# The Impact of Adding Carbon Nanotubes to 3D Printed Denture Base Resin on Denture Adaption, Diametral Compression, and Tensile Strength

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**Abstract**

Denture performance and quality depend on 3D-printed denture base polymers' mechanical characteristics, including tensile strength and diametral compression strength, when determining material suitability. This study evaluates the performance of a resin used in denture base 3D printing, focusing on its adaptation properties, diametral compression, and tensile strength with the addition of carbon nanotubes (CNTs).

Ninety specimens were printed: thirty denture bases for denture adaptation test, thirty disk-shaped specimens for diametral compression test and thirty dumbull-shape specimens for tensile strength test. Each test has three groups (n = 10). Every test had unreinforced 3D-printed denture base resin as the control group; the other groups were reinforced with 0.5% and 0.7% by wt. CNTs. Exocad software was used to assess denture adaptation, and a universal testing machine was used to assess diametral compression and tensile strength.

There was a substantial change in the denture adaption, diametral compression, and tensile strength of the 3D-printed denture base resin when CNTs were added. The mean values of tensile strength and diametral compression increased with 0.5% and 0.7% of CNTs, respectively, as denture adaptation increased.

CNTs can enhance the mechanical and adaptability qualities of the base resin used in 3D-printed dentures.

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## Introduction

The material of choice for removable dental prosthesis is typically polymethylmethacrylate (PMMA), which offers a number of benefits such as low cost, reasonable strength, ease of manufacture and repair, aesthetics, and intraoral stability. Nevertheless, the material's low mechanical and physical qualities as well as the fabrication time are its limitations [1,2]. Computer-aided design and computer-aided manufacturing (CAD-CAM) technology produce digitally manufactured dentures in less time than conventional dentures, using 3D-printable or milled denture base materials [3,4]. However, studies comparing the denture retention or mucosal surface molding precision generated with additive manufacturing to conventional processes have been published, still many questions remain to be answered [5].

CAD/CAM milled dentures outperformed conventionally produced dentures in terms of elastic modulus and flexural strength, according to in vitro studies. Additionally, they were tougher,

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had less tooth movement, and fit more accurately [6]. The location and degree of deformation that happened during the production of full dentures was found using a variety of techniques. Among these is the digital milling method, which is considered a helpful instrument for evaluating the dimensional alteration caused by denture manufacturing. When CADCAM dentures were tested for fit on clinical bases, the printed denture base, created using the digital light processing technique (DLP), proved to be more fitted within 100 µm than the subtracted denture base manufacturing approach [7]. Jin et al., 2019 compared various construction angles on DLP-3D printed complete dentures across groups and found no statistically significant changes in the surface adaption [8].

Nevertheless, the adaptability of full dentures using traditional, milled CDBs and 3D-printed CDBs processes has not been extensively studied in published research. However, the results of this study indicate that the latter approach seems to be an optimistic one that requires further attention and development [9]. The denture base materials that are milled and traditional have higher surface hardness and flexural strength than those that are 3D printed [3]. Despite the fact that the flexural strength is nearly identical to the 65 MPa ISO approved standard, these drawbacks prevent 3D printing from being used for denture base construction and restrict its clinical applications [10,11,12]. Therefore, in order to get over the aforementioned restrictions and take advantage of 3D printing technology, earlier research looked into a variety of variables influencing the characteristics of 3D printed resin, including printing orientation, post polymerization time, and printing layer thickness [13,14].

By adding various fillers, 3D printing can be used in a variety of specialized industries to give them distinctive qualities [15]. Among these, carbon nanotubes (CNTs) have a much greater length-to-width ratio than conventional carbon black particles, which produces a more noticeable reinforcing effect when introduced to polymers [16]. Many researchers have devoted their time to creating sophisticated carbon nanotube-reinforced composites (CNT-RCs) and researching how the presence of CNTs affects the functionality of these composites since the discovery of CNTs [17]. Because of their remarkable mechanical, thermal, and electrical capabilities, CNT-RCs have been the subject of much research over the last few decades. As a result, they have emerged as a new class of advanced materials that can replace numerous existing ones in a variety of engineering areas [18]. The impact and flexural strengths of PMMA were found to be greatly enhanced by the addition of 1% carbon nanotubes (CNTs), but its hardness was reduced [19]. Additionally, it was discovered that 1.5% of single-walled carbon nanotubes greatly improved PMMA's transverse strength and impact resistance while drastically lowering its surface hardness [20]. On the other hand, a study found that the flexural strength of PMMA was not significantly affected by the addition of single-walled carbon nanotubes [21]. The flexural strength and resilience of PMMA were enhanced by the addition of 0.5% and 1% of multi-wall carbon nanotubes (MWCNTs), but its fatigue resistance was reduced at higher concentrations of MWCNTs [22].

Additional research looked into altering 3D-printed materials by adding various nanofillers [23,24]. ZrO2 NPs added to 3D printed denture base resin improve denture adaption and reduce diametral compression. Furthermore, ZrO2 NPs shown a considerable rise in antifungal activity, and when 1% ZrO2 was added, the tensile strength also increased significantly [10]. The association between the tensile and diametral compression strengths following the addition of ZrO2 NPs was assessed by another researchers. They discovered that there is a negative correlation and that enhancing one characteristic does not always entail improving another [10,25,26].

As far as the authors are aware, no prior research has been done on the impact of CNTs on the tensile strength, diametral compression, and denture adaptation of 3D-printed resin. In light of this, the current study assessed the impact of adding CNTs to 3D-printed resin. The study's null hypothesis stated that these three properties of the 3D-printed resin dentures would not be significantly affected by the addition of 0.5–0.7% by weight of CNTs.

## Materials and methods

The ethics committee of the University of Baghdad's College of Dentistry approved this research, which was conducted in the department of prosthodontics. The materials utilized were 3D-principled denture base resin (Optiprint Laviva, Dentona business, Germany) and CNTs (Multiwalled carbon nanotubes with purity of >99%, VT 05141, Cambridgeport, USA). The fact that the carbon nanotubes (CNTs) had an average diameter of 37.4 nm was demonstrated using a particle size analyzer.

For this study, a total of ninety specimens were used. Thirty denture bases were printed for the denture adaption teat following maxillary edentulous definitive casts that were chosen for their anatomical similarity to the type A classification of residual ridge morphology according to the American College of Prosthodontists (ACP) [27]. Thirty disc-shaped specimens were used for the diametral compressive test. The diameter of the specimens was 16 mm, which is twice the thickness of the disc for the diametrical compressive test. The thickness of the specimens was 8 mm, as stated by the manufacturer because this is the highest curing depth for 3D-printed samples. Thirty dumbbell-shaped specimens, the dimensions of which were specified by ASTM specification D-638M (1986) [28], were utilized for the tensile strength test. The specimens were split into three groups of ten for each test, with a weight-based concentration of CNTs of 0%, 0.5%, and 0.7%.

The DLP open system dental printer (Microlay Versus 385, EU) was utilized. The light pink 3D-printed denture foundation material was put into multiple dark bottles with deterioration. Before adding the CNTs, the pure resin was thoroughly mixed for 1.5 hours at room temperature using a mechanical mixer. Following weighing with a three-digit electrical scale (DM3, England), the CNTs were added in the specified concentrations. The mixture was then thoroughly mixed with a magnetic stirrer (Stuart Scientific, UK) at 60 °C for 30 minutes to reduce the material's viscosity (a higher viscosity will affect the quality of the print), and stirring was then continued at room temperature for eight hours to create a well-mixed homogenous mixture that was ready for the printing process [29]. Sending the sample's STL file, or software design, to the printer initiated the printing process.

The material's software was configured as per the manufacturer's instructions, which specified for a 50 μm layer thickness in (1.61) s/slice along the vertical Z-axis. After printing, the specimens were cleaned of any remaining uncured resin using 99.9% isopropyl alcohol. To finish the polymerization, glycerol painting and 20 minutes in an ultraviolet (UV) light polymerization apparatus were used. Using a low-speed rotary handpiece and a polishing machine and cloth in a wet state, the supports and base were removed [30]. Prior to the testing process, the specimens were submerged in distilled water at 37 °C for 48 hours [31].

**Characterization of the 3D-printed samples:**

**Field emission Scanning electron microscopy (FE-SEM):** To evaluate the dispersion of CNTs inside the 3D printed resin, a FE-SEM (FEI, INSPECT F 50, Netherlands) machine was utilized. Analysis was done on two randomly selected experimental samples with either 0.5wt% or 0.7wt% CNTs, along with one randomly selected control sample. At 400–4000 $cm^{-1}$ the resolution was set.

**Fourier transforms infrared spectroscopy (FTIR):** The usage of FTIR (spectrometer–Spectrum Two, Perkin Elmer, USA) was employed to ascertain whether a chemical reaction occurred between the CNTs and the 3D printed resin material. Three samples were tested, one at random from each of the categories (Control, 0.5 wt%, and 0.7 wt%).

**Testing procedure:**

**Denture adaptation test:** A three-dimensional image of every stone cast was taken with a (vinyl 3D scanner: smart optics). In compliance with ISO 12836, the die was scanned with a precision of 6 meters using a completely automated Z-axis scan, in which the scanner automatically directs the object into the measurement field. Using the Exocad program, which simulates a full denture, a virtual denture foundation was designed. It was then saved as an STL file and manufactured using a 3D printer for printing. Following the completion of printing 30 denture bases with the precise concentration of CNTs, the intaglio surfaces of each manufactured denture base were scanned using the same vinyl 3D scanner from Smart Optics. This process resulted in the creation of an STL file for each denture's intaglio surface. Using the same software (Exocad in-lab DentalCAD), the STL file of each denture was superimposed on the STL file of the matching reprocessed cast with four layers (cast, denture base after processing, cast/denture base combined, and the overlay guide).

The cast/denture foundation layer served as a guide to help the denture find its proper location. To standardize the measurement, this software was used to take measurements for each of the 30 dentures at 50 points. With 50 points painted on it in precise placements to cover the complete anatomical landmark, the overlay guide layer acted as a representation of one of the best-fitting denture bases [10]. Anatomical landmarks throughout the entire cast were distributed at 50 points. The crest of the ridge (12 points), midline (10 points), posterior palatal seal (PPS) (9 points), denture border (11 points), and palate (8 points) were the five main zones into which the cast was divided. As illustrated in Figure 1, fit discrepancies were assessed at 50 points, including the palate, posterior palatal seal area, median palatine suture, denture border, and crest of the ridge, for each denture base based on surface matching and measurements.

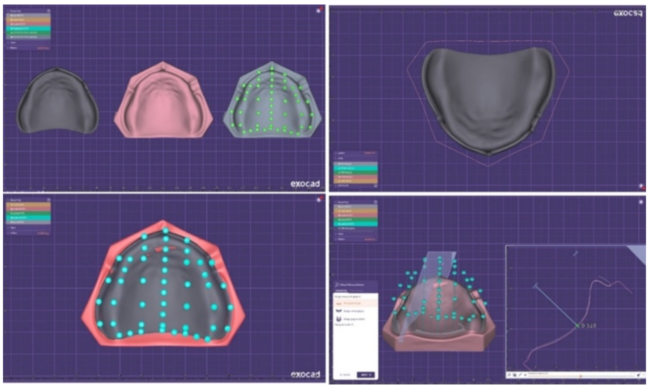


**Figure 1.** design of a virtual denture foundation.

**Diametral compression test:** The computer controlled electronic universal compression testing machine (LARYEE, WDW-20, China) was used to test each specimen. This approach involves compressing a disk made of 3D-printed acrylic denture base resin diametrically in a testing machine until it fractures (splints). Due to the compressive stress placed on the test subject, the Poisson effect causes the material to undergo tensile stress in the direction of the force supplied by the test equipment. By using the following formula, the indirect tensile stress (σx) is directly proportional to the load (P) applied in compression:

$$\sigma x = \frac{2P}{\pi DB}$$

Where P is the load, D is the diameter, and B is the thickness of the specimen, the disk specimen's center point is where the maximum vertical tensile tension is found [32,33].

**Tensile strength test:** The tensile strength of every specimen was assessed using a universal testing apparatus (LARYEE, WDW-20, China). Usually, the ends of the material specimen are clamped on two jigs that are separated from one another by a predetermined amount. This causes the specimen to stretch as the two jigs separate until the specimen sustains damage [33]. The formula used to determine tensile strength was:

$$\text{T.S. } MPa = \frac{\text{Maximum force } (N.)}{Area\ (mm^2)}$$

**Statistical Analysis:** GraphPad Prism (version 9.0) was used to examine the data. The Shapiro-Wilk test and the Brown-Forsythe test were employed to ascertain the data's normal distribution and homogeneity of variance, respectively, and the analysis of variance (one-way ANOVA) table was utilized. To identify the significant differences across groups, the Bonnferroni multiple-comparison test was used. Probability (P) value greater than 0.05 (P>0.05) was regarded as statistically not significant (NS), whereas P≤0.05 indicated statistically significant (S).

## Results

### FTIR outcomes:

As can be seen in Figure 2, there was no chemical interaction and the inclusion of CNTs had no effect on the resin's spectrum range after 3D printing. The FTIR was simply used to verify whether or not there was a chemical reaction; one test sample evaluation was adequate to compare the outcomes with the control group. The absorption peaks in the FTIR spectrum are indicative of the functional groups' vibrational modes within the sample. It is possible to identify the distinctive peaks of the common functional groups—OH, C=O, NH, CH, etc.—in order to verify the existence of certain chemical bonds. The 0.5 wt.% and 0.7 wt.% of CNTs with 3D printed acrylic resin in Figure 2 demonstrate the presence of a peak at approximately 3410 $cm^{-1}$, which is caused by the N-H bending vibration in $NH_3$. The formation of the network structure resulted in a steric effect, which is why the O-H bonds were responsible for the weak peak at 2927 $cm^{-1}$. A sharp peak caused by C=O vibrations was visible at 1100 $cm^{-1}$. Stretching vibrations of C=O give rise to a high peak at about 1728 $cm^{-1}$. Peaks in the aromatic ring at 1635–1532 $cm^{-1}$ are caused by C=C stretching vibrations. There are weak peaks at N-H, C-O-H, C-Cl, C-Br, and C-I at 1457 $cm^{-1}$, 797 $cm^{-1}$, 619 $cm^{-1}$, and 486 $cm^{-1}$, respectively.

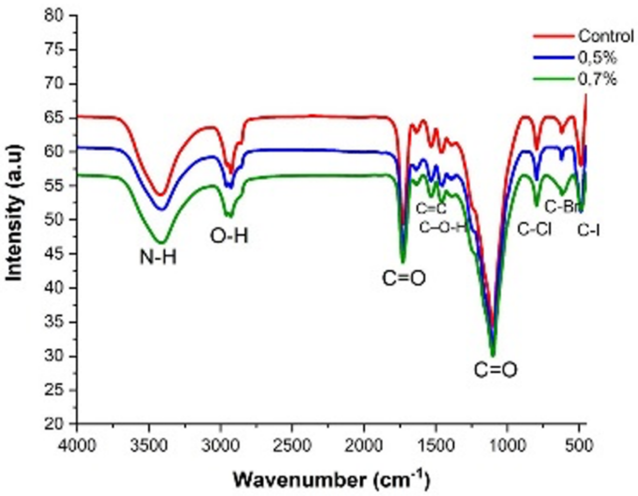


**Figure 2.** 0%, 0.5%, and 0.7% by weight of CNTs added in denture resin 3D printed materials. spectrum of FTIR. The wavenumber $cm^{-1}$ and transmittance percentage are represented by the X and Y axes, respectively. The wavenumber of its peak is matched by the bonds displayed in the figure.

**FESEM Outcomes:**

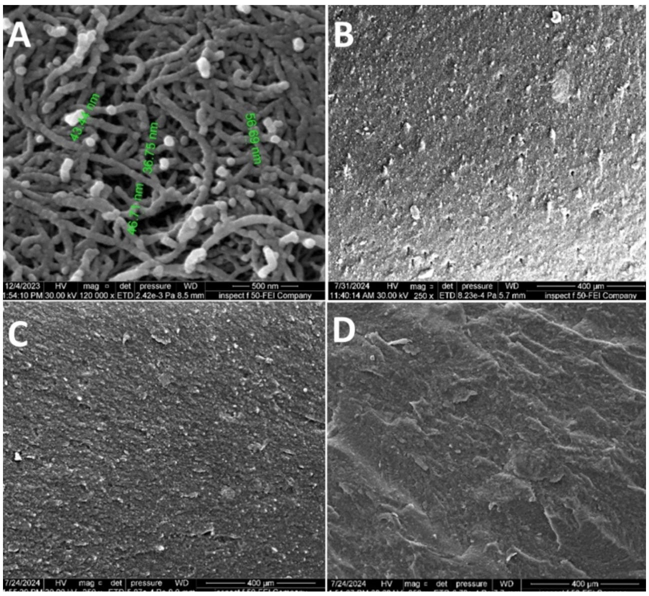


**Figure 3.** The FE-SEM micrograph shows (A) CNTs powder at a magnification of 120 000x (500 nm); (B) a control tensile test specimen at the interior structure's fracture site; (C) 3D-printed resin/0.5% by wt. CNTs in the interior structure after fracture of tensile specimen; (D) sample reinforced with 0.7% CNTs after fracture (magnification at 250x, 400 µm).

FE-SEM scans clearly demonstrated that the diameter of the nanotubes was within the nanometer range, as shown in Figure 3(A). Figure 3 (B) shown resin as it was initially, prior to any modifications being performed, the section of the scan at the internal structure in fracture site. (tensile test specimen). Furthermore, FESEM demonstrated that the morphology of the CNTs/3D-printed resin specimen was well integrated into the final printed structure, as shown in Figure 3(C and D). The distribution of the CNTs in the matrix appears to be reasonably even. The presence of some pits, which are more noticeable in the internal structure of printed pieces, suggests that porosity exists. The internal morphology of a fractured specimen is shown in Figure 3 C&D. The bulk has properly incorporated the CNTs that were discovered.

**Denture adaptation outcomes:**

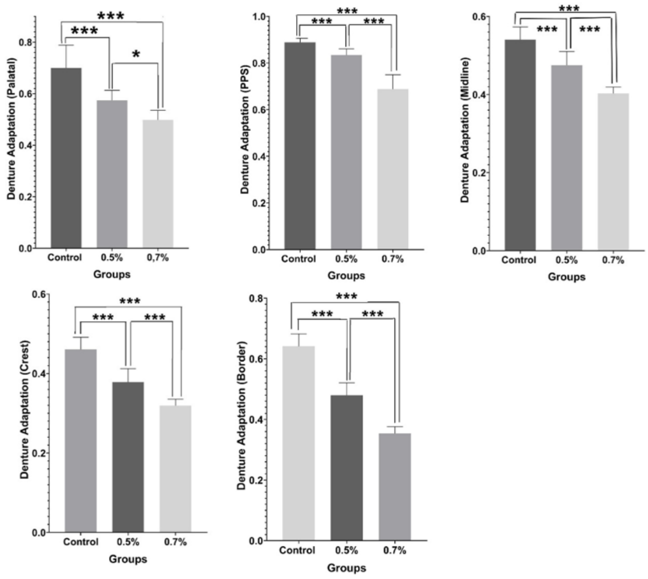


**Figure 4.** Bar charts showing the control group and the 0.5% and 0.7% by weight CNTs experimental group for the denture adaptation test over all specified locations. *** high significant P value = 0.0001, * significant P value = 0.0260.

The mean values for all the selected areas decreased with 0.7% by weight of CNTs, which was the lowest mean value [Palatal area (0.4978±0.03683), PPS area (0.6881±0.06204), Midline area (0.4029±0.01629), Crest of the ridge area (0.3191±0.01634), Border area

(0.3537±0.02240)], followed by 0.5% by weight of CNTs. The control group had the highest mean [Palatal area (0.6995±0.08868), PPS area (0.8887±0.01777), Midline area (0.5402±0.03310), Crest area (0.4606±0.03098), Border area (0.6412±0.04118)]. One-way ANOVA was used to compare the means of the experimental groups' results, and the results were significant. Figure 4 shows that the most significant and effective proportion for enhancing denture adaptability in all regions of interest is 0.7% by weight of CNTs, as determined by Bonferroni's multiple comparison test.

**Diametral compression outcomes**:

The mean and standard deviation were computed for the diametral compression test (Figure 3). In comparison to the control group, the mean values of the experimental groups increased when the CNTs were added, according to the data. The group with 0.7% weighted CNTs had the greatest mean (32.38±1.282), while the control group had the lowest mean (23.05 ±0.8644). Using the ANOVA table to compare the means of all the tested groups produced significant results (P value < 0.0001). The multiple comparison showed significant differences between the control and 0.5% by wt. CNTs, also significant differences between the control and 0.7% by wt. CNTs, as shown in Figure 5.

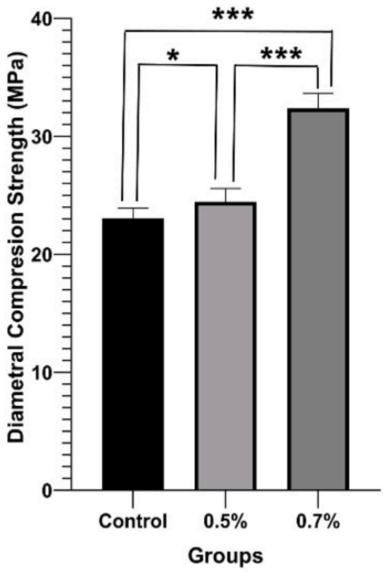


**Figure 5.** Bar chart displaying the mean and SD for diametral compression test. ***high significant P value = <0.0001, *significant P value = 0.0273.

**Tensile test outcomes**:

The mean and standard deviation were calculated. The finding indicates that, in comparison to the control group, the experimental groups' mean values increased when the CNTs were added, according to the data. The group with 0.7% by weight concentration of CNTs had the highest mean (38.26±0.9572), while the control group had the lowest mean (18.02±0.7969). One-way ANOVA was used to compare the experimental groups' means for the tensile test results, and the outcome was highly significant (P value <0.0001). As illustrated in Figure 6, Bonferroni's multiple comparison test was used to compare the mean values across all study groups. The results indicated significant differences between the control and 0.5% by weight CNTs, as well as between the control and 0.7% by weight CNTs, and no significance between 0.5% and 0.7% by weight CNTs.

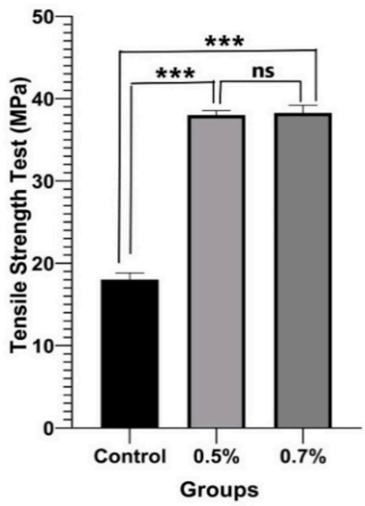


**Figure 6.** Bar chart displaying the mean and SD for tensile strength test. *** high significant P value = < 0.0001, ns not significant P value = >0.9999.

**Discussion**

To achieve satisfactory retention and stability for complete dentures, denture bases must be accurately tailored. Complete dentures can be manufactured using a variety of techniques. Reaching a balance between biocompatibility, adaptability, and minimal deformation is the noble goal of any technique [34].

Reduced laboratory processes and simplicity characterize CAD-CAM complete denture fabrication. Moreover, it provides standardized production and increased dimensional accuracy [35]. Due to the wide range of machines that are accessible, the minimal waste of raw materials, and the ability to print complicated shapes, digital technology has the advantage of versatility. Additionally, the digitized data enable the future fabrication of dentures, should that be required [36].

The printing method's key shortcomings are the staircase effect, low repeatability, and need for supporting structures. More time and resources are needed for these supporting structures [37,38]. The accuracy of printed products is affected by every stage, including designing in CAD software, printing, and cutting in printing software; light intensity, direction, and printing angle; the number of layers; the software; shrinkage between layers; the quantity of supporting structure; and the post-processing procedure [39].

To achieve proper adaptation to the mucosa, denture base deformation during manufacturing must be kept to a minimum. In addition to the processing technique, the material and thickness of the base affect the degree of this distortion [40]. The supporting system of the denture base was designed using the software in relation to the 3D-printed dentures. The denture base's orientation was modified to ensure that the supporting arms made touch with the polished surface, preserving the tissue surface's accuracy and adaptability. Researchers are looking at using carbon nanotubes as augmentation fillers, particularly for polymer [41]. The intrinsic features of nanotubes reinforced in polymers were exploited by improving the interface interaction between the nanotube surface and polymer. In order to prevent dimensional changes, excellent stress transfer from the polymer to the nanotube is the outcome of this proper adhesion. By adding carbon nanotubes to polymethylmethacrylate (PMMA) resins, prostheses become stronger and can endure greater forces during mastication. It can also be utilized in fixed partial dentures and other prosthesis because of the exceptional strength of this enhanced material. As much as 200 times stronger than carbon fibers, carbon nanotubes have tensile strengths up to 4000 times greater than those of steel. Comparatively mild van der Waals forces allow carbon nanotubes to bind to matrices like PMMA polymer. There is a significant increase in the mechanical fatigue strength and compression strength due to the high adhesion strength of carbon nanotubes in the PMMA matrix [42]. Thus, it was selected for this investigation.

According to this investigation, CNTs greatly enhanced the denture base's adaptability, and the denture's increased fit against the upper mold was directly correlated with the concentration of CNTs. Given that the nanofillers' size helps to internally fill the matrix and replace the resin, resulting in reduced shrinkage, the improvement in the denture base's overall adaptability may be attributed to their effective dispersion [43]. This is consistent with a study that investigated how adding glass fibers to a denture base polymer enhanced its accuracy and discovered that the dimensional alterations decreased with increasing fiber concentration [44]. Another study that compared the polymerization shrinkage of denture base acrylic resin with and without micro-additions of carbon nanotubes (CNTs) agreed with the findings. The results unambiguously demonstrate that polymerization shrinkage does not occur when 0.5% of carbon nanotubes are incorporated into PMMA resin, and that shrinkage is reduced when 0.25% and 0.125% carbon nanotubes are used in comparison to 0% carbon nanotube in PMMA resin. These results are in line with earlier research by Firtell et al., and Yeung and Chow which revealed that total polymerization shrinkage in PMMA resins was greatest in the absence of nanotubes compared to their presence [45].

The flexural strength of a material is shown by the combination of its compressive, tensile, and shear strengths. When the tensile and compressive strengths of the material rise, so does the force needed to fracture it. In terms of the diametral compression and tensile strength, the addition of CNTs at two different concentrations (0.5% and 0.7% by weight) significantly increased these parameters when compared to the control group in the 3D-printed denture base resin. These results are consistent with other research that demonstrated the addition of CNTs significantly improved the mechanical properties [46]. Previous research has demonstrated that strengthening effects on composites can be enhanced by utilizing fillers with a small average particle size and a limited size range [47].

And this connected with earlier research on the effect of titanium oxide addition on denture base tensile strength by Mutiara et al [48]. Additionally, it has been observed that a comparatively small weight proportion of nanoparticles can lead to a notable improvement in mechanical properties [49].

The agglomeration of the nanoparticles incorporated within the 3D resin, which act as stress concentration spots in the matrix and this lead to decreasing the mechanical properties, could explain why an increase in CNT concentration might result in a decrease in tensile strength. This finding is consistent with the findings of Chladek et al. (2013), who found that the mechanical properties of nanocomposites reinforced by silver NPs decreased as NPs concentration increased [50,51,52]. Similarly, Chatterjee (2010) demonstrated that the tensile strength decreased with an increase in titanium oxide nanoparticles [52]. Additionally, agglomerated fillers which create loosely bounded clusters and change the crack propagation mechanism also reduce the tensile strength[51,52].

Nevertheless, the pure form of the particles may act as impurities within the polymer matrix, potentially causing printed parts to fail, due to the incredibly weak bond between the polymer chains and the added particles. It may be feasible to minimize negative effects and greatly improve mechanical performance by employing NPs with oriented geometries and robust bonding abilities [53]. Because of the way that 3D printing works, fillers usually align along the deposition lines; this might enhance the components' mechanical, thermal, or electrical conductivity properties [53,54]. Each of these elements could have an impact on the behavior of the material under various stress patterns, with differing outcomes, either directly or indirectly. The 3D-printed denture base resin's tensile and diametral compressive strengths are impacted by the addition of CNTs. This event highlights the critical requirement for precise control in dental material formulations by highlighting the sensitivity of mechanical qualities to NP concentration [55]. The present study offers crucial novel knowledge about how to modify the mechanical characteristics of denture base resin that is 3D printed by adding CNTs. The noted increases in tensile strength and diametral compression showed promise for improved performance in dental applications. Since the lingual aspect of the mandibular denture and the midpalatine region of the maxillary denture are more likely to fracture, CNT-incorporated resin has been used in these areas therefore, the denture's strength can be increased without sacrificing the patient's aesthetics [56]. The current in vitro study was limited by the use of a single kind of resin and no color changes assessment was performed when the proportion of MWCNTs increased.

## Conclusions

The study's conclusions, which have significance for both future research and clinical application, add to the continuing investigation of innovative materials for 3D-printed dental prosthesis. Within the limitations of this investigation, it was found that adding CNTs to 3D-printed denture base resin significantly enhances the material's behavior as denture adaptation, and that the amount of CNTs added directly correlates with the improvement in denture adaptation. The addition of CNTs resulted in a considerable increase in both tensile strength and diametral compression, with the increase being directly proportional to the CNT concentration. To avoid negatively affecting other qualities, care must be taken when choosing the right concentration of CNTs.

## Declaration of Interest

The authors report no conflict of interest.

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