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CHARACTERIZATION OF INNOVATIVE DENTAL RESIN REINFORCED WITH ZIRCONIA NANOPARTICLES OBTAINED BY 3D PRINTING

Andreea BORŞ[1], Melinda SZEKELY[2], Zsuzsanna BARDOCZ VERES [3], Iuliana CORNESCHI[*4], Robert CIOCOIU[5], Aurora ANTONIAC[6], Catalin Ionel ENACHESCU[7]

Three-dimensional printed resins are gaining significant interest in dentistry. The demand for advanced materials with improved mechanical properties is on the rise to fulfill the growing need for technological developments. The incorporation of zirconia to reinforce three-dimensional (3D) printed resin has demonstrated significant potential in the field of dental restorations. These fillers have been found to improve the mechanical and biological characteristics of dental resins, thereby establishing them as a highly promising alternative dental material in restorative dentistry. Zirconium oxide is a metal oxide that exhibits commercial viability, affordability, non-hazardous properties, and sustainability, hence rendering it suitable for a wide range of prospective applications. The objective of this study was to evaluate the mechanical characteristics of 3D printed resin that has been enhanced with modified Yttrium stabilized zirconia (YSZ) nanoparticle additions. The specimens were analyzed via scanning electron microscopy (SEM), surface-free energy (SFE) measurements, and Shore® (Durometer) test. The results suggest that YSZ nanoparticles could improve the mechanical properties of the reinforced resin. The findings have the potential to enhance the advancement of indirect restorative dental materials.

Keywords: microstructure, mechanical properties, three-dimensional printing, additive manufacturing, Yttrium stabilized zirconia, reinforced resin

[1] Lect., Faculty of Dental Medicine, *George Emil Palade* University of Medicine, Pharmacy, Science, and Technology of Targu Mures, e-mail: andreea.bors@umfst.ro

[2] Prof., Faculty of Dental Medicine, *George Emil Palade* University of Medicine, Pharmacy, Science, and Technology of Targu Mures, e-mail: szekely.melinda@umftgm.ro

[3] Assistant, Faculty of Dental Medicine, *George Emil Palade* University of Medicine, Pharmacy, Science, and Technology of Targu Mures, e-mail: zsuzsanna.bardocz-veres@umfst.ro

[4] Student, Faculty of Materials Science and Engineering, National University of Science and Technology POLITEHNICA Bucharest, e-mail: iuliana.corneschi@stud.sim.upb.ro

[5] Lect., Faculty of Materials Science and Engineering, National University of Science and Technology POLITEHNICA Bucharest, e-mail: robert.ciocoiu@upb.ro

[6] Researcher, Faculty of Materials Science and Engineering, National University of Science and Technology POLITEHNICA Bucharest, e-mail: antoniac.aurora@gmail.com

[7] Doctor, Department of Dermatology, *Elias* Emergency University Hospital, Bucharest, e-mail: catalin_enachescu@yahoo.com

1. Introduction

Advances in computer-aided design and computer-aided manufacturing (CAD/CAM) emerging as remarkable technologies in the dental field have simplified the fabrication process of indirect restorations. An easier, faster, and more accurate method of production is to use a completely digital workflow using an intraoral scanner followed by design with CAD software and computer-aided subtractive or additive manufacturing techniques [1].

Manufacturing with the subtractive technique involves cutting a uniform disc or an individual block using a milling machine which is commonly used by dentists or dental laboratories [2]. However, it has some drawbacks. It causes waste of raw materials, requires instrument sustainability. and leads to difficulties in obtaining precise complex dental shapes rapidly [3,4]. In addition, the technology of using milling devices includes expensive machines, hard to reach for many dental practices. To overcome these shortcomings, our study has focused on additive manufacturing techniques.

The use of additive manufacturing (AM) for the construction of dental restorations is a relatively recent development in prosthetic dentistry [1]. Different materials and technologies like vat photo-polymerization, binder and material jetting, and powder bed fusion, are available at this moment [5]. Stereolithography (SLA) can be used for 3D printing of CAD/CAM models with low mechanical anisotropy [6]. The low anisotropy is because the parts printed by SLA have completely uniform layers. After all, they are packed more densely and have lower hardening energies. The process involves the polymerization of the liquid resin layer by layer using ultraviolet (UV) light. To obtain models that can be applied clinically, after a layer is printed, it is subjected to a post-polymerization process in order to complete the solidification [7].

In dentistry, 3D printing is used to print personalized impression trays, computer-guided implant surgical templates, or rapid prototyping skulls [8-10]. Due to the lack of printable materials, there are few studies on definitive indirect dental restorations [11-13]. With the evolution of 3D printing techniques and the discovery of new materials for printing, it will be possible to obtain long-lasting prostheses. These prostheses will have increased resistance to stress and resistance to the corrosive processes that take place in the oral cavity and will also satisfy safety and aesthetic requirements [14].

Against this backdrop, this study aimed to determine whether a novel 3D-printed resin reinforced with modified Yttria-stabilized zirconia (YSZ) nanoparticles could be used for manufacturing permanently fixed prostheses by comparing the microstructure and mechanical properties of two printable materials. The null hypothesis was that specimen types of printable resins do not affect their physical properties.

2. Materials and methods

2.1. Sintered yttria-stabilized zirconia powder with particle size range from 14–50 nm (yttrium oxide 9%) was obtained from zirconia discs (Multilayer Cercon XT-Dentsply Sirona) processed in milling machine (DWX-52D, by DG Shape, Figure 1) and sintered in furnace (Tabeo-1/M/Zirkon-100, MIHM Vogt, Figure 2). The fully sintered zirconia is described as having a lower volume fraction of pores, a greater strength, and an improved resistance to hydrothermal aging [15], therefore we decided to use this type of powder in our study. The residual zirconium oxide powder resulting from milling was collected and sintered at 1500^0C. The mean particle sizes were measured with a scanning electron microscope to provide topographical and elemental information at different magnifications.
The coupling silane agent Z Prime (batch 2300011450, Bisco) was used to accelerate the interaction between the resins and the zirconium nanoparticles thus resulting in a reactive group. The amount of coupling agent was determined based on Arkle's equation (Equation 1) as follows [16,17].

$$Amount\ of\ silane\ (g) = \frac{Amount\ of\ nanoparticles\ (g) \times Surface\ area\ (m^2/g)}{Minimum\ coating\ area\ of\ silane\ (m^2\ /g)} \quad (1)$$

2.2. The 3D-printed dental resin was purchased from Asiga Resin DentaTOOTH (Asiga), a biocompatible material for the production of dental teeth with increased resistance to wear and stain-resistant.

YSZ powder was dried and coated with silane (40ml). Silane solution was dropped wisely under magnetic stirring for 10 minutes (Thermo Fisher Scientific, Ceramic).

The YSZ nanoparticles used were added gradually, under continuous stirring, in percentages of 1% and 3% (w/w), respectively, compared to the printable resin solutions used.

The Asiga 3D Max UV digital printer (Figure 3) was used for 3D printing, while the design of the disc specimens (Φ =18mm) was done by the CAD software (Exocad, DentalCAD, Figure 4). A Composer 4.0 (Asiga) software was used to cut the generated stereolithography (STL) files which were then sent to a 3D printer.

Thirty discs of 18mm diameter were obtained from the modified materials ($n_{1\%}$=10, $n_{3\%}$=10) and the other ten from unmodified resin ($n_{0\%}$=10).

After printing, in order to remove the excess of uncured resin, the obtained specimens were cleaned by sonication in isopropyl alcohol for 5 minutes and rinsed twice in distilled water. The samples were subjected to a post-curing process to achieve maximum strength in a HiLite Power3D Kulzer high-performance photopolymerization unit for 20 minutes at 200W (Figure 5).

Fig. 1. The milling machine (DWX-52D, by DG Shape) used for milling zirconia discs.

Fig. 2. The sintering furnace (Tabeo-1/M/Zirkon-100, MIHM Vogt) used in the study

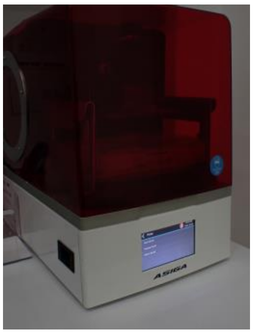

Fig. 3. Asiga 3D printer used to computer-aided manufacture the disc specimens.

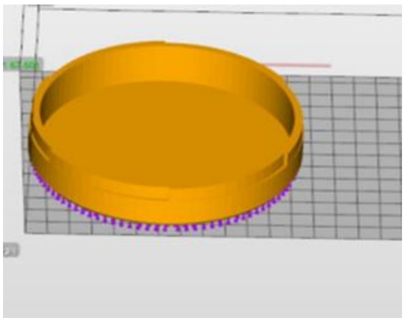

Fig. 4. Computer aided design with Exocad for the 18 mm diameter discs.

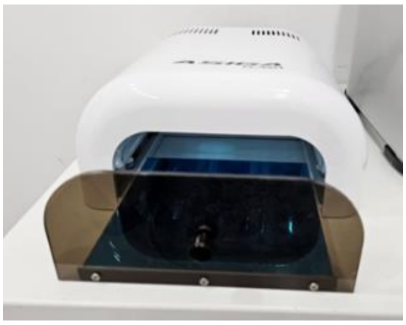

Fig. 5. The light curing unit used (HiLite Power3D; Kulzer).

2.3. Microstructure

Coated YSZ nanoparticles were viewed by scanning electron microscopy (ESEM Quattro™ microscope; Thermo Fischer Scientific, Hillsboro, OR, USA).

2.4. Surface free energy

Surface free energy (SFE) is an important parameter that characterizes the material surfaces and is determined by measuring the contact angle using the sessile drop method. The contact angle was measured using a Krüss Drop Shape Analyzer - DSA100, Hamburg, Germany.

The Extended Fowkes or OWRK method (geometric mean) was used in the study being one of the more common approaches to determining the surface free energy of solids using contact angle measurements [16].

The method involves the use of three liquids, diiodomethane (D), ethylene glycol (E), and water (W), with high values of surface-free energy and distinctive surface-free energy components [16].

2.5. Shore microhardness test

In our study, the Shore D scale was used using a microhardness tester. To determine the hardness, the Shore test was used, which determines the resistance of plastic materials to indentation. The test provides an empirical value for hardness, a value that is later correlated with other material properties. Hardness using the Shore A scale is a method used in the case of plastic materials such as polyolefins or fluoropolymers, while Shore D hardness is determined in the case of harder polymer materials.

2.6. Statistical analysis

The obtained data were analyzed using the ANOVA test (GraphPad InStat) and the post-hoc test for the comparison of pairs at the statistical significance of the value $p < 0.05$. To generate statistical significance in the case of surface free energy and Shore hardness results, repeated measures ANOVA tests were performed.

3. Results and discussion

3.1. Microscopic characterization

The image of YSZ powders is displayed in Figure 6 with Canon 550D camera, adapted to IOR ML 3.

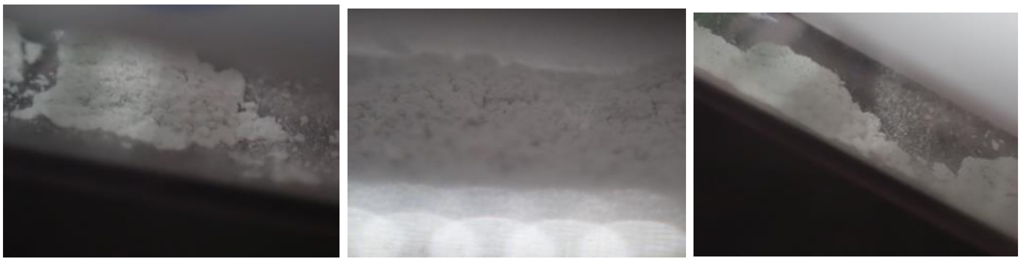

Fig. 6. Detailed photography of the milled and sintered zirconia powder 0.87× magnification Canon 550D camera.

The size of YSZ particles was measured with an SEM microscope. The results are shown in the below figures.

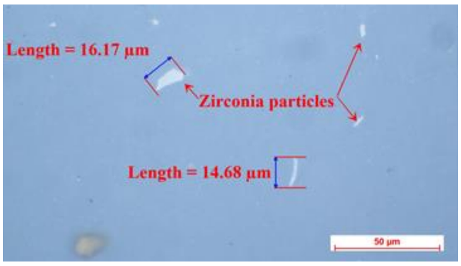

Fig. 7. Microscopic characterization of YSZ particles at X50000 magnification.

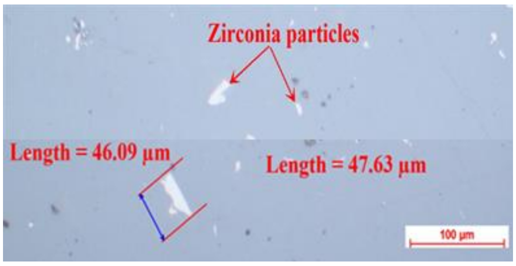

Fig. 8. Microscopic characterization of YSZ particles at X100000 magnification.

Fig. 9. SEM aspect of resin reinforced with 1% YSZ nanoparticles X15000 magnification.

Fig. 10. SEM aspect of resin reinforced with 3% YSZ nanoparticles X15000 magnification.

3.2. Determination of surface free energy using the OWKR method

The distribution of the contact angle (OWRK method) values for resins with YZS addition suggested the premise of its uniform distribution in volume (inherent on the surface investigated), the analyses were carried out considering the presence of two zones dictated by the contact angle values.

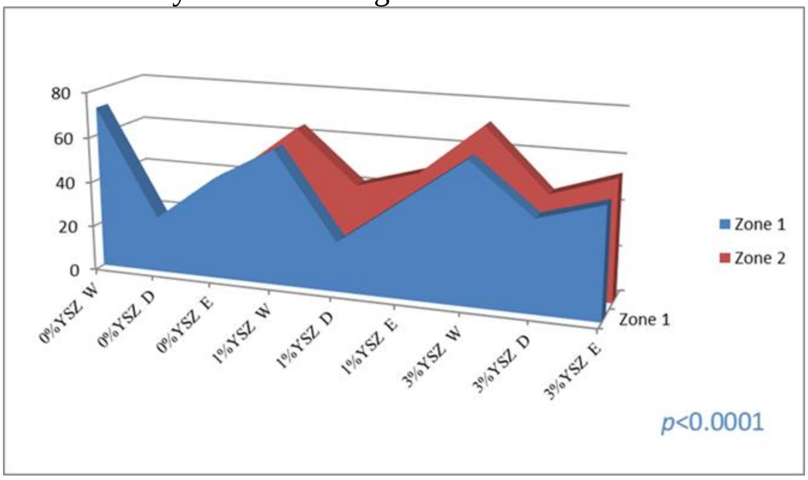

Fig. 11. Measured contact angles for the resins with YZS addition (three liquids was used).

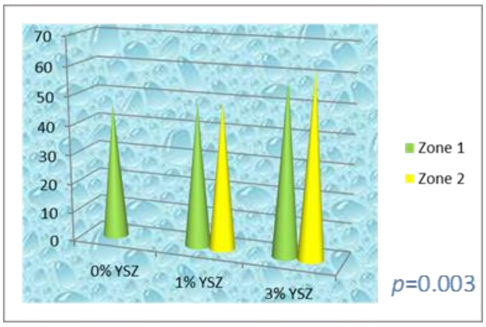

Fig. 12. Surface free energy (SFE) of the tested specimens (ml/m^2).

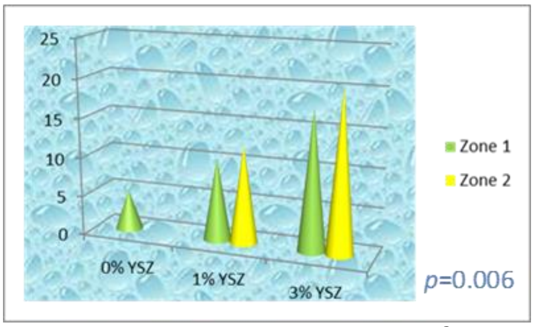

Fig. 13. Polar component of SFE (ml/m^2).

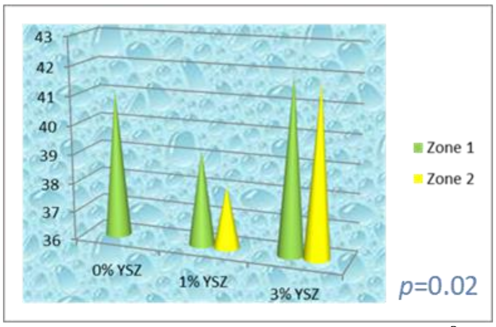

Fig. 14. Dispersive component of SFE (ml/m^2).

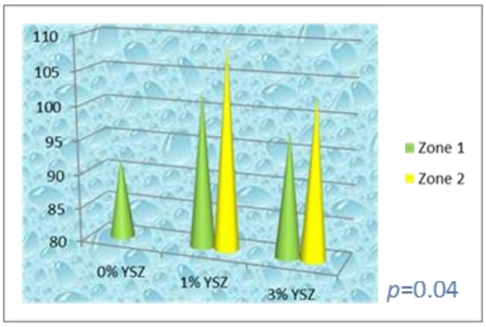

Fig. 15. Adhesion to water of the tested specimens.

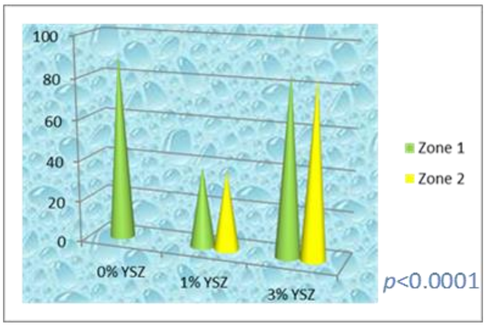

Fig. 16. Adhesion to diiodomethan of the tested specimens.

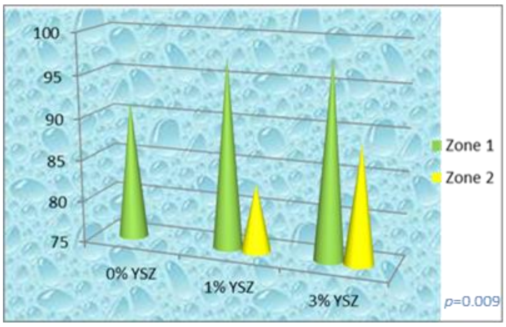

Fig. 17. Adhesion to ethilenglycol of the tested specimens.

3.3. Hardness Shore D

Shore D microhardness measurements of the resins with YZS addition (0%, 1%, and 3% YSZ) predict the preferential distribution of YSZ in the structure of 3D printing resins, followed by a small amount of YSZ accelerating a more intense effect on microhardness ($n_{0\%}$=80.25±0.69, $n_{1\%}$=85.50±0.32 compared with $n_{3\%}$=86.79±0.27, p=0.0006).

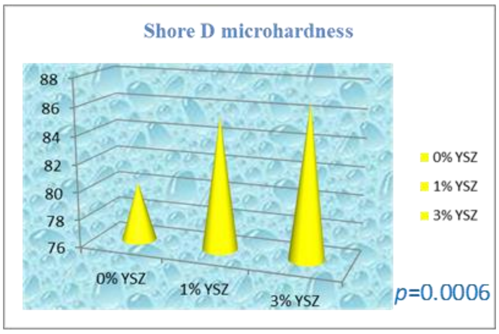

Fig. 18. Hardness measurements of the tested specimens.

Our research focused on the microstructure and mechanical properties of 3D printing resin films reinforced with YSZ and fabricated by additive process. Due to the different sizes and amounts of added YSZ nanoparticles are expected to have different effects on the microstructure and mechanical properties, which indirectly explains the variation of the surface energy and microhardness of the 3D resin films.

In order to detect possible manufacturing defects, a microscopic analysis of both types of reinforced samples (1% and 3%) was carried out using the ESEM microscope. In 3D printing of the sample discs, it was observed that there were no defects, not even at the level of the overlapping of the layers on top which should be visible as a result of the extrusion deposition process. The SEM images of all reinforced printing resins showed an average distribution throughout the near-surface region with a noticeably higher density of YSZ particles in the samples with 1% YSZ and a hyperdensity in the samples with the highest concentration of YSZ (3%). All 3D printing resin films with max % added YSZ (3%) showed the highest surface energy values for both zones (1 and 2), which can be attributed to the different concentrations of YSZ as well as the agglomeration effect. With the smallest incorporation of YSZ nanoparticles at contents of 1% (w/w) as well as for the control sample, the lowest polar ($p=0.06$) and dispersive ($p=0.02$) values were evaluated for the multicomponent system. In addition, adhesiveness for water ($p=0.04$) and diiodomethan ($p=0.0001$) increased with the proportion of YSZ. In contrast, adhesion to ethilenglycol ($p=0.09$) was indirect in proportion compared to the weight of YSZ.

The smaller the size of the particles is, the more densification of the electrolyte powders is obtained. This aspect is due to the higher surface energy of the particles. The results obtained in the case of the sample with 3% nanoparticles, the superior densification of the resins, suggest that other factors have a significant role in determining the microstructure and the densification behavior. These factors could be the powder synthesis method, particle size distribution, and post-processing of the powders.

Nowadays, there has been a notable focus in dentistry research on improving the overall quality of 3D-printed dental materials, with a specific emphasis on dental bridges and crowns. The objective is to ensure their optimal utilization in clinical settings. This involves enhancing the biocompatibility and durability of the materials [18].

Moreover, the quality of the final product can be affected by the following factors: printing parameters, the degree of polymerization or the addition of reinforcing materials [19-21]. So, a continuous evaluation of these factors is very important in the selection of appropriate materials. Mechanical properties are essential to withstand biting forces.

In this study, the effect of zirconia particles from 3D printed specimens on the structure, surface free energy, and hardness of the material was evaluated. We found that the addition of nanoparticles in the 3D-printed resin have significant difference in mean values compared to the control 3D-printed resin.

Based on the results, it was demonstrated that both the surface free energy and the hardness of 3D printed resins increase by adding nanoparticles. This aspect is correlated with previous studies that demonstrated the effect of different nanoparticles on 3D-printed resins [14,22].

The advantages of additive manufacturing technologies include the reduction of material waste, decreased production time, simplified manufacturing processes, the capacity to personalize production, and the availability of a wide range of materials. Nevertheless, despite these benefits, there exist certain constraints when utilizing this technology throughout various domains of production, such as dentistry. In the context of fabricating patient-specific models, it is not feasible to employ MRI equipment for data collection in patients with metallic implants during (AM) procedures. One further constraint is the incompatibility of certain materials, rendering them unsuitable for processing through additive manufacturing. The fabrication and replacement of these materials may provide challenges in terms of complexity and cost-effectiveness in their development [23].

The incorporation of nanoparticle fillers has been demonstrated as a successful strategy for improving the microstructure and mechanical properties of dental 3D resins [24]. Additionally, previous studies have demonstrated that this methodology can improve the tensile strength and wear resistance, as well as the elastic modulus, while also reducing the polymerization shrinkage and exhibiting other desirable features [25].

4. Conclusion

The incorporation of two different amounts (1 wt% and 3 wt%) of the YSZ into the 3D resin matrix causes an enhanced change in the microstructure and mechanical properties of the 3D printing material. No defects are noticed in the structure of the purchased 3D resins so it can be concluded that adding the prepared YSZ did not show deficiencies in the manufacturing process. The microstructure of YZS-based 3D resins depends on the YZS filler loading and is closely related to the size and distribution of YZS in the polymer matrix.

Since the materials generated in this investigation meet ISO criteria for dental applications, it can be concluded that resins reinforced with YZS nanoparticles in 3D printing technology present a feasible alternative for the production of components that might potentially be utilized in dental fixed prostheses (FDPs). However, additional research is required to evaluate the clinical significance of additive manufacturing technologies in the production of FDP components.

The assessment of the mechanical characteristics and biocompatibility of 3D-printed materials in comparison to traditional alternatives is crucial in establishing their appropriateness for extended clinical application in dental restorations. A comprehensive examination of these variables can contribute to the advancement of dental materials and the optimization of patient care.

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R E F E R E N C E S

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