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

Mohammed K. Jawad, B.D.S. [(1)]
Abbas F. Ali, B.D.S., Ph.D. [(2)]

ABSTRACT

Background: The objectives of this study are to evaluate the effect of addition of Multi-Wall Carbon Nano Tubes (MWCNTs) of different concentrations (0.05 mg.mL^{-1},0.25 mg.mL^{-1},0.5 mg.mL^{-1}and1 mg.mL^{-1}) on dimethyl sulphoxide DMSO and distilled water (DW) on tooth enamel. It intends to evaluate enamel microhardness in (Kg. m^{-2}) pre and post the application of Multi-Wall Carbon Nano Tubes (MWCNTs).

Materials and Methods: Thirty specimens prepared for the present study to measure the hardness of the enamel.

Results: The results showed that a significant increase in the enamel microhardness for groups 0.05 mg/mL (group B), 0.25 mg/mL (group C), 0.5 mg/mL (group D) and 1 mg/mL (group E) compared with control group (group A) in dimethyl sulphoxide media. Also, the results showed a significant increase in the enamel microhardness for polished samples compared with unpolished samples in DMSO media.

Conclusion: The final conclusion highest mean value obtained was 1 mg/mL (group E) in the enamel microhardness suspension in and dimethyl sulphoxide media.

Key words: Multi-Wall Carbon Nano Tubes, enamel hardness. (J Bagh Coll Dentistry 2016; 28(1):169-173).

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 formulating of 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 µm 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 ".[(8)] More simply speaking, one nanometer is one-billionth or 10^{-9} of a meter[(7-9)]**.** Nanotechnology can be classified in terms of application into three broad and extensively overlapping categories [(10)] they are**:** Nanoelectronics, Nanomaterials/particles and Nano-biotechnology.

Carbon nanotubes (CNT) are a new crystalline form of carbon. Wound in a hexagonal network of carbon atoms constituting a graphene nanofoil, hollow cylinders can have diameters as small as 0.7 nm with lengths that can be ranged from a few micrometres to 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)]. The Hardness of Knoop (KHN) and Vicker (VHN) reported approximately the same value [(15)]. The average hardness value of enamel and dentin is between 270 to 350 Knoop microhardness or from 250 to 360 Vickers microhardness and from 50 to 70 Knoop microhardness respectively [(16)].

MATERIALS AND METHODS

Activation of Commercial Carbon Nano Tube[(17)]. One gram of Multi-Wall Carbon Nano Tubes was transferred into a glass beaker and (10

(1)Master student, Department of Basic Science, College of Dentistry, University of Baghdad.
(2)Assist. Professor, Department of Basic Science, College of Dentistry, University of Baghdad.

cm^3) of nitric acid were added. Then ($30cm^3$) of sulphuric acid were added drop wise to the mixture and placed in two-neck round bottomed flask enquired with a condenser to continue stirring and heated to 50 ◦C for 24 hrs after which the MWCNTs were filtered off using Cellulose filter paper (pore size 0.45 micrometer). 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 set at 150◦C for 2hr. In the third step 0.02 g from MWCNTs were put in 20 ml DW and DMSO. The MWCNTs did not mixed with DW instead formed a suspension, While the MWCNTs are properly mixed with DMSO. The whole solution is transferred into sonicator.

Teeth Specimens Preparation

The total number of samples were 54 (24 samples in DW and 24 samples DMSO in different concentrations and 6 samples control) from mandibular first premolar for micro hardness test were prepared. Samples divided the microhardness samples into polished samples and unpolished samples and was polishing the polished samples by hand piece device with pumice material and repeat the polishing more than once until the surface become roughness.

Samples were collected from healthy teeth of female 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. All samples we kept in water for further tests. The samples were shaken in the vibrator for limited period of time ten minute for three times in six continuous days.

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: Vickers Test: $HV= 1854\ F/d^2$.

Where HV: Vickers hardness number, in kg $.m^{-2}$, F: Test force, in kg, d: Diagonal length of the indentation, in m^2.

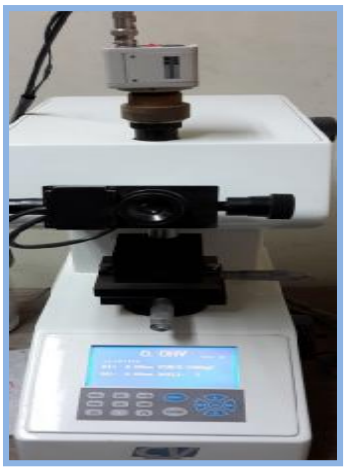


Figure 1: Micro-Vickers Hardness Testing Machine (CV-400 DM).

Sample Preparation to Measure the Hardness

The total number of samples was 54 samples to measure the hardness of the enamel, the group is divided into subgroups as follows:

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

Group B (0.05 mg/mL): (3 unpolished enamel surface and 3 polished enamel surface samples in DW) and (3 unpolished enamel surface and 3 polished enamel surface samples in DMSO).

Group C (0.25 mg/mL): (3 unpolished enamel surface and 3 polished enamel surface samples in DW) and (3 unpolished enamel surface and 3 polished enamel surface samples in DMSO).

Group D (0.5 mg/mL): (3 unpolished enamel surface 3 polished enamel surface samples in DW) and (3 unpolished enamel surface and 3 polished enamel surface samples in DMSO).

Group E (1 mg/mL): (3 unpolished enamel surface and 3 polished enamel surface samples in DW) and (3 unpolished enamel surface and 3 polished enamel surface samples in DMSO).

Statistical Analysis

Statistical analysis was done by using the software SPSS version 17.0; the results were expressed as mean ± standard deviations (mean ± SD). 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 used to evaluate enamel hardness in ($Kg.m^{-2}$) after MWCNTs application with DMSO in different concentration treatment.

Enamel Hardness Test

Control group compared with groups dealing with MWCNTs application with DMSO in different concentration treatment and different surfaces treatment (Fig. 2,3).

Enamel Microhardness Test in Difference Groups

Table (1) showed that the results of LSD test after ANOVA a statistically highly significant differences among groups (A compared with B, C, D, E), (B compared with C, D, E), (C compared with E only but compared with D a statistically significant differences) and (D compared with E) in unpolished state in DW media, and also a statistically highly significant differences among groups (A compared with B, C, D, E), (B compared with C, D, E) , (C compared with E only but compared with D a statistically significant differences) and (D compared with E) in polished state in DW media.

In DMSO media a statistically highly significant differences among all groups in unpolished state and polished state.

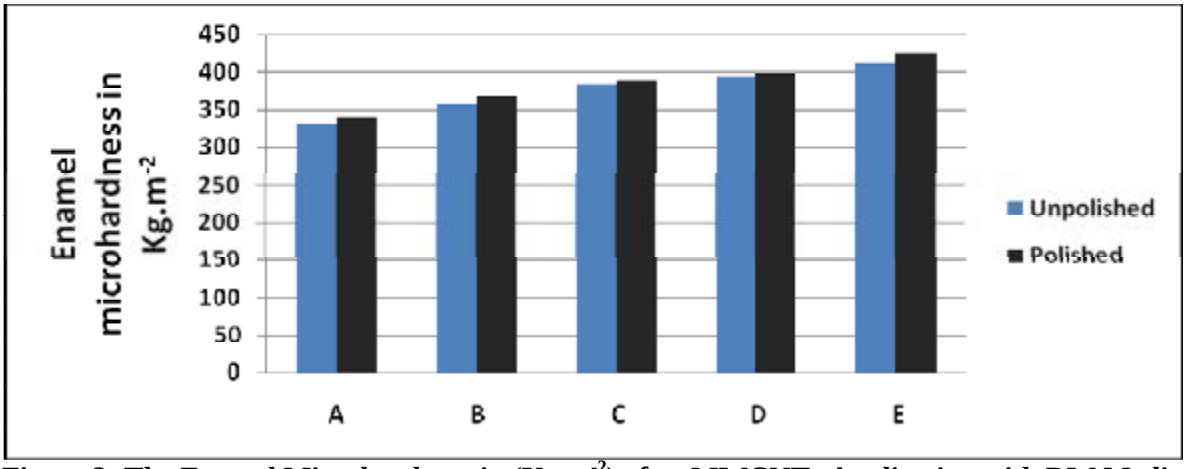


Figure 2: The Enamel Microhardness in ($Kg.m^{-2}$) after MWCNTs Application with DW Media

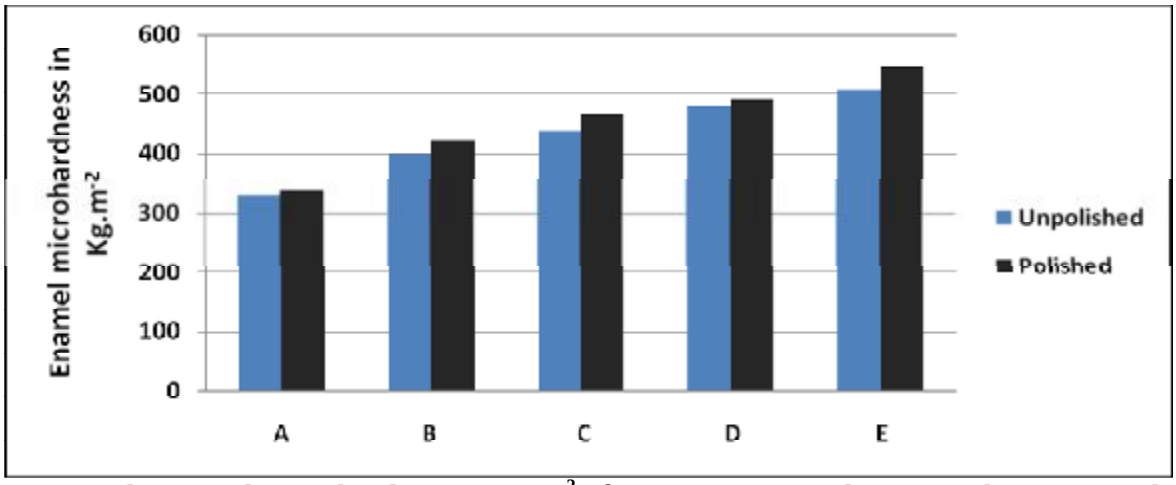


Figure 3: The enamel Microhardness in($Kg.m^{-2}$)after MWCNTs Application with DMSO Media.

Table 1: LSD Test and ANOVA of Enamel Microhardness

State	Groups		Media			
			D.W.		DMSO	
			Mean Difference	p-value	Mean Difference	p-value
Unpolished	A	B	-26.03	0.000 (HS)	-65.97	0.000 (HS)
		C	-54.00	0.000 (HS)	-107.37	0.000 (HS)
		D	-62.97	0.000 (HS)	-148.97	0.000 (HS)
		E	-79.83	0.000 (HS)	-177.00	0.000 (HS)
	B	C	-27.97	0.000 (HS)	-41.40	0.000 (HS)
		D	-36.93	0.000 (HS)	-83.00	0.000 (HS)
		E	-53.80	0.000 (HS)	-111.03	0.000 (HS)
	C	D	-8.97	0.019 (S)	-41.60	0.000 (HS)
		E	-25.83	0.000 (HS)	-69.63	0.000 (HS)
	D	E	-16.87	0.000 (HS)	-28.03	0.000 (HS)
Polished	A	B	-27.37	0.000 (HS)	-82.30	0.000 (HS)
		C	-49.33	0.000 (HS)	-125.70	0.000 (HS)
		D	-58.23	0.000 (HS)	-150.17	0.000 (HS)
		E	-85.50	0.000 (HS)	-207.63	0.000 (HS)
	B	C	-21.97	0.000 (HS)	-43.40	0.000 (HS)
		D	-30.87	0.000 (HS)	-67.87	0.000 (HS)
		E	-58.13	0.000 (HS)	-125.33	0.000 (HS)
	C	D	-8.90	0.046 (S)	-24.47	0.009 (HS)
		E	-36.17	0.000 (HS)	-81.93	0.000 (HS)
	D	E	-27.27	0.000 (HS)	-57.47	0.000 (HS)

DISCUSSION

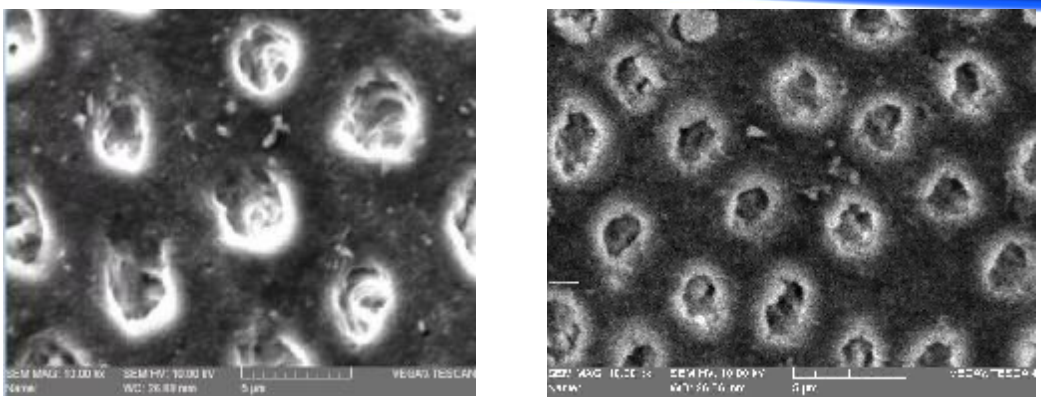
Based on the findings of the current study, the average value of Vickers enamel microhardness was 334.87 ± 2.91, which is similar to the findings of Panich and Poolthong [18], enamel hardness depends on different factors such as degree of enamel mineralization, enamel prisms and enamel tufts variations 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 of 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 Microhardness in Difference Groups

The results of the microhardness are reported in table (1) showed that the results of LSD test after ANOVA have a statistically highly significant differences among groups (A compared with B, C, D, E) , (B compared with C, D, E) , (C compared with E only but compared with D a statistically significant differences) and (D compared with E) in unpolished state in DW media, and also a statistically highly significant differences among groups (A compared with B, C, D, E) , (B compared with C, D, E) , (C compared with E only but compared with D a statistically significant differences) and (D compared with E) in polished state in DW media. In DMSO media a statistically highly significant differences among all groups in unpolished state and polished state.

Peter Atkin`s and Julio de paula [20] described that the well-known CNTs are thin cylinders of carbon atoms that mechanically strong. The intentional integration of two or more distinct materials into one composite material would make use of preferred properties of each material. The MWCNTs reported to be the stiffest and strongest fibers ever produced with Young's modulus reach up to 1 TPA experimentally four times stronger than steel.

The hexagonal structure with a separation of planes is about 0.353 nm which will enables those tubes to penetrate as deep as many micrometers inside the teeth enamel rods. At the same time, the increase in microhardness is due to the increase in concentration of MWCNTs. The tremendous surface area of CNTs is up to 200 m2.g-1 which 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] as shown in figure (4).



A B

Figure 4: SEM: A: Unpolished Sample with MWCNTs, B: Polished Sample with MWCNTs in 5µm.

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