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SYNTHESIS OF BIS-GMA AND UDMA NANOFIBERS FOR REINFORCING EXPERIMENTAL RESIN-COMPOSITES: INFLUENCE ON DEGREE OF CONVERSION, DEPTH OF CURE, FLEXURAL STRENGTH, FLEXURAL MODULUS AND FRACTURE TOUGHNESS

Samy M El-Safty* *and* El-Refaie S Kenawy**

ABSTRACT

Objectives: To study the degree of conversion, depth of cure, flexural strength, flexural modulus and fracture toughness of experimental resin-composites reinforced with Bis-GMA and UDMA nanofibers synthesized by electrospinning technique.

Materials and methods: Bis-GMA (Bis-GMA+TEGDMA+PEGDMA) and UDMA (UDMA+PEGDMA) nanofibers were synthesized by wet electrospinning technique and characterized by Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). After ball-milling to a nanoscale size (< 100 nm) in a ball-milling machine (Retsch – PM 400, Haan, Germany), these nanofibers were added to a prepared experimental resin-composite. According to the percent and type of added nanofibers, this study was divided into eight groups (*n*=10/group): one control group, three groups reinforced with 7, 11 and 15 wt% Bis-GMA nanofibers and four groups reinforced with 7, 11, 15 and 20 wt% UDMA nanofibers. For each of these groups, the degree of conversion (DC), depth of cure (DoC), flexural strength (FS), flexural modulus (E_f) and fracture toughness (FT) were studied. DC was studied using the FTIR method (FTIR, Model: EQUINO X55, Bruker, Germany). DoC was measured according to ISO 4049: 2009a. FS testing (and E_f calculation) was carried out according to ISO 4049:2009 by a three-point bending test. FT testing was conducted according to ISO/FDIS 6872:2007. Data were collected and submitted to One-way ANOVA and *post-hoc* Tukey test with the significance level set at ($p \leq 0.05$).

Results: Pure forms of Bis-GMA (70-100 nm) and UDMA (50-100 nm) nanofibers were confirmed by SEM and FTIR. One-way ANOVA revealed significant differences for flexural strength ($p = 0.001$), flexural modulus ($p = 0.001$) and fracture toughness ($p = 0.001$) but not for neither degree of conversion ($p = 0.078$) nor depth of cure ($p = 0.879$). For both types of nanofibers, compared to the control group, reinforced groups showed greater FS and FT and comparable DC

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* Lecturer, Department of Dental Biomaterials, Faculty of Dentistry, Tanta University, Tanta, Egypt.

** Professor, Department of Chemistry, Director of Technology Transfer office, Faculty of Science, Tanta University, Tanta, Egypt.

and DoC results. For E_f, except the group reinforced with 7 wt% Bis-GMA,all groups exhibited lower values than that of the control group. Within the range of studied properties, Bis-GMA nanofibers exhibited more favourable results than UDMA nanofibers.

Conclusions: Synthesis if Bis-GMA and UDMA nanofibers could be successfully accomplished by electrospinning to be used for resin-composite reinforcement. At a certain ratio (7 wt%), these fibers recorded improvement in FS and FT while keeping E_f, DC and DoC unchanged.

Keywords: Electrospinning; Nanofibers; Bis-GMA; UDMA; Degree of conversion; depth of cure; Flexural Strength; Flexural Modulus and Fracture Toughness.

INTRODUCTION

Restoring both anterior and posterior teeth with resin-composite materials is now an established clinical practice and the substitution of dental amalgam restorations by resin-composite restorations is increasing. The clinical performance and durability of these restorations are determined by a number of factors: (i) the filling technique applied to produce the restoration, (ii) the patient's oral habits and the relevant masticatory loading, and (iii) the physical and mechanical properties of the restorative materials themselves [1-3]. The properties of resin-composite materials depend on several factors related to the polymer matrix, the filler particles and the coupling between filler and matrix [4].

Production of resin-composites of different mechanical properties may be desirable. This is because the clinician can choose the appropriate material according to the intended use. In certain situations, the material should be stiff and strong, in others, flexibility is more important and strength not a critical factor. Toughness or resilience may be the property of interest in a different case. By the wise choice of the relative content of monomer components and in conjunction with a proper selection of filler, resin-composites may be designed to fulfil the needs of specific indications for use [5].

Bis-GMA (2, 2-bis-[4-(2-hydroxy-3 methacryloyloxypropoxy) phenyl] propane) developed by R.L. Bowen [6] more than five decades ago has been the most popular cross-linking dental dimethacrylate. Bis-GMA is characterized by many properties that make it superior to other dimethacrylates. The relatively high molecular weight (512 g/mol), stiff partially aromatic molecular structure with low polymerization shrinkage (6.1 vol.%), rapid hardening, low volatility, good adhesive and outstanding mechanical properties of the cured resins are some of the preferred features of Bis-GMA [7]. However, compared to methyl methacrylate, Bis-GMA is relatively cytotoxic. The high viscosity (1.0-1.2 kPa s at 23ºC) limiting the attainable filler loading of composites and the low degree of C=C bond conversion resulting in a relatively high amount of leachable monomer through oral fluids are further shortcomings of it [8].

UDMA (1,6-bis-(2-methacryloyloxyethoxycarbonylamino)- 2,2,4-trimethylhexane is well-established in dentistry as a resin monomer for dental composites [9,10]. It was first introduced in 1974 by Foster and Walker [11] as an alternative monomer to Bis-GMA. It is produced by the reaction of 2,4,4- trimethylhexamethylene diisocyanate and 2-hydroxyethyl methacrylate (HEMA). UDMA has a molecular weight of about 470 g/mol and also shows a relatively low polymerization shrinkage (6.5 vol.%). In addition, it has a significantly lower viscosity (8-10 Pa s at 23ºC) compared to Bis-GMA. However, the polymerization of UDMA alone results in more flexible materials, therefore, UDMA is only used in combination with Bis-GMA [12].

Most of dental restorative resin-composites marketed today are classified as particulate resin-composites. They are usually made up of ceramic-based particles with sizes ranging from 5 nm to 50 μm surrounded by a photopolymerizable methacrylate matrix based mainly on blends of Bis-GMA and TEGDMA [13]. For improvement of the physico-mechanical properties of resin-composite materials, filler modification, in terms of percent of filler loading, size, type, surface treatment… etc., attracted the vast majority of interest between researchers. However, modification of the matrix monomers is of great importance to enhance the physico-mechanical characteristics of these materials.

Synthesis of organic nanofibers can be valuable in the enhancement of some properties of resin-composites. This is because fiber fillers are superior to the particulate fillers in many aspects. These include: i) the large specific surface area, high aspect-ratio and unique configuration that lead to greater interfacial bonding force between fibers and resin [14], ii) distribution of stresses and inhibition of crack initiation and propagation [15], and iii) the ability to improve crucial mechanical properties such as flexural strength and fracture toughness [16]. Lately, electrospinning has been applied to produce nanofibers from different materials for a variety of purposes. One of these applications is the fabrication of nano-scaled fibers for the reinforcement of resin-composite materials. Basically, it applies an electrical charge to draw nano-sized fibers from a solution. It has been applied to produce metallic, ceramic and polymeric nanofibers from their precursor materials [17, 18].

The degree of conversion (DC) in a given resin system has repeatedly been studied by dental researchers as it is considered an important indicator for the prospective properties of such systems [19]. To produce a resin-based restorative material with enhanced mechanical properties with a minimum of unreacted, leachable components, a relatively high DC is preferable. However, increasing the double bond conversion may require the addition of low-viscosity diluents such as TEGDMA (triethylene glycol dimethacrylate) that produce composites with reduced properties and greater polymerization shrinkage [20]. The best conversion in the Bis-GMA- and UDMA-resin based systems was found to be at higher concentrations of TEGDMA. Nevertheless, though the DC is highest for the diluent-rich systems, other properties such as flexural strength and polymerization shrinkage - that are affected by the crosslink density - become compromised at low concentrations of basic monomers [21].

Studies [22, 23] shown the inverse relationship that exists between the remaining double bonds in a resin system and its mechanical properties. Other studies [24, 25] showed that monomer viscosity and glass transition temperature relate directly to polymerization shrinkage and degree of conversion. It was reported that the conversion percent of double bonds is majorly affected by two factors: the type of resin used in the organic matrix and the mode of curing used [26].

A major problem related to the photo-polymerized resin-composites is the depth of cure (DoC) limitation and possibility of inadequate monomer conversion at deeper parts of restoration [27]. Insufficient polymerization has been reported to adversely affect the physico-mechanical [28] and biological [29] properties of these materials. The depth of cure - referring to the thickness of a resin-based composite that is adequately cured [30] - can be influenced by several parameters related to the cured material - type, shade, translucency, filler size and distribution, refractive index mismatch and photoinitiator - [31], the curing unit - light output, wavelength range, exposure time and distance from cured material - [32] and the placement technique, e.g., incremental- or bulk-placement [33,34].

Evaluation of strength-related properties of experimental and commercially available dental resin-composites are very essential for accepting such materials as restoratives materials. One good aspect of the flexural strength testing is that the material is evaluated under three main types of stresses; compressive, tensile and shear [35]. In the same stream, flexural modulus is an essential testing procedure to verify the capacity of a restorative material to serve successfully in the oral cavity. It is directly related to the composition and the interatomic bonding [36] and affected by monomer chemistry [37], monomer structure [38], filler content [39] and filler/matrix interactions [40, 41]. As an important indicator of performance of restorative materials, fracture toughness testing has been applied for thorough evaluation of such materials. It defines the resistance to crack propagation from a pre-existing flaw [42]. Resistance to crack propagation over time is very essential for making a durable restoration in oral environments [43]. Despite of the crack may be small to the extent that it can not be detected initially, it progresses under masticatory functional loads or other stresses and fracture of the restoration and its related clinical complications may result [44].

Therefore, the main purposes of this study were: firstly, to synthesize Bis-GMA and UDMA nanofibers by electrospinning technique for the reinforcement of experimental resin-nano-composites. Secondly, to characterize the synthesized nanofibers by scanning electron microscopy (SEM) and Fourier-transform infra-red spectroscopy (FTIR). Thirdly, to compare the effect of added Bis-GMA nanofibers with that of UDMA nanofibers on some properties of experimental resin-composite; degree of conversion, depth of cure, flexural strength, flexural modulus and fracture toughness.

Our null hypotheses were: i) the electrospun organic nanofibers will have no significant effect on the studied properties of the experimental resin-composite and ii) there will be no difference between the effect of Bis-GMA nanofibers and that of UDMA nanofibers on the examined properties of experimental resin-composites.

MATERIALS AND METHODS

Materials: Materials used in this study are listed in Table 1.

Methods:

Preparation of nanofibers by electrospinning:

Bis-GMA and UDMA nanofibers were prepared in an electrospinning unit (Nano-01A Electrospinning setup, MEC C Co., LTD, Tokyo, Japan) that consisted of four main components: i) a syringe pump that controls the feeding rate of the polymeric solution to be electrospun, ii) a capillary tube with a small-diameter needle that contains the

TABLE (1) Information and percentages of chemical ingredients used in preparing the experimental resin-composite and electrospun organic (Bis-GMA and UDMA) nanofibers.

Characterization	*Supplier*
A) Resin 27 wt%: 1) Bisphenol A diglycidyl ether dimethacrylate (Bis-GMA). 2) Tri (ethylene glycol) dimethacrylate (TEGDMA) 3) Urethane Dimethacrylate (UDMA). 4) Bisphenol A polyethethylene glycol diether dimethacrylate (Bis-EMA). 5) Polyethylene Glycol Dimethacrylate (PEGDMA). **B) Nano-fillers 72 wt%:** <50 nm nanoparticles and 0.3 μm loosely agglomerated clusters of silica and zirconia. **C) Initiator and accelerator 1wt%:** 1) Camphorquinone (CQ). 2) Ethyl-4-(N,N'-dimethylamino) benzoate (4EDMAB). **D) Silane:** 3-methacyloxypropyltrimethoxysilane.	Sigma Aldrich, St Louis, Missouri Ltd, USA

polymer solution held by its surface tension, iii) a high voltage source that stretches the solution into ultrafine fibers and iv) a metallic collector covered with an aluminum foil upon which a mat of the electrospun nanofibers can be collected. Upon application of a high voltage, the polymer solution inside the needle becomes highly electrified and tends to form a conical shape known as the Taylor cone. Upon further increase in the electric field in which the repulsive electrostatic force surpasses the surface tension of the solution, the charged jet of the solution is ejected from the tip of the Taylor cone to become very long and thin electrospun nanofibers. The randomly oriented negatively charged fibers, in the form of mat, are collected on a positively charged metallic surface covered with an aluminum foil [45, 46].

Preparation of Bis-GMA nanofibers:

A solution consisting of 60 wt% of Bis-GMA (MW = 512.599 g/mol), 20 wt% TEGDMA (MW = 286.324 g/mol) and 20 wt% PEGDMA (MW = 350 g/mol) was prepared for electrospinning. This solution was vigorously stirred in a magnetic stirrer (DAIHAN MaXtir™ 500S Hi-performance Digital Magnetic Stirrers, SRICO, South Korea) for 2 h at 37 °C in a glass vial in oil bath then placed in a vacuum oven (Napco model 5851, Capovani Brothers, Inc., Scotia, New York 12302, United States) for 24 h at 37 °C to remove any air bubbles. The capillary tube with a small diameter needle (18 gauge) was connected to the positive terminal of a high-voltage supply (Spellman SL30) generating 20 kV DC. At a flow rate of 0.7 ml/h and a distance of 10 cm between the needle tip ejecting the nanofibers and the metallic collector, the nanofibers were produced. Nanofibers were dried in a vacuum oven (Napco model 5851, Capovani Brothers, Inc., Scotia, New York 12302, United States) for 36 h at room temperature.

Preparation of UDMA nanofibers:

For the production of these nanofibers, a solution was prepared from 80 wt% UDMA (MW = 470.563 g/mol) and 20 wt% of PEGDMA. This solution was stirred with the magnetic stirrer for 1 h at room temperature in a glass vial then placed in the vacuum oven for 24 h at room temperature to remove any air bubbles. The electrospinning conditions applied for Bis-GMA nanofibers were applied for UDMA nanofibers as well.

Characterization of nanofibers:

Characterization of the prepared organic nanofibers was carried out by: Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR).

Scanning electron microscopy (SEM):

Scanning electron microscopy (SEM) was done after the nanofibers were prepared and ball-milled. Nanofiber specimens were coated with a gold coating (SPI-Modules Vac/Sputter Coater). Specimens were scanned by an electron microscope (JEOL-JSM-5200LV, Tokyo, Japan) at a magnification of 20000 x.

Fourier transform infrared spectroscopy (FTIR)

This investigation was carried out using an FTIR unit (FTIR, Model: EQUINO X55, Bruker, Germany) to identify the functional groups of the synthesized nanofibers. The ball-milled nanofibers were added to Potassium Bromide (KBr) at the ratio of 1:80 respectively. The mixture was pressed under a hydraulic press to form a tablet. Ten scans were recorded between the wave number of 5000 to 200 cm^{-1} with a resolution of 1 cm^{-1} and averaged.

To make sure that the organic nanofibers will be adequately milled to be added as a filler component to the resin matrix, an assigned FTIR at the range of 2000 to 1000 cm^{-1} was carried out to the solutions (Bis-GMA/TEGDMA/PEGDMA) and (UDMA/PEGDMA) used for preparing these nanofibers. Each 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, both types of 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 mats. To obtain fibers at the nanoscale (≤ 100 nm), these mats of fibers 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 in diameter, at a speed of 350 rpm, for 7 h.

Silanization of nanoparticles

Silanization of inorganic filler particles (silica and zirconia nano-particles/clusters) was accomplished with 5 wt% silane coupling agent (3-methacyloxypropyltrimethoxy-Silane) and 95 wt% acetone solvent [47]. Each type of nano-particles/clusters was dispersed in acetone in a separate bottle. The silane agent was then added to each solution at a percent of 5 wt% at room temperature and the mixture was vigorously stirred in the magnetic stirrer, described above, at 150 rpm for 15 h. Each solution was then filtered in order to collect the silanized nanoparticles. To assure the complete removal of solvent, the mixture was stored for 24 h at 37 °C. After storage, the mixtures were sieved through a 300 nm then 100 nm sieve and kept in a sonication device (Power sonic 405, Hwashin Technology Co, Korea) for 10 min. the nanoparticles/clusters were then dried under vacuum in an oven (Vacuum drying chambers, Binder, Bohemia, North American) at 110 °C for 3 h.

Formulation of experimental resin-composites

The method described by Asmussen and Peutzfeldt [5] for the reparation of the resin matrix of the experimental resin-composite was followed in this study. The organic matrix that forms 27 wt% of the resin-composite was prepared by mixing Bis-GMA, UDMA and Bis-EMA as the forming monomers. In addition, TEGDMA was added as a diluent co-monomer and PEGDMA as a cross linking agent. Firstly, TEGDMA and PEGDMA were mixed in proportions of 50:50 (wt%) to form a diluent solution. Mixing process was performed by Vortex mixer (Vortex, Ika, Sigma Aldrich, St, Louis, Missouri, LTD, USA) at a speed of 100 rpm for 6 h at room temperature. Then, TEGDMA/PEGDMA mixture was mixed with UDMA and Bis-EMA in proportions of 1:1:1 (wt%) at 100 rpm for 24 h at room temperature. Finally, 30 wt% of Bis-GMA was added to 70 wt% of the previously prepared solution [(TEGDMA/PEGDMA)/ UDMA/Bis-EMA] and the solution was mixed at 200 rpm for 24 h at room temperature.

Preparation of the filler component of the experimental nanocomposite was performed according to previous published works [48, 49]. Silanized ZrO_2 nanoclusters (20 wt%) were mixed to 80 wt% of silanized ZrO_2 nanoparticles in a mechanical stirrer with vertical blade (5040001 RW28, Atlanta, USA) at a speed of 20 rpm for 2 h at room temperature to form ZrO_2 nanofiller mixture. This process was repeated for silica nanoclusters/nanoparticles in the same proportions and conditions to form silica nanofiller mixture. Twenty percent of ZrO_2 nanofillers mixture and 80 wt% of SiO_2 nanofillers mixture were mixed in the mechanical stirrer at 20 rpm for 5 h at room temperature to form the filler component of the experimental resin-composite.

This filler mixture was then divided into the study groups to be investigated; one group without nanofibers. Other three groups were formed by adding Bis-GMA nanofibers at the ratio of 7, 11 and 15 wt% at the expense of the nanoparticles. More four groups were formulated by addition of UDMA nanofibers at the ratio of 7, 11, 15 and 20 wt% at the expense of nanoparticles. The added nanofibers were thoroughly mixed with the nanoparticles in the mechanical stirrer at 50 rpm for 6 h at room temperature to ensure even distribution of the nanofibers throughout the fillers. The photoinitiator (camphorquinone) and co-initiator (4EDMAB) were mixed in a proportion of 1: 1 wt% in the mechanical stirrer at 10 rpm for 1 h at room temperature to form the photo-activation system. Finally, each group of the experimental resin-composite was prepared in the proportions of 27 wt% organic matrix, 72 wt% fillers and 1wt% photo-activation system. Mixing process was achieved in a centrifugal mixing device (Speed-Mixer, DAC 150 FVZK, Hauschild Engineering, Germany).

Grouping

Group I: Experimental composite without nanofibers.

Group II: Experimental composite reinforced with 7 wt% Bis-GMA nanofibers.

Group III: Experimental composite reinforced with 11 wt% Bis-GMA nanofibers.

Group IV: Experimental composite reinforced with 15 wt% Bis-GMA nanofibers.

Group V: Experimental composite reinforced with 7 wt% UDMA nanofibers.

Group VI: Experimental composite reinforced with 11 wt% UDMA nanofibers.

Group VII: Experimental composite reinforced with 15 wt% UDMA nanofibers.

Group VIII: Experimental composite reinforced with 20 wt% UDMA nanofibers.

Studied properties

Degree of conversion (DC)

Two equal weights (100 mg) of cured and uncured experimental resin-composite of each group were prepared. The degree of conversion (DC) was studied using the FTIR method (FTIR, Model: EQUINO X55, Bruker, Germany). The cured composite specimens were milled in a ball-milling machine (Retsch – PM 400, Haan, Germany) with a ball size of 10 mm in diameter at a speed of 350 rpm for 4 h. Each cured and uncured composite specimen was then added individually to Potassium Bromide (KBr) at the ratio of 1:80 respectively. The mixture was pressed under hydraulic press to form a tablet. Ten scans for each specimen were measured between wave number of 5000 to 200 cm^{-1} were recorded with a resolution of $1cm^{-1}$. DC (%) was calculated from the equivalent aliphatic (1638 cm^{-1})/ aromatic (1608 cm^{-1}) molar ratios of cured (C) and uncured (U) specimens according to the following expression [50]: DC = (1- C/U) × 100 (%).

Depth of cure (DoC)

Depth of cure (DoC) was measured according to International Organization for Standardization ISO 4049: 2009a [51]. Half-split stainless steel cylindrical molds of 4 mm in diameter and 6 mm in thickness were used for specimen preparation (*n*=10). Mold was put on the glass slide covered with Mylar strip and separating medium was applied to the wall of the mold with a brush. The composite material was applied to mold cavity with a plastic instrument. After that, a glass slide covered with Mylar strip was applied on top of the mold with a gentle pressure. Curing was carried out only on top of specimens before removal from the mold. Curing was accomplished by light-emitting-diode LED curing unit for 20 s that radiated the light in 430-485 nm spectral wavelength range with irradiance of 1200 mW/cm^2 output intensity.

After light curing, the half-split mold was gently opened and specimens were removed from the mold and the uncured resin-composite material was scrapped away with a plastic spatula. The absolute length (ΔL) of the cylindrical specimens of cured resin-composite was then measured with a micrometer caliper. The absolute length (ΔL) was divided by two and the depth of cure was calculated as follows:

Depth of cure by ISO (D_{ISO}) *(mm)* $= \Delta L/2$.

Flexural strength (FS)

Flexural strength (FS) testing was performed according to ISO 4049:2009 by a three-point bending test [51]. A half-split stainless-steel mold was used to prepare bar-shaped specimens (2 mm depth x 2 mm width x 25 mm length). The mold was put on top of a glass slide covered by Mylar strip. A separating medium was applied to mold wall with a brush, then the composite material was applied to the mold cavity using a plastic instrument. Another glass slide covered with Mylar strip was applied on the top of the mold with a gentle hand pressure. Curing was done on from the top and the bottom sides of the specimens before removal from the mold. The resin-composite was photo-polymerized by LED curing unit for 20 s with three overlapping light exposures to cure the entire length of specimen. After polymerization, all the specimens were stored in distilled water at 37°C for 24 h.

The flexural strength test was performed in a universal testing machine (INSTRON, 3600 series, USA). The test assembly consisted of two supporting wedges placed 20 mm apart and a loading wedge that applies load at a cross-head speed of 0.75 mm/min. The applied force and strain during bending was measured as a function of deflection. The flexural strength (MPa) was calculated according to the following formula:

$$\mathbf{FS} = 3F\, d/2wh^2$$

Where F = maximum force (N), d = distance between the two supports, w = width of the specimen, h = height of the specimen (all in mm).

Flexural modulus (E_f)

After recording the flexural strength, the flexural elastic modulus (E_f) in GPa was calculated according to the following formula:

$$E_f = FL^3/4BH^3d$$

Where F is the maximum force (N), L is the distance between the supports, B is the width of the specimen, H is the height of the specimen, and d is the deflection (all in mm).

Fracture toughness (FT)

Testing of Fracture toughness of our specimens was conducted according to ISO/FDIS 6872:2007 [52]. Bar-shaped specimens (25 mm length × 5 mm width × 2 mm depth) from each group (*n* = 10) were prepared in half-split stainless steel molds. Packing of the resin-composite material, curing and storage of specimens were performed as described for the flexural strength specimens. A single edge V-notched beam (SEVNB) at mid-span of each specimen was prepared using a disc 0.5 mm width (13014, Patterson Dental, New York, USA). The notch depth was one third (1/3) the specimen depth. A ruler and pen marker were used to standardize position, direction and length of the notch with accepted accuracy of ±0.1 mm.

Fracture toughness was determined on a single-edge notch specimen using the three-point bending method according to the procedures outlined in ISO/FDIS 6872, 2007. A three-point bending test [span length= 20 mm with the notch centrally located on the tensile side] was carried out in a Universal Testing Machine (Model 3600; Instron Industrial Products, Norwood, MA, USA) with a load cell of 5 kN. At a crosshead speed of 0.5 mm/min, loading of specimen was continued until fracture. Load-deflection curves were recorded by the help of a computer software (Instron® Bluehill Lite Software). Calculation of fracture toughness (Griffith = MPa. $m^{1/2}$) by the single-edge notched method was done according to the following equation:

$$K_{Ic} = F/B \times S/W^{1.5} \times f(c/w)$$

$$f(c/w) = 2.9(c/w)^{1/2} - 4.6(c/w)^{3/2} + 21.8(c/w)^{5/2} - 37.6(c/w)^{7/2} + (c/w)^{9/2}$$

Where F=Maximum Load, B=Specimen width, S=Supporting span, w=Specimen height, c=notch length, f(c/w)=a function of c and w

Statistical analysis

Data were collected, tabulated and statistically analyzed using an IBM compatible personal computer with SPSS statistical package version 20 (SPSS Inc. Released 2011. Armnok, NY: IBM Corp.). A one-way analysis of variance (ANOVA) with the significance level established at ($p \leq 0.05$) was applied for the statistical analysis of the results of the investigated properties. As ANOVA revealed significant differences between groups of flexural strength, flexural modulus and fracture toughness, Levene's test for homogeneity of variances was carried out for the data of each property ($p \leq 0.05$) to choose the appropriate test for multiple comparisons. Equal variances were confirmed ($p > 0.05$); therefore the Tukey test was used to determine differences between groups of each property.

RESULTS

Characterization results:

Scanning electron microscopy (SEM):

Bis-GMA nanofibers:

At a magnification of 20000 x, SEM image (Figure 1) shows smooth surface of Bis-GMA organic nanofibers. The diameter of the synthesized nanofibers ranged between 70 and 100 nm.

UDMA nanofibers:

Figure 2 shows SEM image of UDMA nanofibers at a magnification of 20000 x. The nanofibers diameter ranged from 50 to100 nm.

Fourier transform infrared spectroscopy (FTIR):

Bis-GMA nanofibers:

Formation of mixed organic nanofibers (Bis-GMA/TEGDMA/PEGDMA) is indicated by the IR spectra of the aromatic (Bis-GMA) and aliphatic (TEGDMA/PEGDMA) compounds which displayed intense peaks at 3457 cm^{-1} due to O-H stretching, at 2965- 2873 cm^{-1} due to C-H stretching of CH_2, at 1608 and 830-810 cm^{-1} due to C=C stretching, at 1509 cm^{-1} due to C-C stretching, at 1245-1100 cm^{-1} due to C-O-C stretching and at 1450 cm^{-1} due to C=O stretching. In addition, IR spectra displayed peaks at 1600-1625 cm^{-1} due to benzene ring stretching in Bis-GMA (Figure 3).

UDMA nanofibers:

Figure 4 presents an FTIR that displays specific absorption bands attributed to urethane NH (3500-3320 cm^{-1}), the vibrations of the CH_2 groups (2870-2950 cm^{-1}) and carbonyl unit (CO) from the urethane, as well as to the ester moieties (1717 cm^{-1}). The absorption bands for carbon-carbon double bond on the methacrylate function can be detected at 1608 and 810 cm^{-1}, the C-C vibration at 1535-1509 cm^{-1}, the C-O-C unit in the region 1100-1245 cm^{-1}, at 1368 cm^{-1} due to C-H stretching in CH_3 and at 1450 cm^{-1} due to C=O stretching.

With respect to the "assigned" FTIR that was conducted twice (one time for the solutions of both types of nanofibers prepared for electrospinning and another time for the electrospun nanofibers) at the range of 2000 to 1000 cm^{-1}, adequate polymerization was confirmed by the increase in the single bond at the expense of the double bond indicating partial polymerization as can be seen in Figures 5A and 5B for Bis-GMA nanofibers and Figure 6A and 6B for UDMA nanofibers, respectively.

Results of investigated properties:

Means and standard deviations of degree of conversion (DC), depth of cure (DoC), flexural strength (FS), Flexural modulus (E_f) and fracture toughness (FT) of all studied groups are listed in Table 2. Results of multiple comparisons (Tukey test) are shown in Table 2 by superscript letters as well, ($p \leq 0.05$).

Statistical analysis revealed significant differences for flexural strength ($p = 0.001$), flexural modulus ($p = 0.001$) and fracture toughness ($p = 0.001$) but not for neither degree of conversion ($p = 0.078$) nor depth of cure ($p = 0.879$).

Though no significant differences were found between studied groups for DC, all reinforced groups (with both Bis-GMA and UDMA nanofibers) showed greater DC than the control group. Groups reinforced with UDMA nanofibers recorded slightly higher DC than those reinforced with Bis-GMA nanofibers. This slight increase becomes greater between corresponding groups (with the same percent of added nanofibers) when the percent is higher. In both categories of groups reinforced with Bis-GMA and UDMA nanofibers (within the range selected, 7 - 20 wt%), there was a systematic increase in DC with increasing the nanofibers.

Only groups reinforced with 7% nanofibers (both Bis-GMA and UDMA) recorded slightly greater DoC than the control group. The remaining reinforced groups showed similar or slightly lower DoC than the control group. For both types of nanofibers, there was no evident correlation between the added percent of nanofibers and the resulting DoC, where 7% Bis-GMA nanofibers recorded slightly greater DoC than the control group and groups reinforced with both 11% and 15%. Similarly, the control group and groups reinforced with 11%, 15% and 20% UDMA nanofibers showed slightly lower DoC than that recorded for the group reinforced with 7%.

All groups reinforced with both types of nanofibers recorded significantly greater FS mean values than the control group. For both types, FS values showed a systematic increase with increasing the percent of nanofibers. For a given percent of nanofibers, Bis-GMA nanofibers enhanced FS of the experimental resin-composites more than UDMA nanofibers. The flexural modulus (E_f) mean values for all groups reinforced with both nanofibers were significantly lower than the control group except that reinforced with 7% Bis-GMA nanofibers. On the contrary to the flexural strength, for both types of nanofibers, there was an inverse relationship between the added percent of nanofibers and the resulting E_f.

Compared to the control group, all reinforced groups exhibited significantly greater FT. Within the range selected (7 – 20 wt%), higher percent of nanofibers of both types enhanced FT of the experimental resin-composites systematically. For a given percent of added nanofibers, groups reinforced with Bis-GMA nanofibers showed slightly greater FT than those reinforced with UDMA nanofibers.

TABLE (2) Means and standard deviations (in parentheses) of degree of conversion, depth of cure, flexural strength, flexural modulus and fracture toughness. Each value represents the mean of ten specimens. Different superscript letters indicates statistically significant differences between groups of each column ($p \leq 0.05$).

Type of nanofibers	Percentage of nanofibers (%)	Investigated Properties				
		Degree of Conversion (%)	Depth of Cure (mm)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Fracture Toughness (MPa. $m^{1/2}$)
None	Control group (0%)	75.55 (2.74) ^{a}	2.54 (0.13) ^{b}	98.20 (9.35) ^{a}	11.01 (0.91) ^{a,c,e}	1.163 (0.140) ^{d}
Bis-GMA nanofibers	7 %	76.30 (2.98) ^{a}	2.55 (0.17) ^{b}	113.92 (6.74) ^{b}	11.27 (0.65) ^{c}	1.653 (0.167) ^{a}
	11 %	76.81 (4.44) ^{a}	2.50 (0.11) ^{b}	131.65 (3.96) ^{c,e}	10.35 (1.02)^{c,e,f}	1.950 (0.132) ^{b}
	15 %	77.03 (2.86) ^{a}	2.54 (0.27) ^{b}	145.47 (4.84) ^{d}	9.84 (0.88)^{c,e}	2.542 (0.266) ^{c}
UDMA nanofibers	7 %	76.52 (3.56) ^{a}	2.58 (0.16) ^{b}	103.94 (6.80) ^{a}	10.51 (0.98) ^{c,e,j}	1.580 (0.163) ^{a}
	11 %	77.44 (1.78) ^{a}	2.47 (0.11) ^{b}	124.54 (4.29) ^{c}	9.71 (1.27) ^{b,d,e}	1.812 (0.127) ^{a,b}
	15 %	78.89 (2.93) ^{a}	2.54 (0.21) ^{b}	139.02 (5.34) ^{d,e}	9.47 (0.98) ^{b,f,j}	2.422 (0.119) ^{c}
	20 %	79.92 (3.21) ^{a}	2.53 (0.14) ^{b}	155.38 (4.64) ^{f}	8.49 (0.97) ^{b}	2.945 (0.178) ^{e}

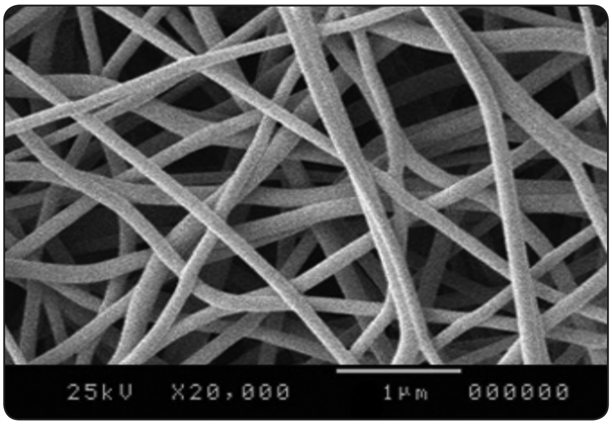

Fig. (1) SEM image (20,000 x) showing Bis-GMA nanofibers (70-100 nm).

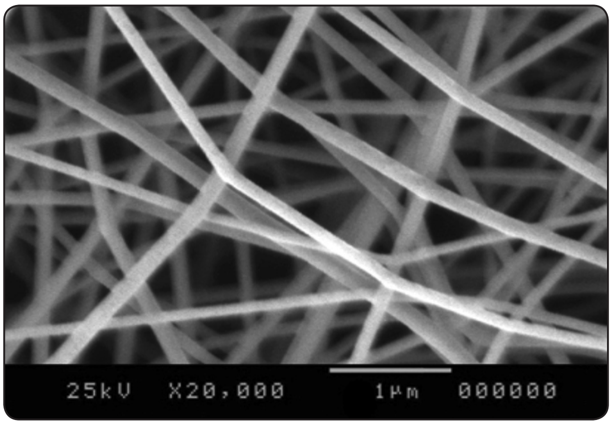

Fig. (2) SEM image (20,000 x) showing UDMA nanofibers (50-100 nm).

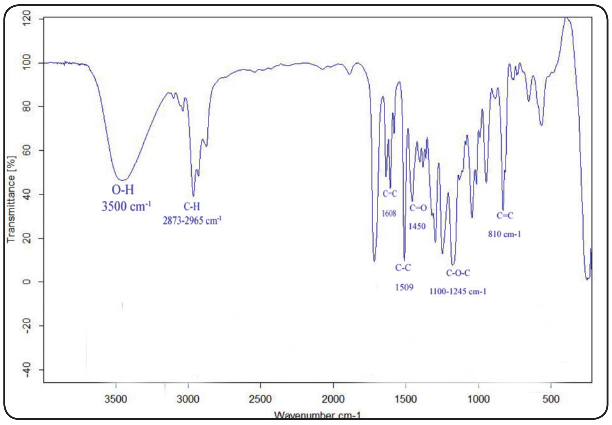

Fig. (3) FTIR spectra of Bis-GMA nanofibers made up of (Bis-GMA/TEGDMA/ PEGDMA).

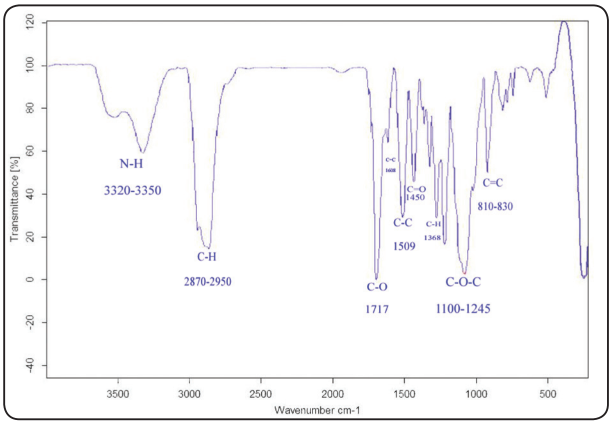

Fig. (4) FTIR spectra of UDMA nanofibers made up of (UDMA/ PEGDMA).

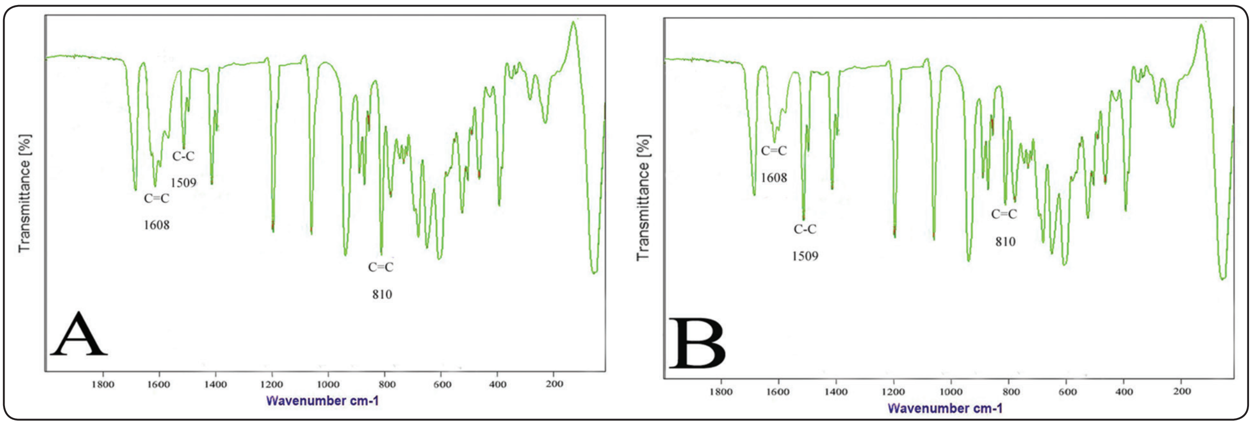

Fig. (5) An assigned FTIR (2000 -1000 Cm^{-1}) for the solution used to prepare Bis-GMA nanofibers (A) and for the electrospun nanofibers (B) revealing an increase in the single bond/double bond ratio indicating partial polymerization.

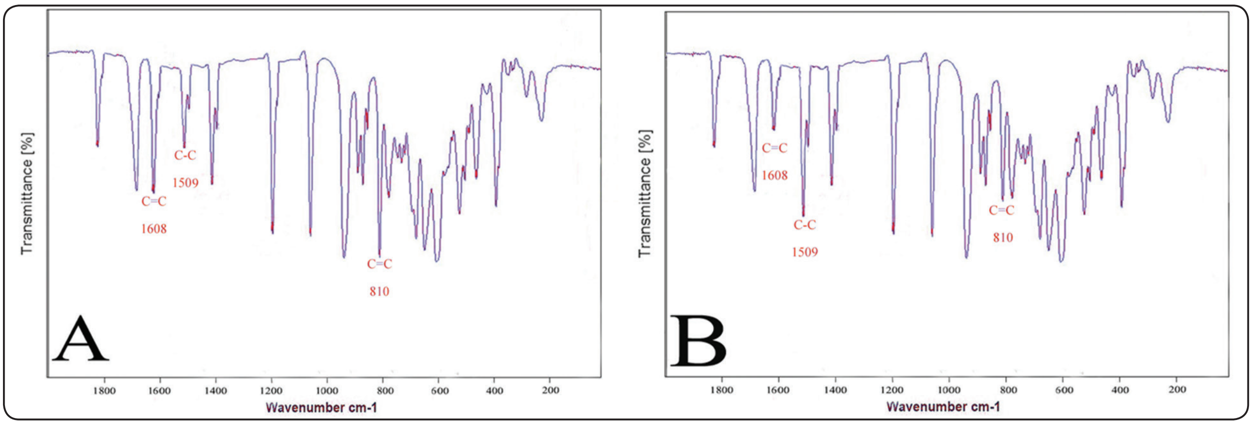

Fig. (6) An assigned FTIR (2000 -1000 Cm^{-1}) for the solution used to prepare UDMA nanofibers (A) and for the electrospun nanofibers (B) revealing an increase in the single bond/double bond ratio indicating partial polymerization.

DISCUSSION

Though the toughening effect of reinforcing fibers in dental resin-composites has been tested for several years, the reinforcing effect is still questionable. Poor toughening and strengthening effect recorded for some fiber-reinforced materials may be attributed to utilization of short discontinuous fibers [53-55]. Currently, the concept being applied in reinforcing resin-composite materials with fibers is based on the "bilayered composite system" in which the fiber-reinforced composite base is made of discontinuous fibers with length of the fibers exceeding the critical fiber length in the dimethacrylate polymer matrix [56]. In such a material, the base layer provides more toughness and prevention of crack propagation and the superficial layer gives more wear resistance and enhanced polishability. The combination of these two layers in the bilayered resin-composite structure is considered as a biomimetic restoration system by mimicking the fibrous structure of dentin-enamel complex [57].

In the present study, the electrospinning technology was utilized to synthesize nanofibers from the two monomers most commonly used in the resin-based systems (Bis-GMA and UDMA) to reinforce experimental resin-composites. Several previous studies used inorganic nanofibers such as glass nanofibers[58], hydroxyapatite nanofibers[59], nanofibrillar silicate[60] and zirconia nanofibers[61] to reinforce resin-composite materials. Other studies utilized polymer nanofibers such as nylon 6 nanofibers[62], polyacrylonitrile polymethyl methacrylate (PAN-PMMA)[63], polyvinyl alcohol (PV-OH) nanofibers[64] to enhance the physico-mechanical properties of these materials as well.

However, synthesis of nanofiber fillers from the same resin matrix material can be advantageous in many respects. Firstly, it is well-established between authors that one major reason of failure of restorative resin-composites is the poor adhesion between fillers and resin matrix. In such a situation, when the material is loaded, the load may not be transferred from the weak resin matrix to the stronger filler component leading to existence of points of stress concentration throughout the resin matrix ending with failure of the material. In our study, the synthesized Bis-GMA and UDMA nanofibers, when mixed with the matrix monomers, become cross-linked within the matrix and a network structure forms between the reinforcing nanofibers and resin matrix after photopolymerization. This remarkably improves the interfacial properties between fibers and matrix. Secondly, silane coupling agent is commonly used to promote filler-matrix adhesion. However, improper silanation may result in weak unstable bond between fillers and resin that can be degraded by water absorbed by the resin-composite[65]. In our work, the synthesized organic nanofibers do not need silanation to be bonded to the matrix because of the chemical bonding that takes place between the nanofibers and matrix monomers after light curing.

Thirdly, dissimilarity of critical properties - such as refractive index, coefficient of thermal expansion/contraction - between fillers and resin may result in shortcomings in the produced resin-composite material. Poor aesthetics due to refractive index mismatching, debonding because of different thermal properties between the two phases, fillers and resin, stress concentration and crack formation may be some of these drawbacks. Preparation of a filler component - Bis-GMA and UDMA nanofibers - from the same material of the matrix enables us to avoid a lot of these negative outcomes. Fourthly, when subjected to friction either by opposing restoration or natural dentition, resin-composites reinforced with such nanofibers exhibit wear in both the resin matrix and reinforcing nanofibers equally leaving smooth surface without irregularities. These irregularities, in inorganic fillers-filled restorations, can be caused by either existence of harder inorganic filler particles on the restoration surface or due to pores created by dislodgment of these particles. Keeping the restoration surface without such irregularities remarkably adds to the good aesthetics of the restoration. Lastly, preparation of such polymeric nanofibers is so far cheaper and easier than a lot of inorganic nanofillers, either particulate fillers or fibers.

Choosing the range 7–20 wt% of nanofibers that were used for reinforcing the prepared experimental resin-composites was based on pilot studies conducted to the investigated properties, particularly FS and FT. The nanofiber percent was increased gradually as long as there was an increase in the mean value of the tested property. For Bis-GMA nanofibers, the maximum percent that recorded enhancement was 15 wt% while for UDMA nanofibers was 20 wt%. The lower viscosity of UDMA, compared to Bis-GMA, allowed more fiber fillers to be incorporated into the mixture. Increasing the percent of added nanofibers beyond 15 wt% for Bis-GMA nanofibers and 20 wt% for UDMA nanofibers recorded results, though greater than the control group, lower than groups reinforced with lower percents. Starting with 7 wt% nanofibers was because there are some studies that applied that percent for reinforcing resin-composites with both inorganic [62] and polymer nanofibers [63]. Another important point regarding why these organic nanofibers were roughly termed Bis-GMA and UDMA nanofibers though other ingredients were incorporated in the initial mix of each. This is because the main component in both types of synthesized nanofibers were Bis-GMA and UDMA, respectively. Addition of TEGDMA as a diluent in case of Bis-GMA nanofibers was just to enable us to prepare a solution suitable for electrospinning. PEGDMA, as a crosslinking agent, was added in both types of nanofibers to enhance the mechanical properties of the produced nanofibers.

As the statistical analysis revealed significant differences between the reinforced groups, with both types of nanofibers, and the control group for FS, E_f and FT, the first null hypothesis was rejected. This null hypothesis, however, was accepted for DC and DoC because of the absence of statistical significant differences between studied groups. Both types of nanofibers produced remarkable enhancement in FS of reinforced groups over the control group with better results, at a given percent, for Bis-GMA nanofibers than those of UDMA nanofibers. This improvement was, within the range studied 7-20 wt%, directly proportional to the added percent of nanofibers. There have been, however, studies that utilized polymer nanofibers to reinforce resin-composites but the results revealed decrease in flexural properties. This reduction was attributed to limitation of bonding between the nanofibers and resin matrix. Another reasoning was based on incomplete wetting of the nanofibers by the infiltrating resin, thus resulting in inclusion of air voids that ultimately compromised the strength [66]. In the present study, improved FS of experimental resin-composites upon reinforcement with Bis-GMA and UDMA nanofibers emphasizes that there was a good bonding between the resin matrix and nanofibers as well as adequate wetting of these nanofibers with resin. Production of these polymeric nanofibers by electrospinning technique initiates some polymerization in these nanofibers. Partial polymerization of the freshly electrospun nanofibers was majorly thought to be due to exposure to the high voltage (20 kV) and heat accompanying the electrospinning process. Whatever the kind and intensity of the activating source, because of the very thin diameter "nano-scale" of these nanofibers, it would be able to induce polymerization, even partially, to these fibers. Such nanofibers, with still adequate unpolymerized monomers, when mixed with the resin part of the composite material form chemical bonding and creates good entanglement and crosslinking between the resin matrix and reinforcing nanofibers.

In agreement with our findings that revealed enhanced FS of resin-composites upon reinforcing with polymer nanofibers, a study [62] applying electrospun nylon 6 nanofibers to reinforce a resin-composite based on Bis-GMA/TEGDMA reported that FS was improved by 36 % upon impregnation of 5 % (mass fraction) of these nanofibers into the resin matrix. In the same stream, Lin et al. [63] concluded that the FS of a resin-composite reinforced with 7.5wt % of PAN-PMMA nanofibers was increased by 18.7 %.

Mean values of flexural modulus (E_f) showed different behaviour than that of FS. Except the resin-composite reinforced with 7 wt% Bis-GMA all reinforced groups, with both types of nanofibers, revealed lower E_f than the control group. More impregnation of nanofibers of both types into the resin matrix recorded more reduction in E_f. This finding can be attributed to the fact that the material's modulus is an inherent property and is directly related to the material's composition and interatomic bonding [36]. Accordingly, we can say that addition of polymeric nanofibers which are weaker and softer - compared to the inorganic particulate fillers - at the expense of the inorganic fillers led to reduction in the E_f values. Reinforcement with 7 wt% Bis-GMA nanofibers, however, exhibited slightly greater E_f (11.27 GPa) than that of the control group (11.01 GPa). This can be attributed to removal of just 7 wt% of inorganic particulate fillers and replacing them with polymeric nanofibers did not do much change in the final composition of the experimental resin-composite. This was not the case with other groups reinforced with higher percents of nanofibers or even with the same percent of UDMA nanofibers that recorded lower E_f (10.51 GPa). The poorer mechanical properties of UDMA, compared to Bis-GMA, explain this reduction of E_f. In disagreement with our results, there are some studies that reported enhancement of E_f of resin-composites reinforced with polymeric nanofibers such as nylon 6 nanofibers [62] and PAN-PMMA nanofibers [63]. Different characteristics and percents used of reinforcing nanofibers may explain different influence of polymeric nanofibers on E_f of resin-composites.

Fracture toughness (FT) of reinforced experimental resin-composites with both types of nanofibers was significantly improved compared to the control group. This improvement was proportional to the percent of added nanofibers, within the range studied 7 – 20 wt%, with slight better superiority for Bis-GMA nanofibers than UDMA ones, at a given percent. This enhancement in FT, as well as FS, could be attributed to the inherently cross-linked fiber structure that resulted in cross-linked polymer matrix-nanofibers interfacial bonding. In terms of prevention of crack opening, it was reported [60, 67] that because of the high aspect ratio (length to diameter) of the polymeric nanofibers, there would be an enhanced intermolecular hydrogen bonding between these fibers and the resin matrix. In addition, because of the length of these nanofibers, if a micro-crack is initiated in the matrix upon loading, the nanofibers remain intact across the crack planes and support the applied load. This helps to resist crack-opening and the matrix is reinforced.

Though results showed slight improvement of degree of conversion (DC) of reinforced groups over the control group, there were no significant differences between DC of all studied groups. Absence of significant differences can be attributed to the organic nature of added nanofibers to the resin-composite groups. That is to say, a certain ratio of partially cured resin in the form of nanofibers was added to all groups of studied resin-composites with no much, if any, change in the DC of the entire material (resin and filler). Groups reinforced with UDMA nanofibers exhibited more enhanced (insignificant) DC than those reinforced with Bis-GMA nanofibers. This is in agreement with the well-established knowledge that UDMA resin has a greater DC than that of Bis-GMA resin because of the inherent viscosity of each [9, 68]. This study showed inconsistent influence of reinforcing nanofibers of both types on the depth of cure (DoC) of studied resin-composite groups. Groups reinforced with 11wt% Bis-GMA, 11 wt% and 20 wt% UDMA nanofibers recorded slightly lower DoC than the control group while remaining groups exhibited equal or slightly greater DoC. Though it may be difficult to interpret this inconsistency of DoC results, light scattering at particle interfaces and absorption by the photoinitiator and pigments may had a role. Both factors were reported to cause variations in DoC of studied resin-composites [69].

Second null hypothesis was partly rejected because there were statistical differences between the effect of Bis-GMA nanofibers and that of UDMA nanofibers on FS, E_f and FT but not on DC and DoC. For DC and DoC, both types of nanofibers exhibited comparable results that were not significant from that of the control group. For FS and FT, greater enhancing effect - that was better than the control group - was recoded for Bis-GMA nanofibers compared to that of UDMA nanofibers, at a given percent. On the contrary, E_f of all reinforced groups - except that with 7 wt% Bis-GMA - was lower than that of the control group with better results for Bis-GMA nanofibers over UDMA ones. The superior results of Bis-GMA nanofibers - in case of FS, E_f and FT - could be attributed to the greater mechanical properties that Bis-GMA resin possesses than that of UDMA resin [70, 71]. Though UDMA resin has a DC - that has an impact on mechanical performance of the restorative material - greater than that of Bis-GMA resin, it was reported that certain mechanical properties, such as strength, hardness and others, are influenced not only by the DC but also by the nature of the monomeric subunits in the polymer [9, 70].

Improvement of FS and FT of studied experimental resin-composites while maintaining the DC and DoC unchanged is advantageous. However, decrease of E_f of these materials is a shortcoming. This can be outlined from a general look at our study. Upon having a deeper insight, however, into the results and the ratios of added nanofibers of both types, we can say that the best results obtained were when the experimental resin-composites were reinforced with 7 wt% Bis-GMA nanofibers. With this ratio, while keeping the DC, DoC and E_f comparable to or slightly better (insignificant) than that of the control group, there was a significant improvement in FS and FT ($p \leq 0.001$). For UDMA nanofibers, the best results were obtained with 7 wt% as well. There was a significant enhancement in FT ($p \leq 0.001$), an insignificant increase in FS ($p = 0.388$), DC ($p = 0.997$) and DoC ($p = 0.999$) and an insignificant decrease in E_f ($p = 0.949$). Despite the greater enhancement in FS and FT recorded for higher ratios (11 – 20 wt%) of nanofibers of both types, they showed undesirable decrease in E_f.

CONCLUSIONS

- Bis-GMA and UDMA nanofibers could be successfully synthesized by electrospinning technique to be effectively used for resin-composite reinforcement.
- When added to the experimental resin-composite with a certain ratio (7 wt%), these fibers recorded enhancement in FS and FT while keeping E_f, DC and DoC unchanged.
- Within the range of studied resin-composite properties, Bis-GMA nanofibers proved superior enhancement than UDMA nanofibers.

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