MECHANICAL PROPERTIES

EVALUATION OF DENTURE BASE PMMA ENHANCED

WITH SINGLE-WALLED CARBON NANOTUBES

By

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DEDICATION

To my parents, Armando and Marlene

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INTRODUCTION

In the mid 1980's, Smalley and co-workers at Rice University developed the chemistry of fullerenes. Fullerenes are geometric cage like structures of carbon atoms that are composed of hexagonal and pentagonal faces. Recent theoretical and experimental studies, suggest that Carbon Nanotubes (CNTs) are 10-100 times higher than the strongest steel at a fraction of the weight. There are two main types of CNTs that can have high structural perfection. Fullerenes are geometric cage like structures of carbon atoms that are composed of hexagonal and pentagonal faces.[1] In 1991, the Carbon Nanotubes (CNTs) were discovered. Recent theoretical and experimental studies, suggests that CNTs have remarkable mechanical and electrical properties.[2] CNTs have shown extremely high mechanical properties with reported strengths 10-100 times higher than the strongest steel at a fraction of the weight.[2, 3] They are extremely strong, resilient and very light weight. One of their most important characteristics is that under certain conditions, the CNTs will form cylindrical stable structures on their own.[4] There are two main types of CNTs that can have high structural perfection. Single-walled nanotubes (SWNTs), that consist of a single graphite sheet seamlessly wrapped into a cylindrical tube and Multi-walled carbon nanotubes (MWNTs), that comprise an array of such nanotubes concentrically nested like rings of a tree trunk.[2] In addition to the exceptional mechanical properties associated with CNTs (elastic modulus of 1TPa. diamond: 1.2 TPa), they also posses superior thermal and electric properties: thermally stable up to 2800° C in vacuum, thermal conductivity about twice as high as diamond, and electric current-carrying capacity 1000 times higher than copper wires.[2] To unlock the potential

of CNTs for application in polymer nanocomposites, one must fully understand the properties of CNTs as well as the interactions between the nanotube/matrix interfaces. Although this requirement is not different from that for conventional fiber reinforced composites, the scale of the reinforcement phase diameter has changed from micrometer to nanometers.[5]

Reinforcement of denture base material has been a subject of interest to the dental material community. Denture Base acrylics resins are subjected to many different types of stresses. Intra-orally, repeated masticatory forces lead to fatigue phenomena, while extra-orally high impact forces may occur as a result of dropping the prosthesis. As a consequence, fracture of the denture base can result. Impact failure is a predominant mode of failure due to accidental dropping. Clinical studies have shown midline fractures (due to fatigue and impact) to be a common problem in maxillary complete dentures[1, 6] whereas for mandibular dentures, 80% of fractures are caused by impact.[6] Poly (methyl methacrylate) (PMMA) is the principal material of dental prosthesis. To improve the properties of PMMA many have incorporated an ample variety of additive materials into the polymer, including glass fibers, long carbon fibers, and metal wires, among others. Success has been limited.[1, 7] However, the effects of CNT reinforcement on the mechanical properties of denture base material have not been explored so far. Although Biocompatibility is beyond the scope of this study, the effect of CNTs on living cells is still being studied. Until now, no known adverse effects have been reported.[2]

LITERATURE REVIEW

DENTURE REINFORCEMENT

Several studies have investigated the incidence and types of fracture of dentures. In a study made by Darbar et al[8] it was reported that 33% of the repairs carried out were due to debonded/detached teeth and 29% were repairs to midline fractures more commonly seen in upper complete dentures. The midline fracture in a denture is often a result of flexural fatigue. Impact failures usually occur due to sudden blow to the denture due to accidental dropping.[9]

FULLERENES – RELATED CARBON NANOTUBES.

In 1985, Rice and colleagues did a series of experiments on the vaporization of graphite. In the distribution of gas-phase carbon clusters, detected by spectrometry, C60 was the dominant species. Especially a C60 closed cluster containing 60 carbon atoms. These molecular carbon fibers consist of tiny cylinders of graphite, closed at each end with caps that contain precisely six pentagonal rings. Dividing C60 parallel to one of the three-fold axes results in the zigzag nanotube, while bisecting C60 along one of the five fold axes, produces the armchair arrangement of hexagons around the circumference. There is a third class of structure in which the hexagons are arranged helically around the tube axis, which are less perfect than the idealized version, either single or multi – layered.[10]

ATOMIC STRUCTURE AND MORPHOLOGY OF CARBON NANOTUBES

CNTs can be visualized as a sheet of graphite that has been rolled into a tube. Graphite is formed as a 2-D sheet of carbon atoms arranged in a hexagonal array. "Rolling" sheets of graphite into cylinders forms CNTs. The atomic structure of nanotubes is described in terms of tube chiralty, or helicity, which is defined by the chiral vector *Ch* and the chiral angle θ. The angle determines the amount of "twist" in the tube. The two limiting cases exists were the chiral angle is at 0 and 30, zigzag and armchair respectively[2]

NANOTUBE SYNTHESIS AND PROCESSING.

SWNTs and MWNTs are usually made by carbon-arc discharge, laser ablation of carbon, or chemical vapor deposition. Nanotube diameters range from ~0.4 to >3 nm for SWNTs and ~1.4 to at least 100 nm for MWNTs.[4]

MECHANICAL PROPERTIES OF CARBON NANOTUBES

Besides their experimental observations, Ijima et al[11] examined the response of nanotubes under compression using molecular dynamics simulations. They simulated the deformation properties of single- and multi-walled nanotubes bent to large angles. Their experimental and theoretical results show that nanotubes are remarkably flexible. The bending is completely reversible up to angles in excess of 110 degrees.[4]

The high modulus and the low weight of carbon fibers make them ideal reinforcing agents in a variety of composite materials. Although only bending experiments on CNTs have been performed so far. CNTs seem to behave as "ideal carbon fibers" that can be stiff, yet flexible, accommodating its molecular structure to different conditions, associating very high modulus with very high strength.[12, 13]

Some of the earliest theoretical work in this area was carried out by the Tomanek group from Michigan. This group employed the Keating potential to determine the structural rigidity of short, single-walled nanotubes containing 100, 200 and 400 atoms. Tomanek results imply a Young's modulus in the range of 1500-5000 GPa[10] The North Carolina research group (NCUU) studied nanotube buckling under extreme deformations, using molecular dynamics and macroscopic approaches. The NCUU did not observe fracture in their simulations of axial compression or bending of nanotubes, but the application of tension does eventually produce fracture. The first quantitative TEM measurements of mechanical properties of nanotubes were made by Treacy, Ebbesen and Gibson in 1996. By analyzing the mean-square amplitude as a function of temperature it was possible to obtain estimates for the Young's modulus, which ranged from 415 GPa to 4150 GPa with a mean of 1800 GPa.[10]

REINFORCED PMMA COMPOSITES

Although PMMA has been widely used as a main component of denture base polymer for many years, this material is sometimes fractured or cracked in clinical use. One of the factors that cause fracture is considered to be low resistance to impact.[14] Rubber reinforcement has remained the most effective method of toughening PMMA for several decades, its greatest problem being significant additional cost. Fiber reinforced composites have the advantage that if the matrix should fail catastrophically, then the fractured portions are likely to remain in close proximity, held together by the fibers. [15] Many attempts have been made to enhance the strength properties of acrylic denture bases including the addition of metal wire. The primary problem of using metal reinforcement is poor adhesion between the wire and the acrylic. [6]

CARBON NANOTUBE COMPOSITES

The incorporation of carbon fibers into a matrix not only confers strength and elasticity to the material but also greatly enhances toughness.[10] Research on nanotube composites has concentrated on polymer-MWNT –based materials, wherein they exhibit mechanical properties that are superior to conventional polymer-based composites due to their considerably higher intrinsic strengths and moduli, and the fact that the stress transfer efficiency can be 10 times higher than that of traditional additives. It is generally believed that most MWCNTs have a "Russian doll" structure in which each constituent tubule is only bonded to its neighbors by weak Van der Waals forces. This immediately raises a problem when one is considering incorporating carbon nanotubes into matrices.[10]

Many have tried to improve the mechanical properties of bone cement [acrylic] by adding small amounts of metal, glass, polymer or carbon fibers as reinforcing materials, but these efforts resulted in limited success. Inadequate dispersion, poor fiber-matrix bonding and filler-damage scale mismatch are potential reasons for these sub-satisfactory results. Scale compatibility is one key reason why the discovery of CNTs gives new hope for fiber reinforcement of bone cement. The small diameter (10 nm) of this nanomaterial is far more comparable to the size of the polymer chains and the scale of fatigue damage compared to the size of conventional ($10^4 – 10^6$ nm) fibers.[16]

Often, carbon black, glass fibers, and phenolic resin are incorporated into the polymer hosts, resulting in significant improvements in mechanical properties, including impact strength and tensile and compressive moduli (stiffness) over that of the nonfilled polymer. SWNTs exhibit extraordinary mechanical properties[1, 2] such as tensile strength of 50 to 200 GPa, estimated Young's moduli of 1 to 5 TPa and high strengths. Further,

when released from strain, bent SWNTs recover their original form without direct fracture. On the base of these properties, CNTs are excellent candidates for the development of nano reinforced polymer composite materials. Polymer-SWNT composites show more promise than MWNT-based nanocomposites as potential high performance engineering materials. Independent experiments on PMMA-SWNTs at low concentrations (<1wt %) indicate that the polymer is intimately mixed with the nanotubes. Furthermore, measurements of the melt rheology of polystyrene-SWNT nanocomposites indicate a substantial increase in the viscosity and elasticity of the system at low shear rates, even at 1wt% SWNT loadings.[4] Ajayan *et al*. embedded purified tubes into an epoxy resin. They were interested in obtaining cross-sectional images of nanotubes and then cut the hardened composite into thin slices with a diamond knife. The nanotubes were found to have become aligned in the direction of the knife movement. The main importance of this work is in providing a graphic demonstration that unidirectional nanotubes can be prepared, this also proves the self-assembly property of CNTs.[10] Transparent nanotube sheets have been produced, drawn from a sidewall of multiwalled nanotube (MWNT) forests synthesized by catalytic chemical vapor deposition, using acetylene gas as the carbon source.[17]

In 2009, Marrs et al[5] successfully dispersed MWCNT into an acrylic matrix with two heated (220 ºC) stainless steel counter-rotating sigma rotors in the mixing chamber of a Haake Rheomix machine. Other proposed methods include sonic dismembranators, chemical modification; as proposed by Marrs[5] and Spin casting as used by Safadi et al[18] in order to produce thin films of MWNT-filled composites (0.5 vol. %).

Sui and Wagner[19] observed unusually large deformation in PMMA electrospun fibers under tension when multiwall or single-wall CNTs were included as a second phase in the fibers. The addition of CNTs caused a striking, visible transformation in the deformation mode of PMMA ES fibers. In pure PMMA fibers, sparse and unstable polymer necking occurs under increasing tension, leading to failure at relatively small strains. However, the presence of either SWCNTs or MWCNTs causes the failure strain to reach comparatively enormous values[19]

According to Marrs[16] MWCNTs are believed to effectively bridge cracks and reduce the extent of plastic deformation experienced by a PMMN matrix. MWCNTs can successfully reinforce the craze by strengthening the fibrils and bridging the recesses or submicron voids to prevent their coalescence, thus enhancing the fatigue performance of the material.

FUTURE USES FOR CARBON NANOTUBES AND IMPORTANCE OF CONTINUED RESEARCH

Recently, a new field of study related to CNTs and its use in drug delivery has gathered attention. The new "intelligent materials" will not only have greater mechanical properties, but they will also help fight disease when needed. A research group has studied the use of "nanosensors" for *Candida* detection. The technique uses field-effect transistors (electronic devices that contain an electrode source and a draining electrode connected to a transducer) based on CNTs and with *Candida albicans* specific antibodies. The *Candida* samples, which can be obtained from blood, serum or vaginal secretions, are placed directly on the biosensor, where the interaction between antigens and antibodies changes the electric current of the devices. This change is recorded and makes it possible to measure the amount of yeast present in a sample. By using this biosensor it

will be possible in future to obtain a rapid diagnosis of infection with this pathogen, which will help to ensure administration of the correct prophylactic treatment[20]. In 2005, Zhang et al[17] produced thin, transparent sheets of CNT's trough a filtration process. In the future this technique could be adapted for the production of color - stable denture acrylic eliminating the concerns with esthetics.

PURPOSE OF THIS INVESTIGATION

This investigation is undertaken to study the effect of CNT reinforcement on the mechanical properties of commercially available denture base material.

The null hypothesis is that the addition of carbon nanotubes (Single-Walled Carbon Nanotubes in 1% or less by weight) does not alter the overall mechanical properties of prosthetic PMMA. The alternative hypothesis is that due to the mechanical properties of CNTs, their addition into a PMMA matrix will improve the mechanical properties of the prosthesis.

MATERIAL AND METHODS

PMMA MATERIAL

The denture base material used was Lucitone 199® (Dentsply International Inc., York, PA, USA). The CNTs were Single-Walled, highly purified nanotubes (MK Nano, Nississaqua, Ontario, Canada). SWCNTs were chosen because of their less complicated atomic structure that will ease the preparation and interactions within the composite matrix.

SPECIMEN GEOMETRY

Flexural Strength: the mould for this group was fabricated as bar shaped mould prepared in standard denture flasks, using a template measuring 70 mm x 40 mm x 3 mm. Each mould was prepared and cut to obtain the specimen tested, which had measurements of 70 mm x 10 mm x3 mm.

Flexural Modulus: the mould for this group was fabricated as bar shaped mould prepared in standard denture flasks using a template measuring 70 mm x 40 mm x 6 mm. Each mould was prepared and cut to obtain the specimen tested which had measurements of 70 mm x 10 mm x 6 mm.

Fracture Toughness: the mould for this group was fabricated as bar shaped mould prepared in standard denture flasks using a template measuring 70 mm x 40 mm x 3 mm. Each mould was prepared and cut to obtain the specimen tested, which had measurements of: 70 mm x 8 mm x 4 mm

Hardness: The fractured piece from the flange of the three point bending specimens was used for hardness testing.

SPECIMEN FABRICATION

The specimens were fabricated using the aforementioned denture base resin, Lucitone 199® original shade. Following manufacturer's instructions; the powder/liquid ratio: 21 g. (32 cc) /10 ml and the mixing time: 15-30 seconds.

The SWCNTs were added as received from manufacturer to the measured acrylic powder at 0.25 wt %, 0.50 wt % and 0.75 wt % of total weight volume (acrylic + monomer) in a glass beaker. The liquid monomer was then added to the powder and mixed for 15 seconds to assure wetting of all powder particles. The mix was covered and allowed to reach packing consistency. (Approx. 9 minutes at room temperature of 73 +/- 2 ºF) The mix was packed using conventional denture flasks (Hanau Type, Whip-Mix Corporation, Louisville, Kentucky, USA) not exceeding 10 minutes of work time. The closed flasks, (locked by spring clamp) were cured in a water bath for a period of 9 hours at 160 ºF, followed by a cooling time of ½ hour in water at 60-80 ºF. The flask was bench cooled for 30 minutes and submerged in cool water for 15 minutes before deflasking**.** Although distortion after processing has been reported, it is considered clinically insignificant.[21] The specimens were removed from the flasks and cleaned from stone particles. The specimens were sequentially polished with SiC paper (600 grit.) to achieve smooth edges. Each specimen was cut to obtain the final testing sample by using a Hamco Sectioning Machine (New York, USA), in order to obtain a final sample of the following dimensions: 70 mm x10 mm x 3 mm, 70 mm x10 mm x 4 mm for flexural

strength and modulus respectively and 70 mm x 8 mm x 4 mm for fracture toughness. Each specimen was visually inspected, calibrated, and polished again if necessary.

TESTING SUMMARY

Flexural strength and modulus:

- Sample: 70 mm x 50 mm x 3 mm
- Cut Sample: 70 mm x 10 mm x 3 mm (test sample)
- Span Width: 50 mm.
- Loading rate: 5 mm/min.
- Soaking wet specimens in 37 ºC water. Condition in 23 ºC water for 60 min. Remove sample and dry with paper towel.

Fracture Toughness

- Sample: 70 mm x 50 mm x 6 mm
- Cut Sample: 70 mm x 8 mm x 4 mm (test sample)
- Notch made with cutting wheel at specimen center.
- Soaking wet specimens in 37 ºC water. Condition in 23 ºC water for 60 min. Remove sample and dry with paper towel.
- Span Width: 35 mm
- Loading rate: 1 mm/min.

Microhardness

- Sample: fractured flange of flexural strength sample

FLEXURAL STRENGTH AND FLEXURAL MODULUS

The flexural strength and flexural modulus were determined using the three-point bending test as specified by the ISO specification 20795-1:2008. A total of four groups

were prepared, at 0.0 wt %, 0.25 wt %, 0.50 wt %, and 0.75 wt % with 20 samples per group. The specimens were tested using a universal testing machine (Sintech Renew 1121, Instron Engineering Corp., Canton, MA, USA). A standard three point bending jig was attached to the machine and connected to a computer with a specifically designed program (Test-Works 3.0 MTS Systems Co., Eden Prairie, MN, USA). This software controlled the testing machine and recorded the breakage load and beam deflection. Before each test, the specimen thickness and width were recorded with a digital micrometer and introduced into the computer. The specimens were then placed on the jig and the test carried out using a crosshead speed of 5 mm/min (for flexural strength and modulus) and 1 mm/min for the fracture toughness test.

The flexural strength (S) was calculated using the following formula:

$S = 3FL / 2bd^2$ where (S): Flexural strength in *MPa,* (F): the load at break or yield in *N*. (L=50 mm) the span of specimen between supports, (b=10 mm) the width and (d=3 mm) the thickness.

The flexural modulus (E) = *MPa,* was calculated using the following formula:

$E = F_1 L^3 / 4bd^3 D_1$, where (F_1) is the force at deflection, (L = 50 mm) is the span of specimen between supports, (b = 10 mm) the width, (d = 3 mm) the thickness, D_1 the deflection at linear region of load deflection curve.[22] For the wet specimens testing, the samples were conditioned in water at 37 ºC +/- 1 ºC for 7 days +/- 2 hours prior to testing.[23]

FRACTURE TOUGHNESS

According to ISO 20795-1, each specimen was fixed with a holding device and marked at the centerline, midway from the edges of the specimens. A pre-crack was cut

with a diamond saw to a depth of 3.0 +/- 0.2 mm along the marked centerline. A sharp notch was then made at the bottom of the main notch with a sharp blade and a gentle tapping. The notch depth was in the range of 100 μm to 400 μm. An optical microscope was used to check the crack depth. The specimens were then stored in a container with water at 37 ºC for 7 days. The specimens were then conditioned in water at 23 ºC for 15 minutes prior to testing. The dried specimen was placed between supports of the test rig and tested with a constant load of 1 mm/min. The test was considered finished when the load was reduced in 5% or when the machine crosshead reached its limit. After completion of the test, two measurements were recorded under an optical microscope (Nikon Measurescope UM-2, Japan). Measure one identified as “a prime” was recorded as the distance from the specimen surface to the pre-crack notch, and measure two, identified as “a” was recorded as the measure from the specimen surface to the fracture line.

According to ISO 20795-1, the fracture toughness was calculated by using the following formulas:

$$K_{max} = \int P_{max} l_t / (b_t h_t^{3/2}) \quad x \sqrt{10^{-3}} \quad \text{MPa m}^{1/2}$$

where:

$\int$ is a geometrical function dependent on χ:

$$\int(\chi) = 3\chi^{1/2} [\, 1.99 - \chi(1-\chi)(2.15-3.93\chi + 2.7\chi^2) \,] / [\, 2(1+2\chi)(1-\chi)^{3/2} \,]$$

and:

$$\chi = a/h_t$$

P_{max} is the maximum load exerted on the specimen, in Newton’s

a , h_t b_t and l_t expressed in mm where a is the crack length (no longer than 0.4mm) h_t is the height, (8 +/- 0.2 mm) b_t is the width and l_t is the span (32 +/- 0,1 mm)

MICROHARDNESS

The hardness test was made for each sample in the dry condition. A piece of broken flange from the flexural strength test was taken and evaluated on a Knoop hardness tester. (Leco® Corp. M-400 St. Joseph, Michigan, USA). A 100g load and 15 sec. dwell time was used. Each sample was tested three times and a Knoop number was obtained.

The Knoop hardness number (KHN) is the ratio of the load applied to the area of the indentation calculated from the following formula:

$KHN = L / l^2 C_p$

In this equation, L is the load applied in kgf, l is the length of the long diagonal of the indentation in mm, and C_p is a constant relating l to the projected area of the indentation. The units for KHN are also kg/mm^2. Higher values represent harder materials.

STATISTICAL METHOD

The effect of carbon nanotube reinforcement (0.0%, 0.25%, 0.50%, and 0.75%) and conditions (wet, dry) on flexural strength, impact strength, modulus and microhardness was assessed using analysis of variance (ANOVA). The ANOVA for microhardness also included a random effect for sample to correlate the 10 measurements within each sample. A 5% significance level was used for all tests. If the reinforcement-condition interaction effect is significant, pair-wise comparisons of the treatment combinations was examined for significance using the Fisher's Protected Least Significant Differences method. If the interaction effect is not significant, the main effect was examined for significance. If the main effects were significant, pair-wise comparisons between the levels within each factor was examined using the Fisher's Protected Least Significant Differences method. The distributions of the measurements were examined and a transformation (logarithmic, rank, etc.) may be necessary to satisfy the assumptions required for the ANOVA.[1, 24]

RESULTS

FLEXURAL STRENGTH

Two main groups were tested in dry and wet conditions. In both, dry and wet conditions, the control group is higher than the experimental groups ($p < 0.05$), except for the 0.5% group. In the Control group (dry), mean values of 97.74 MPa were obtained and 84.65 MPa for the Control (wet). No statistical difference could be observed between wet and dry conditions in the Control group. In the 0.25 % 0.50% and 0.75% no statistical difference was found between the groups. Mean values ranged from 83.53 MPa for the 0.25% group, 82.68 MPa for the 0.50% group and 80.98 MPa for the 0.75% group. A statistical difference was found between the Control and Experimental groups ($p < 0.05$). (See table I and II)

FLEXURAL MODULUS

Two main groups were tested in dry and wet conditions. In both, dry and wet conditions, the control group is higher than the experimental groups ($p < 0.05$). The Control group (dry) was statistically higher than the other three experimental groups. No statistical difference was found between experimental groups (dry or wet). The control group (dry) had a mean value of 2.64 GPa with a maximum of 2.72 GPa. The control group (wet) had a mean value 2.16 GPa with a maximum of 2.22 GPa. The experimental groups had values ranging from 2.00 to 2.70 GPa with mean values of 2.43 GPa (0.25 %), 2.38 GPa (0.50%) and 2.42 GPa (0.75%). (See table I and III)

FRACTURE TOUGHNESS

All groups were tested in wet condition. There was no statistical difference in fracture Toughness between the control and the experimental groups, with the exception of the 0.75% group which was statistically lower than the rest. The control group had a mean value of 2.14 MPa-$m^{1/2,}$ in the experimental groups; the 0.25 % group had a mean value of 2.15 MPa-$m^{1/2}$ the 0.50% had a mean value of 2.22 MPa-$m^{1/2}$ and the 0.75% had a mean value of 1.92 MPa-$m^{1/2}$. (See table I and IV)

MICROHARDNESS

All groups were tested in the dry condition. In all samples, the experimental group showed higher values than the control group. The control group had a mean value of 17.86, while in the experimental groups the 0.25% group had a mean value of 20.93, the 0.50 % a mean value of 21.24 and 19.63 for the 0.75 % group. (See table I and V)

TABLES

TABLE I

General results obtained for all samples. (Mean values)

	Control	0.25 %	0.50 %	0.75 %
Flexural Strength (dry) (MPa)	97.74	83.53	82.68	80.98
Flexural Strength (wet) (MPa)	84.65	74.29	79.65	71.20
Flexural Modulus (dry) (GPa)	2.64	2.43	2.33	2.35
Flexural Modulus (wet) (GPa)	2.16	2.16	2.17	2.16
Fracture Toughness (wet) (GPa)	2.14	2.15	2.22	1.92
Microhardness (Knoop)	17.86	20.93	21.24	19.63

TABLE II

Mean Values of flexural strength.
Comparison table between groups (dry and wet samples)

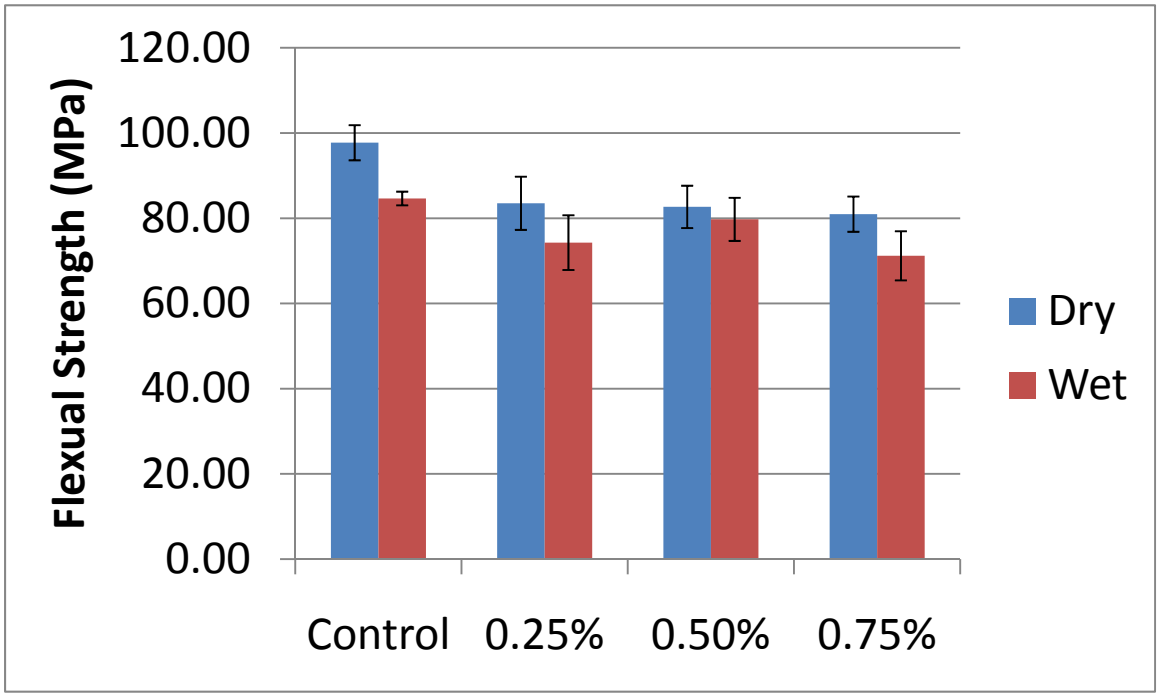

TABLE III

Mean Values for flexural modulus.
Comparison table between groups (dry and wet conditions)

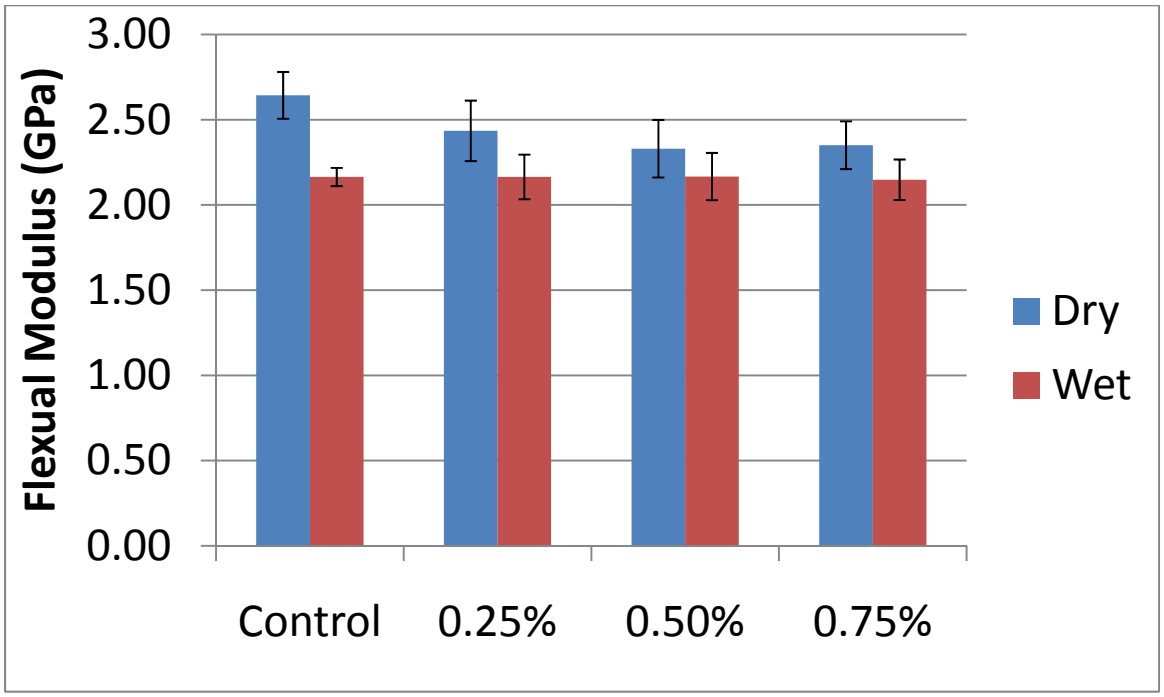

TABLE IV

Mean Values of fracture toughness for all samples (wet condition)

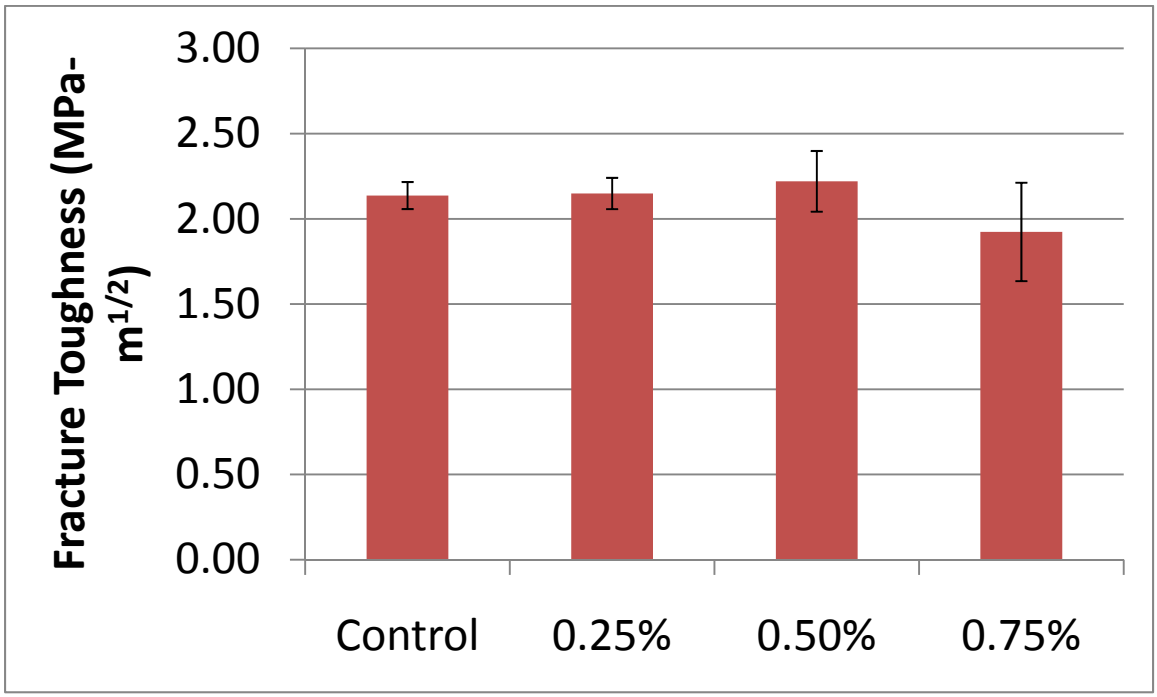

TABLE V

Mean Values of Microhardness for all samples

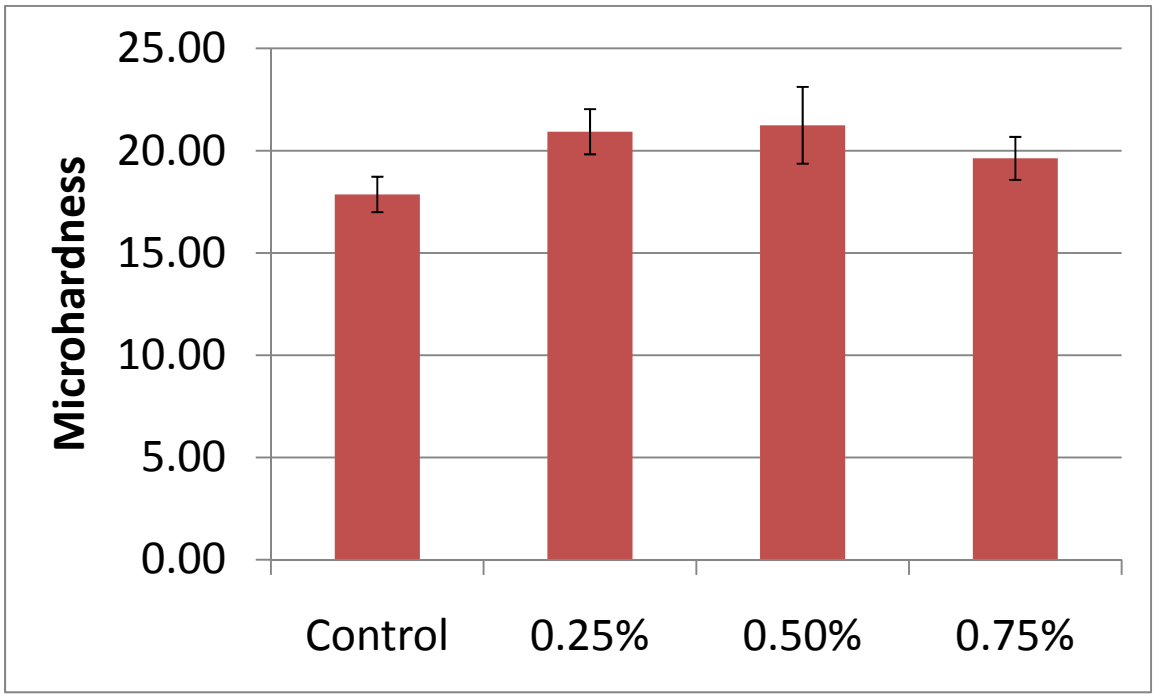

TABLE VI

Table extract from Marrs et al[5]
Mean Values from 3-Point Bending test for
Bone Cement (PMMA) augmented with MWNTs

% MWNTS (wt %)	Flexural Strength (MPa)	Bending Modulus (MPa)
0	**80.3 +/- 6.2**	**3402 +/- 44**
0.5	**85.7 +/- 3.8**	**3405 +/-44**
1	**78.3 +/- 7.4**	**3500 +/- 58**
2	**90.6 +/- 3.2**	**3528 +/- 66**
5	**84.9 +/- 5.6**	**3823 +/-127**

FIGURES AND ILLUSTRATIONS

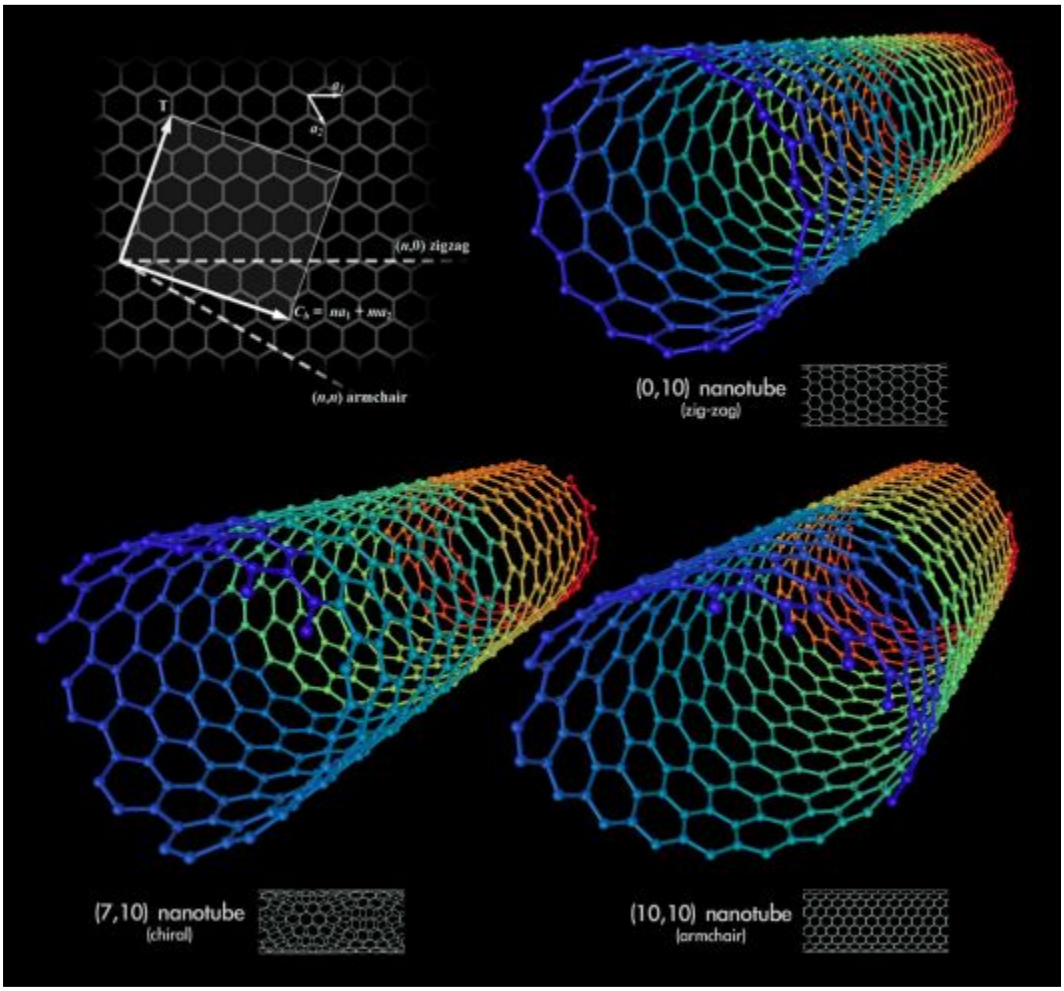

FIGURE 1. Molecular configurations of CNTs

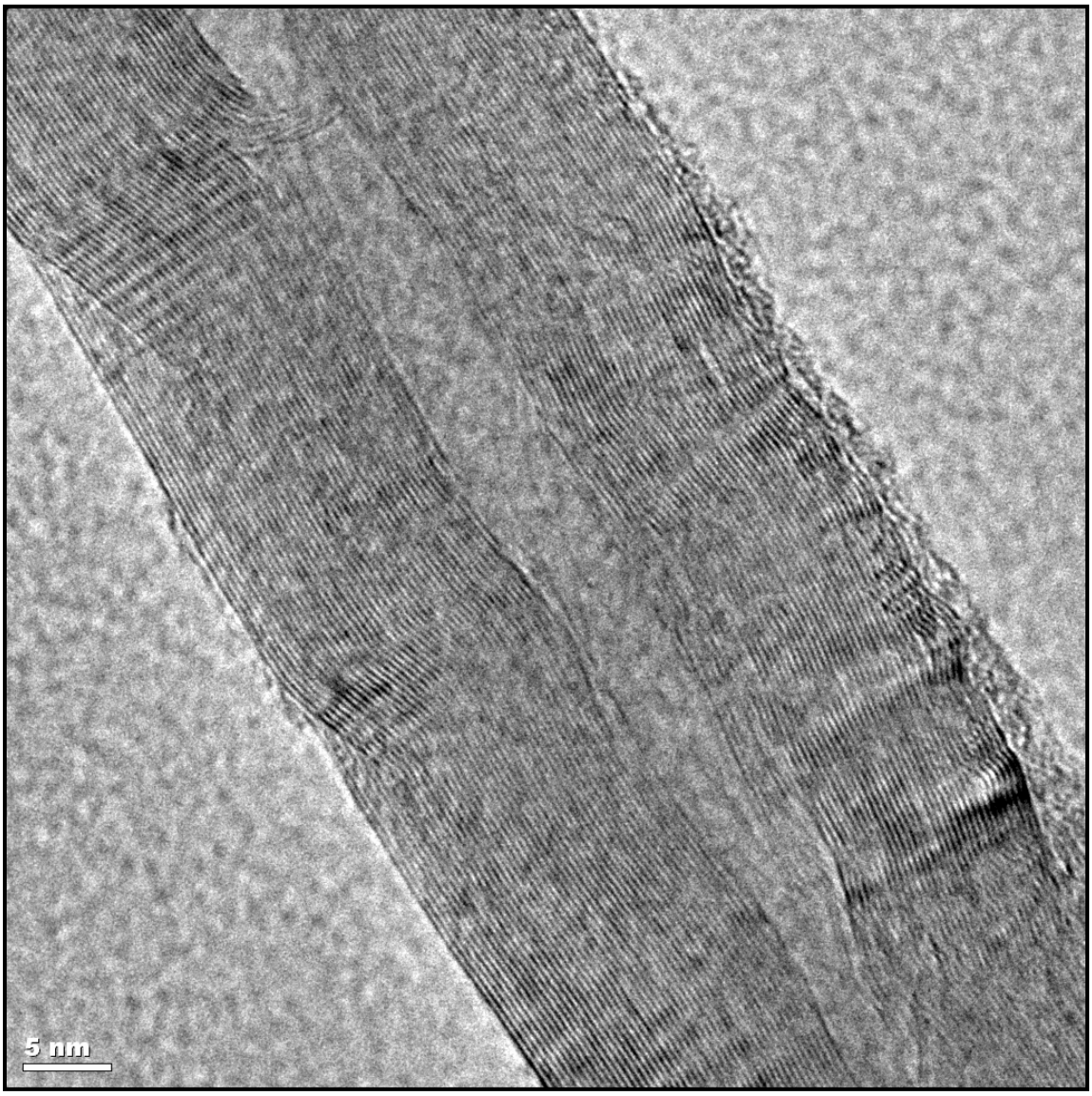

FIGURE 2. TEM picture of an array of Carbon Nanotubes.

FIGURE 3. Image of denture flask and plastic mould used for sample fabrication.

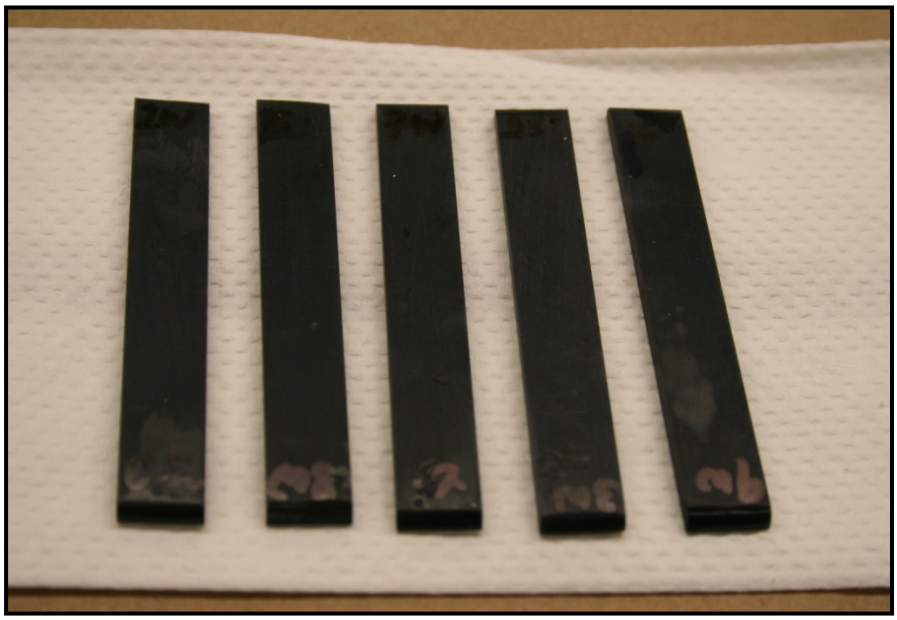

FIGURE 4. Image of experimental samples.

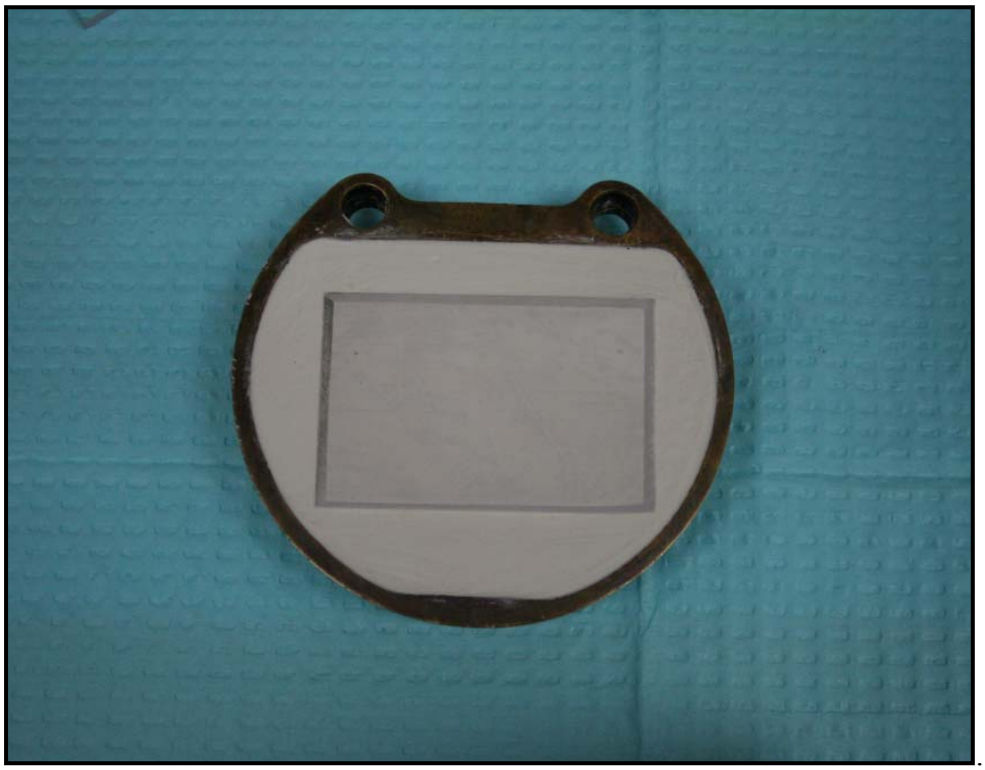

FIGURE 5. Image depicting part of the process of mould fabrication.

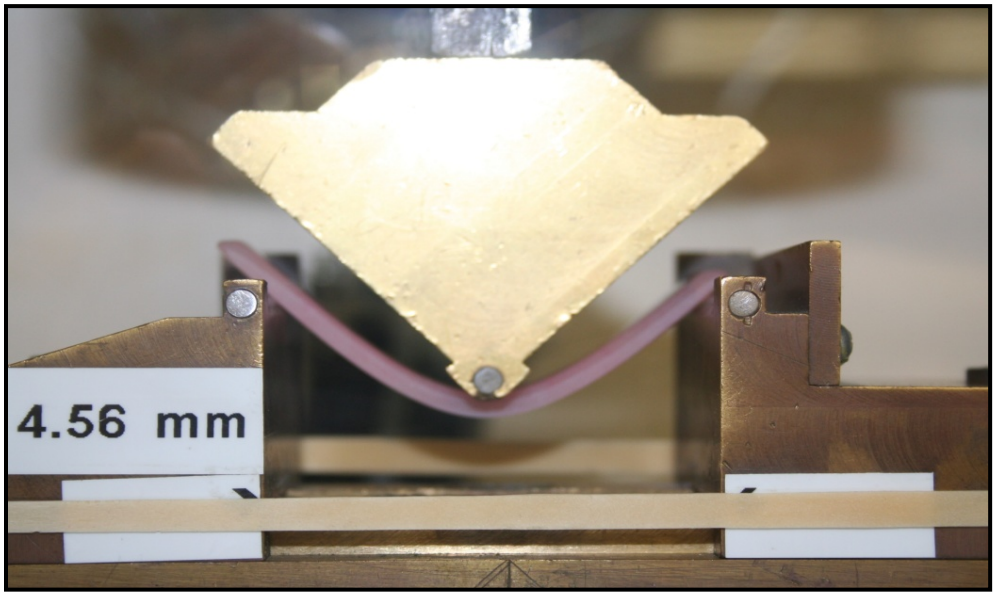

Figure 6. Image of the control samples being tested for flexural strength and modulus.

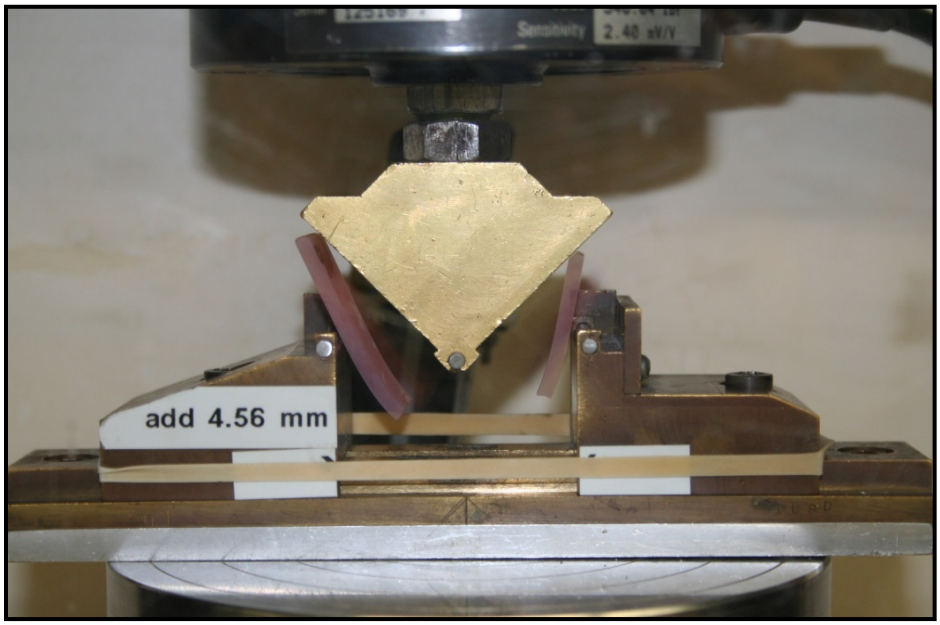

FIGURE 7. Image depicting the breakage of a control sample during flexural strength testing.

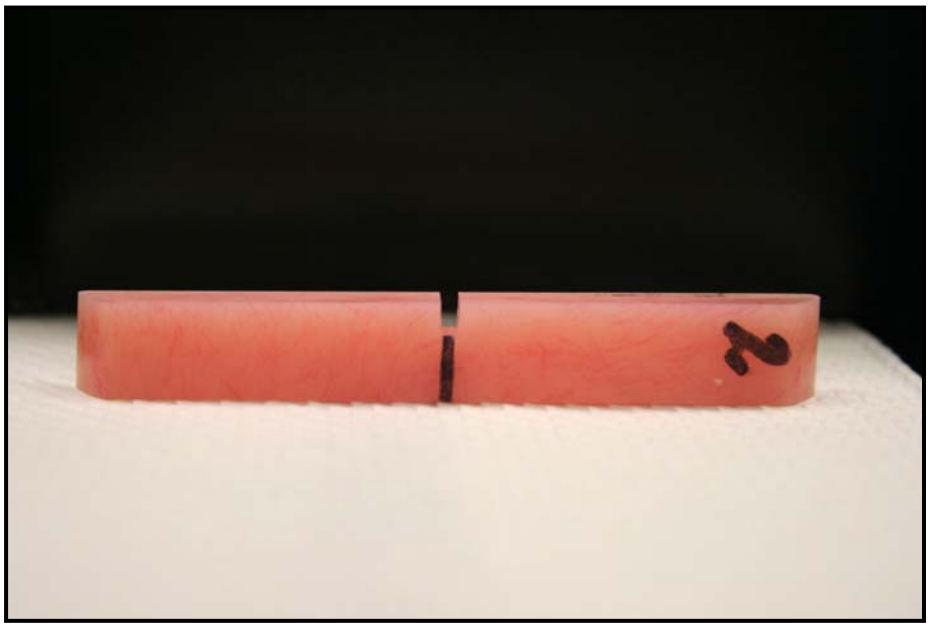

FIGURE 8. Control sample with notch prior to fracture toughness testing.

FIGURE 9. Micrograph taken from Vigolo *et al*[25] showing the exceptional flexibility of carbon nanotube based fiber (15μm radius fiber).

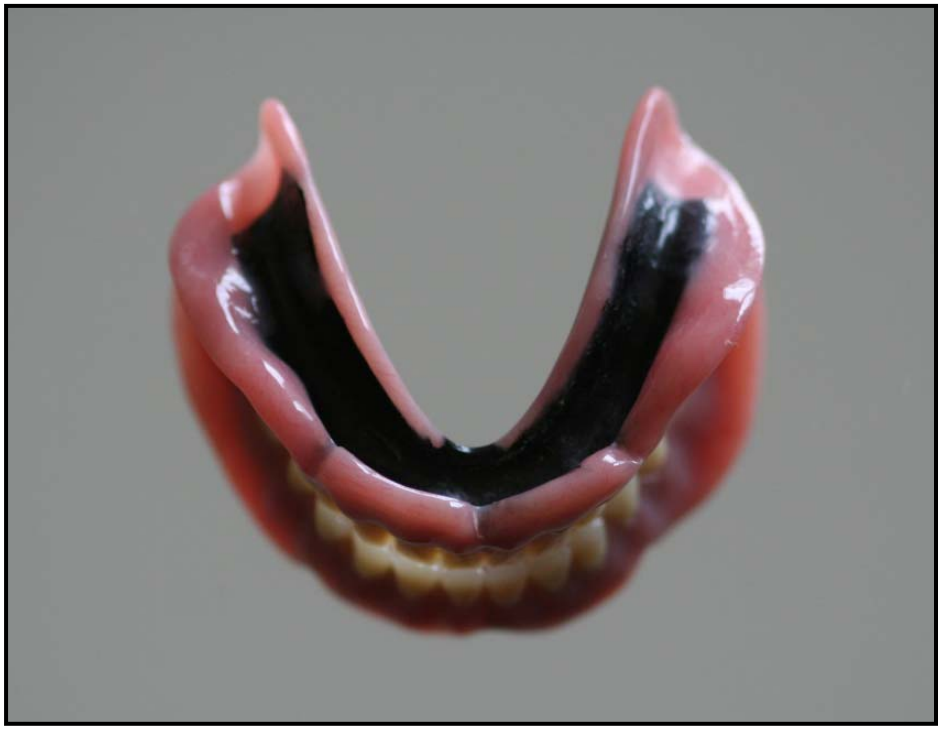

FIGURE 10. Image of proposed method of reinforcement. The reinforced material acts as a substitute for a metal bar.

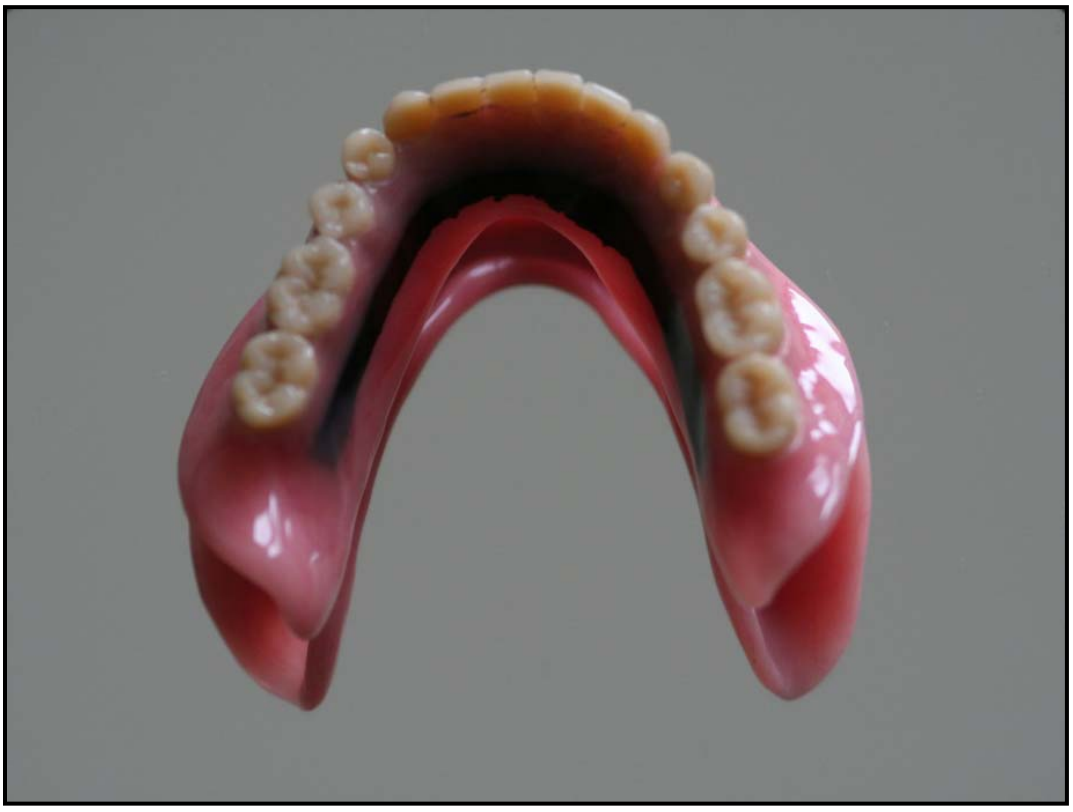

FIGURE 11. Image of proposed method of reinforcement. The reinforced material is placed on weak and non-esthetic areas of the denture.

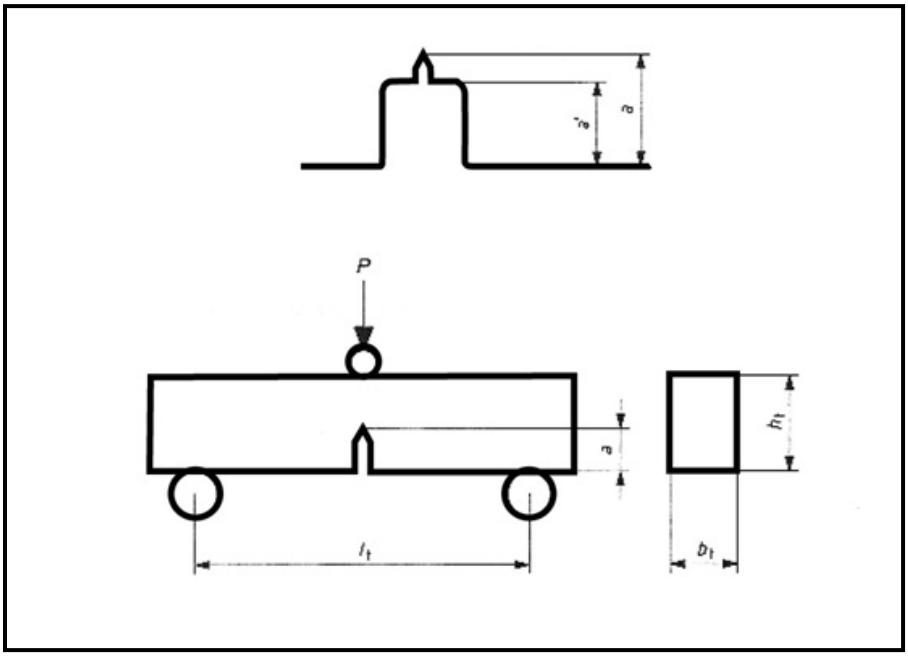

FIGURE 12. Fracture toughness test design.
Image legend:

- a : notch + pre-crack measurement
- a’ : notch measurement
- P: load
- *l*t : distance between supports

DISCUSSION

LUCITONE 199® PMMA: PREVIOUS RESEARCH

The material studied for this research was Lucitone-199®. Previous studies have reported control values of the material for flexural strength, flexural modulus and fracture toughness. Zappini et al[1] and Puri et al[23] reported a control fracture toughness for Lucitone 199® in the range of 2.53 MPa $m^{1/2}$. Fracture toughness is a simpler test to obtain information about the mechanical properties of denture resin; it measures the sensitivity of the material to the presence of sharp notches (crack initiation). Machado et al.[26] reported flexural strength values of 87.12 MPa. Similar values were reported by Meng[27] and Dixon[21]. Hill et al[28] reported Modulus values in the range of 2200 MPa for Lucitone 199®, fracture toughness values of 2.67 MPa $m^{1/2}$ and determined that denture base acrylic adhere to the laws of LEFM sufficiently for K_{ic} to be satisfactorily calculated. Smith et al[29] reported values of Knoop microhardness for Lucitone 199® of 14 (KHN number) and Loh et al[30] reported values of 15.8 for Lucitone 199®. All of the previous values for mechanical properties are in the same range of the ones obtained for the control group in this research for all tests performed (See table I).

PMMA REINFORCEMENT

Acrylic denture resin has been the object of many studies. Several methods of reinforcement have been tried with more or less success. Dentures still fracture at certain weak areas where stress is concentrated due to masticatory forces or due to impacts outside the oral cavity. Factors that contribute to stress concentration enable initiation of

cracks. Most failures occurred in the labial frenum area where a deep notch is located. This has been reported by authors including Darbar[8] and Zappini[1]. The conditions in this study were designed to stimulate clinical conditions. All samples were prepared following manufacturer's instructions and were conditioned for testing according to ISO parameters.

The use of carbon fibers as strengtheners has been investigated in previous studies with success. With the advent of nanotechnology, and with the discovery of CNT's by Ijima[11] in 1991, a new field of study was opened for PMMA reinforcement. The excellent properties of CNTs could replace heavy metal alloys as advocated in previous studies.[5] An array of strengthener materials has been tried over the years. Vourinem et al[22] demonstrated the effect of polyphenylene – based RRP fillers on the flexural properties of denture base polymer. Addition of particulate RRP fillers increased the modulus and surface microhardness, but made no effect or even decreased the flexural strength of the specimens. This unfavorable result is attributed to the adhesion and dispersion of the particulate, the main reason for the similar results in the flexural strength values obtained in this research. Franklin et al[15] used glass flakes to reinforce PMMA. This study showed that fracture toughness was increased in 69% (only property tested). Although glass flakes might offer a way of reinforcement, the use of CNTs may be more promising due to their nano scale size and inherent properties that could increase the strength of a nano-composite in a range of 600% as reported by Ci[31]. Grave et al[32] compared the transverse strength of samples of cross linked acrylic resin with samples containing various percentages of aramid fibers (Kevlar) and reported weaker values

mainly due to adhesion and fiber size. Other products such as glass fibers and metal inserts have been tried with limited success.

FRACTURE TOUGHNESS, FLEXURAL STRENGTH AND MODULUS.

In the fracture toughness test, Lucitone 199® exhibited ductile fracture with an irregular fractured surface, same results as previously reported by Zappini et al[1]. The experimental samples did not enhance nor decrease the values of this particular test compared with the control group. Several factors may influence the values for fracture toughness, including sample geometry and test conditions. Further research is needed to understand the behavior of reinforced materials under tension, even though the values for the control sample in this research are similar to those found in the literature.[28] Marrs et al[5] reinforced PMMA used in bone cement with CNTs. This research obtained values that showed an increase in the mechanical properties of the acrylic. Mean values of 90.6 MPa (12% increase) for flexural strength and 3500 MPa for bending modulus (40 % increase) were recorded when 2 wt% of MWNTs where added. (See table VI).

HARDNESS

The microhardness (compressive test) results of this research are similar to those obtained by Bierbuck et al[33] in which resistance to indentation increased by up to 3.5 times on loading up to 2% SWNTs. Knoop hardness numbers of 14-17 have been reported in the literature[29, 30]. It seems that even with random dispersion, the CNT's increase the strength under compression. (See table V)

CNTs NANOCOMPOSITES PREPARATION AND DISPERSION

A maximum concentration of 0.75 wt% of the material was used in this research for various reasons. Several authors, including Marrs et al[5, 16], Gong et al.[34] and Safadi at al[18] have observed that the best results in concentration of CNTs is around 0.5 wt% and 2.0 wt%, a greater percentage causes agglomeration that result in clump formation and failure. Despite the excellent properties of the CNTs, it was observed that the addition into a matrix for nano-composite formation can be challenging. A key phase of the process is dispersion. Although successful dispersion is possible,[5, 16, 35] it has been proven difficult due to random aggregation and formation of clusters upon mixing. These clusters form areas of deformation that impedes mechanical improvement and can even hamper the acrylic resin inherent properties.[16, 19] Gong[34] improved dispersion and interfacial bonding of nanotubes in epoxy matrix composites with a non-ionic surfactant. He increased the elastic modulus in 30% with the addition of 1wt % of nanotubes.

The Microhardness test may explain the problems regarding dispersion. Values are higher due to the increase in density of the polymer and the compression nature of the test. Microhardness values changed and peaked depending on their location within the matrix. This characteristic of the material can be explained by the study of Ci et al[31] where compressive stress – strain for nanotube composites were evaluated. The CNTs were dispersed randomly and in longitudinal structural formation. It was observed a remarkable increase in both samples, but the arranged array showed the most desirable characteristics. This shows why the PMMA-CNTs matrix does not behave in a desirable fashion under tension due to the random dispersion and distribution of the nanotubes.

Even though that successful dispersion has been achieved with several methods[5, 16, 31, 36] it will certainly involve more complicated procedures and chemical modification.

THERMAL BENEFITS OF CNTS

According to Marrs[5] and Kim[37], the addition to of CNTs to PMMA may also offer thermal benefits due to their high thermal conductivity. MWCNTs may reduce the high temperatures observed at PMMA – bone cement interfaces in the case of bone cement PMMA. Also, the use of MWNTs may help avoid polymerization induced "hot" spots and even reducing curing temperature, hence improving failure rates due to thermal shock during PMMA fabrication. According to Salvelat et al[12], the flexibility of CNTs at room temperature is not due to any plastic deformation but to their strength and to the unique capability of the hexagonal network to distort for relaxing stress.

SUMMARY AND CONCLUSIONS

The data obtained from this study showed that all values obtained for the control group were in the range of acceptance as compared with previous studies. The experimental samples did not reinforce the material in the flexural strength, modulus and fracture toughness. The material did enhance the hardness of the samples tested. The reasons for these results were attributed to a factor that seems to be a key in Poly(methyl methacrylate) composites: dispersion. Even though that the material used is in the nano-scale, its distribution within the matrix alters the characteristics of the acrylic. In the control group, values of 97.74 MPa were recorded for flexural strength; lower values were observed in the experimental groups (80-83 MPa). The experimental samples behaved better under compression were all values were higher than the control group. The values ranged 19-21 in comparison with the control group (16-17 KHN).

The continuation of this pilot research is important due to the promise of this new material, not only as reinforce for PMMA, but also due to its thermal and biological characteristics that makes it unique. With the advancement of the technology and with new procedures it will be possible to produce in the future composites that will be extremely strong and cost-effective.

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ABSTRACT

MECHANICAL PROPERTIES

EVALUATION OF DENTURE BASE PMMA ENHANCED

WITH SINGLE-WALLED CARBON NANOTUBES

By

Kevin Scotti

Recent theoretical and experimental studies, suggest that Carbon nanotubes are 10-100 times higher than the strongest steel at a fraction of the weight. There are two main types of CNTs that can have high structural perfection. Single-walled nanotubes (SWNTs) consist of a single graphite sheet seamlessly wrapped into a cylindrical tube. Multi-walled carbon nanotubes (MWNTs) comprise an array of such nanotubes concentrically nested like rings of a tree trunk.

Denture base acrylics have been reinforced with different materials with limited success. No single reinforced material has showed a great statistical difference in mechanical improvement. The goal of this investigation was to study the effects of Single Walled Carbon Nanotubes reinforcement on the mechanical properties of commercially available denture base PMMA. Denture Base material was reinforced with Single-walled Carbon Nanotubes (SWNTs) at dispersion of 0.25 wt % (group 1), 0.50 wt % (group 2), 0.75 wt % (group 3) and 0.0 wt % (group 4, control). Samples from each group were evaluated for microhardness, flexural strength, flexural modulus, and fracture toughness. The samples were tested in two conditions, as manufactured (dry) and after storing at 37 C for 7 days (wet). Data from four experiments was analyzed by ANOVA. All control sample

values were in the range of acceptance compared with previous studies. Higher values were obtained for the control groups for flexural strength and modulus compared with the experimental samples. ($p < 0.05$) There was no statistical difference regarding fracture toughness between control and experimental groups. A statistical difference was observed in Hardness. The experimental group showed higher values under compression.

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