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Mechanical Properties of Denture Base Materials Modified with Zirconia Nanotubes

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Abstract

Background and Aim: Several studies have investigated the effect of addition of fillers on mechanical strength of denture base materials. This study aimed to evaluate the mechanical properties of heat-cure denture base materials incorporated with different concentrations of zirconia nanotubes (ZNTs).

Materials and Methods: In this in vitro study, 90 specimens were fabricated from each denture base resin material (Trevlon and DPI) and divided into three groups (n=30) based on the mechanical properties to be tested (flexural strength, impact strength, and surface hardness). Thirty specimens in each group were further subdivided into 5 subgroups (n=6) based on the weight percentage (wt%) of ZNTs (0.0wt%, 0.5wt%, 1.0wt%, 2.0wt%, and 5.0wt%). The specimens were subjected to flexural strength, impact strength, and surface hardness testing using a universal testing machine, IZOD impact testing machine, and Vickers hardness tester, respectively. One-way ANOVA and post-hoc tests were used for statistical analyses (alpha=0.05).

Results: The maximum flexural strength was observed following the inclusion of 2.0wt% and 1.0wt% ZNTs in Trevlon and DPI, respectively. The maximum impact strength was obtained with the addition of 1.0wt% ZNTs to both Trevlon and DPI. The surface hardness of Trevlon and DPI increased significantly with an increase in the concentration of ZNTs (P=0.005). Flexural strength (P=0.000) and surface hardness (P=0.005) were significantly different among various concentrations of Trevlon and DPI, but the impact strength (P=0.013) was significantly different only in DPI.

Conclusion: The optimal concentration of ZNTs to obtain enhanced mechanical properties of denture base resins was found to be 1.0wt%.

Keywords: Flexural Strength; Hardness; Polymethyl Methacrylate; Zirconium Oxide

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Introduction

Polymethylmethacrylate (PMMA), originally introduced to the field of dentistry by Walter Wright in 1937, remains as a highly regarded exemplary denture base material [1]. Its exceptional characteristics, including biocom-

patibility, stability in the oral environment, esthetic appeal, precise fit, ease of fabrication and adjustment, reparability, and cost-effectiveness render it a versatile choice for dental prostheses [2,3]. However, despite its numerous advantages, PMMA exhibits certain inherent limitations such as inferior mechanical properties, which can lead to the fracture of denture base and consequently affect the durability of dentures [4]. In fact, denture fracture stands as one of the most frequently encountered clinical complications, with reports indicating failure in approximately 68% of denture wearers within a span of 3 years [5].

The primary cause of denture fracture can be attributed to material fatigue resulting from repetitive application of masticatory forces [1,6]. Thus, dental prostheses must possess not only adequate strength to withstand such forces but also resistance to abrasion during cleaning procedures. Failure to meet these criteria may result in development of a rough denture surface, which promotes the adherence of food particles and debris, ultimately leading to unhygienic dentures and the potential onset of denture stomatitis [7]. Furthermore, microcracks within the denture structure serve as stress concentrators. These microcracks, exacerbated by the mechanical stresses incurred during mastication, progressively contribute to denture fractures [8]. Additionally, fractures may also occur due to impact forces when dentures are accidentally dropped on hard surfaces during patient-initiated cleaning procedures [9]. Consequently, researchers have directed their efforts toward modifying the composition of PMMA or incorporating filler materials to formulate novel materials with enhanced properties [1].

Various fillers like glass fibers, polyethylene and polypropylene fibers, and different forms of alumina, titania, and zirconia have been added to denture base materials [10]. Zirconia (ZrO_2) is a metal oxide that has gained attention because of many advantageous properties like biocompatibility, high flexural strength, excellent toughness, high hardness, and corrosion resistance making it a good choice for polymer reinforcement [11,12]. Numerous studies have suggested that addition of zirconia has a significant effect on surface hardness [12-15], flexural strength [12,14], transverse strength [13,15], impact strength [4,13], solubility, and sorption [15] of PMMA.

Nanotubes, distinctive tubular structures characterized by an enhanced surface area-to-volume ratio, offer improved interfacial interaction and mechanical integration within resin matrices [16]. Consequently, nanotubes have been explored as potential fillers in resins, serving as an alternative to nanoparticles. The inclusion of titania nanotubes has demonstrated a significant impact on flexural strength, microhardness, and fracture toughness of denture base resin [16]. Zirconia nanotubes (ZNTs) have received substantial interest for biomedical applications due to their biocompatibility and impressive mechanical and tribological properties. Additionally, they exhibit favorable thermal and chemical stability along with low electrical conductivity [17]. Despite these promising attributes, the utilization of ZNTs in denture base polymers remains an underexplored area of research.

Therefore, this study was designed to incorporate various concentrations of ZNTs into heat-cure acrylic resins and assess their effect on mechanical properties. The null hypothesis considered was that the addition of ZNTs would not have any significant effect on flexural strength, impact strength, and surface hardness of denture base resins.

Materials and Methods

Trevlon (Dentsply India, Gurgaon, India) and DPI (Dental Products of India, Mumbai, India) heat-cure denture base materials and ZNTs (Nano Research Lab, Jamshedpur, Jharkhand, India) were used in this in vitro study.

Preparation of the mold:

Custom-made plastic molds were fabricated with specified dimensions of 65 mm x 10 mm x 2.5 mm, 50 mm x 6 mm x 4 mm, and 20 mm x 2 mm to fabricate specimens for evaluation of flexural strength [12], impact strength, and surface hardness [6], respectively. Wax was rolled, softened, and pressed into the mold space. The wax specimens were flasked using type III dental stone (Goldstone, Asian Chemicals, India) to create a mold space [6].

Preparation of acrylic specimens:

Acrylic resin powder and monomer were mixed in 3:1 ratio by volume as per the manufacturer's instructions. The experimental groups with varying concentrations of ZNTs were designed, and a control group without nanotubes was also considered. The ZNTs were added to the monomer at different concentrations (0.0wt%, 0.5wt%, 1.0wt%, 2.0wt%, and 5.0wt%) and thoroughly wetted by stirring using a glass rod followed by addition of acrylic resin powder. The mixture was homogenized using the glass rod. Once it attained a dough-like consistency, the mass was collected, kneaded, and packed into the mold space. Subsequently, the dental flask was sealed and subjected to a hydraulic bench press with 4 lbs. pressure, followed by bench curing for 30 minutes. The flask was later placed in a thermostatically controlled water bath (Labormat SD-Dreve Dentamid GmbH, Unna, Germany), where the temperature was gradually raised to 74°C within 30 minutes and maintained for 8 hours during the curing process. After curing, the flask was removed from the bath and allowed to cool on the bench for 30 minutes. The flask was then carefully opened, and the specimens were retrieved and examined for defects such as porosities and voids. Defective specimens were discarded and replaced. Excess material was trimmed, and the specimens were sequentially finished with 120-, 220-, and 400-grit Emery papers and polished with a pumice slurry. The same methodology was employed to fabricate specimens for various tests using both the heat-cure acrylic materials [6].

A total of 180 specimens (90 from each heat-cure acrylic resin) were fabricated. The 90 specimens fabricated from each denture base resin material were divided into 3 groups (n=30) for assessment of flexural strength, impact strength, and surface hardness. The specimens from each group were further divided into 5 subgroups (n=6) based on the concentration of ZNTs incorporated (0.0wt%, 0.5wt%, 1.0wt%, 2.0wt%, and 5.0wt% ZNTs). All the specimens were stored in distilled water at 37°C for 7 days before testing [12].

Flexural strength testing:

The specimens were mounted on the anvils of flexural grip of the universal testing machine (AE-UTM-LC2; Advanced equipment, Thane, India) with a span length of 50 mm, and the load was applied at a crosshead speed of 2 mm/minute until the specimen fractured. The fracture load was recorded in Newtons (N). The flexural strength was calculated in megapascals (MPa) using the formula:

$$S=3WL/2bd^2$$

Where S is the flexural strength (MPa), W is the fracture load in Newtons (N), L is the distance between the supports/span length (mm), b is the specimen width (mm), and d is the specimen thickness (mm).

Evaluation of impact strength:

A notch with 1 mm depth was made at the center of the test specimens using a carborundum disc. The specimens for the evaluation of impact strength were mounted in the specimen holder of the IZOD impact tester (Advanced equipment, Thane, India) and the specimen was struck at the notch by the pendulum. The impact strength was measured in kJ/mm2 and computed automatically by the machine itself.

Evaluation of surface hardness:

The test specimens were mounted on a Vickers hardness tester (Daksh Quality Systems Pvt Ltd., India) and the lens was focused to identify the location to make an indentation. The lens was replaced with a diamond indenter with an angulation of 136 degrees, and a maximum of 50 g load was applied at a dwelling time of 30 seconds. Then, the load was retracted, and the indenter was replaced with the lens. The lens was focused on the indentation, and the length of diagonals was measured. Five indentations were made for each specimen in various locations, and the mean values of indentations were averaged as the Vickers hardness number (VHN) value of the respective specimen in kg/mm2 [6,12].

Scanning electron microscope (SEM) assessment:

The fracture modes (brittleness or ductility) of the specimens were analyzed using a scanning electron microscope (ThermoFisher XL-30 ESEM, ThermoFisher Scientific Inc., USA). Brittle fracture in polymers is a mode of material failure that occurs with minimal or no plastic deformation prior to rupture. The resulting fracture surface is typically smooth and flat, indicating a sudden and rapid fracture. In contrast, ductile fracture in polymers involves significant plastic deformation before rupture, resulting in a fracture surface that is rough and fibrous, reflecting the material's ability to absorb energy and deform under stress. The fractured unmodified and modified acrylic specimens were gold sputtered and underwent SEM assessment and imaging with an acceleration voltage of 30 kV at different magnifications (×250, ×1000, ×2000). The SEM images were used for analyses.

Statistical analysis:

The obtained data were subjected to statistical analysis using SPSS version 25.0 (IBM SPSS Statistics for Windows, IBM Corp., Armonk, NY, USA). One-way ANOVA was used for intragroup comparison, and post hoc comparisons were performed by the Tukey's HSD test for inter-group comparisons. $P<0.05$ was considered statistically significant.

Results

The mean and standard deviation of flexural strength, impact strength, and surface hardness of unmodified and modified denture base materials are presented in Table 1 (for Trevlon) and Table 2 (for DPI).

Flexural strength:

In Trevlon, addition of ZNTs from 0.0wt% to 2.0wt% caused a gradual increase in flexural strength. However, addition of 5.0wt% of ZNTs yielded the least flexural strength (Table 1). In DPI, addition of ZNTs from 0.0wt% to 1.0wt% increased the flexural strength. However, ZNT concentrations higher than 1.0wt% caused a gradual decrease in flexural strength of heat-cure denture base materials (Table 2). One-way ANOVA showed significant differences (P=0.000) among different concentrations of ZNTs in both Trevlon and DPI denture base materials (Tables 1 and 2).

In post-hoc analysis (Table 3), the unmodified Trevlon group showed significant differences in flexural strength with 1.0wt% (P=0.007) and 2.0wt% (P=0.000) concentrations of ZNTs. Among the modified groups, Trevlon modified with 0.50wt% ZNTs had significant differences with 1.0wt% (P=0.018) and 2.0wt% (P=0.000) ZNTs. Trevlon modified with 5.0wt% ZNTs also exhibited significant differences with 1.0wt% (P=0.000) and 2.0wt% (P=0.000) modified groups (Table 3). The unmodified DPI showed significant differences with 1.0wt% (P=0.003) and 2.0wt% (P=0.025) modified groups. Among the modified groups, 0.5wt% group displayed significant differences with 2.0wt% group (P=0.044); 1.0wt% group showed significant differences with 5.0wt% group (P=0.007, Table 4).

Impact strength:

Both Trevlon and DPI heat-cure denture base materials displayed a constant increase in

impact strength by increasing the concentration of added ZNTs from 0.0wt% to 1.0wt%. However, a decrease in impact strength was observed in both denture base materials with higher concentrations (2.0 and 5.0wt%) of ZNTs (Tables 1 and 2). One-way ANOVA showed a significant difference in impact strength (P=0.013) among different concentrations of ZNTs in DPI denture base material (Table 2). However, no significant difference (P=0.563) was observed among different concentrations of ZNTs in Trevlon denture base materials (Table 1).

In post-hoc analysis, no significant differences were observed between the unmodified and modified groups and also between the modified groups of Trevlon denture base material (Table 3, P>0.05). The unmodified DPI showed significant differences with 1.0wt% group (P=0.025). Among the modified groups, 1.0wt% group had a significant difference with 5.0wt% group (P=0.021, Table 4).

Surface hardness:

The surface hardness increased by addition of different concentrations of ZNTs to both Trevlon and DPI denture base materials (Tables 1 and 2). One-way ANOVA showed significant differences in surface hardness (P=0.005) among different concentrations of ZNTs in both Trevlon and DPI denture base materials (Tables 1 and 2).

In post-hoc analysis, unmodified Trevlon group showed significant differences in surface hardness with 5.0wt% (P=0.002) group. The unmodified DPI material showed significant differences with 2.0wt% (P=0.021) and 5.0wt% (P=0.009) modified groups. However, no significant differences were observed between the modified groups of Trevlon and DPI denture base materials (Tables 3 and 4).

SEM analysis:

In SEM analysis, the control group specimens (Figure 1) of both denture base materials exhibited smoother surfaces indicating a brittle fracture. However, the denture base materials modified with various concentrations of ZNTs (Figures 2,3) demonstrated irregular surfaces with sharp multiple lamellae indicating a ductile fracture except with 5.0wt% ZNTs. Incorporation of 5.0 wt% ZNTs (Figure 4) displayed the same fracture mode as the control group.

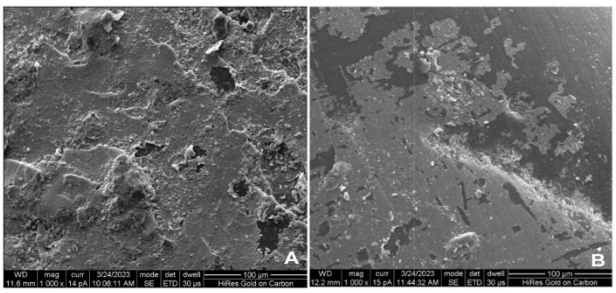

Figure 1. (A) SEM micrograph of DPI with 0wt% ZNTs; (B) SEM micrograph of Trevlon with 0wt% ZNTs

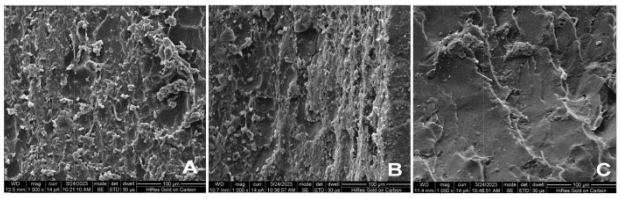

Figure 2. (A) SEM micrograph of DPI with 0.5wt% ZNTs; (B) SEM micrograph of DPI with 1.0wt% ZNTs; (C) SEM micrograph of DPI with 2.0wt% ZNTs

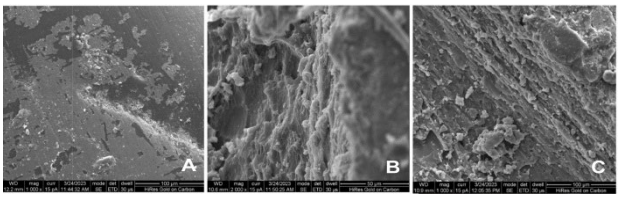

Figure 3. (A) SEM micrograph of Trevlon with 0.5wt% ZNTs; (B) SEM micrograph of Trevlon with 1.0wt% ZNTs; (C) SEM micrograph of Trevlon with 2.0wt% ZNTs

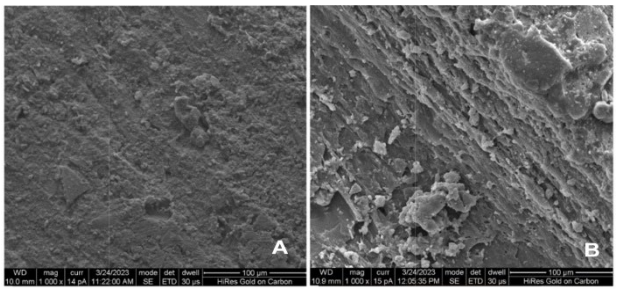

Figure 4. (A) SEM micrograph of DPI with 5.0wt% ZNTs; (B) SEM micrograph of Trevlon with 5.0wt% ZNTs

Table 1. Comparison of flexural strength (MPa), impact strength (kJ/mm$^{2)}$ and microhardness (Kg/mm$^{2)}$ of Trevlon heat-cure denture base material modified with different concentrations of ZNTs

Concentration of ZNTs	Flexural strength		Impact strength		Surface hardness	
	Mean ± SD	P value	Mean ± SD	P value	Mean ± SD	P value
0.0wt%	112.942±9.482		2.688 ± 1.34		25.840±6.974	
0.5wt%	114.542±7.497		3.086 ± 1.054		31.813±6.661	
1.0wt%	128.510±7.818	0.000*	3.506 ± 1.157	0.563	32.995 ± 2.75	0.005*
2.0wt%	138.28 ± 5.59		2.798 ± 0.820		33.785±1.566	
5.0wt%	107.127 ± 4.21		2.564 ± 0.832		38.397 ± 4.82	

*Statistically significant difference according to one-way ANOVA, SD: Standard deviation

Table 2. Comparison of flexural strength (MPa), impact strength (kJ/mm$^{2)}$ and microhardness (Kg/mm$^{2)}$ of DPI heat-cure denture base material modified with different concentrations of ZNTs

Concentration of ZNTs	Flexural strength		Impact strength		Surface hardness	
	Mean ± SD	P value	Mean ± SD	P value	Mean ± SD	P value
0.0wt%	106.277±12.655		1.901 ± 0.496		27.015±7.023	
0.5wt%	107.915±10.3		2.515 ± 0.918		30.420±7.77	
1.0wt%	132.827±12.42	0.000*	3.33 ± 1.1	0.013*	35.418±4.477	0.005*
2.0wt%	127.453±5.66		2.047 ± 0.55		37.492±3.44	
5.0wt%	108.340±13.577		1.875 ± 0.56		38.623±2.87	

*Statistically significant difference according to one-way ANOVA, SD: Standard deviation

Table 3. Inter-group comparison of flexural strength, impact strength, and microhardness for Trevlon

Groups		Flexural strength		Impact strength		Surface hardness	
		Mean Difference±SD	P value	Mean Difference±SD	P value	Mean Difference±SD	P value
0.0wt%	0.5wt%	1.599 ± 4.133	0.995	0.398 ± 0.611	0.965	5.973 ± 2.900	0.269
	1.0wt%	15.568* ± 4.133	0.007*	0.818 ± 0.611	0.671	7.155 ± 2.900	0.131
	2.0wt%	25.337* ± 4.133	0.000*	0.111 ± 0.611	1.000	7.945 ± 2.900	0.076
	5.0wt%	5.816 ± 4.133	0.629	0.123 ± 0.611	1.000	12.557* ± 2.900	0.002*
0.5wt%	1.0wt%	13.97* ± 4.133	0.018*	0.420 ± 0.611	0.957	1.182 ± 2.900	0.994
	2.0wt%	23.740* ± 4.133	0.000*	0.288 ± 0.611	0.989	1.972 ± 2.900	0.959
	5.0wt%	7.415 ± 4.133	0.399	0.522 ± 0.611	0.911	6.583 ± 2.900	0.188
1.0wt%	2.0wt%	9.77 ± 4.133	0.159	0.708 ± 0.611	0.775	0.790 ± 2.900	0.999
	5.0wt%	21.384* ± 4.133	0.000*	0.942 ± 0.611	0.547	5.401 ± 2.900	0.363
2.0wt%	5.0wt%	31.153* ± 4.133	0.000*	0.234 ± 0.611	0.995	4.612 ± 2.900	0.517

***** Statistically significant difference according to the Tukey HSD test; SD: Standard deviation

Table 4. Inter-group comparison of flexural strength, impact strength, and microhardness for DPI

Groups		Flexural strength		Impact strength		Surface hardness	
		Mean Difference±SD	P value	Mean Difference±SD	P value	Mean Difference±SD	P value
0.0wt%	0.5wt%	1.638 ± 6.516	0.999	0.614 ± 0.44	0.634	3.405 ± 3.160	0.816
	1.0wt%	26.550* ± 6.516	0.003*	1.429* ± 0.44	0.025*	8.403 ± 3.160	0.090
	2.0wt%	21.177* ± 6.516	0.025*	0.146 ± 0.44	0.997	10.477* ± 3.160	0.021*
	5.0wt%	2.063 ± 6.516	0.998	0.026 ± 0.44	1.000	11.608* ± 3.160	0.009*
0.5wt%	1.0wt%	24.912* ± 6.516	0.006*	0.815 ± 0.44	0.366	4.998 ± 3.160	0.522
	2.0 wt%	19.538* ± 6.516	0.044*	0.47 ± 0.44	0.822	7.072 ± 3.160	0.199
	5.0wt%	0.425 ± 6.516	1.000	0.64 ± 0.44	0.598	8.203 ± 3.160	0.102
1.0wt%	2.0wt%	5.373 ± 6.516	0.920	1.283 ± 0.44	0.052	2.073 ± 3.160	0.964
	5.0wt%	24.487* ± 6.516	0.007*	1.455* ± 0.44	0.021*	3.205 ± 3.160	0.846
2.0wt%	5.0wt%	19.113 ± 6.516	0.050	.0172 ± 0.44	0.995	1.132 ± 3.160	0.996

***** Statistically significant difference according to the Tukey HSD test; SD: Standard deviation

Discussion

Denture fracture is the most commonly reported clinical failure due to a fatigue mechanism that involves small flexural stresses initiating cracks propagating through the denture, resulting in fracture [5,18]. Numerous researchers investigated the impact of various fillers on the mechanical strength of dentures with varying results [4,19,20]. Nanofillers have received significant attention because of their small size (nano-meter dimension), large surface area, and strong interfacial interaction with organic polymers causing unique properties [21]. However, the main disadvantage of using these nanoparticles is non-homogeneous dispersion within the resin matrix due to agglomeration of nanoparticles [15]. As an alternative, linear nanotubes provide significantly higher surface area for interaction with PMMA denture base resin when compared with nanoparticles [22]. Various nanotubes including titania [16], carbon [23,24], and halloysite [25] were experimentally added to PMMA resin. This study investigated the effect of incorporation of different concentrations of ZNTs on the mechanical properties of heat-cure denture base materials.

The flexural strength of a prosthetic material often counteracts the flexural forces generated during mastication. In this study, incorporation of 2.0wt% ZNTs into Trevlon heat-cure acrylic resin (138.28 ± 5.59 MPa), and addition of 1.0wt% ZNTs into DPI heat-cure acrylic resin (132.827 ± 12.42 MPa) resulted in a higher flexural strength compared with other modified and unmodified groups. The filler shape, type, size, distribution, and concentration, the interaction of nano-fillers within the polymer matrix, and curing time influence the mechanical and physical characteristics of denture base resins [3,4,26].

The tubular open-ended structure of nanotubes allows for the methyl methacrylate monomer to diffuse into the nanotubes via the capillary action and polymerize; thereby, increasing the mechanical interlocking of the matrix and ZNTs exhibiting higher flexural strength [27,28]. Incorporating ZNTs and polymer molecules might create an improved matrix with greater crosslinking, leading to increased load transfer. In addition, zirconia exhibits transformation toughening, a mechanism that absorbs stress at the crack tip, induces phase transformation, and inhibits crack propagation. Crystal transformation causes expansion of zirconia nanocrystals, and the areas of cracks are held in a state of compression, thereby arresting crack propagation [3,29].

Moreover, the flexural characteristics of reinforced resin are mostly affected by the interactions between the incorporated fillers and the resin matrix. The high contact area of the ZNTs with the PMMA resin also enhances load transfer [12]. Furthermore, because of the interfacial friction between the nanotube and matrix resulting from the extremely high surface area of the nanotubes and the strong interfacial shear strength between the ZNTs and PMMA matrix, the nanotube "pull out" effect may significantly increase the fracture resistance. This increase in fracture resistance is particularly noticeable in nanocomposites reinforced with a small amount (2.0wt%) of nanotubes that exhibit homogeneous nanofiller dispersion [27,28]. These reasons might justify the superior flexural strength of nanotube-reinforced acrylic resins.

The quantity of filler is another factor that affects the strength of acrylic resins. The concentration of added fillers should be sufficient to allow uniform distribution of nanostructures throughout the resin matrix without impairing the continuity of the matrix [4,13]. Khaled et al. [27] reported agglomeration of nanotubes with higher filler loading at the fracture plane resulting in void formation. The

current investigation observed a reduction in flexural strength as filler loading increased beyond 1.0wt% in DPI and 2.0wt% in Trevlon denture base resins. This decrease in flexural strength at higher concentrations of ZNTs could be due to the formation of voids at the interface of the nanotubes and polymer matrix. These voids could be responsible for crack propagation through local stress concentrators. Furthermore, increased filler loading may also cause poor adhesion between the resin matrix and nanotubes, resulting in protrusion under stress. The difference in flexural strength among the two heat-cure denture resins can also be attributed to differences in their composition [27].

The type of curing cycle also influences the mechanical strength of acrylic-based dentures. Francis et al., [30] and Athar et al. [31] stated that the mechanical properties of Trevlon and DPI were higher in the long-curing group due to higher degree of conversion and minimal residual monomer. The samples in the present study were also polymerized using a long curing cycle.

The present results were in agreement with those of Yu et al., [32] and Al Badr [33]. They also reported that higher concentration of nanofillers in the resin matrix reduced the flexural characteristics. On the contrary, Ahmed and Ebrahim [34] and Albasarah et al. [28] reported a constant increase in flexural strength of heat-cure acrylic resin by addition of zirconium oxide nanofillers in concentrations from 0.0wt% to 5.0wt%. They reported that the nanoparticles were incorporated in the spaces between the polymer chains. Also, due to the transformation toughening process, absorption of crack propagation energy could have helped in enhancing the fracture resistance.

Another factor commonly causing denture fracture is lack of adequate resistance against impact. This study reported the maximum impact strength following addition of 1.0wt% ZNTs to both denture base materials (Trevlon: 3.506 ± 1.157 kJ/mm2, and DPI: 3.33 ± 1.1 kJ/mm2). The denture base resins with more than 1.0wt% ZNTs demonstrated a reduction in impact strength. In the current study, the increase in impact strength by addition of up to 1.0wt% ZNTs can be attributed to greater surface area of the hollow nanotubes providing high contact area; thereby, the capillary action allows for the monomer and powder to pass through and polymerize, enhancing mechanical interlocking between ZNTs and PMMA matrix. Also, there will be an increase in resistance to fracture due to "pull out" effect of ZNTs [27,28]. The decrease in impact strength by addition of ZNTs in concentrations higher than 1.0wt% of ZNTs was due to agglomeration of ZNTs at the fracture plane causing void formation. These agglomerated nanotubes may also interfere with crosslinking of polymer chains [27]. Furthermore, improper wetting of these agglomerates by the resin material may have resulted in voids acting as stress concentrators [35].

The present results were in agreement with those of Gad et al. [3], and Ali and Safi [36]. They reported that addition of higher concentrations of nanofillers decreased the impact strength due to their agglomeration, resulting in loose cluster formations through which cracks may propagate. Similar to the present study, Kurakalva Soundarya et al. [37] also reported that addition of 1.0wt% zirconia nanoparticles significantly enhanced the impact strength compared to the control group. On the contrary, Begum et al. [38] reported that unmodified groups displayed greater impact strength compared to zirconia nanoparticle-modified PMMA groups. They observed a gradual decrease as the concentration of nanoparticles increased in PMMA. However, all the referred

studies have used nanoparticles as reinforcing materials.

Hardness predicts the wear resistance of dentures. It is sensitive to residual monomer content within the polymer. Measurement of hardness is an indirect method of assessing polymerization depth and degree of conversion of PMMA resin matrix. In the current study, the highest surface hardness was attained with addition of 5.0wt% ZNTs to both denture base materials (Trevlon: 38.397 ± 4.82 Kg/mm2, DPI: 38.623 ± 2.87 Kg/mm2). The surface hardness of Trevlon and DPI improved by increasing the concentration of ZNTs. In the current study, this gradual increase in surface hardness can be attributed to the alignment of ZNTs that may help in maintaining the stability of the reinforced resin matrix [16]. The present results were in agreement with those of Abdulrazzaq Naji et al. [16], and Ahmed and Ebrahim [34]. They reported an increase in the hardness of acrylic resins with an increase in concentration of titania nanotubes. A similar pattern was observed with the addition of ZNTs in the current study. However, the denture base materials modified with ZNTs in the present study exhibited superior mechanical properties compared to titania nanotube incorporation as reported by Abdulrazzaq Naji et al. [16]. Furthermore, nanofillers may form a thick immobilized resin matrix close to the surface that resists indentation forces. Aging of specimens is another factor that influences hardness [7]. Aging increases the degree of polymerization, resulting in improvement of microhardness of acrylic resin modified with various nanofillers [7]. In the present study, the test specimens were soaked in distilled water for a duration of one week before testing.

Based on the SEM analysis, the enhancement of flexural strength and impact strength by increasing the concentration of ZNTs from 0.5wt% to 2.0wt% may be the result of proper nanotube distribution. ZNTs fill the interstitial spaces of the acrylic resin matrix, preventing the propagation of cracks and demonstrating a ductile fracture. In accordance with the present study, Gad et al. [3] reported that addition of nanofillers displayed ductile fracture with enhanced flexural strength.

This study had some limitations. It only investigated the flexural strength, impact strength, and surface hardness. This in vitro study did not simulate the oral environment. The degree of polymerization also influences the properties of polymers and was not considered in this study. Surface treating of fillers is known to influence their bonding to the polymer matrix. The present study used untreated nanotubes. Further research may be focused on assessing the properties of ZNTs incorporated in denture base polymers by simulating the oral environment, measuring the degree of polymerization, and silane treatment.

Conclusion

Within the limitations of this in vitro study, the following conclusions can be drawn:

The maximum flexural strength was observed by incorporating 2.0wt% ZNTs in Trevlon and 1.0wt% in DPI denture base material. However, no significant difference was found between 1.0wt% and 2.0wt% groups. Hence, 1.0wt% or 2.0wt% ZNTs can be used as filler to enhance the flexural strength of denture base resin. The maximum impact strength was obtained after the addition of 1.0wt% ZNTs to both Trevlon and DPI denture base materials. Hence, incorporation of 1.0wt% ZNTs may enhance the impact strength of denture base resin. Both the denture base materials demonstrated a constant increase in surface hardness with the increase in concentration of added ZNTs. Maximum surface hardness was observed by incorporating 5.0wt% ZNTs into PMMA.

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