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Comparative Evaluation of Microhardness, Water Sorption and Solubility of Biodentin and Nano-Zirconia-Modified Biodentin and FTIR Analysis

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Abstract: Aim: This study compares the microhardness, water sorption and solubility of nano-zirconia-reinforced biodentin groups to commercially available biodentine. Materials and Methods: Samples were prepared by adding different percentages of nano zirconia to biodentin. Four groups were categorized as follows: group 1 used Biodentin as the control group, group 2 used 10% nano zirconia and 90% Biodentine, group 3 used 20% nano zirconia and 80% Biodentine, and group 4 used 30% nano zirconia and 70% Biodentine. A Vickers microhardness tester was used to measure the microhardness of the groups according to ISO 4049/2000. The water sorption and solubility of the divided groups were assessed using disk-shaped molds. The second weight was measured on an electronic weight machine after two weeks, and values were recorded. FTIR analysis was performed. Vickers microhardness, water sorption and solubility were analyzed using a one-way ANOVA, and for multiple comparisons, a post hoc Tukey's HSD test with a significance level of $p < 0.05$ was performed. Group 3 had the highest mean microhardness measurement among all groups. The microhardness values for all groups in descending order are as follows: group 3, group 2, group 1 and group 4 ($p = 0.008$). Group 2 showed the lowest mean of water sorption compared among all groups. Group 2 has the lowest mean of water sorption, followed by group 3, group 1 and group 4 ($p = 0.002$). Group 4 showed the highest water sorption among all groups. Group 4 exhibited the highest solubility mean among all groups. Group 1 had the lowest mean of solubility, followed by group 2, group 3 and group 4 ($p = 0.000$). The FTIR spectra of different types of biodentin showed the absorbance peaks of the precipitates of each modified biodentin. The absorbance peaks fell between 474.63 cm^{-1} and 3438.33 cm^{-1}. Conclusion: Biodentin is a competitive biomimetic material, but it lacks hardness and has more solubility. Thus, adding nano zirconia improved microhardness and reduced water sorption. The solubility of 20% nano zirconia added to biodentin was almost close to biodentin but with no significance. The 20% nano-zirconia-modified biodentin showed overall better properties compared to biodentin. The 20% nano-zirconia-modified biodentin can be used in deep cavities as a single restorative material instead of multi-layered restorations to increase longevity without microleakage and failure of restoration.

Keywords: biodentine; biomimetic materials; microhardness; nano zirconia; restorative

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1. Introduction

Hydraulic calcium silicate cements have successfully replaced the conventionally available materials in dentistry since their introduction due to their properties such as biocompatibility, bioactivity, radiopacity, their ability to stimulate the repair of tissues and the remineralization of dentin [1,2]. These materials require water to set and do not deteriorate in a wet environment, such as in the presence of blood, tissue fluid, saliva or water [3]. They are broadly used in various procedures such as direct and indirect pulp capping, the restoration of carious teeth, apexification, perforation, root repair, root end filling and endodontic surgeries [2,4]. MTA, biodentine, bio aggregate, Theracal, calcium-enriched mixture cements and endo sequence root repair materials are some of the few calcium silicate cements, but the principal focus is on the material Biodentine [5].

Biodentine is acknowledged as a prominent representative of calcium-silicate-based cements, as it is radiopaque, antimicrobial and biocompatible with good sealing ability and marginal integrity. It has the shortest setting time, does not discolor and possesses good physio-mechanical properties [6,7]. The powder contains tricalcium silicate as the main core material, calcium carbonate as the filler and zirconium oxide acting as a radio pacifier. The liquid consists of calcium chloride, water and hydrosoluble polymer [8]. It sets via a hydration reaction and releases calcium hydroxide once set, which initiates the secondary dentin formation when placed above the pulp, and hence this material is popularly known as the "dentine substitute" [9]. All the aforementioned properties make it a suitable material for numerous clinical conditions, such as for pulp capping, pulpotomy, furcation or perforation repair, root end or root canal filling and as a dentin tissue replacement material [10].

Zirconia, a metal oxide with a natural white color and high toughness, is favorably used in dentistry due to its superior physio-mechanical and biological properties. It is biocompatible and bioinert with steady chemical features, radiopacity and good corrosion resistance [11]. Nano zirconia is extensively used to repair dental tissues. Nano-zirconia-reinforced groups of polymethyl methacrylate denture base significantly increase surface hardness, flexural strength and impact strength compared with un-reinforced groups [11,12]. Similarly, adding nano zirconia to GIC increases its surface microhardness, compressive strength and flexural strength, resulting in overall mechanical properties [13,14].

Microhardness, a significant material property, especially when placed for posterior restoration, is the resistance of restoration to permanent deformation. Vickers microhardness testers are used to determine hardness by marking three indentations on the surface and calculating the value of the diagonals [12]. Water sorption is the phenomenon of absorption and adsorption, in which water is absorbed into the body of a material and adsorbed on the surface. Solubility is the amount of the substance, the solute, that dissolves to form a solution in a given amount of solvent [6].

Several studies have been conducted on adding nano zirconia to different materials in dentistry [14–17], but there are no data available regarding the enforcement of nano zirconia to biodentine. Hence, this study was conducted to determine the microhardness, water sorption and solubility of nano-zirconia-reinforced groups in different percentages with biodentine.

2. Materials and Methods

The materials used in this study included Biodentine™ (Septodont, Saint-Maur-des-Fosses Cedex, France) and nano zirconia (Jiangsu Xfnano materials Tech, Nanjing, China). Four groups were categorized using the materials mentioned earlier, and they are as follows:

Group 1: Biodentine™, the control group.
Group 2: 10% nano zirconia by weight and 90% Biodentine by weight.
Group 3: 20% nano zirconia by weight and 80% Biodentine by weight.
Group 4: 30% nano zirconia by weight and 70% Biodentine by weight.

2.1. Preparation of Samples

Group 1: Equivalent to 700 mg, 100% Biodentine by weight was used as the control group. Group 2: Sample preparation was performed using 90% Biodentine by weight, equivalent to 630 mg, which was weighed on a digital scale (Sartorius BSA423S), as well as 10% nano zirconia by weight, equivalent to 70 mg. All the contents were mixed in a given weight proportion and were transferred to an air-tight container, followed by centrifugation using a centrifugal machine (Eppendorf, centrifuge 5804, Mississauga, Canada). Then, the contents were subjected to ultra-sonification in an ultrasonic stirrer (Branson 3510). The volume and weight of groups 3 and 4 were obtained via the same method as mentioned earlier and tabulated in Table 1.

Table 1. Weight proportion of Biodentine and nano zirconia in all groups.

Groups	Weight of Biodentine in mg	Weight of Nano Zirconia in mg
Group 1	700 mg	
Group 2	630 mg	70 mg
Group 3	560 mg	140 mg
Group 4	490 mg	210 mg

The powder content of all groups was mixed with liquid as per the manufacturer's instructions and was triturated in an amalgamator (Promix TM; Dentsply Caulk, York, PA, USA) for 30 s. The mixture was then transferred to disk-shaped acrylic molds of 5 ± 1 mm thickness and 2 ± 1 mm diameter and was placed on a glass slide (Sail Brand, China) with a mylar strip (Ruwa Matrix Strips; Austenal Dental Products Ltd., Harrow, UK). The molds were slightly overfilled with material, and another strip and slide were placed on the top with pressure to avoid voids and to obtain a smooth surface. Then, the cement was set at room temperature overnight and was placed in an incubator (Memmert GmbH +Co. KG, Schwabach, Germany) for 24 h at 37 °C and 100% humidity to allow the material to completely set.

2.2. FTIR Analysis

Fourier-transform infrared spectroscopy (Perkin Elmer spectrum 100 FTIR spectrometer) was performed in the spectral range of 450–4000 nm. It is a non-destructive technique that provides insight into the chemical characterization of material and also gives information about the organic and inorganic components of the respective materials. The samples were crushed into powder with a pestle and mortar, and a KBr pellet was made in a 1:10 ratio using potassium bromide and the samples. The KBr pellet was then further analyzed.

2.3. Evaluation of Microhardness

Vickers microhardness (the mode- VM 50, fuel instruments and engineers Pvt LTD, India) was measured according to ISO 4049/2000 using disk-shaped acrylic molds of 5 ± 1 mm thickness and 2 ± 1 mm diameter (10 molds of each group). A pyramid-shaped diamond indenter was used to analyze them with a 1 kg load for 10 s. Three indentations were marked on the surface of each specimen at three different locations. The Vickers microhardness value (*VHN*) was calculated using a standard chart, and it was cross-checked with the values obtained by the following formula:

$$\frac{VHN = 2F\ \sin\left(136^{\circ}/2\right)}{d^2} = \frac{1.854F}{d^2}$$

F is the load in kg.
d indicates the mean of two diagonals in mm.

2.4. Evaluation of Water Sorption and Solubility

Disk-shaped molds were divided according to the groups and were allowed to set at room temperature for 24 h. After the material was set, the samples were de-molded, and the initial weight was recorded on an electronic weight machine. Then, samples were vertically immersed in a beaker containing 20 mL of distilled water and were placed in an incubator for two weeks at 37 °C and 100% humidity. The second weight was checked after two weeks, and the values were recorded. The weight difference between the initial set samples and the immersed samples was noted. Finally, samples were kept in a drier for 24 h to evaporate the water, and then the final weight was measured and compared with the weight of the initial set samples to evaluate the amount of material dissolved in distilled water.

2.5. Statistical Analysis

According to the Kolmogorov–Smirnov test, all data were distributed normally. Thus, differences between the four groups regarding their Vickers microhardness, water sorption and solubility were analyzed using a *one-way ANOVA*, and for multiple comparisons, a *post hoc Tukey's HSD* test was used at a level of significance of $p < 0.05$.

3. Results

3.1. FTIR Analysis

The FTIR absorbance spectra of the precipitates on different sets of biodentin and modified biodentin are shown in Figure 1. The absorption peaks ranged between 522.00 and 3438.33 cm^{-1} for group 1, i.e., Biodentin, 522.00 and 3643.26 cm^{-1} for group 2, 522.00 and 3438.33 cm^{-1} for group 3 and 522.00 and 3643.26 cm^{-1} for group 4 (Table 2).

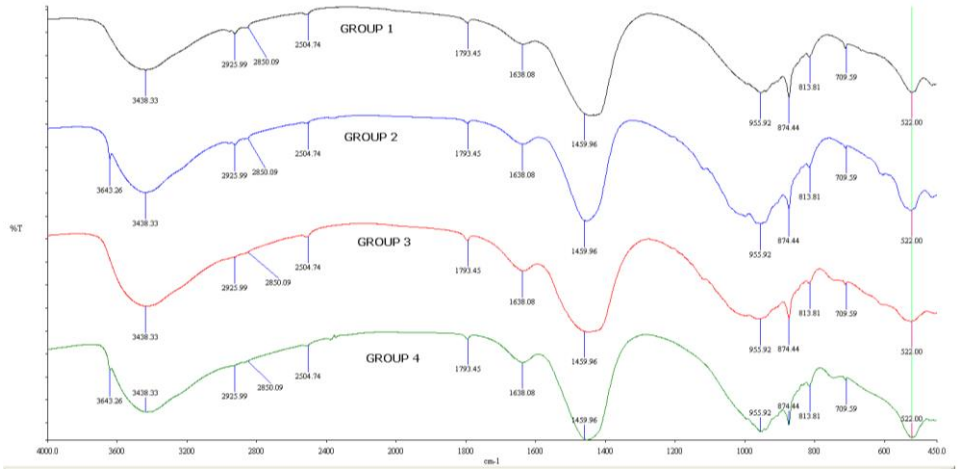

Figure 1. FTIR spectra of different types of cured Biodentin showing the absorbance peaks of the precipitates of each modified biodentin. Absorbance peaks ranging from 474.63 cm^{-1} to 3643.26 cm^{-1} are seen.

The FTIR spectra of biodentin and different groups of nano-zirconia-modified biodentin are shown in Figure 1 and Table 2, showing the main infrared absorption of biodentin and modified biodentin. The OH stretching vibrations of biodentin gave a broad band at 3438.33 cm^{-1}. As seen in the spectra of biodentin and its nano-zirconia-modified groups, the stretching vibration shifted from 3643.26 cm^{-1} for group 2 to 3438.33 cm^{-1} for group 3 and 3643.26 cm^{-1} for group 4. The absorption bands for group 1, the control group, and group 3 had the same value: 3438.33 cm^{-1}. Aliphatic C-H stretching and C-H stretching were also seen in the range of 3000–2800 cm^{-1}. Not much variation was seen in this region of absorption. In the absorption range of IR 2000–1650 cm^{-1}, the formation of C=C of aromatic ring stretching indicated a medium interactive bond between nano zirconia and components of biodentin. At absorptions of 709.59 cm^{-1} and 813.81 cm^{-1}, there were

trisubstituted and monosubstituted molecules. All these sharper peaks were assigned to a broader new peak with an idealized formula ($Ca_8(Si_6O_{18}H_2)(OH)_8(Ca.6H_2O)$ with a C/S ratio > 1.5).

Table 2. Band assignment for FTIR spectra.

Absorption (cm^{-1})	Group	Compound	Comments
3643.26	O-H stretch	Alcohol	Free
3438.33	O-H stretch	Alcohol	Intermolecular band
2925.99	Aliphatic C-H stretch	Carboxylic acid	
2850.09	C-H stretching	Alkane	Doublet
1793.45	C=O stretching		anhydrite
1638.08	C=C Aromatic ring stretch	Alkene	Substituted
1459.96	C=H	Inorganic carbonate alkane	Methyl group
955.92	C=C bending	Alkene inorganic carbonate and Aroganite	Methyl substituted
874.44		Aroganite	
813.81	Aromatic ring bends out of a plane		Monosubstituted
709.59	-CH out-of-plane aromatic band		Trisubstituted
522.00			

3.2. Analysis of Microhardness

Table 3 reveals the difference concerning microhardness between the groups. Group 3 exhibited the highest mean value of microhardness, followed by group 2, group 1 and group 4.

Table 3. Microhardness measurement of all groups.

Groups	Mean (SD)	F(df)	*p*-Value
Group 1	32.449 (9.910)		
Group 2	33.874 (12.552)		
Group 3	34.876 (14.618)	4.579 (3, 39)	0.008 *
Group 4	17.658 (10.175)		

* Significant at 0.05 level with one-way ANOVA.

Furthermore, there was a significant difference among the groups; hence, a post hoc test was conducted. Table 4 shows the multiple comparisons test with group 4, indicating that group 4 significantly differed in the mean of microhardness measurement with all the groups. However, there was no significant difference in the mean of microhardness between group 1 and group 2 (*p*-value = 0.993), group 1 and group 3 (*p*-value = 0.969) and group 2 and group 3 (*p*-value = 0.998).

Table 4. Multiple comparisons test for microhardness.

Group		Mean Difference	*p*-Value	95% Confidence Interval	
				Lower	Upper
Group 1	Group 4	14.791	0.043 *	0.375	29.207
Group 2		16.216	0.022 *	1.800	30.632
Group 3		17.218	0.014 *	2.802	31.634

* Significant at 0.05 level with post hoc Tukey's HSD test.

3.3. Evaluation of Water Sorption

Table 5 shows the comparison of water sorption values among the groups, which reveals that group 2 had the lowest mean of water sorption, followed by group 3, group 1 and group 4. Furthermore, a multiple comparisons test was conducted, which showed a significant difference in the mean of water sorption between group 2 and group 4 and between groups 3 and 4. However, no significant difference was found between group 1

and group 2 (p-value = 0.085), group 1 and group 3 (p-value = 0.225) and group 1 and group 4 (p-value = 0.628) (Figure 2).

Table 5. Comparative evaluation of water sorption of all groups.

Group	Mean (SD)	F (df)	p-Value
Group 1	0.0019 (0.0009)	5.898 (3, 37)	0.002 *
Group 2	0.0009 (0.0008)		
Group 3	0.0012 (0.0008)		
Group 4	0.0025 (0.0011)		

* Significant at 0.05 level with one-way ANOVA.

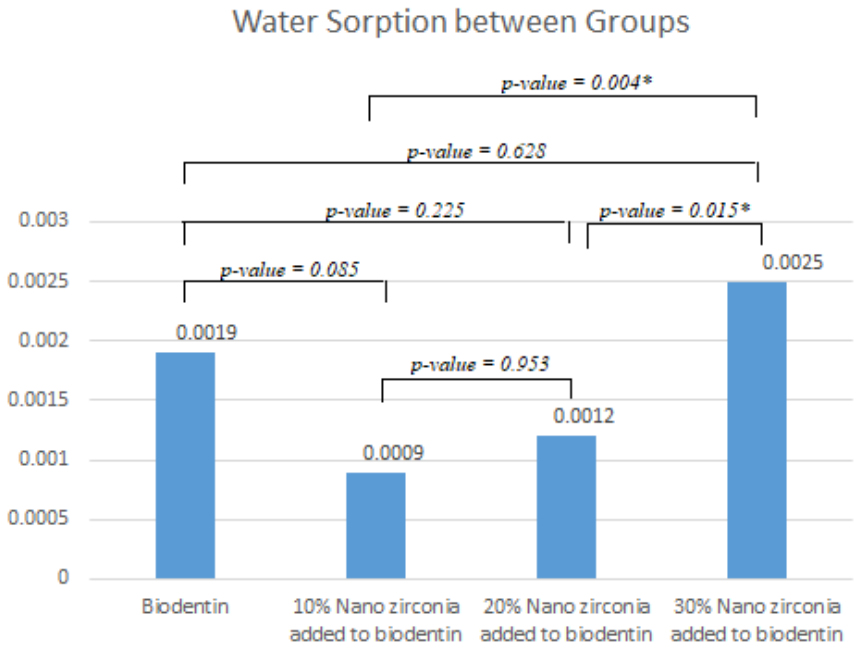

Figure 2. Water sorption between groups. * significant difference.

3.4. Evaluation of Solubility

Table 6 indicates the mean solubility value of all the groups, in which group 4 had the highest solubility compared with group 3, group 2 and group 1, and it also had the most negligible value. Further post hoc test results (Figure 3) revealed a significant difference in mean solubility between groups 3 and 1 and between groups 3 and 2. It also showed the difference between groups 4 and 1 and between groups 4 and 2. There was no significant difference in the mean solubility between groups 1 and 2 (p-value = 0.954) and between groups 3 and 4 (p-value = 0.668).

Table 6. Comparative evaluation of solubility of all groups.

Group	Mean (SD) (Weight in gms)	F (df)	p-Value
Group 1	0.0212 (0.0030)	10.959 (3, 37)	0.000 *
Group 2	0.0218 (0.0032)		
Group 3	0.0253 (0.0014)		
Group 4	0.0265 (0.0018)		

* Significant at 0.05 level with one-way ANOVA.

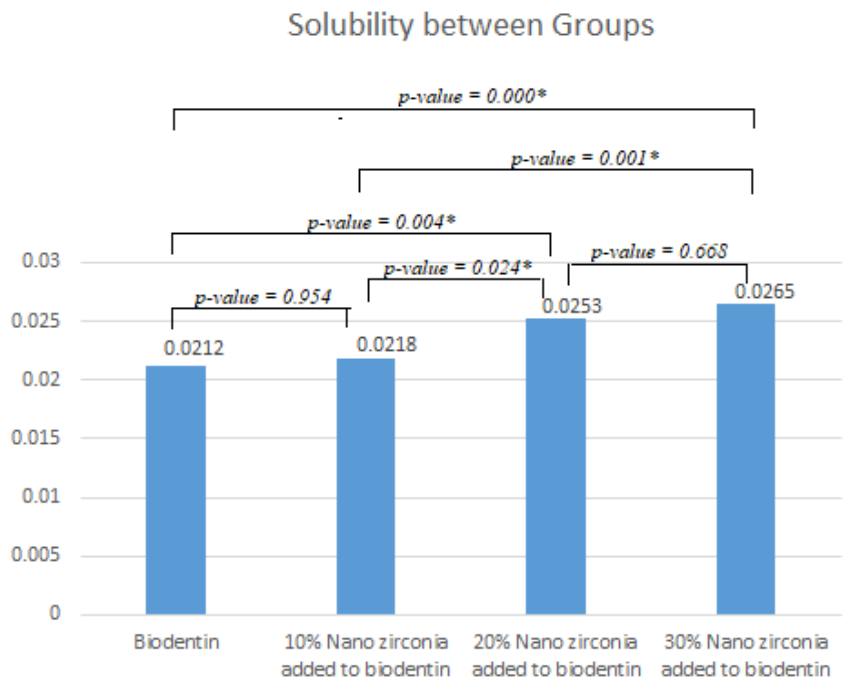

Figure 3. Solubility between different groups. * significant difference.

4. Discussion

This study aimed to evaluate and compare the effect of adding nano zirconia to biodentine in different percentages, such as 10%, 20% and 30%. Using FTIR, microhardness, water sorption and solubility were checked accordingly. Biodentine, the 'dentine replacement' material, gained popularity quickly after its introduction to dentistry in 2009 due to its phenomenal properties, which have allowed its use in numerous dental procedures, ranging from permanent restoration and direct and indirect pulp capping to root-end filling, perforation and apexification [7]. Nanomaterials are another essential emerging topic in dentistry, as they promise to enhance the material properties applied in the dental field to treat or prevent oral diseases [18]. Nano zirconia, used as a nanomaterial in this study, is allegedly able to enhance the properties of the material. It has increased mechanical strength, higher biocompatibility and good overall biological and surface characteristics [19].

4.1. FTIR

Dental materials used in dentistry for various vital procedures must be biocompatible, inhibit bacterial growth, prevent microleakage and form a bond between the tooth and the material. Knowing the material's composition and structural and chemical features is desirable, as they are placed directly or closely to vital tissues [20]. Fourier transform infrared spectroscopy is a vibrational technique popularly used to know the chemical and structural properties of a material. It absorbs the energy in the IR region, resulting in the transfer of photons from lower to higher energy, causing molecular bond vibrational movement [21].

Morphological and chemical analyses of biodentin have found that the FTIR spectrum shows characteristic absorption bands of phosphate and hydroxyl groups. In addition, Camilleri et al. [4] reported that Biodentine contains calcium hydroxide in its composition.

The FTIR spectra of biodentin and different groups of nano-zirconia-modified biodentin are shown in Figure 1. Table 2 shows the main infrared absorption of the biodentin and modified biodentin. The OH stretching vibrations of biodentin gave a broad band at 3438.33 cm^{-1}. As seen in the spectra of biodentin and its nano-zirconia-modified groups, the stretching vibration shifted from 3643.26 cm^{-1} for group 2 to 3438.33 cm^{-1} for group 3 and 3643.26 cm^{-1} for group 4. There was an interaction between the biodentin components and the nano zirconia in all groups, and there were some free functional groups for bonding

in group 2 and group 4, as the absorption band was 3643.26 cm^{-1}. The absorption bands for group 1, the control group, and group 3 were the same: 3438.33 cm^{-1}. In accordance with this, the results for all objectives of our research also show that group 3 had better and equal properties compared to biodentin. Aliphatic C-H stretching and C-H stretching were also seen in the 3000–2800 cm^{-1} range. Not much variation was seen in this region of absorption. In the absorption range of IR 2000–1650 cm^{-1}, the formation of C=C of aromatic ring stretching indicated a medium interactive bond between nano zirconia and components of biodentin. At absorptions of 709.59 cm^{-1} and 813.81 cm^{-1}, there were trisubstituted and monosubstituted molecules (Table 2). All these sharper peaks were assigned to a broader new peak with an idealized formula ($Ca_8(Si_6O_{18}H_2)(OH)_8(Ca.6H_2O)$ with C/S ratio > 1.5).

4.2. Microhardness

Microhardness is dental materials' most significant mechanical property, mainly when used in vital pulpal treatment. It is the principal indicator that denotes resistance against deformation and dramatically influences the elasticity or strength of a material [22]. The surface microhardness of Biodentine is equal to that of natural dentine [23]. As per Camilleri et al., the hardness of the bodentine was around 130 HV and then decreased to 90 HV after etching with 35% phosphoric acid for 1 min, considered the highest value compared with other materials in the study [9]. Similarly, Grech et al., in another study, reported a hardness value of 48.4 HV, which was, again, the highest value compared with materials such as bio-aggregate and IRM when immersed in HBSS for 28 days [6]. As per Kaup et al., the hardness of biodentine was 62.35 HV, which was double that of Pro Root MTA, and Daawood et al. stated that the microhardness of biodentine is 45.4 HV. As mentioned above, differences in values are mainly due to varying protocols followed in the respective studies [24,25]. A reduced water powder ratio and the formation of a tag-like structure are the principal reasons that biodentine is a structurally more resistant material against forces, permitting it to be used broadly [22,26].

In our study, the hardness of the control group, i.e., Biodentine™, was 32.39 HV when following the aforementioned methodology. Adding nano zirconia in different percentages to elevate the properties of biodentine was the new approach. Nano zirconia, the 'nano material' with enhanced physio-mechanical properties, was added to PMMA to increase the repair strength of the denture base. Different studies have shown the increased transverse strength, flexural strength and microhardness of nano-zirconia-reenforced groups compared with un-reinforced groups [16,17,27]. The incorporation of nano-silica into MTA in different percentages leads to a reduction in setting time and increases compressive and flexural strength accordingly [28]. Hence, it is clear from the details mentioned above that the addition of nano materials significantly enhances the material's properties.

In the present study, when nano zirconia was added to different groups, group 3 with 20% nano zirconia showed favorable results with increased microhardness compared to the control group, as mentioned (Tables 3 and 4). In contrast, the values were reduced in group 4. Major factors determining the outcome are the size of the used nanoparticles, the percentage of nanofillers added and the type of material into which nanofillers are incorporated [12]. Nano zirconia can form strong bonds between the fillers and material, which in turn establishes strong molecular bonds that permit increases in desirable material properties [15]. The homogenous distribution of filler particles that fill the gap and that establish inter-atomic solid bonds is the utmost important factor for the desired outcome [16,17,29,30]. A decrease in or an inappropriate percentage of nanofillers does not make any statistical difference. An increased percentage of nanofillers results in poor adhesion and agglomeration. There can be the formation of multiple voids or the complete saturation of nano zirconia with the material [27,29]. When a higher content of filler is added, it leads to the formation of defects and weakening of the material. When the matrix reaches a saturation point, it cannot accept more filler, and if fillers are added to it, this results in the interruption of the continuity of

the matrix and thus results in decreased strength [31]. Henceforth, when the percentage of nanofillers increases or decreases to a certain level, it can cause structural defects in the material and adversely affect its properties. Therefore, in this study, the 20% addition of nano zirconia to biodentine is considered the ideal ratio for enhancing microhardness and obtaining a statistically significant increase in the values compared with the control group.

4.3. Water Sorption and Solubility

The water sorption and solubility of the dental restorative material must be minimized to increase its lifespan by preventing microleakage and expansion in the oral environment [32]. Biodentine exhibits increased solubility compared with other restorative materials but is lesser than other calcium-silicate-based cements, likely due to its controlled water–powder ratio [33]. Solubility is the loss of material; the higher solubility of biodentine is mainly due to the increased release of calcium and hydroxide ions during the hydration process, which is necessary to maintain its bioactivity [34]. Calcium ions mineralize and proliferate the pulpal cells. Moreover, it maintains the mineralization of dentin and helps in the formation of dentin bridges. However, the increased solubility of Biodentine is condemnatory when it is used as a restorative material because the hydrolysis of calcium hydroxide causes the denaturation of collagen, resulting in the crystallization of dentinal tubules. Water sorption is related to the level of the porosity of the material. The water sorption of biodentine is a result of increased hydration and a water-reducing component in its composition [32–34].

The mechanism responsible for water sorption and solubility is the diffusion of water into the matrix, resulting in the formation of voids, weakening the material strength, resulting in its deterioration and thus reducing the lifespan of restoration [35]. The addition of nanofillers reduces water sorption and solubility because they are insoluble in water, reducing fluid uptake [18].

In the present study, group 2, with 10% nano zirconia, showed the most negligible water sorption value among all the compared groups, with group 4 exhibiting the highest value (Table 5, and Figure 2), and the most insignificant solubility was noticed in group 1, which was the same as group 2, as there was no significant difference between them. Group 4 showed the highest solubility (Table 6 and Figure 3). This can be explained by the study by G Ergun et al., who stated that adding nano zirconium dioxide fillers to denture liners reduces water sorption and solubility [19]. Another study, in which silver nanoparticles were added to calcium silicate cements, showed favorable results [36]. Fatma Hussein et al. also supported the results of the current study; they added nano titania to conventional GIC and induced a reduction in its water sorption and solubility [18], which is in harmony with the studies by Dehis et al. [37] and Subramaniam et al. [38]. An increase in the nanofiller percentage causes an increase in water sorption and solubility, as noted by group 4, which could be due to the formation of multiple voids and the presence of more free molecules [27,29].

5. Conclusions

Biodentin is a competitive biomimetic material but lacks higher hardness and has less sorption; hence, adding nano zirconia improved its microhardness and water sorption properties. The solubility of the 20% nano zirconia added to biodentin was close to that of biodentin but with no significance. Further research is required to improve biodentin's mechanical properties as well as its water sorption and solubility. The 20% nano-zirconia-modified biodentin showed overall better properties compared to biodentin and may provide applications with better prognoses. The 20% nano-zirconia-modified biodentin can be used in deep cavities as a single restorative material instead of multi-layered restorations to increase longevity without microleakage and failure of the restoration.

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