. The application of liner bake 1 and 2 resulted in storage moduli of 205 GPa and 209 GPa, respectively. Shoulder bake, as well as both dentin bakes and stain bake, increased E’, whereas the maximum E’ was found after dentin bake 1 (222 GPa). A subsequent reduction of E’ to 209 GPa could be determined after the correction bake. With the final bake, E’ reached the level after sintering (216 GPa). Steam cleaning changed E’ by about 4 GPa. None of the changes were statistically significant (p>0.075) (Fig. 2.3).
Fig. 2.3: Change of E’ [GPa] in relation to E’ after sintering; influence of the surface or heat treatment (median, 25%/75%).

Neither annealing (5 GPa) nor a 90d storage in acid (2GPa) or water (7 GPa) had a significant influence on the ΔE’ (Fig. 2.4) when the specimens were investigated with the treated side on top (pressure zone). Turning the specimens around and placing the treatment on the support side under tensile stress caused a ΔE’ values of -6 GPa (annealing), 8 GPa (90 days acid) and 22 GPa (90 days water). The application of veneering resulted in a highly significant (p>0.75) reduction of E’bi. With veneering, the thickness ratio of veneering:core of the bars was 1.2:1. The application of the liner increased thickness by 0.05 ± 0.008 mm.
The influence of the glass-ceramic veneering on the bi-layer system was stringent: under optimal fabrication conditions, the storage modulus $E'_{\text{bi}}$ decreased to values between 84 and 125 GPa for both types of veneering (Fig. 2.5).

**Fig. 2.5:** $E'$ [GPa] after veneering in layer- or press technique (specimens were loaded with treatment in pressure or in tensile zone; median, 25%/75%).

No significant differences were found between layering and press ceramic application when the veneering was placed on the bottom of the bar. Influenced by the fabrication process, $E'$ decreased to values between 57 and 62 GPa for both types of veneering (Fig. 2.6; below). In this case, when the veneering was placed on the bottom of the bar, a further decrease of $E'_{\text{bi}}$ was found. The application of veneering in the press-technique caused a higher decrease of $E'_{\text{bi}}$ in comparison to the layer application.

Effective $E'_{\text{bi}}$ increased when ignoring the increase of thickness due to veneering material and relating $E'_{\text{bi}}$ on core thickness (0.5 mm). The plain increase in thickness due to application of the liner, dentin or stain masses caused an increase of $E'_{\text{bi}}$ up to 268 GPa (liner), 592 GPa (dentin) and 670 GPa (stain) with the veneering on the top side of the bar. Smaller increases up to 248 GPa (liner), 391 GPa (dentin) and 422 GPa (stain) were found, when the veneering was applied on the bottom. The main differences were caused by the application of dentin masses, whereas stain ceramic had no further effect (Fig. 2.6, above).
Fig. 2.6: Storage modulus (E’ [GPa]): influence of applied liner, dentin or stain masses; above: related to core thickness; below: related to thickness core + veneering specimens were loaded with treatment in pressure or in tensile zone; median, 25%/75%).

Surface roughness varied between 0.1 and 0.2 μm, but no significant differences between the various heat treatments were found. EDX analysis revealed differences only after air abrading. Alumina particles (1.6 wt%) could be detected on the zirconia surface. All other treatment had no EDX-visible effects.

2.5 Discussion

The storage modulus E’ of 216 GPa, which could be determined with DMA, correlates with the modulus of elasticity of 210 GPa in the literature [13]. E’ showed a decrease of about 5%
in the dental application temperature range between 5°C and 80°C. This decrease is associated with a dimension change of 20 μm and a damping response that is shown by a dipole peak (\(\tan \delta \) of 0.04) at about 120°C. This phenomena is described as a stress-induced reorientation of elastic dipole moments (Yzr’ Vo”’) [14, 15] and may be a helpful tool to differentiate between different types of dental zirconia.

Although SEM figures (Fig. 2.2) showed changes of the zirconia surface with different treatments, only small variations of E’ could be determined. Sandblasting, which showed the highest optical superficial changes and additional Alumina on the surface, as well as steam cleaning had no effect on the storage modulus. Roughness due to surface treatment did not change significantly.

The simulated liner bake (970°C) reduced the median E’ by about 5%. These results corresponded with a reported 5% decrease of flexural strength with heat treatment [16], which is caused by t-m transformation. Subsequent temperature programs with temperatures down to 830°C (dentin bake) increased median E’ again, whereas further heat treatments down to 680°C had only a small influence on E’. Sundh et al. showed that the temperature of a heating treatment of zirconia had an influence on the fracture strength of fixed partial dentures. With treatments above 900°C fracture strength halved, whereas treatments of about 750°C caused a reduction of only approximately 23% [17]. However [5, 6], the same authors [17] found no difference in fracture results dependent on whether a zirconia core was veneered or not.

It has been described that sandblasting improves the mean strength of zirconia at the expense of its reliability [18], but we found only small, non-significant changes of E’. It was supposed that particle abrasion may cause a superficial t → m transformation [16], creating a layer of compressive strength that works against the previously induced flaws [9, 18]. Flaws, which may not reach deeper than the compressive zone, may explain the strength increase with abrading. Longer flaws, in contrast, would result in weakening of the material. However, flaws on the tensile-loaded surface may grow to slow crack growth mechanisms [13, 19]. Abrading caused high deviation of the flexural strength and reliability, which might affect clinical use [9, 16, 18].

No influence on E’ of storage in water or acid could be determined when the sandblasted surface was tested in a pressure zone. Turning around the bar and subjecting the sandblasted and stored surface to tensile loading resulted in partially different results. Storage in acid showed only small changes, while storage in water resulted in a median change of about 10% of E’. It was described that besides increased temperature (about 250°C) and high grain size, water/humidity is responsible for transformation processes in the zirconia ceramic. Water forms superficial zirconium hydroxides due to water chemisorption and causes strain energy accumulation and m → t transformation. On the other hand water might react with yttrium.
forming yttrium hydroxide, which depletes the stabilization causing m->t transformation [9]. Ardlin et al. described that storage in ringer solution had no effect on zirconia [20]. In contrast to wet storage, storage at 120°C for 120hrs caused only small variations [8] and even after 30 months no substantial change in bending strength could be found [21]. In particular, aging under low temperature had no effect on the flexural strength of zirconia bars [9]. Aging is supposed to influence the amount of yttrium, which is responsible for the grain size, which in turn influences zirconia transformation [22].

The nearly doubled thickness of the testing bar with veneering led to a seemingly strong increase of E’bi with extreme variations up to 100%, regardless of whether the veneering was placed on top or bottom of the bar. When E’bi was calculated with the real thickness of the bar, E’bi was reduced by about 60% with veneering, reaching the modulus of the individual veneering ceramics. Under optimal manufacturing conditions, small differences were found between layering and press ceramics, which may be attributed partly to the application of liner for the layering technique or the recommended glass-pearl treatment before performing the press method. Dimensional influences, especially due to varying edge stability, may not be excluded. Specimens with defects or insufficient bonding between the two ceramic components caused an extreme decrease of E’. The results indicated, that the veneering with a “weak” ceramic had a strong influence on the whole specimen. This is in accordance to microtensile investigations [4], finite element analysis [23] or bending tests [6] where the veneering had predominant effects on the properties. These results are significant for the fabrication of bridges where one source of defects is the fracture of the pontic on the tensile side of the connector [24, 25]. Chipping may be avoided by considering modulus and veneering thickness, because both parameters have influence on the stress ability of the restorations [12]. Although an increase of the core thickness (maintaining the total thickness core + veneering constant) is not supposed to improve the stress of the bi-layered system [26], the change in the modulus of elasticity in a bi-layer (or even multi-layer system taking cement or tooth substance into account) may influence the strength of restorations [27]. Differences in modulus cause variation of energy absorption/dissipation and, in the end, may cause chipping, interfacial chipping or fracture.

It can be concluded that the veneering of zirconia with glass-ceramic materials may have a strong influence on the modulus of the dental restorations. Long-term storage in water may contribute to further deterioration. Especially for the application of the glass-ceramic in tensile stress, a weakening of fixed partial dentures should be expected. Heat treatment of the zirconia core during firing of the veneering had no significant influence on the storage modulus.
2.6 References
