

Original Article

## Fractography and Mechanical Properties of Urethane Dimethacrylate Dental Composites Reinforced with Glass Nanoparticles

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### Abstract

**Statement of Problem:** Dental resin composites are becoming prevalent in restorative dentistry and have almost replaced amalgam nowadays. Consequently, their mechanical properties and durability are critical.

**Objectives:** The aim of this study was to produce Pyrex glass nano-particles by wet milling process and use them as reinforcement in dental resins for anterior restorations and then examination of fractographic properties of these composites.

**Materials and Methods:** The glass nano-particles were achieved via wet milling. The surface of the particles was modified with 3-(Trimethoxysilyl) propyl methacrylate ( $\gamma$ -MPTMS) silane in order to improve their surface. Fourier transform infra-red (FTIR) analysis showed that the silane groups provided double bonds to the surface of the particles and prevented agglomeration. Then, the composite resins were made with different weight percentages of Pyrex glass. The mechanical properties of samples flexural test were evaluated. The required energy for fracture of the specimens was achieved via this test. The fracture surfaces of the samples were analyzed using a scanning electron microscope (SEM) in order to explain the mechanisms of fracture.

**Results:** The results and analysis showed that increasing the glass nano-particles mass fraction had a great effect on mechanical properties of the composites due to the mechanisms of crack propagation and crack deflection as well as preventing void formation. The effective energy dissipation mechanisms such as crack pinning and deflection, was observed in SEM micrographs.

**Conclusions:** Void formation in the low filler content composite is one of the mechanisms to decrease the energy required for fracture of these composites and eventually weaken them.

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### Introduction

Dental resin composites consisting of a polymerizable resin matrix and appropriate filler are becoming prevalent in modern dentistry [1]. To-date, dental resin

composites have almost replaced dental amalgam as filling materials in small-sized operations due to the fact that an amalgam filling has disadvantages such as toxicity, difficulty in fixing and lack of bioactivity [2]. Since the invention of resin composites in the 1960s

by Bowen [3], there has been great progress both in research and application of these materials. However, using these materials in heavy-load (such as, posterior areas) and large area restorations has been limited because of several disadvantages like high polymerization shrinkage, low wear resistance and secondary caries. Studies on modifications in resins and inorganic fillers have been increased significantly to improve the mechanical properties due to the function of resin composites [2].

Resin composites typically consist of a dispersed phase composed of glass filler particles such as zirconia/silica based that are distributed to reinforce a polymerizable resin matrix, and silane coupling agents. The organic compounds are glycidyl methacrylate (BIS-GMA), urethane dimethacrylate (UDMA), and triethylene glycol dimethacrylate (TEGDMA), which are cured during application. Due to the good aesthetic properties and strength of these composites, they are the most commonly used materials to restore hard tissues like dentin and enamel [4].

In addition, since particles in nano scale improve the strength and wear resistance, they are attractive as filler for dental composites [5]. Many different methods are used for the production of inorganic nano-particles [6]. One of the most convenient and promising techniques to produce nano-particles powder is mechanical milling [7]. Planetary milling is an efficient method to produce nano-particles, among the high-energy milling such as oscillating, attrition jetting and vibration milling. The selection of the appropriate milling parameters for specific equipment to produce fine powders, especially dry nanoparticles, is necessary. Drying generally causes agglomeration of fine particles due to high interaction between them [8]. Compounds such as alcohol, ketones, amines, carboxylic acids, and esters are used to prevent particle agglomeration during the production of fine particles [9].

In order to appropriately disperse nano-particles in a polymer matrix and improve compatibility between the nano-fillers and polymer matrix, using several coupling agents including silanes to modify the nano-particle's surface is very common. The proper modification of nano-particle's surface can also make a durable chemical junction between the two phases because of chemical and physical interactions with the inorganic matrix [10].

Although many studies have focused on the strength values of dental composite, little has been done about fractographic analysis. This is really

critical, since material strength alone is not sufficient to show the causes of restoration failure or clinical durability [11]. Outside the dental field, fractographic analysis is commonly used to make systematic relations between strength test values and performance of components in brittle materials [12]. A study on commercial glass-ceramics that are usually used in dental field showed that while different batches had identical properties like elastic moduli, microstructures, and fracture toughness, they had highly different failure loads because of the difference in defect type [13]. In order to determine the critical flaw and prediction of component strength in brittle materials, fractographic analysis is essential. Among all brittle materials, resin composites with high filler ratio are quite neglected in fractographic studies [14]. This group of materials is put between polymeric and ceramic materials. Fractographic specialists in both fields discover the issues difficult to distinguish when they are covered by rough microstructures that are so common in failed composite materials [15].

The present study first aimed to modify the glass nano-particles which were produced via wet comminution process and use them as fillers to reinforce dental polymers. We also aimed to observe the fractured surfaces of these new composites after failure under flexural tests and study the mechanisms of their fracture.

## Materials and Methods

### *Production of glass powder*

A borosilicate Pyrex glass (Schott Co., Mainz, Germany) with composition of 81 wt% SiO<sub>2</sub>, 13 wt% B<sub>2</sub>O<sub>3</sub>, 4 wt% Na<sub>2</sub>O + K<sub>2</sub>O and 2 wt% Al<sub>2</sub>O<sub>3</sub> was utilized. A planetary mill (Fritsch-GMBH, Idar-Oberstein, Germany) was employed for glass comminution experiments. The grinding bowl volume was 500 ml and the grinding balls were made of tungsten carbide (wolfram carbide: WC). The comminution process was performed with 7.5 weight ratios of balls to glass particles in the 500 ml grinding bowl and WC grinding balls. The glass was milled for 30 hours with 400 rpm speed. Hexane was used as the liquid dispersion medium.

### *Modification of glass particle size*

Having been milled, the glass particles were silanized with  $\gamma$ -MPTMS; then, the particle size and distribution were determined according to the previous work [16]. Fourier transforms infrared spectroscopy

py (FTIR) of glass particles and SEM photos were recorded before and after silanization.

*Production of composites*

Producing dental matrices with uniformly dispersed nano-scaled fillers has always been a challenge [17]. Acetone was a medium to explore the optimal procedure for dispersing the silanized glass particles in the resin matrix. Although the silanized particles could be highly separated and uniformly dispersed in acetone, it might not be able to achieve the same high degree of separation and dispersion in UDMA/TEGDMA. Hence, the modified glass particles with different weight fractions (5, 7.5 and 10 wt %) were dispersed in acetone by sonication to achieve uniform dispersion and the solution was added to the resin (70/30 UDMA, TEGDMA in weight percentage). Surrounding the mixture by an ice enclosure inhibits heating of the mixture. Then, acetone was removed by evaporation. This was followed by addition of camphorquinone (CQ) and ethyl 4-(dimethylamino) benzoate (4EDMAB) (in 0.5/0.5 weight ratio). Finally, the composite was placed in an ultrasonic bath to remove air bubbles and better mixing.

*Fabrication of samples and flexural test*

Composite bars with 2mm × 2mm × 25mm dimensions were fabricated in steel moulds for flexural strength test, according to ISO 4049. Three bar-shaped samples were made in each group. These specimens were light cured with 520 mW/cm<sup>2</sup> intensity (Demetron LC Curing light) for 45 seconds on each side, and then carefully removed from the

moulds. In order to simulate the mouth environment, the samples were stored in distilled water at 37°C incubator for 24 hours. The flexural strength was measured via 3-point bending test using a universal testing machine (STM-20 Santam) with a span of 20 mm, at 60 N load cell and a cross-head speed of 0.5 mm/min. Force-displacement curves of all specimens were recorded during the tests and the amounts of work-of-fracture of the samples were calculated by dividing the area under these curves by the specimen’s cross-sectional area. Work-of-fracture is the energy required to fracture a specimen [17]. The flexural strength is calculated by:

$$F.S. = 3PL/2bh^2$$

Where, F.S. is flexural strength, P is force at fracture point, L is span distance (20 mm), b is width of sample and h is the height of the sample.

*Morphology*

A VEGA//TESCAN Scanning electron microscope (SEM) was employed to examine the morphologies of glass particles and the fractured surfaces of the UDMA/TEGDMA dental resins composites containing various mass fractions of glass particles. Prior to SEM examination, the specimens were sputter-coated with gold to avoid charge accumulation.

**Results**

*FTIR analysis of particles*

The FTIR spectra of glass particles before and after milling are given in Figure 1. These spectra show that hexane has no significant effect on glass structures

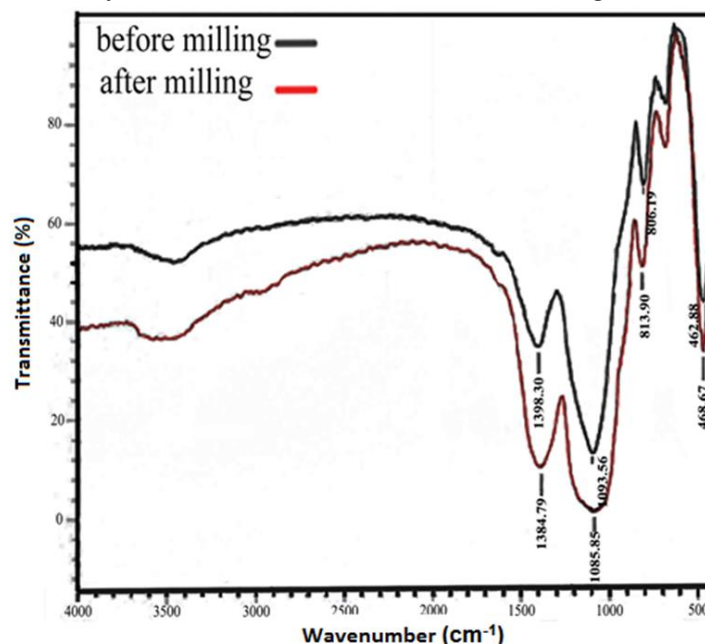
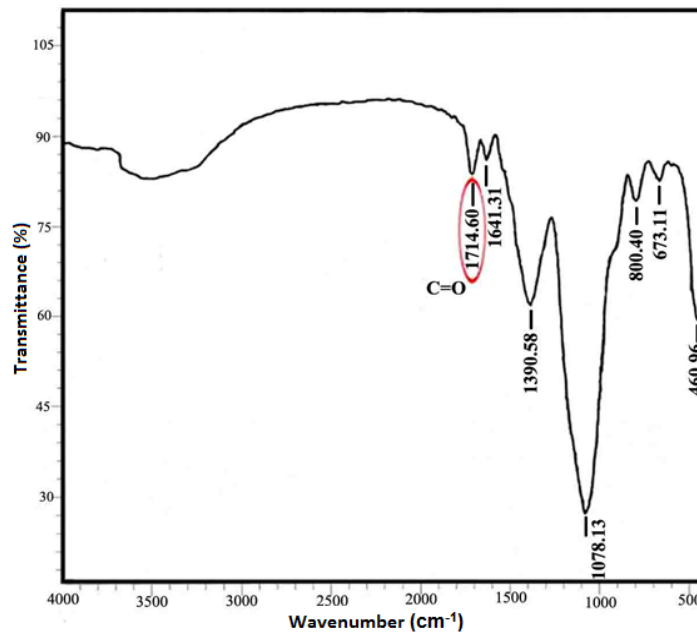


Figure1: FTIR of glass before and after milling

because of the fact that there is no new peak resulting from a new functional group after milling process. Figure 2 shows the FTIR of glass particles after modification with silane.



**Figure 2:** FTIR of silanized glass particles and existence of C = O bond

#### *Morphology of particles*

Figures 3A and 3B show the SEM micrographs of the glass particles before and after silanization, respectively.

#### *Flexural strength and work-of-fracture*

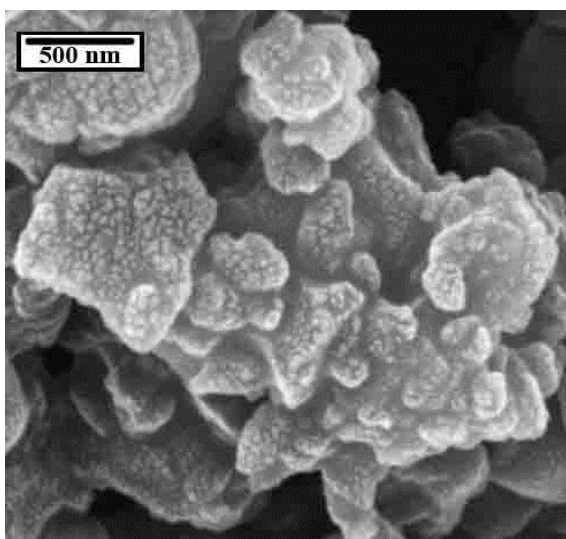
The flexural strength and flexural modulus of the specimens were calculated using 3-point bending formula; the results have been reported in the previous work [16]. Several curves of force-displacement obtained

from the flexural tests of the samples are displayed in Figure 4 as examples. According to these curves, the maximum force and extension at which a composite sample failed were obtained and the values of force

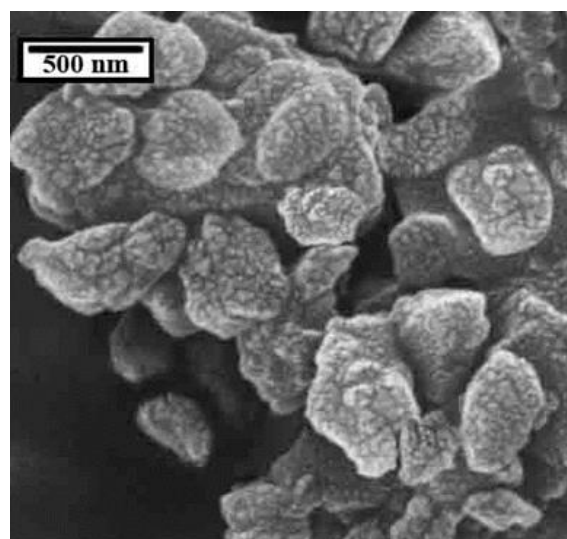
and displacement at the failure point and mean value of work-of-fracture for each group are summarized in Table 1.

#### *Fractography*

SEM photos of the fractured surfaces emanate from 3-point bending tests are shown in Figure 5. Columnar photos in Figures 5 (a), (b), and (c) show the fractured surfaces of 5, 7.5, and 10 wt% glass filler composites, respectively.



**Figure 3A:** SEM photomicrograph of glass particles before silanization



**Figure 3B:** SEM photomicrograph of silanized glass particles

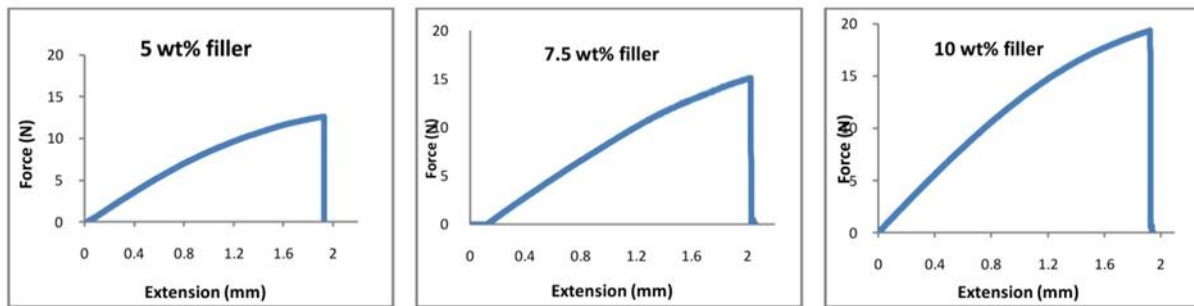


Figure 4: Force-displacement curves of the composites of each group achieved by flexural tests with 5, 7.5, 10 wt% filler

**Discussion**

Comparison of Figures 1 and 2 shows that there is a peak at 1714cm<sup>-1</sup> wave number which is due to the existence of carbonyl (C = O) group and chemical bonds between glass and  $\gamma$ -MPTMS [18]. It can be concluded that modification of glass was successfully carried out through silanization process.

Micrographs 3A and 3B display that agglomerated particles were removed dramatically after modification. The particle size was analyzed in our previous study, showing that the mean particle size of the silanized glass particles was about 140 nm [16].

By increasing the fraction of glass filler from 5 to 10 wt%, the values of flexural strength increase from (64 ± 1.7) MPa to (75 ± 2.5) MPa and flexural moduli increase from (1.2 ± 0.01) GPa to (1.4 ± 0.02) GPa [16]. In other words, flexural strength and flexural modulus of the composites containing 10wt% filler improved by 17.2% and 16.7%, respectively.

The data in Table 1 indicate that work-of-fracture of composite samples increases from (4.07) kJ/m<sup>2</sup> to (5.33) kJ/m<sup>2</sup> with 5 wt% increase in the filler content. It means that work-of-fracture was improved by 30.9%. The results indicated that the impregnation of the silanized nano-glass particles into UDMA/TEGDMA resin could improve the mechanical properties considerably and enhance the resistance of this resin to brittle fracture.

Comparison of Figure 5 (a) with 5 (b) and 5 (c) reveals that the fractured surfaces of composites containing 5 wt% filler have a large smoother area, large hyperbolic marking, ribbon and fracture steps

in the direction of crack propagation (from the bottom left side to top right side). These patterns are proportional to lower resistance to the crack propagation, and a minimum energy is required to fracture the specimen [19]. As calculated above, the composites in this group have the minimal work-of-fracture compared to the other ones; this indicates that this group has the lowest resistance to fracture.

On the other hand, by increasing the weight fraction of glass particles, the fractured surface area became rougher indicating more ductile fracture, which could be attributed to the crack deflection and crack pinning effects of the glass nano-particles [20]. The composites' fractured surfaces in Figures 5 (b) and (c) in contrast to Figure 5 (a) have rougher features such as out of the plane flaking and the thumbnail type marks, crack pinning, and shear yielding which requires additional energy to fail the materials.

As more energy was imparted from the deformation strain of the specimens for the creation of these features, corresponding increases in the flexural strength and work-of-fracture were obtained [19]. The higher values of flexural strength and work-of-fracture of the composites with 7.5 wt% and 10 wt% filler, concluded from force-extension curves are consistent with the morphology of the fractured surfaces of Figures 5 (b) and (c) .

In order to draw a conclusion about the amount of dissipated energy during the fracture, it is important to know how the cracks pass through the materials, and how the particles influence the crack propagation. Particles function as obstacles when cracks interacted them, so the crack front can deviate and branch or

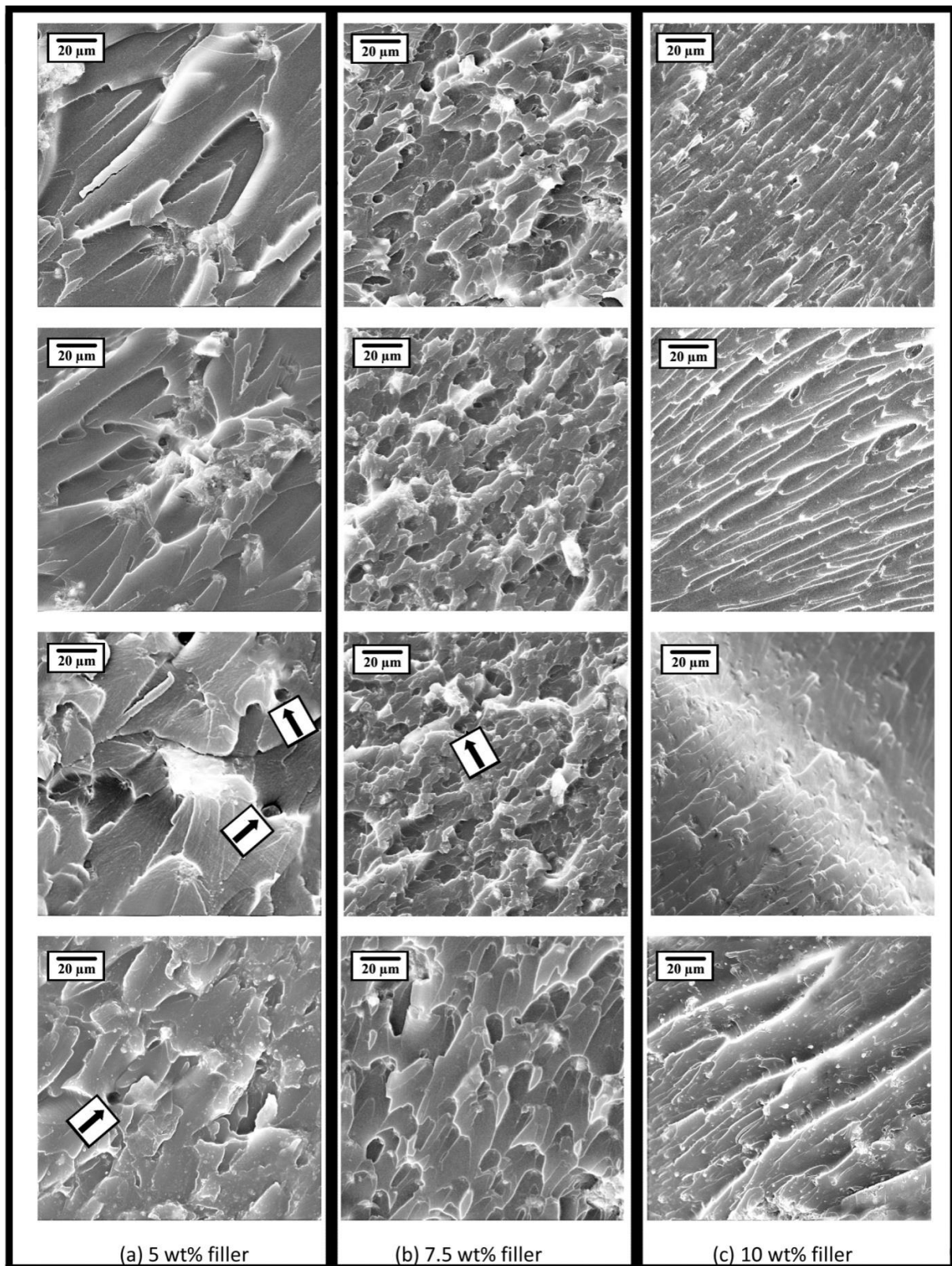
**Table1: The Maximum force, extension and work-of-fracture of the samples at break according to Figure 4**

Glass filler content (wt%)	5	7.5	10
Maximum extension (mm)	1.92	2.02	1.92
Maximum force (N)	12.60	15.13	19.33
work-of-fracture (kJ/m <sup>2</sup> )	4.07 ± 0.04	4.69 ± 0.28	5.33 ± 0.31

even pin in them, which leads to a higher energy absorption in the composite. In addition, the interface has a critical effect in deformation behavior so that under the strong bonding conditions high amounts

of energy will be consumed at the interface of the particle and matrix [19].

The nano-composite reinforced with higher fraction modified glass nano-particles improved the



**Figure 5:** Representative fractured surfaces of three-point flexural specimens: (a): composites with 5 wt% glass filler; (b) composites with 7.5 wt% glass; (c) composites with 10 wt% glass filler. The arrows show voids formation due to failure of the glass particles in the composites with lower filler fractions.

interface and requires more energy to fracture. This leads to a higher flexural strength and a rougher fractured surface. In order to elaborate, it can be observed that some voids are formed on the fractured surface of the composites with lower filler fractions, especially in the composites with 5 wt% filler. These voids are indicated by arrows in Figures 5 (a) and (b). Formation of these voids results from failure of the glass particles. In fact, the filled resin is dramatically weakened because of the agglomeration which functions as structural defects [17].

According to SEM photos and the lower values of work-of-fracture and flexural strength in composites with less filler fraction, it may be concluded that lower content of glass filler in composites has much more tendency to agglomerate which results in weak interface and void formation. In other words, when the glass filler content in the resin matrix is low, the particles' tendency to interact with each other is more than the amount required to interact with the resin matrix. Hence, due to the lack of an efficient interface, the particles are pulled out and the voids are formed by lower forces.

## Conclusions

In this study, glass nano-particles were produced via milling process. It was found that the silane modification has a significant effect on dispersion and stabilization of these particles and removes agglomeration due to the formation of the carbonyl group on the particles' surface.

It was discovered that a little increase in glass nano-particles' mass fraction dramatically improves the mechanical properties of the composite. This raise owes to the effective energy dissipation mechanisms such as crack pinning and deflection, as observed in SEM micrographs. Moreover, void formation in the low filler content composite is another mechanism to decrease the energy required for fracture of these composites and eventually weaken them.

**Conflict of Interest:** None declared.

## References

1. Chao X, Zhong-Yi W, Hui-Ming H, *et al.* Study on the Structure and Mechanical Properties of Dental Barium Glass Particles Surface Modification with Silane Coupling Reagent. *Polym-Plast Technol and Eng.* 2008;47:858-864.
2. Liu Y, Tan Y, Lei T, *et al.* Effect of porous glass-ceramic fillers on mechanical properties of light-cured dental resin composites. *Dent Mater.* 2009;25:709-715.
3. Bowen RL. Particle distribution in reinforced polymer. *J Am Dent Assoc.* 1964;69:481-495.
4. Beyth N, Farah S, Domb AJ, *et al.* Antibacterial dental resin composites. *React Func Polym.* 2014; 75:81-88.
5. Chan K, Nicolella D, Furman B, *et al.* Fracture toughness of zirconia nanoparticle-filled dental composites. *J Mater Sci.* 2009;44:6117-6124.
6. Rozenberg B, Tenne R. Polymer-assisted fabrication of nanoparticles and nanocomposites. *Prog Polym Sci.* 2008;33:40-112.
7. Wang Li-Li, Jiang J-S. Preparation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles by high-energy ball milling. *Physica B Condens Matter.* 2007;390:23-27.
8. Arbain R, Othman M, Palaniandy S. Preparation of iron oxide nanoparticles by mechanical milling. *Miner Eng.* 2011;24:1-9.
9. Garcia F, Le Bolay N, Trompette J-L, *et al.* On fragmentation and agglomeration phenomena in an ultrafine wet grinding process: the role of polyelectrolyte additives. *Int J Miner Process.* 2004;74:43-54.
10. Sabzi M, Mirabedini SM, Zohuriaan-Mehr J, *et al.* Surface modification of TiO<sub>2</sub> nano-particles with silane coupling agent and investigation of its effect on the properties of polyurethane composite coating. *Prog Org Coat.* 2009;65:222-228.
11. Kelly JR. Approaching clinical relevance in failure testing of restorations. *J Prosthet Dent.* 1999;81: 652-661.
12. Quinn GD, Morrell R. Design data for engineering ceramics: a review of the flexure test. *J Am Ceram Soc.* 1991;74:2037-2066.
13. Lewis D. Observations on the strength of a commercial glass-ceramic. *Am Ceram Soc Bull.* 1982;61:1208-1214.
14. Parrington RJ. Fractography of metals and plastics. *Pract Fail Anal.* 2002;2:16-19.
15. Rice RW. Ceramic fracture features, observations, mechanisms, and uses. *Fractography of ceramic and metal failures.* Am Soc Test Mater. 1984;827:5-103.
16. Monfared M, Mirdamadi S, Khavandi A. Synthesis of new dental nanocomposite with glass nanoparticles. *Nanomedicine J.* 2014;1:107-111.
17. Tian M, Gao Y, Liu Y, *et al.* Fabrication and

- evaluation of Bis-GMA/TEGDMA dental resins/composites containing nano fibrillar silicate. *Dent Mater.* 2008;24:235-243.
18. Yuvaraj H, Shim JJ, Lim KT. Organic-inorganic polypyrrole-surface modified SiO<sub>2</sub> hybrid nanocomposites: a facile and green synthetic approach. *Polym Adv Technol.* 2010;21:424-429.
  19. Du M, Zheng Y. Modification of silica nanoparticles and their application in UDMA dental polymeric composites. *Polym Composite.* 2007;28:198-207.
  20. Deng S, Ye L, Friedrich K. Fracture behaviours of epoxy nanocomposites with nano-silica at low and elevated temperatures. *J Mater Sci.* 2007;42:2766-2774.