

## **SURFACE ROUGHNESS, HARDNESS, COLOR STABILITY, WATER SORPTION AND WATER SOLUBILITY OF PMMA DENTURE BASE MATERIAL REINFORCED WITH SYNTHESIZED INORGANIC, ORGANIC, AND HYBRID NANOFIBERS**

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### **ABSTRACT**

**Objective:** The objective of the study was to assess surface roughness, microhardness, color stability, water sorption and water solubility of polymethyl methacrylate (PMMA) denture base resin reinforced with inorganic {silanized ZrO<sub>2</sub>}, organic {Bisphenol A diglycidyl ether dimethacrylate (Bis-GMA)+Triethylene glycol dimethacrylate (TEGDMA)+Polyethylene glycol dimethacrylate (PEGDMA)} and hybrid {silanized ZrO<sub>2</sub>+Bis-GMA+ TEGDMA} Nanofibers.

**Materials and Methods:** The study was divided into four groups according to the added nanofibers (6wt%) to heat curing PMMA denture base material; Control group: PMMA denture-base material without reinforcing nanofibers, Inorganic group: PMMA denture-base material with silanized ZrO<sub>2</sub> nanofibers, Organic nanofibers group: PMMA denture-base material with Bis-GMA/TEGDMA/PEGDMA nanofibers and, Hybrid nanofibers group: PMMA denture-base material with silanized ZrO<sub>2</sub>/Bis-GMA/TEGDMA nanofibers. For each group, 10 specimens were prepared and tested for surface roughness, microhardness, water sorption and water solubility. For each group 11 specimens were prepared and tested for color stability. Surface roughness was measured by optical method. Digital Microhardness tester was used to measure Vickers microhardness. Color stability was evaluated according to ISO/FDIS 20795-1 and ISO 7491, using a Portable Reflective Spectrophotometer. Water sorption (WSP) and water solubility (WSL) were performed according to ISO/FDIS 20795-1. One-way ANOVA was used for comparison between groups and Post-Hoc test (Tukey's tests) was used for multiple comparisons. P-value <0.01 was considered significantly different.

**Results:** One-way ANOVA revealed insignificant differences between the studied groups in surface roughness (p=0.168) and color stability (p=0.806). Significant differences were found in

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microhardness ( $p=0.000$ ), WSP ( $p=0.000$ ) and WSL ( $p=0.000$ ). Post-Hoc (Tukey's test) revealed that: 1) microhardness means of nanofibers-reinforced groups were markedly significantly higher than control group ( $p=0.000$ ). 2) WSP of organic nanofibers reinforced group was significantly lower than that of control ( $p=0.008$ ), hybrid ( $p=0.001$ ) and inorganic ( $p=0.000$ ) groups that were not significantly different from each other ( $p\geq 0.243$ ). 3) WSL of ZrO<sub>2</sub> nanofibers reinforced group was significantly higher than control, organic, and hybrid groups ( $p=0.000$ ). However, the control group was not significantly different from organic ( $p=0.992$ ) and hybrid ( $P=0.018$ ) groups. Organic group was significantly lower than hybrid group ( $p=0.009$ ).

**Conclusions:** Addition of 6% nanofibers prepared by electrospinning technique to PMMA denture resin significantly enhanced microhardness. Surface roughness and color stability were not affected. Water sorption was significantly reduced with organic nanofibers, but was not affected with ZrO<sub>2</sub> and hybrid nanofibers. The highest water solubility for nanofibers reinforced groups recorded in this study was ( $0.46\pm 0.04\mu\text{g}/\text{mm}^3$ ) which is nearly one third of the ISO limit ( $1.6\mu\text{g}/\text{mm}^3$ ).

**KEYWORDS:** Inorganic, Organic, Hybrid Nanofibers, PMMA Denture Base, Microhardness, Surface Roughness, Color stability, Water Sorption and Solubility.

## INTRODUCTION

Polymethyl methacrylate (PMMA) is the most widely used denture base material. Satisfactory aesthetics, low cost, easy fabrication, finishing and polishing, stability in the oral conditions, good fit and easy repair are prominent advantages of PMMA denture base material. However, low flexural, fatigue and impact strengths, insufficient fracture toughness and surface hardness, high coefficient of thermal expansion, low thermal conductivity and lack of radiopacity are annoying drawbacks of this material<sup>[1,2]</sup>.

Surface roughness is an essential property when evaluating a dental material. Rough surface enhances accumulation of dental plaque and residues of food and drinks on the surface of the restoration. This, in turn, decreases the restoration gloss and causes discoloration and surface degradation<sup>[3]</sup>. Also, surface smoothing and hardness of a restorative material has been reported to be in direct proportion to its fracture toughness (FT)<sup>[4]</sup>.

Hardness measures the ability of a material to withstand permanent indentation or penetration and to predict their wear resistance. Hardness is indicative for the material's resistance to be scratched and also its ease of finishing<sup>[5]</sup>. The Hardness is directly related to the conversion rate of

polymerization<sup>[6]</sup>. Moreover, hardness measurement has been successfully used as an indirect method of evaluating polymerization depth of resin-based composites<sup>[7]</sup>. It is well-known that increasing the filler content in restorative material improves its hardness<sup>[8]</sup>.

Important physical properties such as color stability, water sorption and water solubility have to be considered when a research is conducted to improve the mechanical properties of PMMA denture base by different reinforcing means.

The color change in PMMA resin is greatly influenced by hydrophobicity of the monomers and their water absorption. PMMA absorbs water due to polarity of PMMA polymer and the weak secondary bonds between polymer chains. Water sorption (WSP) can cause penetration of staining pigments and plasticization effect which adversely affects the material strength<sup>[9]</sup>. Residual monomer increased WSP and unreacted accelerator result in a yellowish discoloration of the resin<sup>[10]</sup>. PMMA resin water solubility (WSL) test represents the amount of water-soluble ingredients such as; residual monomers and plasticizers that leach out during seven days of water immersion<sup>[11]</sup>. According to ISO specification No. 20795, the amount of water sorption (WSP) and water solubility (WSL) for heat-cured PMMA

resin should not exceed 32 and 1.6  $\mu\text{g}/\text{mm}^3$ , respectively [12].

Most researchers studied the use of different fibers, macro, micro and nano-particulate fillers to overcome some of the mechanical deficiencies of PMMA. Fibers in PMMA resin tend to decrease the surface hardness with no significant increase in strength [13]. Moreover, due to the size of fibers, they tend to increase surface roughness of denture materials and negatively affect their color [14].

Balos et al reported that the surface hardness and FT of PMMA increased with 0.023 vol% silica ( $\text{SiO}_2$ ) nanoparticles (NPs) [15]. In the contrary, da Silva et al [16] reported that with silane surface-treated 0.1, 0.5, 1.0 and 5.0wt%  $\text{SiO}_2$  NPs, the flexural strength (FS) of PMMA improved while hardness was not affected. Another study reported that with 2, 5 and 10%  $\text{SiO}_2$  NPs, FS and WSP decreased, while flexural modulus (FM) and hardness increased [17]. Addition of 1%, 2.5%, 5% and 10wt% fluoride glass (FG) micro-fillers to PMMA decreased microbial adhesion; however with 10wt% FG microfillers, surface roughness of PMMA was significantly increased [18]. Mansour et al [19] reported that the hardness of acrylic resin increased significantly with the incorporation of 20wt% mica microparticles, but its flexural strength was reduced significantly because of the weak bonding between mica and acrylic resin.

Vojdani et al [20] reported significant increase in hardness of reinforced PMMA denture base using 2.5wt% and 5wt% of Alumina ( $\text{Al}_2\text{O}_3$ ) microparticles (3 $\mu\text{m}$ ) but surface-roughness was not affected. While, Pentapati et al [21] studied the addition of 5, 10 and 15wt%  $\text{Al}_2\text{O}_3$  microparticles to PMMA resin and the result showed a significant increase in FS and hardness only with 15wt%  $\text{Al}_2\text{O}_3$ .

Alumina ( $\text{Al}_2\text{O}_3$ ), Magnesia (MgO) and zirconia ( $\text{ZrO}_2$ ) powders were used to reinforce the self-cured acrylic resins. 2%  $\text{ZrO}_2$  exhibited the greatest improvement in FM, FS, FT and hardness [22]. Asar et al [23] concluded that addition of 2%  $\text{ZrO}_2$

microparticles significantly increased impact strength (IS) and FT and significantly lowered WSP ( $17.5 \pm 0.2 \mu\text{g}/\text{mm}^3$ ) and WSL ( $1.4 \pm 0.0 \mu\text{g}/\text{mm}^3$ ) than the control. Another study reported that FS, FT and hardness were enhanced with the addition of  $\text{ZrO}_2$  NPs [24]. Ayad et al [25] reported that with the addition of 5wt% and 15wt%  $\text{ZrO}_2$  powders, an insignificant increase in IS, surface hardness and WSL and an increase in FS and WSP took place. On the other hand, Asopa et al [26] reported that with the addition of 10 to 20wt%  $\text{ZrO}_2$  NPs (5-10nm), a decrease in IS and surface hardness and an increase in FS and WSP were recorded but the results of WSP were within the specification limit and are in agreement with those revealed by other authors who found that the addition of reinforcing particles generally increased WSP [25,27,28].

Ahmed and Ebrahim [29] reported that with 7 wt%  $\text{ZrO}_2$  NPs, FS, FT and hardness increased than the control. On the other hand, Hamid and Abdul Rahman [30] reported that with the addition of 5wt%  $\text{ZrO}_2$  NPs, IS and FS increased, while with 7wt%  $\text{ZrO}_2$  NPs, IS and FS decreased. Also addition of  $\text{ZrO}_2$  NPs slightly increased hardness and surface roughness and decreased apparent porosity. Mohammed and Mudhaffar [31] reported that, the addition of 3wt% and 5wt%  $\text{ZrO}_2$  NPs into acrylic resin resulted in highly significant increase in abrasive wear resistance, tensile and fatigue strengths and highly significant decrease in porosity, WSP and WSL. 0.3 wt% halloysite nanotubes (HNT) significantly increased hardness of PMMA while, adding 0.6 and 0.9wt% HNT significantly decreased hardness of PMMA resin. FS and FM did not show a significant difference with the three HNT concentrations [32].

In a previous recent study was conducted by Abdel-karim and Kenawy [33], adding 6wt% of inorganic ( $\text{ZrO}_2$ ), organic (Bis-GMA/TEGDMA/PTEGDMA) and hybrid ( $\text{ZrO}_2$ /Bis-GM/TEGDMA) nanofibers synthesized by electrospinning technique significantly ( $p=0.000$ ) improved flexural strength, flexural modulus, fracture toughness and impact

strength of PMMA denture base resin compared to the control.

In the current study, the effect of adding these nanofibers on hardness, surface roughness, color stability, water sorption and water solubility of PMMA denture base resin are investigated.

The null hypothesis of this study was that, there will be no significant differences in hardness, surface roughness, color stability, water sorption and water solubility of PMMA resin with or without the addition of different (inorganic, organic and hybrid) nanofibers.

## MATERIALS AND METHODS

**I. Materials:** Materials of this study are presented in table (1).

### II. Methods:

#### *Preparation and characterization of the nanofibers*

Nanofibers preparation was carried out exactly as those methods described in detail in a previous

study conducted by Abdel-karim and Kenawy<sup>[33]</sup>. Characterization of these nanofibers was performed using scanning electron microscopy (SEM) and Fourier transform infra-red spectroscopy (FTIR) as follows:

#### *Scanning electron microscopy (SEM)*

Nanofiber specimens were coated with gold coating (SPI-Modules Vac/Sputter Coater) and then scanned by Electron Microscope (JEOL-JSM-5200LV, Tokyo, Japan) at a magnification of 20000X.

#### *Fourier transform infra-red spectroscopy (FTIR)*

The functional groups of synthesized nanofibers were identified by FTIR method (FTIR, Model: EQUINO X55, Bruker, Germany). All types of nanofibers were milled in mortar and pestle, then added to Potassium Bromide (KBr) powder at a ratio of 1:80, respectively. The mixture was then pressed under hydraulic press to form a tablet. Ten scans were recorded for each tablet between the waves from 5000 to 200  $\text{cm}^{-1}$  with resolution of 1 $\text{cm}^{-1}$ .

TABLE (1): Materials used in this study

Materials	Composition	Manufacturer
<b>Denture-Base material</b>	Heat-cured acrylic denture-base material (type I class I): - <b>Powder:</b> polymethylmethacrylate (methyln-butyl) co-polymer, benzoyl peroxide and mineral pigments. - <b>Liquid:</b> methylmethacrylate, ethylene glycol dimethacrylate (EGDMA) as a cross-linking agent and hydroquinone.	Lucitone 199, Dentsply International Inc. Chicago, USA
<b>Nanofibers Materials</b>	<b>1. Inorganic Nanofibers:</b> Zirconium oxychloride $\leq$ 100 nm and vehicle of Polyvinyl alcohol (PVA). <b>2. Organic Nanofibers:</b> Bisphenol A diglycidyl dimethacrylate (Bis-GMA) + Tri (ethylene glycol) dimethacrylate (TEGDMA) +Polyethylene glycol dimethacrylate (PEGDMA). <b>3. Hybrid Nanofibers:</b> Zirconia nanoparticles $\leq$ 100 nm+(Bis-GMA + TEGDMA) in a ratio of 1:20	Sigma Aldrich, USA
<b>Silane</b>	3-(Trimethoxysilyl) propyl methacrylate (TMSPM)	

Initiator and activator could not be added to the organic and hybrid solution to prevent its polymerization and hardening before electrospinning. In the other hand, organic and hybrid nanofibers should be adequately hard (partially polymerized) after electrospinning to be ball-milled to be added as a filler component to the PMMA powder. A special “assigned” FTIR at the range of 2000 to 1000  $\text{cm}^{-1}$  was carried out to the solution (Bis-GMA/TEGDMA/PEGDMA) used for preparing these nanofibers. This solution was mixed to KBr in a ratio of 1:80 and the mix was pressed to form a tablet for FTIR examination to assess the single bond/double bond ratio. After electrospinning and ball-milling, the nanofibers were submitted once again to the FTIR investigation and the single bond/double bond ratio was measured.

#### **Ball-milling of electrospun nanofibers:**

Normally, electrospun nanofibers are produced in the form of sheets. To obtain fibers at the nano-scale ( $\leq 100\text{nm}$ ), these sheets of nanofibers sheets were ball-milled. Ball-milling was conducted by planetary photon grinder milling machine (Retsch – PM 400, Haan, Germany), with a ball size of 10 mm, at speed of 350 rpm, for 7 h.

#### **Preparation of specimens and grouping:**

Heat-curing PMMA acrylic denture-base material (Lucitone 199 Dentsply International Inc., Chicago, USA) was used. 6wt% of acrylic powder was replaced with each type of reinforcing nanofibers to form three experimental groups in addition to a control group as follows:

- A) Control group: PMMA acrylic denture-base material without nanofibers.
- B)  $\text{ZrO}_2$  group: PMMA acrylic denture-base material with 6wt% silanized  $\text{ZrO}_2$  nanofibers.
- C) Organic nanofibers group: PMMA acrylic denture-base material with 6wt% Bis-GMA/TEGDMA/PEGDMA nanofibers.

- D) Hybrid nanofibers group: PMMA acrylic denture-base material with 6wt%  $\text{ZrO}_2$ /Bis-GMA nanofibers.

Acrylic powder and nanofibers in each group were carefully mixed by a mechanical stirrer (5040001 RW28, Atlanta, USA) at 50 rpm for 30 min to ensure a uniform distribution of nanofibers through the powder. According to the manufacturer, the powder was mixed with the liquid at a P/L ratio of 2.5:1. Upon reaching the dough stage (12 min), the mixture was packed into the mould of the flask and pressed under 14 MPa using a hydraulic press for 30 min to form acrylic plates for testing. The curing process was carried out by placing the flask in a water bath at 78 °C for 90 min. The flask was removed from the water bath and then left to cool slowly to room temperature and the acrylic plate was removed from the flask.

#### **Surface roughness:**

Ten flat and polished specimens (12 mm length  $\times$  12 mm width  $\times$  3 mm height) were prepared for each group<sup>[34]</sup>. The prepared specimens were stored in water at room temperature for 24 h prior to testing. Optical method was used to measure average surface roughness. Specimens were photographed using USB Digital microscope with a built-in camera (Scope Capture Digital Microscope, Guangdong, China) connected to an IBM compatible personal computer using a fixed magnification of 120X. The bitmap images were recorded with a resolution of 1280x1024 pixels per image. Digital microscope images were cropped to 350x400 pixels using Microsoft office picture manager to specify/standardize area of roughness measurement. The cropped images were analyzed using WSxM software (Version. 5 develop 4.1, Nanotec, Electronica, SL). Within the WSxM software, all limits, sizes, frames and measured parameters are expressed in pixels. Therefore, system calibration was done to convert the pixels into absolute real world units. Calibration was made by comparing an object of known size (a ruler in

this study) with a scale generated by the software. Subsequently, a 3D image of the surface profile of the specimens was created. Three 3D images were collected for each specimen, both in the central area and in the sides at an area of  $10\mu\text{m}\times 10\mu\text{m}$ . WSxM software was used to calculate the average height in  $\mu\text{m}$  of every specimen, which can be assumed as a reliable index of surface roughness [25]. The average of the ten examined specimens was taken as the mean surface roughness of each group.

### Hardness (Vickers microhardness):

After completing the surface roughness testing, the same specimens were used to measure the hardness of different groups. Digital Microhardness tester (Zwick/Roell, Indentec, ZHV  $\mu$ -S, West Midlands, England) was used to measure Vickers hardness (VH). VH was determined with the application of a 30 g load for 10 sec. Each specimen was subjected to five indentations with at least 2 mm distance from one another and then averaged. The mean of the ten examined specimens was taken as the hardness of each group. The diagonal length of the indentation was measured by a built-in scaled microscope. VH was calculated as follows:  $VH=1.8544\times P/d^2$  ( $\text{Kg}/\text{mm}^2$ ), where P is the load and d is the diagonal length.

### Color stability

According to ISO/FDIS 20795-1:2013(E) [12], eleven flat disc specimens of each group were prepared with dimensions of  $(50 \pm 1)$  mm diameter and  $(0.5 \pm 0.1)$  mm thickness. Each two specimens were stored in the oven for 24 h at  $37^\circ\text{C}$ , then one specimen of them was stored in the dark in a lab environment ( $23^\circ\text{C}$  and 50% humidity) until the color comparison test was carried out. Half of the second specimen was covered with an aluminum foil and the whole specimen was stored in water at  $37^\circ\text{C}$  and exposed to a xenon light radiation for 24h according to ISO 7491[36]. After exposure, the aluminum foil was removed before color

comparison between covered/uncovered halves of specimen and the first specimen. The color of each specimen was measured using a portable Reflective spectrophotometer (X-Rite, model RM200QC, Neu-Isenburg, Germany). A white background was selected and measurement was performed according to the CIE  $L^*a^*b^*$  color space. The color changes ( $\Delta E$ ) of the specimens were evaluated using the following formula:  $\Delta E_{\text{CIELAB}} = (\Delta L^*2 + \Delta a^*2 + \Delta b^*2)^{1/2}$ . Where:  $L^*$ = lightness (0-100),  $a^*$ = color change of the axis red/green and  $b^*$  = color variation of the axis yellow/blue. Thus, it was possible to compare the color change after immersion treatment by the  $\Delta E$  parameter of CIEL $^*a^*b^*$  system.

### Water sorption and water solubility

The test was performed according to ISO/FDIS 20795-1 [12]. Ten flat disc specimens for each group were prepared with dimensions of 50 mm and thickness of 0.5 mm. The specimens were first conditioned to a constant mass. The specimens were placed in a rack inside a desiccator with freshly dried silica gel (Sigma Aldrich, Milwaukee, WI). The desiccator was placed in an oven at  $37^\circ\text{C}$  for 23 h. Following removal from the desiccator, the specimens were placed in a second desiccator containing freshly dried silica gel at  $23^\circ\text{C}$  for 60 min. The above cycle was repeated until the conditioned mass ( $m_1$ ) was reached when the difference between two successive readings was less than 0.2 mg. At this point, the volume (V) of the specimen was calculated using an average of three diameter readings and five thickness readings. Next, the conditioned specimens were immersed in water at  $37^\circ\text{C}$  for 7 days, then removed from the water with polymer-coated tweezers. Specimens were wiped with a clean dry towel until being free from visible moisture, waved in the air for 15 sec and weighed as the wet mass ( $m_2$ ). After this weighing, the specimens were reconditioned to a constant mass in the desiccator as described above and the reconditioned mass was recorded ( $m_3$ ). The amount

of water sorption (WSP) was calculated as follows:  $WSP (\mu\text{g}/\text{mm}^3) = (m_2 - m_3)/V$ , where  $m_2$  is wet mass in  $\mu\text{g}$ ,  $m_3$  is reconditioned mass in  $\mu\text{g}$  and  $V$  is the volume of specimen in  $\text{mm}^3$ . The amount of water solubility (WSL) was calculated as follows:  $WSL (\mu\text{g}/\text{mm}^3) = (m_1 - m_3)/V$ , where  $m_1$  is the conditioned mass in  $\mu\text{g}$ .

### Statistical Analysis

The recorded values of surface roughness, hardness, color stability, water sorption and water solubility were collected, tabulated and statistically analyzed. Statistical analyses were performed using an IBM compatible personal computer with SPSS statistical package version 20 (SPSS Inc. Armonk, NY: IBM Corp). For each of the studied properties, a one-way ANOVA was used for statistical significance between groups and post-hoc (Tukey's test) was used for multiple comparisons. p-value <0.01 was considered significantly different.

## RESULTS

### Characterization results

#### Scanning Electron Microscopy (SEM)

In Figure 1.A, SEM shows  $\text{ZrO}_2$  nanofibers produced after calcination at  $1000^\circ\text{C}$  at a magnification of 20000 X. After removal of PVA, the zirconia nanofibers are presented with rough surface. The fiber diameter ranged between 40 nm and 80 nm. The organic nanofibers (Bis-GMA/TEGDMA/PEGDMA) are presented in Figure 1.B at a magnification of 20000 X. These nanofibers exhibited a smooth surface and their diameters ranged between 50 nm and 90 nm. Similarly, hybrid (Bis-GMA/ $\text{ZrO}_2$ ) nanofiber are presented at a magnification of 20000 X (Figure 1.C). The hybrid nanofibers have a beaded structure due to the entanglement of  $\text{ZrO}_2$  nanoparticles with the organic nanofibers and having their diameters ranging from 20 nm to 90 nm. Scanning of the ball-

milled nanofibers for the three types is shown in Figures 1.A2, 1.B2 and 1.C2, respectively.

### Fourier Transform Infra-red Spectroscopy (FTIR)

**ZrO<sub>2</sub> nanofibers:** Pure  $\text{ZrO}_2$  was indicated by the IR spectra intense peak at  $520\text{ cm}^{-1}$  and  $750\text{ cm}^{-1}$  after calcination at  $1000^\circ\text{C}$  because of stretching of Zr-O bond (Figure 1.A1). In addition, the complete removal of PVA at this temperature was emphasized by the disappearance of the peaks corresponding to the PVA molecule and the fibers formed were exclusively consisted of pure  $\text{ZrO}_2$ .

**Organic nanofibers:** The formation of mixed organic nanofibers (Bis-GMA/TEGDMA/PEGDMA) was indicated by the IR spectra of the aromatic (Bis-GMA) and aliphatic (TEGDMA/PEGDMA) compounds which displayed intense peaks as follows: at  $2965 - 2873\text{ cm}^{-1}$  was due to C-H stretching of  $\text{CH}_2$ . At  $1608\text{ cm}^{-1}$  was due to C=C stretching. At  $1509\text{ cm}^{-1}$  was due to C-C stretching. At  $1036\text{ cm}^{-1}$  was due to C-O-C stretching and at  $1450\text{ cm}^{-1}$  was due to C=O stretching. Also, IR spectra displayed peaks at  $1600 - 1625\text{ cm}^{-1}$  due to benzene ring stretching in Bis-GMA (Figure 1.B1). For the "assigned" FTIR at the range of  $2000$  to  $1000\text{ cm}^{-1}$  that was carried out twice; one to the solution (Bis-GMA/TEGDMA/PEGDMA) used for preparing these nanofibers before electrospinning and another to the ball-milled nanofibers after electrospinning. Adequate polymerization was emphasized by the increased transformation of the single bond at the expense of the double bond indicating partial polymerization after electrospinning as that can be seen in Figures 2.A and 2.B, respectively.

**Hybrid nanofibers:** The formation of hybrid nanofibers was indicated by the IR spectra of both the organic (Bis-GMA/TEGDMA) and inorganic ( $\text{ZrO}_2$ ) component as discussed above (Figure 1.C1).

### Results of investigated properties

Means  $\pm$  standard deviations (SDs) and statistical

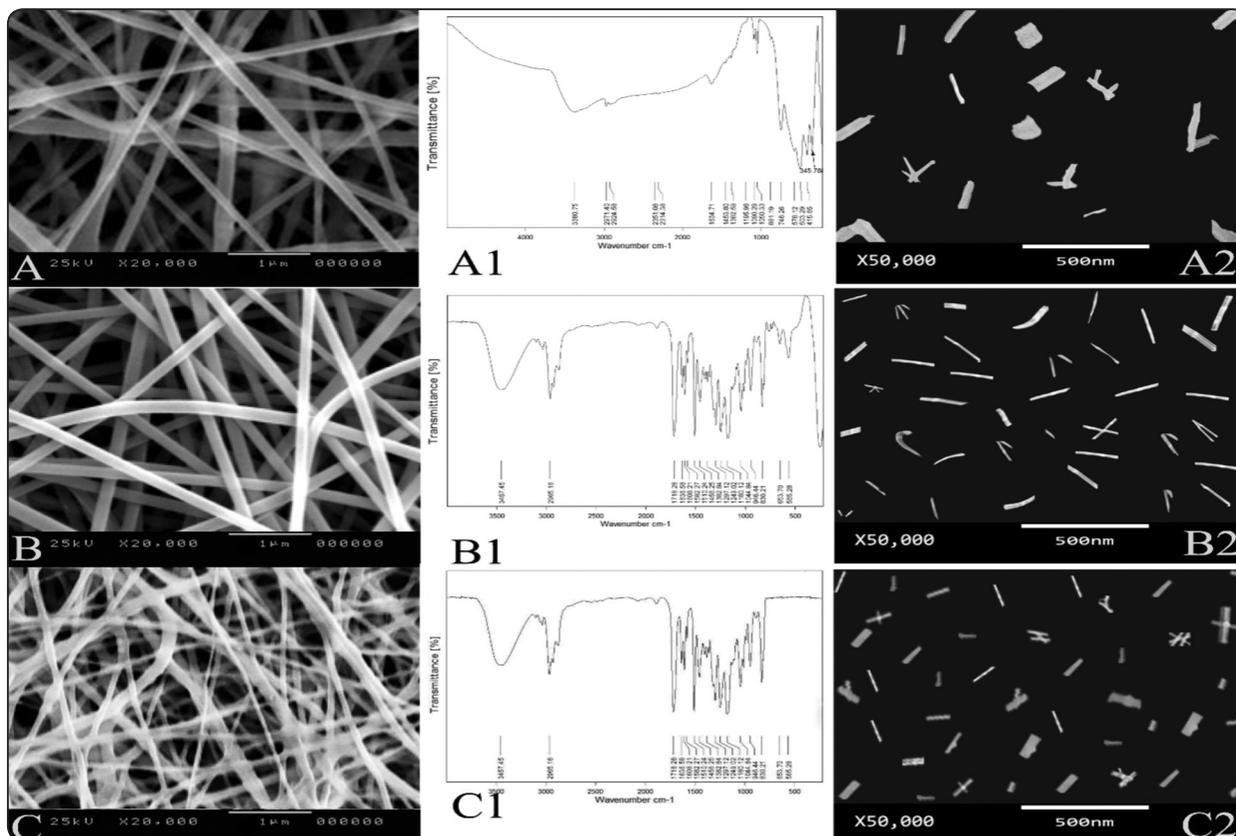


Fig. (1) SEM of the electrospun nanofibers; zirconia, organic and hybrid types: A, B and C, respectively. FTIR of these nanofibers is presented in A1, B1 and C1, respectively. SEM of the corresponding ball-milled nanofibers is shown in A2, B2 and C2, respectively.

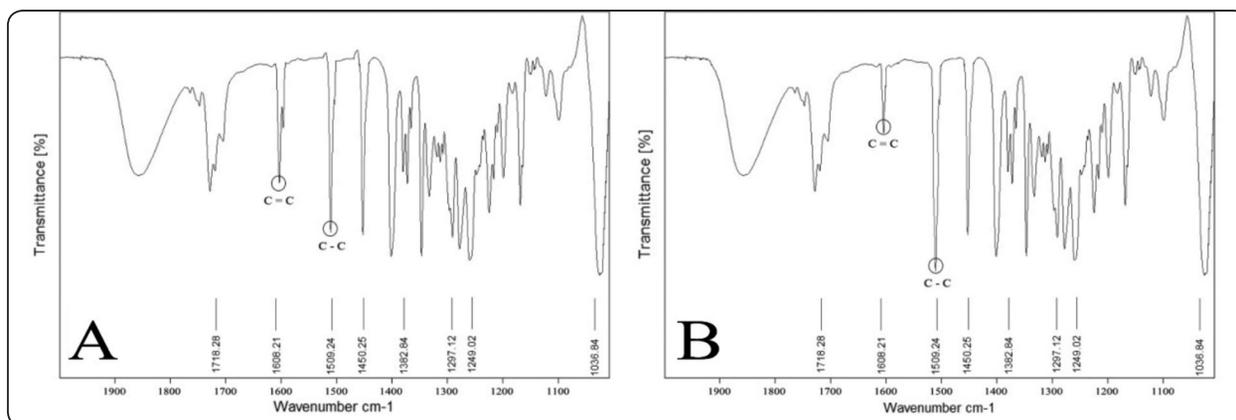


Fig. (2) An assigned FTIR (2000 -1000 Cm<sup>-1</sup>) for the solution used to prepare the organic nanofibers (A) and for the electrospun nanofibers (B) revealing an increase in the single bond/double bond ratio indicating partial polymerization.

analysis of surface roughness, microhardness, color stability, water sorption (WSP) and water solubility (WSL) are listed in Table (2) and presented in Figures (1-5). One-way ANOVA revealed insignificant differences in surface roughness ( $p=0.168$ ) and color stability ( $p=0.806$ ) of studied groups. One way ANOVA revealed significant differences in microhardness ( $p=0.000$ ), WSP ( $p=0.000$ ) and WSL ( $p=0.000$ ) between the studied groups. Post-Hoc (Tukey's test) revealed the following: 1) microhardness means of nanofibers reinforced groups were markedly significantly higher than control group ( $p=0.000$ ). Also, there were significant

differences between microhardness means of all studied groups ( $p=0.000$ ). 2) WSP of organic nanofibers reinforced group was significantly lower than that of control ( $p=0.008$ ), hybrid ( $p=0.001$ ) and  $ZrO_2$  ( $P=0.000$ ) groups that were not significantly different from each other ( $p \geq 0.243$ ). 3) WSL of  $ZrO_2$  nanofibers reinforced group was significantly higher ( $p=0.000$ ) than control, organic, and hybrid groups. The control group was not significantly different neither from organic ( $p=0.992$ ) nor from hybrid ( $p=0.018$ ) groups. Organic group was significantly lower than hybrid group ( $p=0.009$ ).

TABLE (2) Statistical analysis of physico-mechanical properties of studied groups

Groups: 6% Nanofibers (Nfs)	Mean $\pm$ SD				
	Surface Roughness ( $\mu m$ )	Microhardness (VHN) (Kg/mm <sup>2</sup> )	Color Stability ( $\Delta E$ )	Water Sorption ( $\mu g/mm^3$ )	Water Solubility ( $\mu g/mm^3$ )
<b>Control:</b> PMMA without Nfs.	0.131 $\pm$ 0.008 <sup>a</sup>	13.21 $\pm$ 0.16 <sup>a</sup>	0.06 $\pm$ 0.02 <sup>a</sup>	16.15 $\pm$ 0.76 <sup>a</sup>	0.45 $\pm$ 0.02 <sup>ac</sup>
<b>Inorganic:</b> PMMA with silanized $ZrO_2$ Nfs.	0.136 $\pm$ 0.009 <sup>a</sup>	16.67 $\pm$ 0.28 <sup>b</sup>	0.07 $\pm$ 0.02 <sup>a</sup>	17.05 $\pm$ 0.95 <sup>a</sup>	0.55 $\pm$ 0.03 <sup>b</sup>
<b>Organic:</b> PMMA with (Bis-GMA +TEGDMA+ PEGDMA)Nfs	0.127 $\pm$ 0.009 <sup>a</sup>	14.13 $\pm$ 0.15 <sup>c</sup>	0.07 $\pm$ 0.02 <sup>a</sup>	14.53 $\pm$ 1.27 <sup>b</sup>	0.41 $\pm$ 0.02 <sup>a</sup>
<b>Hybrid:</b> PMMA with (Bis-GMA + TEGDMA) + $ZrO_2$ Nfs.	0.131 $\pm$ 0.008 <sup>a</sup>	14.77 $\pm$ 0.14 <sup>d</sup>	0.07 $\pm$ 0.01 <sup>a</sup>	16.48 $\pm$ 1.17 <sup>a</sup>	0.46 $\pm$ 0.04 <sup>c</sup>
<b>F</b>	1.784	601.760	0.326	10.460	38.880
<b>P-Value</b>	0.168	0.000	0.806	0.000	0.000

Different letters are significantly different at  $P < 0.01$ .

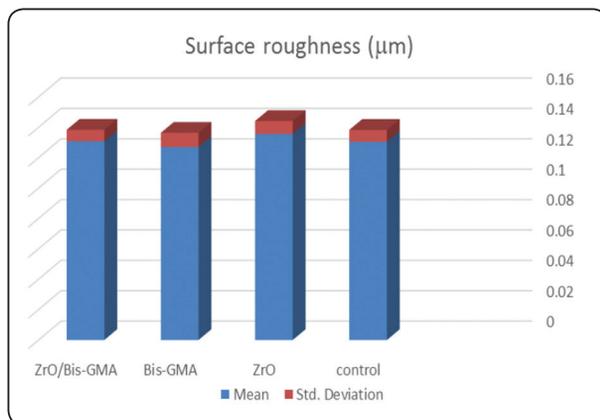


Fig. (3): Surface roughness means  $\pm$  SD of all groups

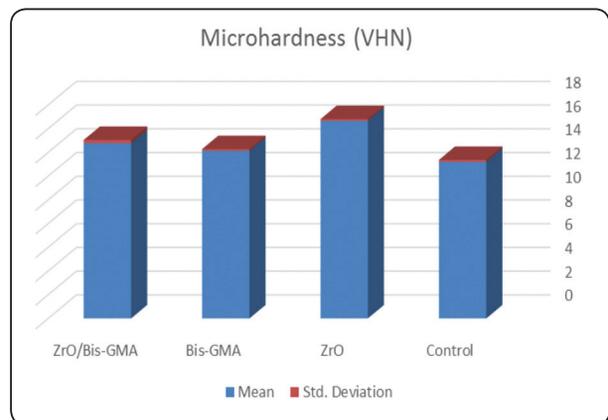


Fig. (4): microhardness means  $\pm$  SD of all groups

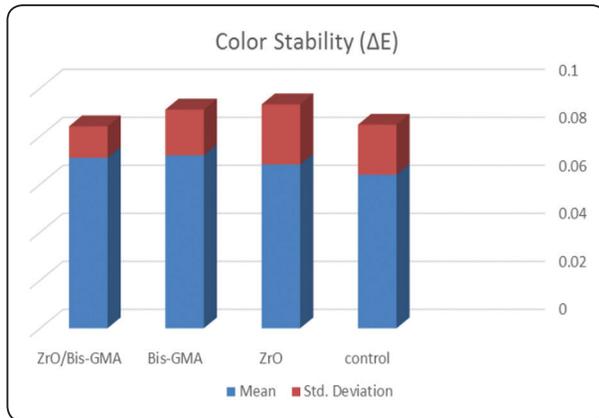


Fig. (5): Color stability means  $\pm$  SD of all groups

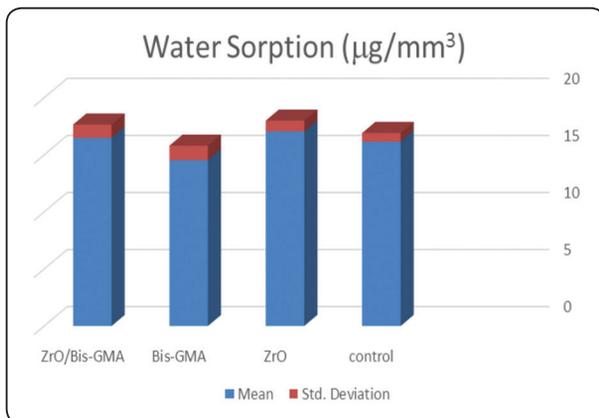


Fig. (6): Water sorption means  $\pm$  SD of all groups

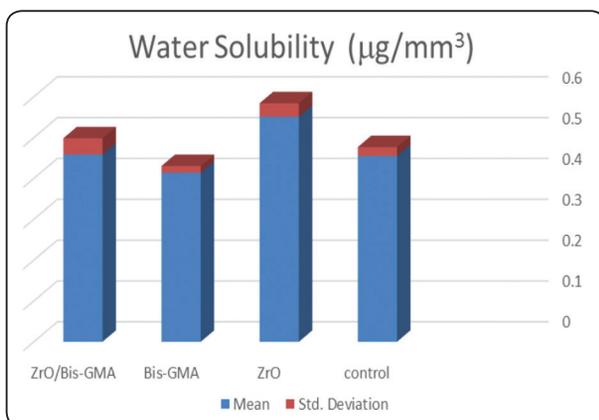


Fig. (7): Water solubility means  $\pm$  SD of all groups

### DISCUSSION

Due to the inferior mechanical properties of polymethyl methacrylate (PMMA) denture base resin, many reinforcing materials have been tried to improve its mechanical deficiency. Physical properties such as color stability, water sorption and water solubility are very critical and must be considered when improving the mechanical properties of PMMA by different reinforcing materials.

A 6wt% of synthesized  $\text{ZrO}_2$ , Bis-GMA/TEGDMA/PEGDMA and  $\text{ZrO}_2/\text{Bis-GMA}/\text{TEGDMA}$  are the materials that were used for synthesis of three types of nanofibers to reinforce PMMA resin.  $\text{ZrO}_2$  is a biocompatible material and presents high mechanical properties with white color which is less likely to alter esthetics [23]. In the current study, 6wt% of  $\text{ZrO}_2$  nanofibers was selected because a percentage above 7% of  $\text{ZrO}_2$  nanoparticles was reported to cause changes in the acrylic color [37]. Bis-GMA is extremely viscous oligomer and it is strong, rigid and elongated organic molecule. Therefore,TEGDMA diluent was added to form a spinnable solution. Also, PEGDMA was added as cross linking agent to produce strong organic fibers [38]. Electrospinning method was used for the synthesis of nanofibers as it is simple and convenient. It enables the synthesis of nanofibers with wanted composition, structure and morphology [39]. Zirconia nanofibers were prepared according to the method described by Shao et al [40], while organic and hybrid nanofibers were synthesized according to that described by Abdel-karim and Kenawy [33].

Surface roughness is presented as finer irregularities of a final restoration surface which resulted from the configuration and manufacturing of the material [41]. In vivo studies of surface roughness have shown that there is a substantial increase in bacteria retention above a threshold of  $0.2 \mu\text{m}$  [42]. Rough surface of a denture base material is positively correlated with bacterial accumulation

and decreases gloss retention and color stability<sup>[20,43]</sup>. Surface irregularities of acrylic resin surfaces increase the likelihood of microorganisms remaining on the denture surface after the prosthesis is cleaned. Generally speaking, the rougher the surface is, the more susceptible the material to be stained<sup>[44]</sup>. Moreover, rough surface increases ability to form cracks on the surface of a material and decreases its fracture toughness<sup>[43]</sup>. In this study, a non-contact optical method<sup>[35]</sup> was used to measure average surface roughness.

The null hypothesis of this study for surface roughness was accepted, as there was no any significant difference between control group (PMMA without nanofibers) and nanofibers-reinforced groups ( $p=0.168$ ). The average surface roughness that was recorded in this study ( $0.13\mu\text{m}$ ) was much lower than surface roughness threshold ( $0.2\mu\text{m}$ ). The result could be attributed to the nano-sized scale of the nanofibers used in this study that might not affect surface roughness. In addition, the reported result of surface roughness was might be reflected by the micro-sized scale of the PMMA polymer in all groups. This assumption may be supported by the very close means and low standard deviations of the control and nanofibers-reinforced groups recorded in this study.

To the authors' knowledge, no studies have been found, reporting the effect of adding nanofibers on the surface roughness of heat-cured PMMA resin. However, in agreement with this study, surface-roughness of PMMA resin was not affected with the addition of 5wt%  $\text{Al}_2\text{O}_3$  3  $\mu\text{m}$  particles<sup>[20]</sup>. Slight increase in hardness and surface roughness of PMMA resin was reported with the addition of 7wt%  $\text{ZrO}_2$  nano-particles (NPs)<sup>[30]</sup>. Addition of 1%, 2.5%, 5% and 10wt% fluoride glass micro-fillers to PMMA decreased microbial adhesion, however with 10wt% micro-fillers, surface roughness of PMMA was significantly increased<sup>[18]</sup>. Despite the insignificant effect of our synthesized nanofibers, microfibers increased surface roughness of PMMA denture base and may adversely affect their color<sup>[14]</sup>.

Another property that can influence the surface characteristics of acrylic resins is the hardness. Hardness indicates the ease of finishing a material and its resistance to in-service scratching and during cleaning procedures<sup>[5]</sup>. For denture base materials, hardness is very critical surface property. This is because if the hardness value is low, surface scratches may lead to crack formation that decreases fracture toughness of the denture. This, in turn, will cause catastrophic failure of the denture even at low masticatory force<sup>[45]</sup>. Vickers microhardness test was used in the current study as it is the most accurate and simple test for measuring the microhardness of a brittle material<sup>[46]</sup>.

The null hypothesis of this study for hardness was rejected, as the results revealed that the microhardness means of nanofibers-reinforced groups were markedly significantly higher than control group ( $p=0.000$ ). This result could be attributed to the advantages anticipated for the added nanofibers. Nanofibers act as a reinforcing mean due to their huge specific surface area, super high aspect-ratio and unique structure which leads to higher interfacial bonding between fibers and resin<sup>[47]</sup>. As the diameter of the fibers is reduced, most of the ions, molecules and functional groups will be available on the outmost layer which can grant high reactivity to nanofibers that are, important characteristic that is not found in their traditional bulk counterparts<sup>[48]</sup>. Moreover, nanofibers act as a stress distributor and have a great potential to inhibit micro-crack initiation and prevent its enlargement<sup>[49]</sup>. It has been reported that nano-scaled fibers possess strength ten times as high as that of most of micro-scaled fibers<sup>[50]</sup>.

Good wettability between fillers and the matrix is an important factor in order to improve the composite's properties. Treatment of  $\text{ZrO}_2$  nanofibers with a silane coupling agent improved the bonding between inorganic  $\text{ZrO}_2$  nanofibers and the organic PMMA resin matrix, which consequently increased the composite material's strength<sup>[51,52]</sup>. In comparison with micron-sized fibers, the nanofibers

are over 10-times thinner and contain significant surface  $ZrO_2$  groups that can readily interact with different silane coupling agents. Consequently, the interfacial bonding between the resin matrix and the silanized nanofibers can be extremely powerful which can inhibit crack propagation<sup>[53,54]</sup>.

Once again, the increase in hardness can be explained also on the basis of good distribution of the nano-sized fibers (50-150 nm) to fill the interstitial spaces between acrylic resin chains microparticles resulting in increased interfacial shear strength between the nanofibers and polymeric chains. This can effectively interrupted the crack propagation and improve the mechanical properties of the material<sup>[54]</sup>. Moreover, for  $ZrO_2$  reinforced PMMA group which recorded the highest hardness value, compressive stress causes the transformation of  $ZrO_2$  from the small tetragonal to the big monoclinic phase. Such transformation effectively arrests the crack propagation<sup>[55]</sup>.

For the organic nanofibers, Bis-GMA, TEGDMA and PEGDMA that formed the organic and most of the hybrid nanofibers are di-functional molecules i.e. they have methyl methacrylate group at each end with double bond that can undergo free radical polymerization on activation. Similarly, PMMA resin has methyl methacrylate group with a double bond. Upon heat activation, linear PMMA micro-molecules chains undergo free radical polymerization and become entangled and a covalently bonded structure is formed with the Bis-GMA, TEGDMA and PEGDMA nanofibers to produce a strong cross-linked network of organic molecules. Upon submitting the organic solution (Bis-GMA/TEGDMA/PEGDMA) used for synthesizing the organic nanofibers to an assigned FTIR investigation (2000-1000  $Cm^{-1}$ ) before electrospinning and another FTIR to the ball-milled nanofibers, adequate polymerization was emphasized by the increased transformation of the single bond at the expense of the double bond. Only partial polymerization is enough in such a case. This is because partial polymerization means

that there is still enough quantity of unpolymerized monomers that will be cured later upon mixing with the resin part of the PMMA which will create better entanglement between the resin and the reinforcing nanofibers. Partial polymerization of the freshly electrospun organic nanofibers was majorly thought to be due to exposure to the high voltage (25Kv) and heat accompanying the electrospinning process. Whatever the kind and intensity of the activating source, because of the very thin diameter “nano-scale” of the nanofibers, it will be able to induce polymerization, even partially, to these fibers. This consequently enhances the mechanical properties of the nanofibers-reinforced PMMA resin [25,56]. The hardness is directly related to the conversion polymerization ratio<sup>[6]</sup>.

In this study, PMMA without nanofibers (control) reported the lowest hardness value as the material is typically low in strength and hardness<sup>[57]</sup>.  $ZrO_2$  nanofibers-reinforced group showed the highest hardness value. This could be justified by the inherent characteristics of the  $ZrO_2$  particles.  $ZrO_2$  possesses strong ionic inter-atomic bonding, giving rise to its desirable characteristics, that is, hardness and strength<sup>[29]</sup>.

In majority of polymer reinforcement, macro-, micro- and nano-particulate fillers have been the most commonly used type. Many reports described the use of nanofibers in dental composites<sup>[48,50,53,54,57]</sup>. There are no studies have been found reporting the effect of adding nanofibers on hardness of heat-cured PMMA. However, in general agreement, it is well known that adding high filler content in composite restoration increases its hardness<sup>[8]</sup>. In agreement with this study, hardness was improved with addition of  $ZrO_2$  microparticles<sup>[22,25]</sup> and  $ZrO_2$  NPs<sup>[24,29-31]</sup> to PMMA resin. In disagreement with this study, hardness was not affected with addition of 5wt% and 15wt%  $ZrO_2$  powders<sup>[25]</sup>. Moreover, a decrease in surface hardness was reported with addition of 10 wt% and 20 wt%  $ZrO_2$  NPs<sup>[26]</sup>. With the addition of other reinforcing materials, Vojdani et al [20] reported significant increase in

hardness of PMMA denture base using 2.5wt% and 5wt% of  $\text{Al}_2\text{O}_3$  microparticles, while, Pentapati et al.<sup>[21]</sup> reported a significant increase in hardness only with 15wt% not with 5 wt% or 10 wt%  $\text{Al}_2\text{O}_3$  microparticles. There is a controversy between studies with regard to the reinforcing effect of silica ( $\text{SiO}_2$ ) nanoparticles on the hardness of PMMA. Some of them reported a significant improvement<sup>[15,17]</sup>, while other reported no effect<sup>[16]</sup>.

Naturally appearing esthetics is very crucial for denture base material; so that the effect of reinforcement materials on color stability of denture based material should be considered. Various methods have been used for measurement of color e.g. colorimeters, digital cameras, and imaging systems. But Spectrophotometer, that was used in this study, is amongst the most accurate, useful and flexible instruments for overall color matching in dentistry<sup>[58]</sup>. The color stability test method used in this study was carried out according to ISO/FDIS 20795<sup>[12]</sup> and ISO 7491<sup>[36]</sup> which are widely employed in the dental research. The color change of the organic resin matrix has been said to be directly related to monomers hydrophobicity and their water absorption properties that lead to penetration of staining pigments<sup>[9]</sup>.

As the statistical analysis for color stability data revealed no significant differences between the studied groups ( $p=0.806$ ), the null hypothesis of this study for color stability was accepted. In agreement with our study, Safi et al.<sup>[59]</sup> studied the effect of zirconia NPs addition on the color properties of PMMA and did not find any noticeable color changes. In disagreement with this study, significant color differences were detected between control group and specimens reinforced with  $\text{ZrO}_2$  nanoparticles (NPs) at different immersion solutions<sup>[37]</sup>.

The null hypothesis of this study for water sorption (WSP) and water solubility (WSL) was partially rejected. This is because the statistical analysis revealed that the WSP mean of organic nanofibers-reinforced group was significantly lower

than that of control ( $p=0.008$ ), hybrid ( $p=0.001$ ) and  $\text{ZrO}_2$  ( $p=0.000$ ) reinforced groups that were not significantly different from each other ( $p \geq 0.243$ ).

In this study, there were no significant differences in WSP between control,  $\text{ZrO}_2$  and hybrid-reinforced groups and in WSL between the control and organic and hybrid-reinforced groups. This could be attributed to the good distribution of these nanofibers in the resin matrix without agglomeration and the good bonding between nanofibers and the resin matrix. Organic nanofibers-reinforced group reported the lowest WSL and significantly the lowest WSP mean values. This could be attributed to polymerization of PMMA chains with the Bis-GMA, TEGDMA and PEGDMA nanofibers to produce a strong cross-linked network organic molecules with decreased interstitial spaces between PMMA polymer chains that consequently might decrease WSP and WSL of nanofibers reinforced PMMA resin.

Studies that reporting water sorption and solubility of nanofibers-reinforced PMMA resin could not be found in the literature. Many studies reported that, the addition of  $\text{ZrO}_2$  powders<sup>[25]</sup> and  $\text{ZrO}_2$  nanoparticles<sup>[26,28]</sup> resulted in increased WSP and WSL, however this increase lied within the ISO specification limit. On the other hand, a study reported that the addition of  $\text{ZrO}_2$  NPs into acrylic resin resulted in highly significant decrease in WSP and WSL<sup>[31]</sup>. Moreover, a study reported that adding 2%  $\text{ZrO}_2$  microparticles significantly lowered WSP ( $17.5 \pm 0.2 \mu\text{g}/\text{mm}^3$ ) and WSL ( $1.4 \pm 0.0 \mu\text{g}/\text{mm}^3$ ) than the control [23]. In the current study, the highest water sorption and solubility reported were nearly one half ( $17.05 \pm 0.95$ ) and one third ( $0.55 \pm 0.03$ ) of that of the ISO limit, respectively. Although,  $\text{ZrO}_2$  nanofibers-reinforced group was reported significantly higher WSP than control and other nanofibers groups. This could be attributed to washing of unbonded  $\text{ZrO}_2$  nanofibers on the surface of the disc specimens as the difference between WSL means of  $\text{ZrO}_2$  nanofibers and control is only  $0.1 \mu\text{g}/\text{mm}^3$ .

## CONCLUSIONS

Adding 6% inorganic, organic and hybrid nanofibers prepared by electrospinning technique to PMMA denture resin resulted in: 1) Highly significantly improved microhardness. 2) Surface roughness and color stability were not affected. 3) Water sorption was significantly reduced with organic nanofibers and was not affected by ZrO<sub>2</sub> and hybrid nanofibers. 4) The highest water solubility mean for nanofibers reinforced groups was 0.55 μg/mm<sup>3</sup> which is nearly one third of the ISO limit (1.6 μg/mm<sup>3</sup>).

## RECOMMENDATION

The results of this study, together with those of a previous one conducted by Abdel-karim and Kenawy<sup>[33]</sup>, that reported high improvement in flexural strength, flexural modulus, fracture toughness and impact strength of PMMA denture base resin reinforced with these nanofibers (p=0.000), an in vitro aging and clinical studies are recommended for comprehensive understanding of the effect of these nanofibers on the denture base PMMA.

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