

Reinforcing Effect of PVDF/MWCNTs Nanofibers on Dental Resin based
Composites

by

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PROJECT REVIEW INFORMATION

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The Project was approved on December 15, 2019 by the following review committee:

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Research Supervisor

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The above review committee determined that the Project is acceptable in form and content and that a satisfactory knowledge of the field was covered by the work submitted. A copy of the Certificate of Approval is available from the School of Graduate and Postdoctoral Studies.

Abstract

In the present study, the restorative composite resin was fabricated by impregnating electro-spun PVDF/MWCNTs nanofiber membrane within the based dental polymer (BisGMA/TEGDMA) using photo-polymerization. The flexural strength (FS) of the base dental polymer resin was significantly improved by the addition of MWCNTs in PVDF electro-spun fabrics (by mass fraction of 0.1 and 0.25 wt%). With respect to the water sorption/solubility analyzing, all nanofiber reinforced dental resin samples showed significantly less W_{sp} values than those for the neat resin samples ($P < 0.05$). On the other hand, the pure PVDF nanofiber reinforced composites had the lowest solubility in water.

KEY WORDS: Dental restorative composites; BisGMA/TEGDMA; Electrospinning; PVDF, MWCNTs

Author's Declaration

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List of Abbreviations and Symbols

PVDF	Polyvinylidene Fluoride
MWCNT	Multi Wall Carbon Nanotubes
Bis-GMA	Bisphenol-A Glycidyl Methacrylate Resin
TEGDMA	Tri-Ethylene Glycol Dimethacrylate
Wsp	Water Sorption
Wsl	Water Solubility
CQ	Camphorquinone
4-EDMAB	

1. Introduction

1.1. Electrospinning process

Over the last hundred years of the progress of the dental material engineering, one of the main issues has been based on improving and producing durable, biocompatible, directly applied restorative dental materials, in particular composites, which can resist to erosive and abrasive oral circumstances. These novel advanced composites are required to have properties of low viscosity for easy applying on the tooth surface and low polymerization shrinkage which ensures good filling adhesion. It would also be preferred to have high mechanical properties such as fracture toughness, surface hardness, low thermal expansion coefficient, and a high aesthetic appearance that fits the teeth. As a result of the efforts mentioned above to provide these properties, polymer composites with silica filled acrylate resins have become known [1]. These recent composites are mostly modified by nanoscale organic particles covalently bonded to an inorganic network. Regarding to the composites as a widely used material, it can be said that there are many natural materials available in nano composite forms consisting of organic and inorganic structures. In consequence, it seems reasonable to apply this concept to reinforce restorative biomaterials, particularly dental composites, by nano-structural modification. From the aspect of composite mechanics, nanofibers as a reinforcing material are more preferable compared to nanoparticles due to providing larger load transfer, also making some toughening mechanisms easier such as fiber bridging and fiber pullout. High strength inorganic fibers show a considerable improvement on the mechanical properties of dental composites [2]. For instance, according to a study in which electrospun Nylon PA6 nanofibers were used to strengthen Bisphenol-A glycidyl methacrylate resin/tri-ethylene glycol dimethacrylate (BIS-GMA/TEGDMA) dental resin in proportion of one to one, the addition of PA 6 nanofibers (5% mass fraction) to the composite resin causes an increase in flexural strength and elastic modulus by 36% and 26% respectively. Interestingly, increasing the mass fraction of nanofibers further than 5% could not make any improvement on the mechanical features of the dental resin. Moreover, under SEM observing, unlike the smooth fracture surface of the neat resin sample which did not include Nylon 6 nanofibers, the roughened fracture pattern of the reinforced resin sample with numerous fracture line and steps have suggested that the crack was deflected by the nanofibers. Considering these findings, it can be concluded that the nanofibers consumed energy and they were aligned along the breaking line [2].

Electrospinning, which is simply applied to and adapted for many different functions, is considered an efficient method for generating long continuous nanofibers from a broad range of materials including composites, polymers and ceramics. By means of a high voltage electrostatic field and a spinneret, the surface of a polymer solution is charged and the ejection of a liquid jet is induced when the field overcomes the surface tension of the polymer drop. As a result of this field, fibers are drawn from the polymer solution by electrostatic forces (Fig.1). Moreover, this electrostatic area adjusts the route of the charged jet [3]. Repulsive forces between the charges which are transferred by the jet generate energy moving against the surface tension. These forces lead to deviating instabilities. As the electric field is intensified, the surface of the solution at the end of the spinneret extends to form a conical body called Taylor cone where a liquid jet begins. The stable jet at the capillary tube becomes unstable under the coulombic attraction as whipping cone formation and stretches through helical loops until it hardens, evaporates or collects on the grounded metal screen such as aluminum [4]. There are various parameters which affect the electrospinning process. These parameters can be categorized as two groups: system parameters such as structure, molecular weight and features of the polymer, such as branched-linear structure, viscosity, surface tension, and process parameters such as electric field potential, flow rate, concentration, distance between the tip of the syringe and the collectors well as environment conditions (temperature, humidity). As the concentration of polymer gets high enough, a polymer entanglement occurs but if it happens too much, the induced polymer motion to the collector is prevented. As charge density and viscosity get higher enough and surface tension decreases, it is expected that the jet is not collapsed. Moreover, the bead density, no matter how centered the polymer is, decreases by decreasing the electric field or increasing the distance between the capillary tip and the collector.

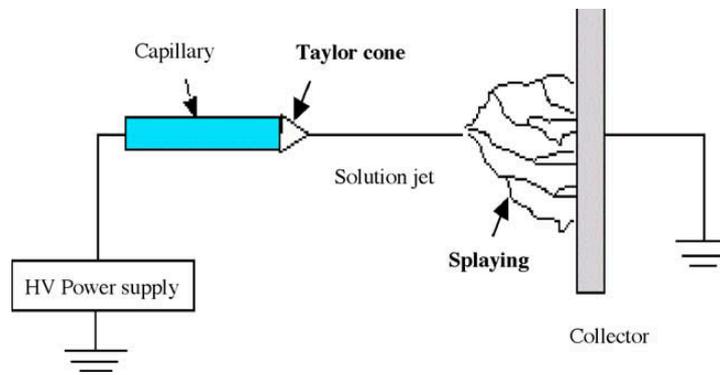


Fig.1. Electrospinning setup [3]

1.2. The properties of Polyvinylidene fluoride (PVDF) required for dental composite applications

The techniques for the reinforcement of dental composites are not recent. Of the reinforcement methods, the adding various fillers to composite resins is the simplest way. There are many fillers, in a great range of materials, that have been tested in a great number of studies, such as calcium phosphates (CaPs), amorphous calcium phosphates (ACP), tetra calcium phosphates (TTCP), dicalcium phosphate anhydrous (DCPA). However, these fillers present some limitations while strengthening the materials that they are incorporated to. Even though Nylon 6, as a nanofiber, has been widely employed to reinforce dental composites in particular Bis-GMA/TEGDMA resins, Nylon 6 can also shrink easily and then reacts with moisture and stain quickly. In current research, it was decided to use polyvinylidene fluoride (PVDF) which is a pure thermoplastic semi-crystalline polymer as a filler particle through dental composites due to its acceptable biocompatibility to the dental hard tissue. Moreover, it has a unique feature of piezo electricity enhancing the migration of cells and stimulating fibroblast activities which is in favor of healing of caries defects[5]. Beside its excellent properties mentioned above, in contrast with other polymers such as PSF (polysulfones), and PES (polyether sulfones), PVDF is relatively more hydrophobic which may make the dental composite fillings resistant to the moisture of oral conditions [6]. Therefore, I also considered this factor when selecting the filler material. Although there are many previous studies that investigated the effects of adding carbon nanotubes on electrospun PVDF nanofibers in terms of thermal, chemical and piezo electric features, PVDF applications to dental composites for reinforcement did not take enough interest among scholars. It was realized there was no evidence based study on reinforced base dental resins where PVDF nano-fibers were modified by carbon nanotubes, a recent popular technique.

1.3. The composite nanofibers with carbon nanotubes

The literature review about the production of nanofibers showed that the electrospinning was a very simple and adaptable procedure for producing ultra-thin fibers from broadly varying materials. In addition, electrospun continuous nanofibers outweigh the discontinuous fibers in terms of cost, mechanical property e.g. [7]. The reinforcement procedures require nanofibers

to be in well-controlled orientation, size and other target features [3]. The next generation of nano-composites with the superior mechanical performance would be produced by the use of carbon nanotubes. Carbon nanotubes (CNTs) are likely the toughest material that will ever exist with a tensile strength greater than steel, but only one sixth the weight of the steel. Of their superb mechanical features, high aspect ratio (length to diameter ratio l/d) provides the nanotubes with an additional advantage over spherical fillers to obtain high property composites [8]. Carbon nanotubes present some drawbacks such as the difficulty of their alignment in the matrices due to the anisotropic structure or their inability of bonding to the matrices as a consequence of having nonreactive graphite surface. Nevertheless, the addition of CNTs into the reinforcement process of dental resins causes an improvement on the mechanical features and biocompatibility by hindering crazing extension and reducing stress as seen in Fig 2.

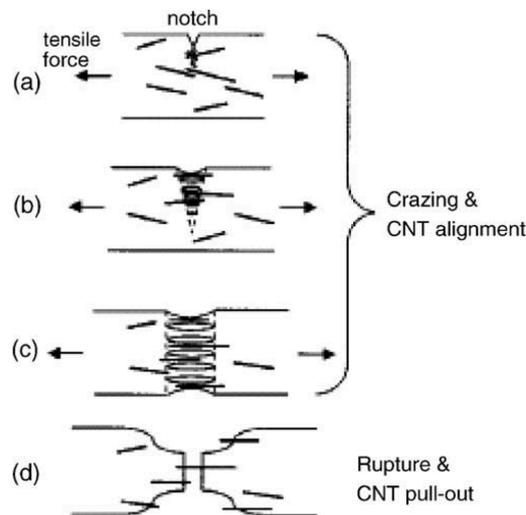


Fig. 2. Schematic illustration of the crazing and rupture of a matrix/CNTs composite fiber [9]

In short, nanotubes are prone to agglomeration which makes their homogeneous scattering in hosting polymer matrices difficult and due to their smooth surface, the formation of the adhesion forces between carbon nanotubes and dental resin composites is prevented. There have been some attempts to improve the dispersion of CNTs such as, solution casting, ball milling, stir-extrusion, sonication (ultrasonic vibration), surfactants treatment and chemical modification. For instance, by means of coating with nano-SiO which is modified, carbon-nanotubes were well dispersed [10,11,12]. Ultrasonication is a functional technique to disperse CNTs in liquids with low viscosity, such as water, acetone and ethanol. If the polymer to get used is either in a solid or viscous liquid state, it should be dissolved or diluted by a solvent before dispersion of CNTs [11]. Besides the methods used to uniformly disperse CNTs, the functionalization of carbon nanotubes is required to modify their surface properties and the interac-

tions between the nanotubes and the polymer. As a result, the inert nature of CNTs with van der Waals interactions leads to an inefficient load transfer across the CNT/matrix interface. These methods can be categorized as chemical functionalizations (covalent method) and physical adsorption (non-covalent method). The main purpose of the surface modification is to provide useful functional groups onto the CNT surface hence the hydrophobic nature of CNT's would change to hydrophilic one. Even though chemical methods using covalent linkages have disadvantages such as the formation of a large number of defects on the CNT sidewalls and the usage of concentrated acids and oxidants considered environmentally unfriendly. They are widely applied to the CNTs in a simple manner and allow the production of prefabricated nano materials. As a result, non-covalent functionalization methods, lower the surface tension of CNT and overcome the van der Waals attraction by electrostatic forces [13].

In order to optimize the handling process of Bis-GMA, which is the most commonly used monomer in the manufacturing of dental composites, TEGDMA is added to dilute the viscosity of resins. Bis-GMA has an importance in terms of reducing volumetric shrinkage preventing the marginal leakage of the dental restoration [10]. As composites are subjected to great loads, huge stress could be distributed by the interaction between nanofibers and dental composites. The electrospun nanofibers frequently used in dental applications also decrease polymerization shrinkage which means they are ideal reinforcing materials. According to the results of a previous study, an addition of hydroxyapatite (HAp) nanofibres with various loading content to some extent would contribute to an increase on biaxial flexural strength of corresponding dental composites. The mass fraction of nanofibers in dental composites has a crucial role affecting the mechanical properties. Incorporating small loading rate of electrospun nanofibers into the dental resins remarkably improved the mechanical properties and the percolation threshold which indicates the critical mass fraction, needs to be around 10%. For instance, compared to unfilled dental resins, the dental resins including HAp nanofibers (10 wt% mass fraction) showed a rise of 22.2% in terms of biaxial flexural strength. Nevertheless, this conclusion would be valid only when the loading content does not exceed a certain point. For example, in this study, after loading with the nanofibers at 40wt%, the biaxial flexural strength was reduced by roughly 60%. Consequently, in case of a uniform dispersion and a certain loading content, generally not too high, it would be expected reinforced dental resin composites to have high mechanical performance [10,14].

1.4. Water sorption (Wsp) and Solubility (Wsl) as a Parameter for the Longevity of Dental Composite Restorations.

Restorative dental composites are constantly subjected to aqueous oral conditions. For this reason dental composite resins may excessively absorb fluids which may lead to detrimental effects on the mechanical and the physical features and subsequently a shortened service life

of dental restoration. Thus two main parameters have become more important when the long term mechanical performance and cytotoxicity of dental composite resins in moist oral conditions are evaluated: Water sorption (Wsp) and solubility (Wsl) [15]. The chemical composition of the resin monomers are responsible for the water sorption of dental composites. Having polar groups makes the monomers hydrophilic through causing them be attracted to water molecules [16]. Some previous studies indicated that diluent monomer such as TEGDMA allows the high amounts of water intaking due to large available gaps between the polymer chains [17].

1.5. Objectives

In consequence, as mentioned above, electrospun nanofibers have been successfully and widely applied to the dental resin composites for along time. Even though there are limited researching studies about their application to strengthen methacrylate resins in dentistry, carbon nanotubes recently have become popular materials. Hence, the purpose of this study was to determine the reinforcing effect of polyvinylidene fluoride nanofibers with multi walled carbon nanotubes in varying mass fractions (0, 0.1, 0.25, 0.5 and 1%) on the flexural strength of BisGMA/TEGDMA dental resin. The fabrication of nanofibers was implemented by electrospinning. Additionally, these strengthening configurations were analyzed whether they had a significant effect on water sorption and solubility of the resin material for its long term clinical success. The hypothesis investigated were twofold: (1) the flexural strength of the nanofiber reinforced resin would rise as MWCNT's content increases; while (2) nano composite fibers containing carbon nanotubes would present lower Wsp and Wsl values compared to the neat Bis-GMA/TEGDMA resin.

2. Research Procedures and Methods

2.1. Materials

Bisphenol-A glycidyl methacrylate resin (Bis-GMA), tri-ethylene glycol dimethacrylate (TEGDMA, diluter) were bought as mixed form (50:50) from Esstech Inc (Essington, PA 19029, USA). In addition, this research utilized Camphorquinone (CQ, photo-initiator) Ethyl 4-dimethylamino benzoate (4-EDMAB, photo-initiator), PVDF polymer and Dimethylformamide (DMF), carboxylic acid functionalized multi walled carbon nanotubes (MWCNT) with 1-2 nm diameters and 1-2 micron length in high purity form (>90%) which were purchased from Aldrich Chemical Co (Sigma, Germany).

2.2. Electrospinnig of PVDF and PVDF/MWCNT Nanofibers

The preparation of PVDF/MWCNT fibers by electrospinning technique was carried out according to the previous methods [9]. Firstly, the electro spinning polymer solution was obtained as a mixture in which PVDF polymer pellets (26wt % of mass fraction in the solution)

were added into DMF solution in a glass beaker. This mixture was stirred on a hot plate magnetic stirrer at 70°C for 2 hours until no pellets remained undissolved. Secondly, MWCNTs were added into the PVDF-DMF solution by changing mass fraction 0.1%, 0.25%, 0.5%, 1% respectively [18]. After this step, MWCNTs were allowed to disperse ultrasonically (ultrasonication) in this final viscous suspension. Subsequently, this solution was placed into a 5 mL plastic syringe that has a capillary tip, and then this syringe was inserted into a programmable syringe pump for the controlled flow rate of the solution. Then, an electrical field between the needle and the collector was provided with a high voltage power supply to generate nanofibers. The polymer solution was connected to the positive electrode through a copper wire and a grounded aluminium foil as a collector was perpendicularly located in front of the needle. According to the review of literature, parameters for the electrospinning set-up were determined as follows: a voltage of 27 kV, a tip-collector distance of 16 cm, a mass flow rate of solutions at a speed of 2.0 mL/h [18, 19]. Despite the fact that the parameters of electrospinning mentioned above were made clear after the literature review, the final optimal settings were determined by means of trial and error. All non-woven fabric mats were prepared by one hour electro spinning process in the same set-up and gathered on a drum collector at 1500 rpm mandrel rotation to obtain uniform and aligned fiber sheets as shown in Fig. 3.

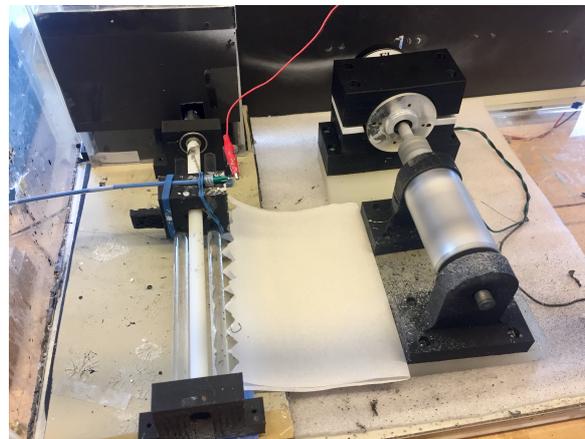


Fig. 3. The electrospinning process

2.3. Preparation of PVDF and PVDF/MWCNT Reinforced BisGMA/TEGDMA Composites

The composite resin samples were prepared following the process described in a previous study [20]. Dental resin matrix which contained monomers (Bis-GMA/TEGDMA, 49.5/49.5, wt%) and initiators (CQ/4-EDMAB, 0.5/0.5, wt%) were uniformly mixed via a magnetic stirrer for 24 hours until a homogeneous resin polymer was obtained. Then the silicon rubber molds were prepared to fabricate rectangular bar shaped composites (25mm x 2mm x 2mm) (Fig. 4a/b).

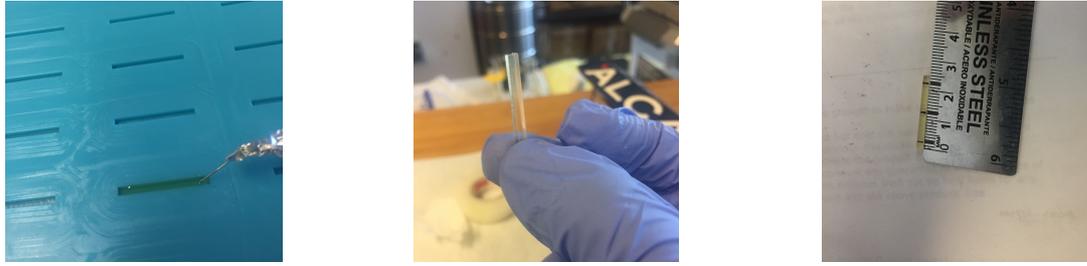


Fig.4. (a) Silicon rubber mold **(b)** Bar shaped neat resin sample **(c)** Markings on samples to locate

The electrospun nanofiber fabrics with various mass fractions of PVDF/MWCNTs nano composites (0.1%, 0.25%, 0.5%, 1%) and PVDF nanofibers without CNTs were stored in petri dishes for one week to remove the solvent then fabric stripes which are 25 mm long and 2 mm wide were cut from the peeled mat (Fig. 5). The thickness of each piece was measured by a digital caliber and recorded as about 60 μ m, and the weight of each fabric strip was measured on a digital balance and it was confirmed whether each piece represented the mass fraction 5% of nanofibers in the composite resin. Then all strips were immersed in the previously activated monomer mixture (BisGMA/TEGDMA-CQ/4-EDMAB) overnight and they were swollen while eliminating air bubbles by ultrasonic vibration. In the manufacturing of specimens for the 3 points bending test, one layer of PVDF/MWCNTs fabric impregnated with the dental resin was placed through the bottom of rubber mold followed by a top resin increment as seen in Fig. 7. Later glass slides were used to cover top of the mold and remove the excessive resin and the bubbles. The samples were photo cured for 1 minute using a light curing unit purchased from Guilin Woodpecker Medical Instrument Co,Ltd/China. The supporting and the loading points of samples were marked by a fine point tip permanent marker in order to correctly locate them on the sample holder (Fig. 4c). As a result, six test groups were categorized according to the composition rate of reinforcement materials as follows in Table 1.

Table 1-Test Groups			
Contents	Dental base resin	Nanofiber (at mass fraction in resin)	Carbon nanotubes (at mass fraction in nanofiber)
Group 1 (as control)	BisGMA/TEGDMA	-	-
Group 2	BisGMA/TEGDMA	PVDF (5 wt%)	-
Group 3	BisGMA/TEGDMA	PVDF (5 wt%)	MWCNTs 0.1 wt%
Group 4	BisGMA/TEGDMA	PVDF (5 wt%)	MWCNTs 0.25 wt%
Group 5	BisGMA/TEGDMA	PVDF (5 wt%)	MWCNTs 0.5 wt%
Group 6	BisGMA/TEGDMA	PVDF (5 wt%)	MWCNTs 1 wt%

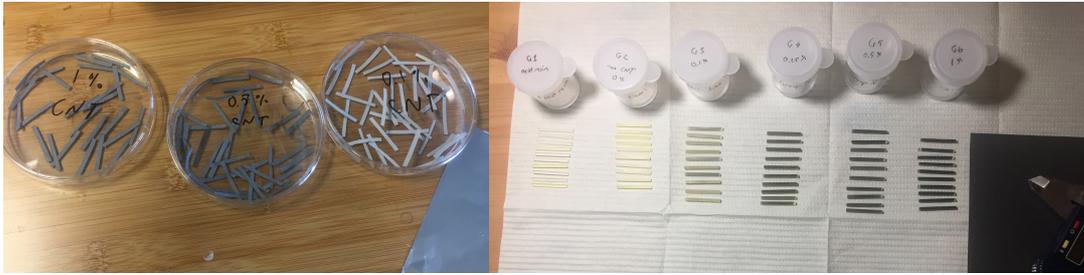


Fig.5. The stripped nanofiber fabrics with various loading rates of CNTs and all specimens for each group.

In regards to the preparation of specimens for water sorption (Wsp) and water solubility (Wsl) analyzing, they were produced the same as those done for 3 point bending test. A circular silicon rubber molds with an internal diameter of 15 mm and a height of 1 mm were prepared. Then the circular shaped pieces were carefully cut from the electrospun nanofiber fabric to fit the rubber mold. These circular fabrics were immersed in uncured dental resin then placed into the molds. After a top resin was incremented over the fabric, the activated resin-fabric complex was cured by 90 second photo-polymerization for each side (Fig. 6).

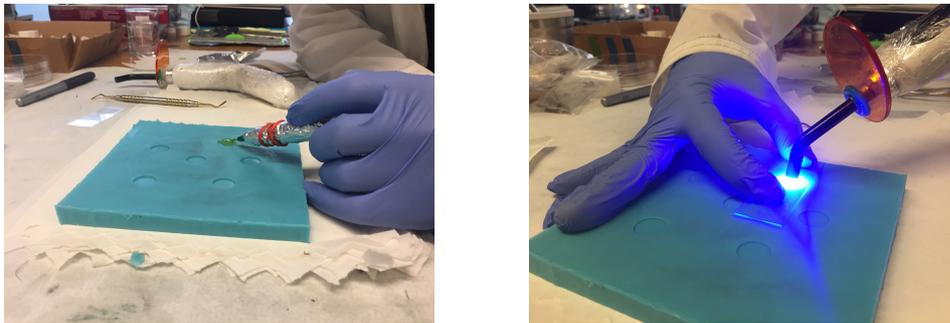


Fig.6. The preparation of composite resin samples for the water sorption and the water solubility analysis

2.4. Testing Methods and Measurements

Flexural strength (F_s) values of the composite samples were measured using a standard 3-points bending test method previously conducted in other research [20, 21]. Flexural strength and elastic modulus were measured using rectangle specimens (25mm x 2mm x 2 mm) produced in rubber molds according to ISO 4049, 9917. All specimens were polished by sand paper with a grit no:1500 and stored in distilled water at 37 C for 24 hours before testing. The bar shaped specimens were fractured in a three-point bonding jig on a computer-controlled Universal Testing Machine (Lloyd LS 100 Plus, Ametek, West Sussex, UK) according to the following specifications: 20 mm of span distance, 0.75 mm/min of crosshead speed, specimen no, n=8 (Fig. 7). The calculations for F_s were made using the following formula:

$$FS = 3PL/2WT^2$$

Where P is the load at fracture, L is the distance between two supports which was set to be 20 mm. W is width of the specimen, and T is the thickness of the specimen, in millimeters at load P .

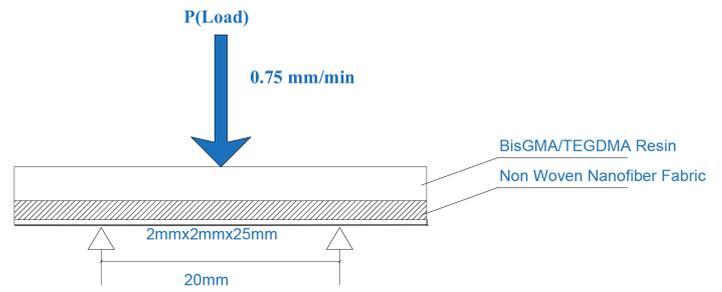
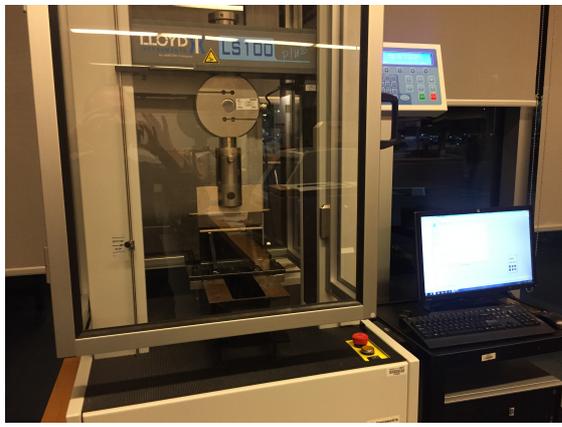


Fig.7 The universal test machine with a loading cell for 3-points bonding test and schematic drawing of 3-point bending test used in this research. The one thin nanofiber strip inside the specimen and located at the bottom (the shadowed area) represents BisGMA/TEGDMA impregnated electrospun PVDF or PVDF/MWCNTs fabric and the area surrounding the fabric strip represents pure BisGMA/TEGDMA resin.

The measurements of water sorption and solubility were conducted with six specimens for each group (n=6), as seen in Fig. 8, according to the some previous studies [22-24]. These light cured samples were stored in dry and dark conditions for 24 h and then placed to a desiccator at 37 ± 1 °C and then weighed through a digital precise balance. These procedures were repeated until the constant mass, **m1** was recorded (with no more than a ± 0.0001 g variation). After drying process, these samples were then immersed in distilled water at 37 ± 1 °C for one week and during this period at certain intervals they were removed, blotted dry and the weight recordings were taken. At the end of the seven day period, the constant value for each sample was recorded as **m2**. Afterwards, the samples were reconditioned at 60 °C until obtaining a constant dry mass as same as described for **m3** was obtained. All of the weight was measured by a digital balance (Mettler Toledo, Columbus OH). The formulation of the percentages of water sorption and solubility were expressed as follows.

$$W_{sp} (\%) = 100 \times ((m_2 - m_1) / m_1)$$

$$W_{sl} (\%) = 100 \times ((m_1 - m_3) / m_1)$$

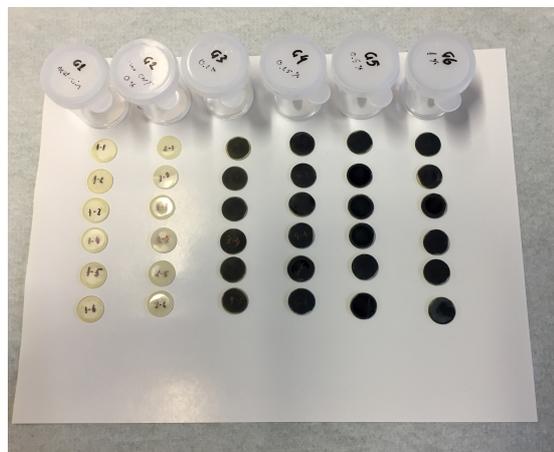


Fig.8 The disc shaped samples for the evaluation of water sorption and solubility.

2.5. Characterization of Nanofiber Structures and Fracture Modes

The optical microscope images (VHX-7000 Series Keyence, Osaka, Japan) were taken from nanofiber fabric samples for each group for the initial characterization. After conducting the three point bending test, the groups representing the highest and the lowest averages were determined, then a scanning electron microscope (SEM, FlexSEM 1000, Hitachi, Fukuoka, Japan) was used to observe the nanofiber structure of fabric samples from these groups and the fracture origins (e.g. air bubbles, nanofiber distributions, CNT agglomerates) and patterns (e.g. fracture or pullout of nanofibers). Prior to SEM imaging, in order to allow for better electrical conduction, a thin layer (~5 nm) of gold coating was applied on these samples.

2.6. Statistical Analysis

The results obtained from the tests were subjected to a statistical analyzing at significance level P of 0.05 by software SPSS 20.0 (SPSS Inc., Chicago IL, 2018). Subsequent multiple comparisons were conducted using a post hoc analysis. In this regard, firstly all tests were sorted out in each group based on variable factor. Then Single Factor Anova was applied to determine whether the means of each group were significantly different or not. As per this analysis if the P value is less than control alpha value 0.05 then to identify significance between the groups, Tukey's HSD and Games-Howell post hoc tests were applied on pair combination of all group times. In regards to the post hoc analyzing, before deciding which test to be applied, it was considered the homogeneity of variances in all groups. Tukey HSD was preferred to analyze the groups which had equal standard deviations whereas Games-Howell testing was conducted for the groups showing no variance homogeneity. In present study, Tukey HSD was employed for the parameters of flexural strength (Fs) and water sorption (Wsp) while Games-Howell test was used to analyze the water solubility values (Wsl).

3. Results

3.1. SEM Morphological Characterizations of PVDF/MWCNTs Nanofibers

The electrospun PVDF nanofibers prepared in this study had diameters ranging from 600 to 1100 nm. Through a backscattered polarized light, different interference colours helped us to detect any change in diameter size of nanofibers. The SEM images in Fig. 9a/b show the morphology and the distribution of electrospun fibers. Although the fibers seemed completely uniform, there was a deviation in the diameter of nanofibers varying within several hundred nanometers. On the other hand, generally nanofibers showed very smooth form without beads. In spite of using drum-type collector at high speed (1500 rpm), the distribution of PVDF and PVDF/MWCNTs nanofibers had a random alignment. In Fig. 9b/11b, it was noticed that there was less uniformity and continuity throughout the fibers in terms of form and diameter as the concentration of MWCNTs in PVDF polymer was increased more than 0.5

wt%. Moreover, under a magnification of 10,000 times, the nanofibers including 1 wt% of carbon nanotubes with a large diameter relative to the others had a more roughness over the fiber surface as seen inside the blue circle (Fig. 10b) while the fibers with a trace amount of CNTs (0.1 and 0.25 wt%) showed a more uniform and smooth contour (Fig. 10a). Apart from these findings the light microscope imaging showed the manner how MWCNTs were arranged throughout the PVDF fibers: the distribution of MWCNTs with 0.1 wt% of loading rate seemed to lead to small changes on the morphology and the diameter of nanofibers (Fig. 11a) whereas the alignment of MWCNTs having 1 wt% of mass fraction caused to damage to the uniformity of fiber outline (Fig. 11b). The comparison of the fractured surfaces between the neat resin (as control) and the nanofiber reinforced composite resin was made by observing the SEM images (Fig.12/13). The broken surface of the resin sample with PVDF/MWCNTs (0.25 wt%) showed significant roughness while the fractured surface of neat resin was very smooth along with straight lines as seen in Fig. 13a and b respectively . The rough fractured surface had at the same time holes and protrusive segments of broken fibers in Fig 13b. In particular, these defects comprised of mostly holes and occasionally grooves might have been caused by the fibers fractured or pulled out.

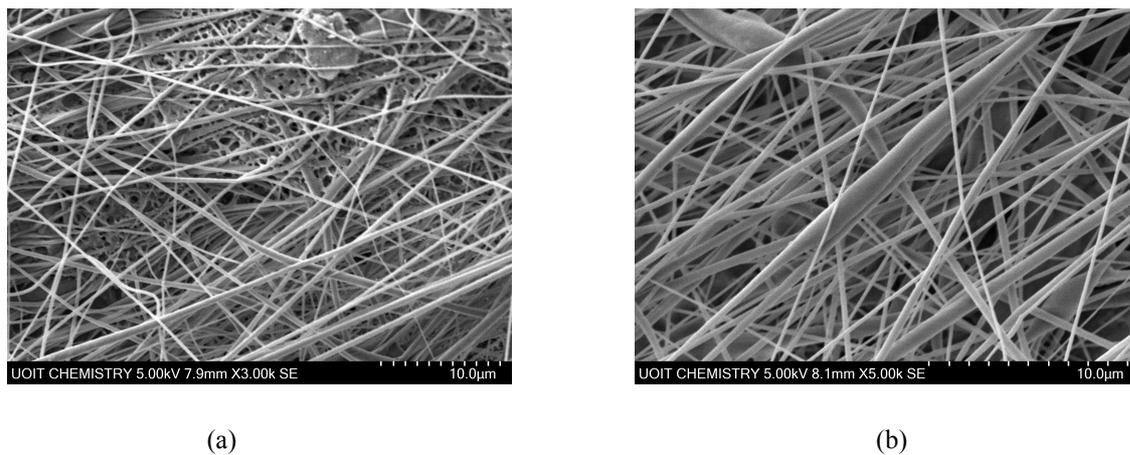


Fig.9. (a) The SEM images of PVDF (non-carbon nanotubes) and (b) PVDF/MWCNTs (1wt %) nanofibers.

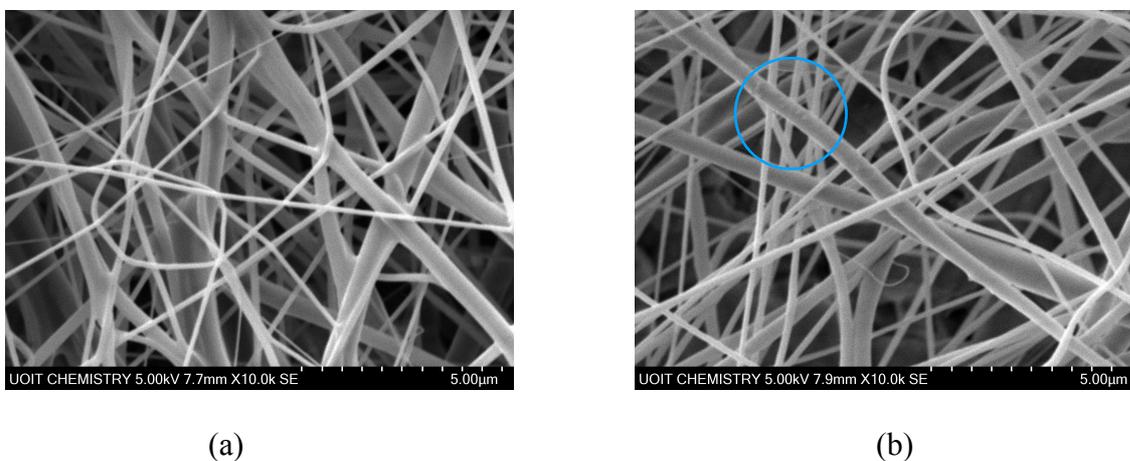
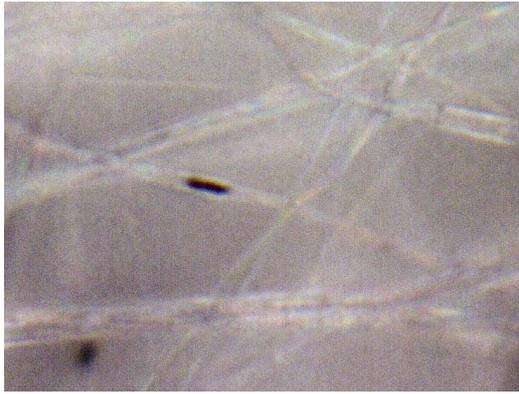
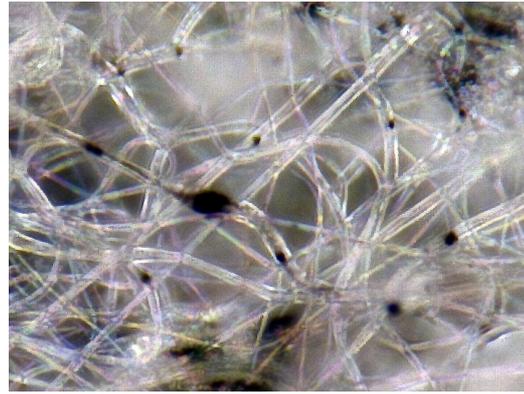


Fig.10. The SEM images of PVDF/MWCNTs (0.25wt %) with magnification of 10,000 times (a). The SEM image of PVDF/MWCNTs (1wt%) at the same magnification level (b).

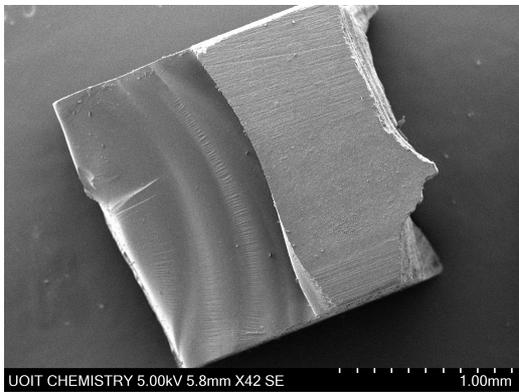


(a)

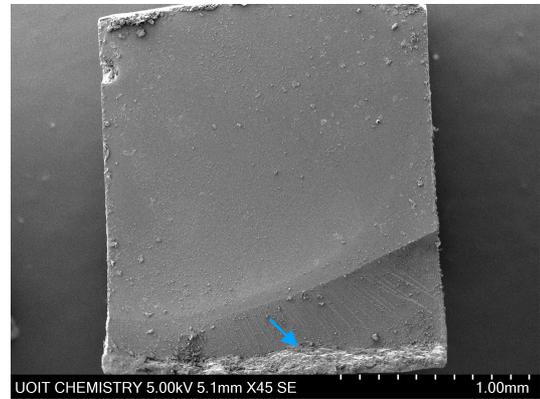


(b)

Fig.11. The images from the light microscope: the PVDF/MCNTs (0.1 wt%) nanofiber reinforced resin (a) and the PVDF/MCNTs (1 wt%) (b)

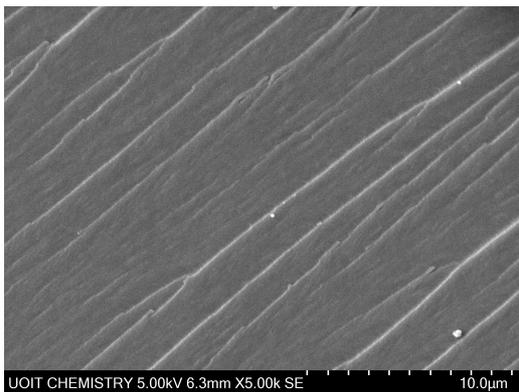


(a)

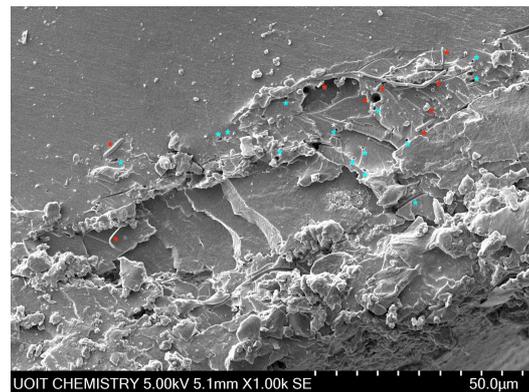


(b)

Fig.12. The SEM images of fractured surface of the bar shaped resin samples for the control group (neat Bis-GMA resin) (a) and the group with PVDF/MWCNTs (0.25 wt%) (b) respectively. In Fig.12 b, the nanofiber concentrated area pointed by the blue arrow is located at the bottom side of the sample.



(a)



(b)

Fig.13. The SEM images of fracture surfaces of representative 3 point bending samples: neat resin without nanofibers (a) and composite resin with one layer of nanofiber fabrics from the group 4 (image taken at the border between fiber concentrated area and the neat resin) (b). As shown in Fig.13 b, the asterisk * and * represent holes and broken fibers respectively.

3.2. Mechanical properties of PVDF/MWCNT Nanofiber Reinforced Dental Composites

The flexural strength (Fs) of Bis-GMA/TEGDMA dental resins containing 5% of PVDF nanofibers with various loading rate of MCNTs were tested and the results are shown in Table 2. Each layer of fabric was equivalent to 5 % of the total weight of neat resin sample which was used as the control group. After conducting the 3-points bending test, the obtained data in the bar chart provides the mean values of eight measurements with standard deviation that are represented by error bars (Fig. 14). The results of flexural strength values (Fs) were shown in Table 2. Compared with the control group, nearly all of the nanofiber reinforced groups had comparable Fs values ($P>0.05$), except for the group III and IV, which had significantly higher Fs than that for the group I ($P<0.05$) via the impregnating and embedding of small contents of PVDF/MWCNTs nanofibers into the dental resin matrix as layer fabric. The Fs of the unfilled resin (mean \pm standard deviation, n=8) were (102.3 \pm 6.8) MPa. For the PVDF nanofiber without MWCNTs reinforced composite, the Fs increased to (111.1 \pm 10.5) MPa. When the 0.1% loading rate of MWCNTs were included to the PVDF nanofiber, the flexural strength was (118.6 \pm 10.2) MPa which corresponded to an increase by 16.3 MPa which was almost twice as much as those obtained for Group II (8.8 MPa). In the Group IV which 0.25 % mass fraction of CNTs were added in, the Fs value reached to the highest point among the all groups by 123.4 \pm 12.2 MPa. However, continuously increasing the MWCNTs' mass fraction to 0.5 % did not further make an improvement on the mechanical properties of the composite resin. On the contrary, there were a decrease for both group V and VI with 0.5 and 1 % of carbon nanotube loading rates respectively as shown Fig. 14. The samples prepared for the group 5 in which 0.5 % MWCNT were added, the Fs (mean \pm standard deviation, n=8) was 114.5 \pm 8.7 MPa. Lastly, in the group VI which had the highest content of MWCNTs through 1% in mass fraction, the Fs was 112.9 which is nearly same as that for the Group II (non MWCNT).

Table 2 - Flexural strength of the fiber-reinforced resin composites

MWCNT incorporation	Fs (Mean \pm SD in MPa)
Group 1 (neat resin) as control	102.3 (\pm 6.8) ^a
Group 2 (PVDF nonMWCNT)	111.1 (\pm 10.5) ^{ab}
Group 3 (PVDF/MWCNT 0.1 wt%)	118.6 (\pm 10.2) ^b
Group 4 (PVDF/MWCNT 0.25 wt%)	123.4 (\pm 12.2) ^b
Group 5 (PVDF/MWCNT 0.5 wt%)	114.5 (\pm 8.7) ^{ab}
Group 6 (PVDF/MWCNT 1 wt%)	112.9 (\pm 11.6) ^{ab}

^a Lower case letters indicate statistical differences with a column (Tukey's test, P=0.05)

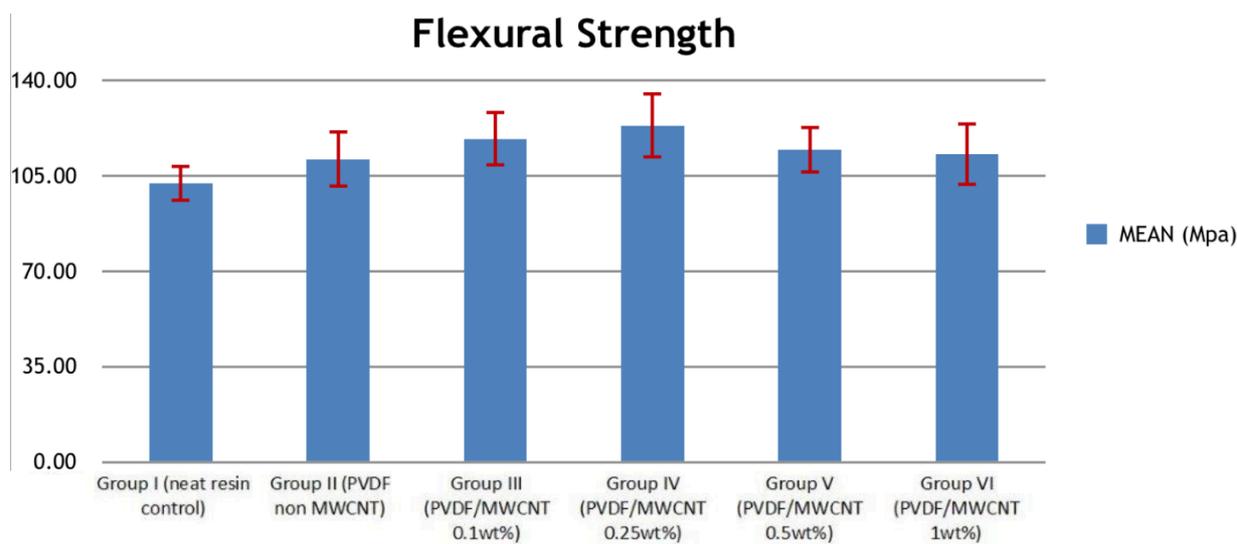


Fig. 14. Mean and standard deviations for flexural strength (MPa) determined by the mass fraction of MWCNT

3.3. Evaluation of Nanofiber Content on Water Sorption and Water Solubility

The results of water sorption and water solubility are shown in Table 2. Group I in which the pure BisGMA/TEGDMA dental resin were used showed the highest values of W_{sp} % (2.56) while in Group IV with the 0.25wt% of MWCNTs incorporation, the lowest value was observed by 2.28 % (± 0.12). On the other hand, the median values of Group II and V were close to each other by 2.37 and 2.36 respectively, and at the same time in Group III and VI, the average water sorption values were identical (2.30%). Interestingly water solubility trends showed different patterns apart from water sorption as seen in Fig. 15, the group II with PVDF nanofibers (non MWCNTs) which had the lowest solubility (0.13% \pm 0.6) was followed by the neat BisGMA/TEGDMA resin (0.22% \pm 0.08). The Groups with PVDF/MVCNTs nano composite fibres had high solubility rates relative to the Groups with no carbon nanotubes.

Table 3 - Water sorption (W_{sp}) and water solubility (W_{sl}) after 7 days in the water (Mean \pm standard deviation)

Groups with contents	W _{sp} (%)	W _{sl} (%)
Group 1 (neat resin)	2.56 (± 0.04) ^a	0.22 (± 0.08) ^{ab}
Group 2 (PVDF nonMWCNT)	2.37 (± 0.10) ^b	0.13 (± 0.06) ^a
Group 3 (PVDF/MWCNT 0.1 wt%)	2.30 (± 0.12) ^b	0.29 (± 0.09) ^b
Group 4 (PVDF/MWCNT 0.25 wt%)	2.28 (± 0.12) ^b	0.33 (± 0.10) ^b
Group 5 (PVDF/MWCNT 0.5 wt%)	2.36 (± 0.07) ^b	0.27 (± 0.04) ^b
Group 6 (PVDF/MWCNT 1 wt%)	2.31 (± 0.15) ^b	0.29 (± 0.19) ^{ab}

^a Lower case letters indicate statistical differences with a column (Tukey's test, P=0.05)

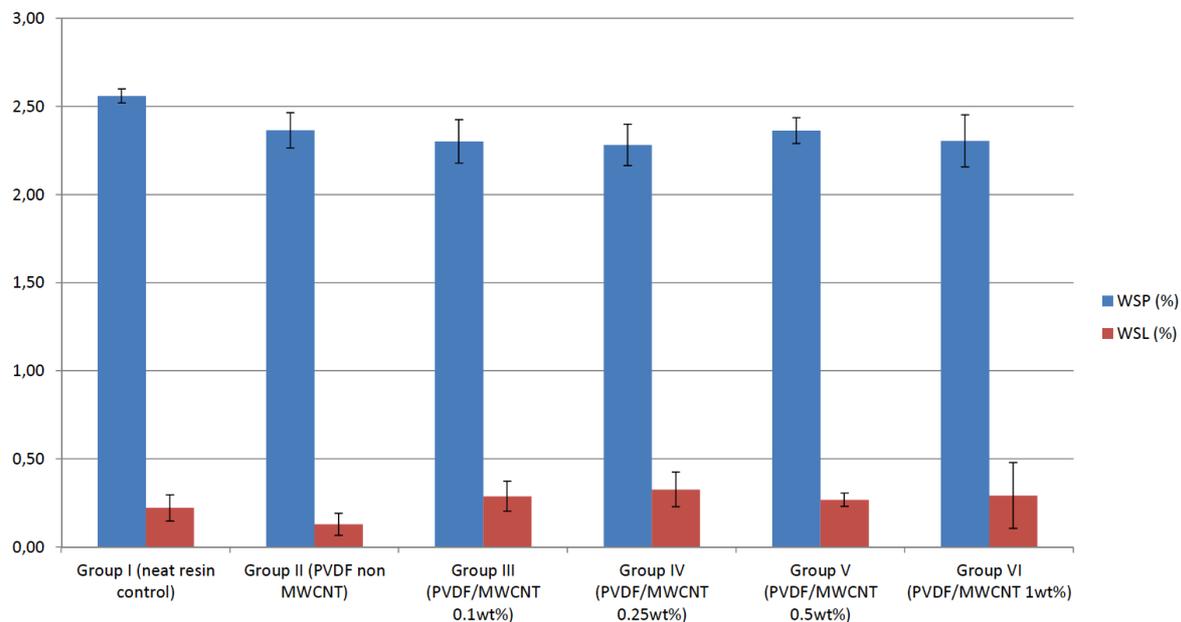


Fig.15. Means and standard deviations for water sorption and water solubility values by nanofiber reinforcement groups.

4. Discussion

Resin based composites have been successfully employed for a long time for dental restorative applications due to their good aesthetic properties. There is no doubt that they are the most popular restorative materials and would remain so until foreseen future although resin based composites include several drawbacks that make them inferior to amalgam from some aspects such as wear resistance, hardness and shrinkage behaviour. As a result of this, filler particles and subsequently nanofibers have been improved to reinforce dental resins. Recently, it has been widely considered that electrospun nanofibers make a significant contribution to the enhancement on the mechanical features of dental composite resins. Particularly, the consideration that fibrous structures which have a high aspect ratio and are also available in nanotubes, may present a significant flexibility. In contrast to nano filler particles in restorative composites which directly transmit the chewing loads into the resin matrix, both nanofibers and nanotubes dissipate the masticatory load that they receive. As a result, this unique feature makes them superior to previous reinforcement materials. Moreover, the high aspect ratio causes nanofibers not only to have flexibility but also interact with resin matrix, namely interfacial adhesion. In the case of the nanofiller strengthening mechanism, the high surface area of electrospun nanofibers could raise the size of entanglement between fillers and surrounding resin matrices, which means that an extremely strong connection between different phases of resultant composites is established [10,14].

PVDF was selected as the polymer of choice, due to its good biocompatibility according to many previous researching projects [25,26]. Furthermore, having piezoelectric characteristic allows biomaterials with PVDF to optimize wound healing by improving the cell migration and fibroblast activities [27]. That is the reason why PVDF, in this study, was considered to be added into the dental restorative material which are applied over wounded dentine tissues. In addition to these advantages, PVDF, unlike some other materials frequently used in elec-

trospinning process such as Nylon-6, is water-insoluble which is a desired feature to resist to intra-oral conditions. With regard to the use of electrospun strips to strengthen the Bis-GMA/TEGDMA resin, the fiber alignment has a positive effect on the flexural strength [28]. Consequently, in this current study in order to acquire aligned nanofibers, the electro spinning process was performed by a rotating collector at high speed (1500 rpm) mandrel rotation.

In regards to the main purpose of the study, it was investigated if there would be a significant difference among the groups in terms of mechanical features of the resin material after the reinforcement of BisGMA/TEGDMA composites by placing PVDF nanofibers fabrics (5 wt%) with MWCNTs in different mass fractions (0, 0.1, 0.25, 0.50 and 1 wt%). Despite the fact that the mean value of the group I (control) with the samples consisting of the neat dental resin indicated the lowest mechanical property among those of all groups by 102.3 MPa, it was still comparable to the others $P > .05$, except for the group III and IV including 0.1 and 0.25 wt% of MWCNTs respectively. For the the group IV, the average flexural strength of the specimens (123.4 MPa) was roughly 20% higher than that for the group I which had no nanofiber content. However, both the group III and IV did not seem significantly different from the other groups with nanofiber reinforcement. In consequence, the addition of carbon nanotubes into the PVDF nanofibers can be considered as the reinforcement process of a reinforcing material. With regard to the multi-walled nanotubes addition to the PVDF fibers, the light micrograph in Fig.11a, demonstrated their successful incorporation. Nevertheless, as shown in Fig.9, the trend of flexural strength means of all groups were not parallel to the raise in mass fraction of the carbon nanotubes. Contrary to the expectation about the addition of 0.5 % and 1 % of MWCNT which would show the highest flexural strength values as suggested by a previous study [28], the Fs average values reached a peak with the group IV including the trace amount of MWCNTs less than these loading rates. Based on these findings, the bar graph of the current study, as seen in Fig.9, showed a curved pattern not slope similar to those of former studies in which the increasing mass fraction of nanotubes led to a rise over Fs means to some extent and then caused these values drop. The first part of the null hypothesis hereby was partially accepted which means flexural strength would not continuously increase but to some extent as MWCNTs are added into the PVDF polymer solution.

The images from the SEM (10a/b) and the light microscope (Fig.11a/b) may be used to explain this situation. As mentioned earlier, carbon nanotubes tend to get accumulated due to their high surface energy which means the distribution of CNTs within PVDF polymer requires some preparations such as surface modification (functionalization) and ultrasonication. In the present study, in spite of providing prefunctionalized carbon nanotubes from the supplier, an overall homogenous mixing of CNTs could not be obtained for the groups having higher loading rates of carbon nanotubes (0.5 and 1% in mass fraction) in comparison with the others. In Fig.11b, it was realized that the bundle of MWCNTs inside of the nanofiber led

to enlargements in the fiber forms and roughness over the fiber surface. All of these changes can be considered to negatively affect the flexibility of nanofibers. As to standard deviations, the group I (control) seemed to have the lowest value by ± 6.8 MPa. Because unlike the other groups in which an accurate placement of the fiber fabrics were required, the preparation of bar shaped neat resin samples was not technically sensitive and therefore the specimens could be produced in a more standardized way and subsequently accompanied by less standard deviations.

As for the characterization of failure modes, it may be suggested that the bonding between nanofibers and BisGMA/TEGDMA matrix was moderately good as the fibers were prone to be broken instead of being pulled out. As a result, this failure manner required much more energy to occur during the three-points bending test. Even though numerous holes which may indicate pullout failure mode were observed over the fracture surface in Fig. 13b, they had superficial depths, which means these holes were the result of fracturing the fibers. Usually when the fibers are broken just under the fracture surface, the broken fragments can be pulled out and then these shallow holes would occur [2, 9]. Meanwhile, the smooth fracture surface with relatively large steps was observed in the control group as seen in Fig. 12a and this pattern indicates the neat resin specimen showed little resistance to the applied loading. In consequence, the SEM images were consistent with and validated the mechanical test results.

The water sorption of dental composites is determined according to the physical and chemical features of them such as the structure morphology, the free volume entrapped within the structure, the soluble uncured part of resin and hydrophilic character [29]. In this research, the water sorption values appeared to be influenced by the placement of PVDF nanofiber fabrics even if they were added into the resin matrix in a small amount (5%), regardless of including the carbon nanotubes. This situation can be explained with the drop of BisGMA/TEGDMA's mass fraction by 5%. In consequence, as a course of its nature, PVDF is hydrophobic and the contact angle of its membrane form with water less than 90° which means, it has no tendency to absorb water as long as not modified [30]. Even though its loading rate was fixed to 5%, PVDF content made a significant difference in terms of W_{sp} value $P < 0.05$ and all strengthened groups by nanofibers had the lower mean values than that for the control group. However, when the W_{sl} means were noted, interestingly all nanofiber reinforced groups with MWCNTs showed a higher water solubility compared to the groups with the neat resin and PVDF/non carbon nanotube. It was realized that because of CNTs concentration and the darkness generated by this CNT's opacity, the light transmission was blockaded during the photo-polymerization. Therefore, the high water solubility of the groups with MWCNTs was attributed to the unreacted monomers entrapped in resin samples. This result was well-matched with those of previous studies which claimed there was a correlation between

degree conversion (DC) and water solubility (Wsl) [24, 31]. As a result, the null hypothesis that the existence of CNTs would lower the Wsl values was rejected.

With respect to the nanofiber reinforcement, fiber incorporation has a critical effect on the results obtained from mechanical testing. In the present study, a single layer of the electrospun fabric was placed within the bar samples. Despite the fact that the fiber rich layer has been mostly located in the middle part of specimens where the neutral axis is available in previous studies. it was preferred to place the fiber strip very close to the bottom part of the specimen. Since the material does not receive the load at the neutral axis in 3-points bending test while the bottom face is subjected to the maximum tensile loading. Hence, in order to correctly test the strength of the material, it may require placing the fabric strips on the bottom of the rubber mold. Finally, electrospun PVDF and PVDF/MWCNT nanofibers were incorporated through BisGMA/TEGDMA polymers as the striped form of non woven fabric however, in actual clinical applications and commercial forms, the composites might be required to have a homogeneous structure in which the much smaller pieces of the reinforcing fabric are mixed well with the dental monomers and distributed within them. On the other hand this process to produce an applicable dental paste is more complex and includes several stages: light activating resin-impregnated fibers, then grinding and milling them into finer powder, subsequently using this resultant powder as a reinforcing agent by mixing with some additives such as colour pigments. In the end, calculating the specific effect of nanofibers in this fabrication concept would be difficult [28]. Therefore, it was aimed to investigate the sole contribution of PVDF/MWCNT nanofibers on mechanical strength of the dental composite resin.

5. Conclusion and Recommendations

5.1. Conclusion

Within the limitations of of the present study, It has been noticed that the addition of trace amount of MWCNTs which is not more than 0.25 wt% had a significant effect on flexural strength. During the water sorption analyzing, it has been seen the hydrophobic nature of PVDF nanofibers led to a significant decrease in the mean of water sorption (Wsp) of neat BisGMA/TEGDMA. However, according to the Wsl results obtained in this study, MWCNT's incorporation, regardless of its amount, caused the water solubility of pure dental resin to significantly increase due to preventing the effective photo polymerization and subsequently resulting in dissolving of uncured resin monomers.

5.2. Recommendations for Future Studies

The following recommendations were presented as a result of this experiment:

1. The present results point to the need for further research which should investigate whether there is a correlation between the outcomes of three-points bending testing and W_{sp}/W_{sl} analyzes. The specifications and standards for both tests should be same. For example, the specimens for mechanical testing are immersed in water at 37 °C for 24 hours while the samples in sorption and solubility analyzing are subjected to different water storing regimes varying from 1 week to 6 months. Even the samples in same shape and size should be used in both test conducted consecutively.

2. In the future, carbon nano-tubes would be more frequently incorporated to the production process of reinforced dental composites in spite of their negative effect on photo-polymerization. Therefore, the elimination of uncured monomers which may be the primary cause of high water solubility then followed by a mechanical failure should be a prior issue for dental material engineering.

3. An additional study should be carried out to investigate the correlation between the composite degree of conversion and the opacity of carbon nanotubes varying from regular to transparent. Finally, there is still demand for a long term clinical trials examining whether the piezoelectricity generated from PVDF fibers has a therapeutic effect on decayed dental tissues or not.

As a result, all these efforts would contribute to the development of highly strong, chemically inert, and biocompatible dental composites.

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