VICTOR BABEȘ UNIVERSITY OF MEDICINE
AND PHARMACY TIMIȘOARA
FACULTY OF DENTAL MEDICINE
DEPARTMENT 1 MD

BEJAN FLAVIA ROXANA

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PhD THESIS

AGING BEHAVIOR OF ZIRCONIA AND HIGH PERFORMANCE POLYMERS USED FOR MONOLITHIC DENTAL RESTORATIONS

A B S T R A C T

Scientific Coordinator
PROF. POROJAN LILIANA, MD PhD

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Monolithic dental restoration obtained from new generations of zirconia or high performance polymers (HPP), using CAD/CAM technologies – represents a current topic in the domain of dental prosthetics, with multiple interdisciplinary implications (dental medicine, dental technique, biomechanics, materials science, chemistry, optics) offering new perspectives in prosthetic applications.

The widespread use of ceramic materials for durable dental restorations has been limited because of their fragility and susceptibility to fracture. They are still the subject of numerous researches and studies, with the main purpose of improving mechanical properties (increasing flexural strength and toughness) along with maintaining their excellent aesthetic properties. Advanced have been made in this field due to their natural, tooth-like appearance, excellent biocompatibility and the possibility of obtaining metal-free restorations (1,2). More recently, with introduction and development of new generations of zirconia with superior characteristics, there has been an increased interest in monolithic restorations, manufactured using CAD/CAM technology and for continuous evolution of the digital workflow.

For the third generation (5Y-TZP), the crystalline structure was modified by increasing the amount of yttria to 5 mol% and implicitly the content of the cubic phase up to 50%, which involves increase in the size of the cubic crystals, a reduction in porosity and increase in light transmission by 43-45%, significantly improving translucency while reducing flexural strength and fracture toughness. The fourth generation (4Y-TZP) is characterized by the addition of 4 mol% Y_2O_3 to stabilize around 25% of the cubic phase in the material. Compared to the previous one, this generation is characterized by higher mechanical strength and lower optical properties. A certain disadvantage of these two new generations is the lower fracture toughness and strength, compared to 3Y-TZP, because they contain smaller amounts of the tetragonal phase, which leads to a reduction in the possibility of the t-m phase transformation, meaning less transformation toughening (3).

The various types of zirconia are differentiated by the tetragonal/cubic phase ratio, which is controlled by the yttria content. The zirconia blanks are also available in monochrome or multilayer versions. The multilayer zirconia contains polychromatic layers that simulate different shades and translucencies of natural teeth, with opacity and chroma ranging from the more opaque layer in the cervical

area, through two transitional layers, to the translucent incisal/occlusal area. The layers have different formulations according to the quantity of dopants and chemical composition, therefore there may be potential differences between layers in terms of physical properties (4).

It was observed that the hardness and strength of zirconia are proportional to tetragonal phase. In the microstructure, when the stress is exerted, the toughening (tetragonal to monoclinic) transformation is induced, stopping the progression of the micro-cracks and eliminating defects (5); for materials with higher cubic content, this mechanism is reduced-that is a disadvantage of these new zirconias and the clinicians should use them, when the aesthetic needs are required.

PEEK and PEKK are commonly used and were introduced in dentistry- as chemically inert and high performance biomaterials. PEEK the most widely used, is hydrophobic and it has a low modulus of elasticity, similar to that of bone, providing better absorption and a damping effect of shocks and functional stress transferred to the tooth abutment, which is an advantage compared to ceramic materials (6,7).

In order to improve their mechanical characteristics, reinforced PEEK with 20% ceramic fillers were developed. Excelent mechanical properties, great polishing potential, posibility of corrections and chemical stability, indicate that PEEK could be an alternative to metallic alloys for obtaining various prosthetic restorations (8). PEKK material show better physical characteristics, low density and acceptable wear resistance.It may be used in dentistry as an implant or prosthetic biomaterial for metal-free restorations (9).

The HPP and zirconia discs or blocks, can be processed using dental CAD/CAM (computer-aided design/computer-aided manufacturing) technology, that performs the scanning, design and manufacturing of the dental restorations. The accuracy of computer-aided impressions can be affected by the principles and scanning method, anti-reflection powder or color displays (10) A major advantage of using CAD/CAM technology is obtaining highly accurate prosthetic restorations, in terms of shape and marginal fit.

It was observed that the surface roughness and the microstructure characteristics of material can be relevant factors that influence the appearance and the final colour. Surface treatments such as glazing and polishing, improve the aesthetics of the prosthetic restoration, reduce the wear of opposing teeth, bacterial accumulation and inflammatory tissue response. They have a significant impact on roughness, microhardness and optical parameters, both before and after aging (11).

Glazing is a laboratory procedure, reduces the roughness, seals the pores and preserves color stability. The aspect of the glazed surface can be influenced by the layer thickness, layer deposition technique, adhesion capacity, interface characteristics resulting in a wavy surface with irregular areas and small defects. After aging, the glaze layer may have a protective role or it can be adversely affected directly, thinned, with cracks, chipped or separated from the material-with a great influence on mechanical properties and external appearance of dental restorations. Slight polishing, due to residual stress, causes tetragonal to monoclinic transformation areas around scratches; resulting in an increase in surface roughness and decrease in translucency; light polishing is recommended (12).

The polishing potential of PEEK surface depends on several parameters: ceramic fillers amount, polishing procedure and devices, velocity and contact pressure. The combination of polishing paste with water induces a fine abrasive action, resulting a glossy, light reflecting surface (13).

For zirconia it is known that, when the quantity of stabilizer is high, the cubic phase content and the surface roughness are increased, meaning they are higher for 5Y-TZP than for 3Y-TZP, and the mechanical properties decreased.

The microstructure, composition of the matrix and the type and amount of filler influence the roughness values of PEEK. Previous studies reported that PEEK (for filled PEEK-more) samples presented higher surface roughness than composite resin and PMMA-polymethyl methacrylate and when several high-performance polymers were compared, pure PEEK recorded the lowest roughness values (13). The microhardness depends on surface condition of the polymers. After thermocycling and longer exposure to food simulating liquids, all tested high performance polymers were affected by an increase in surface roughness associated with a decrease in microhardness values (14).

Light transmission for zirconia depends on crystalline phases and grain size, composition (alumina, oxides), porosity and defects, sintering. Glazing and polishing procedures performed on zirconia surfaces decreased lightness. After glazing an increase in yellowness and after polishing- perceptible color changes ware observed. It was also found that the glaze layer induces a decrease in opalescence, but without affecting the translucency and the polishing surface ensure a more realistic, natural appearance than the glazed one (15).

Discoloration of prosthetic restorations after a prolonged period can be considered an aesthetic failure and is caused in case of high-performance polymers by intrinsic factors such as composition, type of resin matrix, percentage and distribution of the filler, polymerization mode, processing methods, water absorption, dissolution of matrix structure and fiber; or by extrinsic factors, such as staining from liquid and food colorants (caffeine, tannins, theobromine), smoking (nicotine) (16).

Zirconia is susceptible to LTD, which is associated with a slow tetragonal to monoclinic transformation of the particles, starting at the surface that is exposed to moisture. It is known that, hydrothermal and mechanical (polishing, machining) impact can cause stress and unexpected phase transformation on the surface of the material, associate with an increase in roughness. Therefore, the surface-conditioning and treatment procedure should be applied in order to achieve a smoother surface (17).

However, zirconia with higher cubic content underwent almost no monoclinic transformation and hydrothermal degradation.

A significant characteristic of polymers is that of absorbing water, which diffuses trough the resin matrix, and for the modified ones, also through the matrix/filler interfaces, resulting in the detachment of the fibers from the matrix. The crystallinity of the matrix and type of filler, are two relevant factors that influence the matrix/fiber interface in thermoplastic matrix composites. Polymers degradation does not only occur as a result of saliva permeation, factors such as masticatory forces, chemical and thermal dietary changes are also involved. During aging process, the capacity of the polymer to withstand deformation decreases, causing microleakage, detachement of the fibers, secondary caries or fracture of the restauration (18).

However, PEEK is stable at high temperatures and resistant to surface modification, it has demonstrated low water sorption and solubility compared to other polymeric, monolithic materials obtained by CAD/CAM technology (14).

The adaptability of CAD/CAM restoration can be affected by the type of the material, the geometry of the restoration, accuracy of scanning, the wear and the size of the rotary tools, the performance of the milling machine, as well as the characteristics of the cement, its adhesion capacity or resistance to mechanical and thermal stress (17). The loss of marginal adaptability between the dental hard tissues and the adhesive system of the restorations can be attributed to the weakness of cement or to the thermal and elastic stresses induced in the restoration over time.

In this context, the purpose of this research was to investigate the surface characteristics (roughness, micro-hardness), the mechanical and optical properties, adaptability to dental structures and long term stability under the influence of factors similar to the intraoral environment; bringing contributions in order to preserve their properties and increase the lifetime of these restorations, with benefits for patients.

The scientific objectives of these in vitro investigations were:

1. Evaluation of surface properties (roughness, morphology, microroughness) of high and super-high translucent multi-layered zirconia, related to surface treatments (polishing/glazing) and artificial aging (autoclaving, thermocycling)
2. Assessment of optical properties (translucency, opacity, opalescence, level of color change) of high and super-hightranslucent multi-layered zirconia, related to surface treatments (polishing/glazing) and artificial aging (both).
3. Evaluation of the mechanical and optical properties of (unmodified, reinforced), high performance polymers, related to water saturation, thermocycling respectively to staining beverages and simulated cleaning methods.
4. Microcomputed tomography evaluation of marginal and internal adaptability of onlays fabricated from (PEEK, PAEK) high-performance polymers, using CAD/CAM technology.

The first in vitro study, the surface characteristics (roughness, topography, microhardness) of polished and glazed surfaces of STL (4 mol% Y_2O_3), IPS (4 mol%+5 mol% Y_2O_3) and CEZ (5 mol% Y_2O_3) were evaluated before and after thermal aging. The specimens were cut from presintered blocks, sintered and finished-half by glazing and the other half by polishing, then one group of each category was subjected to artificial aging by autoclaving, respectively thermocycling. Surface roughness (Ra, Rz), topography (Sa, Sq), microhardness (HV) were recorded in the three areas (cervical, medium, incisal) of each treated surface. The statistical tests were performed to compare the values among areas of each glazed or polished surface in before, respectively in after aging stage (two-way ANOVA), the same polished-glazed area for a material in before and then in after LTD stage (unpaired Student t-Test), and for the same areas for a zirconia, before-after LTD (paired Student t-Test). Pearson correlation was applied and the straightness of the correlation between surface roughness and microhardness values was calculated.

According to the presented study, the following conclusions can be drawn:

1. Both before and after LTD, surface treatments such as polishing and glazing, affected the surface roughness and topography of the three types of zirconia.
2. Both before and after aging, no significant differences in terms of roughness and microhardness, were recorded between areas of a polished or glazed sample.
3. In the before and after aging stage, the surface roughness values recorded in the same areas for the polished specimens were significanly lower and for microhardness significantly higher than for those glazed - for all studied materials.
4. After autoclaving, the roughness increased significantly for STL (4Y) and insignificanty for CEZ (5Y). After thermocycling, the roughness decreased significantly for glazed CEZ and IPS in medium and incisal areas. For both aged methods-on the polished samples, the situation changes and the STL surface became the roughness among the three materials, and for the glazed samples-CEZ remained the roughness zirconia.
5. After autoclaving procedure-on the glazed surfaces a decrease in microhardness values for STL and a significant increased for CEZ was observed; after thermocycling-no significant impact.
6. Before aging, the negative correlation among roughness and microhardness showed that when the surface roughness is increased,

the surface microhardness decreases; this correlation is no longer valid- after hidrothermal degradation.

7. The 5Y-TZP (super-high translucent) material was less affected by LTD than the 4Y-TZP (super translucent) material. The layers of the 4Y+5Y-TZP (combined) material showed similarities with the other two materials according to their microstructure.

Clinical significance:

1. The roughness of the polished surfaces is lower than the glazed ones, for zirconia with various Y_2O_3 content-before and after aging.
2. After LTD, there was an obvious increase in roughness for 4Y-zirconia, while 5Y-zirconia was not very affected.
3. After autoclaving, for glazed surfaces of the super-high translucent zirconia-the highest microhardness was reported.
4. The 4Y+5Ymaterial- associated the characteristics corresponding to the two microstructure.

The aim of **the second in vitro study,** was to evaluate the optical characteristics and color changes between layers of of three high translucent zirconia with different Y_2O_3 content, and to compare the appearance of the glazed and polished surfaces, before and after aging.

The same polished and glazed surfaces of STL (4 mol% Y_2O_3), IPS (4+5 mol% Y_2O_3) and CEZ (5 mol% Y_2O_3) were evaluated and optical parameters (TP, CR, OP) were recorded in the three areas (cervical, medium, incisal) of each treated surface, before and after LTD (autoclaving, thermocycling).

The statistical tests (two-way ANOVA, unpaired/paired Student t-test) were performed to compare the values among areas on one surface, between glazed and polished surfaces or between stages.

According to the presented study, the following conclusions can be drawn:

1. The translucency (TP) recorded on the glazed samples was lower than that of the polished samples, meaning that surface treatments, as

glazing and polishing, influence aesthetics and optical characteristics of translucent zirconia-both before and after aging.

2. After LTD, the mean TP, OP values-increased for all three zirconias except polished CEZ (autoclaving), respectively, TP increased for all materials and OP only for CEZ (termocycling). The superhigh translucent zirconia (CEZ- 5 mol% Y_2O_3) was less affected by artificial aging.
3. The cervical areas were more susceptible to low thermal degradation and color changes than incisal areas (autoclaving) and incisal areas for CEZ (thermocycling).
4. The glaze layer was found to reduce OP without affecting the TP.
5. LTD affects color stability and translucency of zirconia; the levels of color change (ΔE) ranged between extremely slight and perceivable (autoclaving) and extremely slight and marked change (thermocycling) and marked on combined IPS zirconia (thermocycling).

Clinical significance:

1. Polishing procedure, improve the optical properties of translucent zirconia.
2. After artificial aging, the super-high translucent zirconia (CEZ-5Y) reported superior optical properties then high translucent zirconia (STL-4Y).
3. Regarding TP, the increase rate was lower for the glazed samples than for the polished ones, as well as in the incisal areas compared to the cervical ones.
4. Thermal aging affected the glazed and polished surfaces.
5. IPS (4+5Y) material-associated the characteristics corresponding to the two microstructure.
6. Levels of color change (ΔE)-were perceivable on polished surfaces of high translucent zirconia (autoclaving).

The purpose of **the third in vitro study** was to assess the surface characteristics, topography, microhardness, respectively the optical properties and color stability of three types high performance polymers, related to water saturation and hydrothermal degradation, as well as after staining beverages and mechanical (brushing) and chemical cleaning, simulating certain periods of clinical use.

The plate-shape samples were immersed in distilled water (37°C) and evaluated every 7 days, for a total of 28 days and then were subjected to thermocycling in alternante baths of 5°C to 55°C. For staining beverages experiment, four media were used: distilled water as control, black tea, hot coffee and cold juice. The temperature for experimental baths were chosen to simulate the oral environment.

The mechanical cleaning was achieved using a brushing method with an electric tooth-brushing device and for chemical cleaning, the specimens were chemically cleaned for 3 min./day (total 18 hours) in a hot water solution (60°C).

In the first part of the study, the surface roughness (Ra, Rz), surface topography (Sa, Sq) and microhardness (HV) were recorded and then the optical parameters (TP, CR, OP) and level of color changes were assessed.

According to the presented study, the following conclusions can be drawn:

1. The studied materials, reached water saturation after 7 days of immersion in water, and no significant differences were reported between them. Absorption was related to a decrease in microhardness, and modified PEEK was the most affected.
2. Thermocycling procedure caused a significant increase in surface roughnes, with no statistical differences between materials.
3. In terms of surface roughnes and thopography, modified PEEK was the least afected by aging.
4. Staining beverages such as tea and juice can lead to a significant decrease in the surface roughness of PEEK materials.
5. After the simulated cleaning (brushing/chemical) the roughness values decreased.

6. The level of color changes during water immersion (4 weeks = 1 year simulated aging), was extremely slight to slight, for all studied PEEK.
7. Perceivable color modifications have been found as being selective for J (coffee) and B (tea).
8. Related to simulated cleaninig, after chemical cleaning-perceivable color changes have been observed only for Juvora (juice).

The purpose of **the fourth in vitro study** was to compare and evaluate the internal and marginal fit of CAD/CAM onlay restorations obtained from PEEK and PEKK (high performance polymers-HPP), related to accelerated aging (thermocycling). Discrepancy was assessed using microcomputed tomography.

A typodont-inferior left first molar was prepared for the onlay, in MOD (mesio-oclusal-distal) design, the preparation was scanned to obtain the resin abutment teeth with a 3D printer. Subsequently, the onlays, were processed from the three different monolithic HPPs. and cemented to the abutment teeth using a self-adhesive, dual-cure cement and discrepancy values were measured at twelve reference locations of each mesio-distal section and thirteen locations for each bucco-lingual section, using a microcomputed tomograph.The evaluation was performed both before and after aging stage, achieved by thermocycling (alternante baths of 5°C to 55°C).

Statistcal tests were applied to compare internal and marginal fit of two HPP, or the values recorded before with those after thermocycling (Student t-test), internal and marginal fit between three HPP (one way ANOVA), to find the interaction effect between the material and measurement areas of IG, MG (two way ANOVA), and for multiple comparison of the values, Tukey post hoc test.

The following conclusions can be drawn:

1. For all materials, different levels of discrepancy at reference locations were recorded; the greatest gaps were seen for Pekkton after thermocycling
2. The type of material (composition and microstructure, mechanical characteristics, machinability) significantly influenced the marginal adaptability, especially for Pekkton and BioHPP.

3. MG values were significantly lower then IG values, before and after aging for all three HPPs.
4. At the contra bevel locations, higher values were registered compared to heavy chamfer preparation, for all groups.
5. Thermal aging had an significant impact on marginal and internal adaptability; Pekkton and BioHPP are questionable for fabricating onlays.