

# Effect of Multi-Wall Carbon Nanotubes on the Microhardness of the Tooth Enamel

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## Abstract

**Background:** The object of this study was to investigate the effect of addition of Multi-Wall Carbon Nano Tubes (MWCNTs) in different concentration (0.001g/20ml, 0.005g/20ml, 0.01g/20ml and 0.02g/20ml) in (dimethyl sulphoxide) to tooth enamel. It is intended to evaluate enamel hardness in (Kg .m<sup>-2</sup>) before and after the addition of (MWCNTs).

**Materials and Method:** Thirty specimens were prepared for this study, to measure the hardness of the enamel.

**Results:** The results enamel hardness after MWCNTs application With DMSO showed a significant increase (P<0.01) between groups of 0.001g/20ml, 0.005 g/20ml, 0.01 g/20ml and, 0.02 g/20ml concentration compared with control group. Where the highest mean value obtained was in 0.02g/20ml concentration which had a mean value of  $527.18 \pm 2.904 \text{ Kg .m}^{-2}$ , while the lowest mean value was for control group which had a mean value of  $334.87 \pm 2.904 \text{ Kg .m}^{-2}$ . Polished enamel surface groups showed a significant increase  $452.59 \pm 1.84 \text{ Kg .m}^{-2}$  (P<0.01) in hardness when compared with unpolished enamel surface groups  $430.16 \pm 1.84 \text{ Kg .m}^{-2}$  (P<0.01).

**Conclusion:** The highest mean value obtained was in 0.02g/20ml concentration in the hardness suspended in DMSO. The results showed a significant increase in the hardness for polished enamel surface samples compared with unpolished enamel surface samples in DMSO.

**Key words:** Multi-Wall Carbon NanoTubes (MWCNTs), enamel hardness

## Introduction

Enamel, the outer hard tissue layer of tooth crowns, is a composite material that comparable to other biological tissues like bone or dentin exhibits a unique and complex hierarchical structure (1). The bulk of human teeth consists of two main mineralized tissues, collagen-rich dentine and highly mineralised enamel. They join forming a complex and mechanically durable dentine–enamel junction (DEJ) that contributes to the lifelong success of the tooth structure under thermo-mechanical loadings encountered in the oral cavity under the conditions such as mastication, chemically active environment and thermal shock (2, 3).

Enamel is the hardest tissue in the human body and is considered a nanostructured biocomposite in which its

mineral phase predominates (95-96 wt. %) (4).

In this mineral portion, large hexagonal carbonated hydroxyapatite crystals are tightly packed creating prisms with a keyhole-like structure of about 5  $\mu\text{m}$  in diameter (5). Prisms are aligned and run approximately perpendicular from the dentin-enamel junction to the tooth surface (3). Each prism is separated from each other by a nanometer-thin layer of a protein-based organic matrix (6). The term “Nano” is derived from the Greek word “dwarf”. More simply speaking, one nanometer is one-billionth or  $10^{-9}$  of a meter (7-9). Nanotechnology can be classified in terms of application in three broad and extensively overlapping categories (10):

- Nanoelectronics
- Nanomaterials/particles
- Nano-biotechnology

Carbon nanotubes (CNT) are a new crystalline form of carbon. Wound in a hexagonal network of carbon atoms constituting a graphene nanofoil, these hollow cylinders can have diameters as small as 0.7 nm with lengths that can range from a few micrometres, and reach several millimeters in length (11). Each end can be opened or closed by a fullerene half molecule. These nanotubes can have a single layer (SWCNT for single walled carbon nanotube) or several layers (MWCNTs for multi walled carbon nanotube) of coaxial cylinders of increasing diameters in a common axis. Multilayer carbon nanotubes can reach diameters of 100 nm (12).

Enamel surface microhardness refers to a tooth's resistance to scratching, abrasion, and indentation. A substantial number of mineral ions can be removed from hydroxyapatite latticework without destroying its structural integrity; however, such demineralized enamel transmits hot, cold, pressure and pain much more readily than normal enamel. Microhardness tests are commonly used to study the physical properties of materials, and they are widely used to measure the hardness of teeth (13, 14). Knoop (KHN) and Vicker (VHN) hardnesses have reported approximately the same value (15). The average hardness value for enamel and dentin is in the range from 270 to 350 Knoop microhardness or from 250 to 360 Vickers microhardness and from 50 to 70 Knoop microhardness respectively (16).

## Materials and Method

*Functionalisation of Commercial Carbon Nano Tubes* (17). One gram MWCNTs was transferred into a mixture of nitric acid (10 cm<sup>3</sup>) and sulphuric acid (30cm<sup>3</sup>). This mixture was then heated at 50 °C for 24 hrs after which the MWCNTs were filtered off using Nylon filter paper (pore size 0.45 micrometer). This was followed by subsequent washing with distilled water until the pH was almost neutral. The MWCNTs were then dried under vacuum at room temperature. Then dried in furnace oven for 2hr. In the third step 0.02 g from MWCNTs were put in 20 ml DMSO. The MWCNTs is mixed with DMSO. The whole solution is transferred into sonicator. Twenty four sample in DMSO in different concentration for micro hardness test. The samples should be kept in a water. These samples were

shaken in the vibrator for limited period extend 10min for 3 time in 6 continuous days.

## Grouping of Samples

The group contains 30 samples to measure the hardness of the enamel. Samples were collected from healthy teeth of patients attending a dental teaching hospital at the University of Baghdad collage of Dentistry, also Thi-Qar specialized dental center in department of Orthodontics of the ages ranging between 15 - 24 years. The first selection criterion for the sample was tooth quality. Only teeth with no visible defects were selected, not taking into account any damage at the micro structural level. They were without any caries, no attrition or erosion. The patients were non-smokers and do not consume alcoholic beverages. The second selection criterion was that the teeth belonged to mandibular first premolar.

## The Hardness of a material

The hardness of a material its resistance to penetration under a localized pressure or resistance to abrasion. The baseline of the hardness of base lines was measured through the use of Micro -Vickers Hardness Testing Machine (CV-400 DM, Europe) (Figure1), with a load of 500 g and 1000 g, in 5 seconds.

## Principle of Hardness Determination

The micro hardness test involves a microscopic and static method, of which the results are mostly expressed in terms of Vickers and Knoop hardness numbers. The micro hardness tester is provided with an optical magnifying system. The hardness is determined by penetrating a diamond pyramid indenter under a known test force into the surface of test piece and then measuring the diagonal of the indentation left on the surface after removal of the test force.

The hardness number is calculated upon the below equations.

$$HV = 1854 \frac{4F}{d}$$

Vickers Test

HV: Vickers hardness number, in kg f. mm<sup>-2</sup>, F : Test force, in kg f, d :Diagonal length of the indentation, in mm<sup>2</sup>.

## Sample Preparation to Measure The Hardness

The total number of samples were 30 samples to measure the hardness of the enamel, and divided the group to subgroups upon the following design.

**Control group :** (3 unpolished enamel surface and 3 polished enamel surface *samples*).

**Group (0.001g/20ml) :** (3 unpolished enamel surface and 3 polished enamel surface samples)

**Group (0.005g/20ml) :** (3 unpolished enamel surface and 3 polished enamel surface samples)

**Group (0.01g/20ml) :** (3 unpolished enamel surface 3 polished enamel surface samples)

*Group (0.02g/20ml) : (3 unpolished enamel surface and 3 polished enamel surface samples) Groups (0.001g/20ml, 0.005g/20ml, 0.01g/20ml, 0.02g/20ml) treated with MWCNTs, the special area on the middle third of the labial enamel surface were chosen 5mm away about the cusp tip and whit a line representing axis ( X) for all teeth. All have samples examined for the micro hardness. .*

### Statistical Analysis

Statistical analysis was done using the software SPSS version 17.0; the results were expressed as mean  $\pm$  standard deviations (mean  $\pm$  SE). One way ANOVA was used to compare parameters in different studied groups. P-values ( $P < 0.01$ ) were considered statistically significant.

### Results

Statistical Analysis of the results was used to evaluate , enamel hardness in (Kg .m-2) after MWCNTs application with DMSO in different concentration treatment.

#### Enamel Hardness Test

Control group comport with groups dealing with MWCNTs application with DMSO in different concentration treatment and different surfaces treatment.

MWCNTs application with DMSO in different concentration treatment and different surfaces treatment

Table (1) showed that the highest mean value found in 0.02g/20ml concentration which has a mean value of  $527.18 \pm 2.904$  Kg .m-2 , while the lowest mean value was for the control group which has a mean value of

$334.87 \pm 2.904$  Kg .m-2 . The results of LSD test showed a statistically significant differences between groups in different concentration treatment as in the figure (2). And also table (1) showed that the highest mean value represent in polished enamel surfaces which has a mean value of  $452.59 \pm 1.84$  Kg .m-2 , while the lowest mean value was for in unpolished enamel surfaces which has a mean value of  $430.16 \pm 1.84$  Kg .m-2 . The results of LSD test showed a statistically significant differences between groups in different surfaces treatment as in the figure (3).

Table (1) showed that the highest mean value present a concentration of 0.02g/20ml in polished surfaces which has a mean value of  $547.07$  Kg .m-2 , while the lowest mean value was for the control group in unpolished surfaces which has a mean value of  $330.30$  Kg .m-2 and the results of LSD test showed a statistically significant differences between groups in different concentration treatment and different surfaces treatment.

## Discussion

### Micro Hardness of Dental Enamel

Based on the findings of the current study, the average value of Vickers enamel microhardness was  $334.87 \pm 2.91$ , which is similar to the findings of Panich and Poolthong (18) , enamel hardness depends on different factors such as degree of enamel mineralization, enamel prisms and enamel tufts variations in different areas of enamel, presence or absence of any structural defects in the enamel, type of the teeth (whether it is anterior or posterior), and procedures for preparing the samples to perform the hardness test (13). Other factors influencing enamel hardness are the bio environmental factors, fluoridation of the drinking water, age of the teeth, and different eating habits in different societies (19).

### Enamel Hardness After MWCNTs Application With DMSO

The results of the hardness are reported in Table (1) and figure (2) from which it is observed that the highest mean value obtained was in concentration 0.02g/20ml which had a mean value of  $527.18 \pm 2.904$  Kg .m-2 , while the lowest mean value was for control group which had a mean value of  $334.87 \pm 2.904$  Kg .m-2. The results showed a significant increase in hardness between groups in concentration 0.001g/20ml , 0.005 g/20ml , 0.01 g/20ml and , 0.02 g/20ml compared with control group. Peter Atkin`s and Julio de paula (20)

it's well known that CNTs are thin cylinders of carbon atoms that are mechanically strong. At this time, the increase in hardness due to the increase in concentration of MWCNTs figure (4), the tremendous surface area of CNTs up to 200 m<sup>2</sup>.g<sup>-1</sup> leads to formation of clusters due to Van Der Waals forces. Clustering and non-uniform dispersion of CNTs will lead to inhomogeneous property distribution in the structural component (21). The results of the hardness are reported in Table (1) and figure (3) from which it is observed that the highest mean value of polished enamel surface which had a mean value of 452.59 ± 1.84Kg .m<sup>-2</sup> ,while the lowest mean value of unpolished enamel surface which had a mean value of 430.16 ± 1.84 Kg .m<sup>-2</sup> . The results showed a significant increase in the hardness for polished samples compared with unpolished samples. Because the surface area for polished samples more than unpolished samples. Since the of the polished surface leads to increases the surface area of dental enamel attached to

them MWCNTs material, which leads to increased the permeability of the materials to the inside enamel rods ,this leads to increased material inside dental enamel, gives an increase in the enamel hardness (22).



Figure (1): Micro-Vickers hardness testing machine (CV-400 DM).

Table (1): Descriptive data of enamel hardness in (Kg .m<sup>-2</sup>) after MWCNTs application with DMSO of the relationship between different concentration treatment and different surfaces treatment

Concentration g.mol <sup>-1</sup>	Subjects no.	Unpolished	Polished	Mean ± S.E
Control	6	330.30 g	339.43 g	334.87 ± 2.904 e
0.001/20	6	396.27 g	421.73 e	409.00 ± 2.904 d
0.005/20	6	437.67 e	465.13 d	451.40 ± 2.904 c
0.01/20	6	479.27 cd	489.60 c	484.43 ± 2.904 b
0.02/20	6	507.30 b	547.07 a	527.18 ± 2.904 a
Mean		430.16 ± 1.84 b	452.59 ± 1.84 a	LSD0.01 (concentration) = 9.89
LSD 0.01 (surfaces ) = 6.25				
Concentration vs surfaces LSD 0.01 = 16.02				

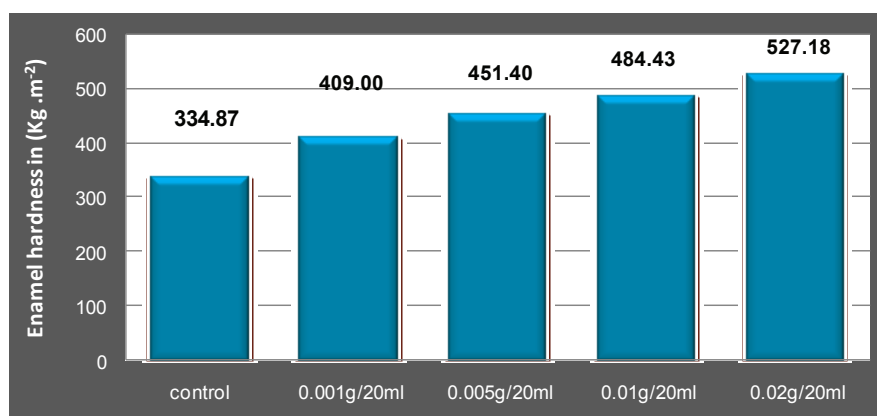


Figure (2): Column chart illustrates the enamel hardness in (Kg .m<sup>-2</sup>) after MWCNTs application with DMSO in different concentration treatment

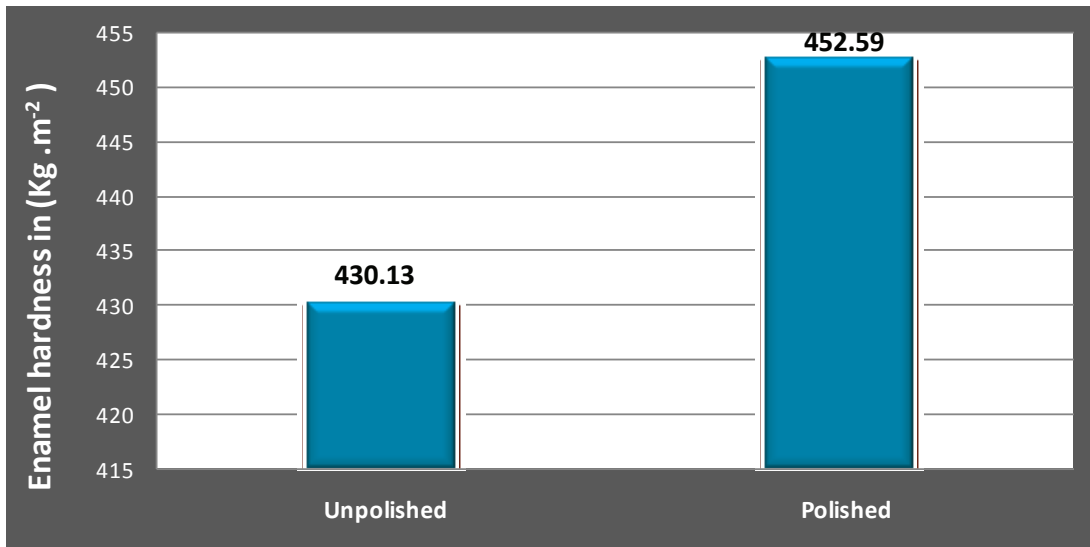


Figure (3): Column chart illustrates the enamel hardness in (Kg .m<sup>-2</sup>) after MWCNTs application with DMSO in different surfaces treatment

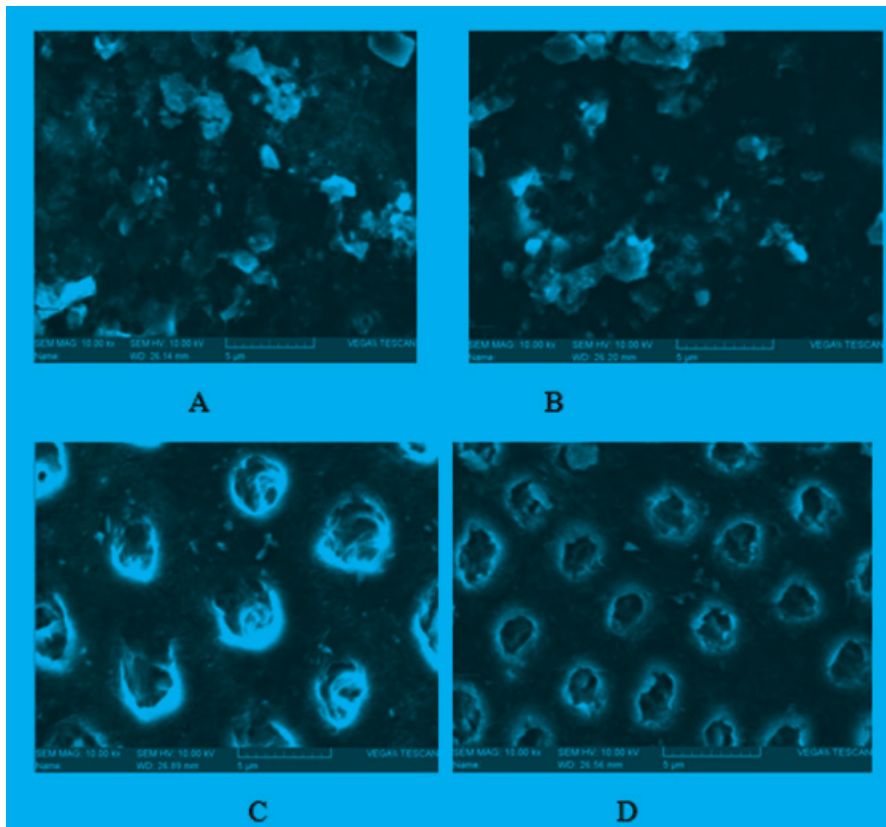


Figure (4):SEM: A:Unpolished sample without MWCNTs, B: Polished sample without MWCNTs, C: Unpolished sample with MWCNTs, D: Polished sample with MWCNTs in 5µm.

**Ethical Clearance:** The Research Ethical Committee at scientific research by ethical approval of both environmental and health and higher education and scientific research ministries in Iraq

**Conflict of Interest:** The authors declare that they have no conflict of interest.

**Funding:** Self-funding

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