



# The Effect of Weight Fraction, Silanization and Size of Fillers on the Mechanical Properties of an Experimental SiO<sub>2</sub> Dental Composite

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## Abstract

**Background:** This research studied mechanical properties of silica-based nanocomposite as a strong restorative material through flexural test method.

**Objectives:** The purpose of this study was to evaluate the effect of weight fraction, silanization and filler size on the flexural properties of silica-based dental nanocomposite.

**Methods:** The prepared composites were made of light-cured copolymer based on Bisphenol A glycolmethacrylate (Bis-GMA) and Triethylene glycoldimethacrylate (TEGDMA) at proportion of 50:50 which reinforced by silica filler. The effect of silanization and weight fraction of the filler was studied with samples containing 10 wt% (n (10)), 20 wt% (n (20)) and 30 wt% (n (30)) nanosilica filler. Samples silanized with ( $\gamma$ -MPS) were also tested. Flexural properties were evaluated with Three-Point Bending test. Flexural strength of the nano SiO<sub>2</sub> based composites were also compared to micro silica glass composites. Flexural data were analyzed with one-way analysis of the variance.

**Results:** The sample with 10 wt% (n (10)) had equal strength as the sample with 30 wt% (n (30)) nanosilica filler. Modulus of the sample n (30) was higher than the other samples, but its toughness was significantly lower. Silanization had not expected positive effect on the flexural properties.

**Conclusions:** Adding low amount of nanosilica improved mechanical properties of the resin composite. Silanization of the particles enhanced workability of the paste, but mechanical properties decreased significantly. Reduction in the size of the filler to nano scale caused better flexural strength in comparison to micro glass silica composites.

**Keywords:** Nanosilica Composite, Flexural Strength, Modulus, Salinization

## 1. Background

Resin composite was introduced to dentistry practice about 60 years ago by Dr. Bowen. During this past 60 years, this technology developed well and today is one of the most popular restorative materials in the world (1).

Resin composite is composed of polymeric matrix, filler and photoinitiation system. The resin is usually reinforced by addition of particles as fillers to promote its physical and mechanical properties. Parameters such as Nature, type, size distribution and surface properties of fillers have considerable effects on the mechanical properties of resin composite (2). Different kinds of fillers such as silica, zirconia, titanium oxide and hydroxyapatite have been used as a dispersed phase in various researches to enhance mechanical properties of this biomaterial (3, 4).

With the advent of nanotechnology, nanomaterials application in biomedical sciences captured great attention. In recent years, the size of the added filler particles in com-

mercial dental composites has decreased from 8 - 30  $\mu$ m to the scale of nanometers (5). Nanomaterials have unique properties such as small size, large surface area, high surface energy and a large proportion of surface atoms. Based on literature it is possible to enhance properties such as modulus of elasticity, surface hardness, polymerization shrinkage, and filler loading of dental resin composites by addition of nanomaterials (6).

In dentistry, silica nanoparticles are more preferred than the other particles as filler, because of their aesthetics and high biocompatibility, therefore in this study silica particles were chosen to be added to reinforce the resin composite (7).

To investigate the effect of spherical nanosilica on the flexural properties of dental composites, flexural strength, flexural modulus and toughness of an experimental dental composite containing different amount of spherical nanosilica as filler were evaluated. Then surface of the sam-

ples with the same amount of fillers was treated by silane coupling agent to improve interactions between the fillers and matrix resin, after that the mechanical tests were done again to compare the effect of silanization. To investigate the effect of size of fillers on Flexural strength, mechanical properties of two nanocomposite samples were compared with a silica glass resin composite with the same filler weight fractions.

## 2. Methods

### 2.1. Materials

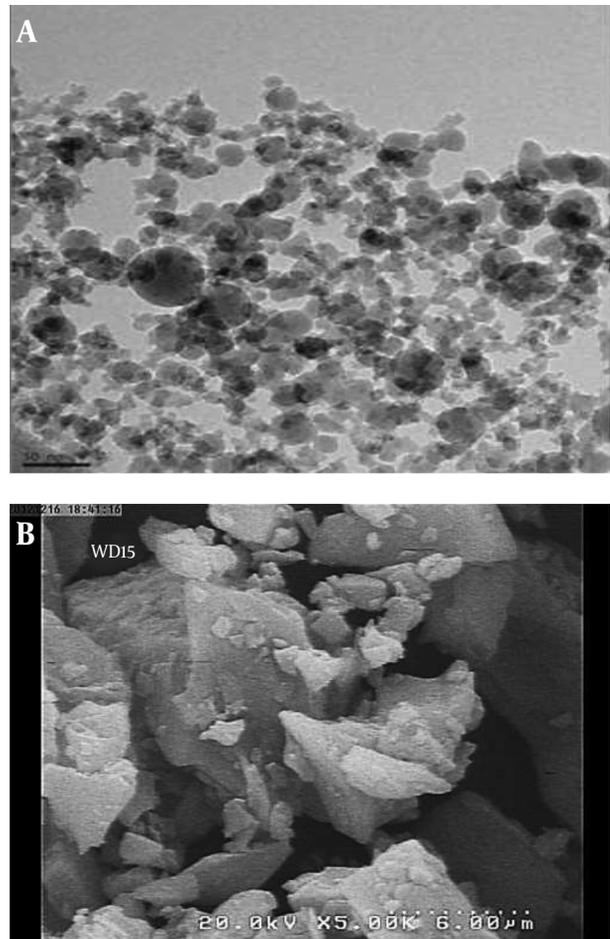
The used resin system was based on triethyleneglycol dimethacrylate (TEGDMA) and 2, 2 -Bis- (4-(methacryloxypropoxy)-phenyl)-propane (Bis-GMA) which were procured from Sigma- Aldrich company (Germany). Photo initiation system which consisted of Camphorquinone (CQ) and Ethyl4-(dimethylamino) benzoate (4EDMAB) was also purchased from Sigma-Aldrich. Silanization process was conducted by N-propylamine and (3-Mercaptopropyl) trimethoxy silane ( $\gamma$ -MPS) which was provided by Merck and Sigma-Aldrich companies, respectively. Nanosilica particle was provided by Nutrino (China). Glass silica was obtained by crushing quartz. [Figure 1](#) shows microscopic shape of both nanosilica and glass silica. Properties of the used fillers are presented in [Table 1](#). Sample codes are provided in [Table 2](#).

### 2.2. Silanization of Silica Nanoparticles

nanosilica particles were silanized with MPS with the method presented by the reference (8). First, the fumed silica ( $5 \pm 0.05$  g), the silane ( $0.5 \pm 0.01$  g), 100 mL cyclohexane and n- propylamine ( $0.1 \pm 0.01$  g) were stirred for 30 minutes at room temperature. Then, the mixture was stirred at  $60^\circ\text{C}$  at atmospheric pressure for another 30 minutes. To elucidate silanized powder and removal of byproducts, the mixture was put in a rotary evaporator at  $60^\circ\text{C}$  for 30 minutes. The powder was then heated at  $95 \pm 5^\circ\text{C}$  for 1 hour in a rotary evaporator. Finally, it was dried at  $80^\circ\text{C}$  by a vacuum oven for 24 hours.

### 2.3. Preparation of Composites

The resin matrix contained Bis-GMA/TEGDMA mixture (i.e. 50:50 by weight) including CQ (0.2 wt%) and 4EDMAB (0.8 wt%) as the photo initiating system. To prepare the resin, TEGDMA was added to viscose Bis-GMA to dilute the polymer, causing incorporation of more filler. Then, the particles were added and mixed by spatula till the color of the paste turned into semi-transparent to assure well dispersion of particles in the paste. Then, photo initiating system was added and the composite was casted into moulds.



**Figure 1.** Microscopic Shape of Fillers a) TEM Image of Nanosilica b) SEM Image of Glass Silica

Finally, the paste was light-cured with the light curing device.

The Photo curing unit had LED lamp, which emitted radiation between 420 and 500 nm with a maximum peak of 470 nm. The intensity of the lamp was  $550 \text{ mWcm}^{-2}$  (Panaloux, China). Samples were casted into  $25 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$  mould upon guidelines on dental polymers from ISO 4049:2009 (9). Since stainless steel mould was not appropriate for separating the specimens, it was replaced by a teflon one. Samples were light-cured by overlapping irradiations for a total of 40s on both sides.

### 2.4. Mechanical Properties

Five specimens for each group were prepared. The flexural modulus was measured using a three-point bending test according to the ISO-4049 specification. Samples were tested by a Santam Machine (Santam 150, Iran) at a speed

**Table 1.** Fillers' Properties

Filler	Shape	Size, nm	Specific surface area, m <sup>2</sup> /g	Purity, %
Nanosilica	Spherical	10 - 15	180 - 270	99.99
Silica Glass	Irregular	5000	43	71.22

**Table 2.** Sample Code, Filler Type and Content

Sample Code	Sample Description
n (10)	Bis-GMA/TEGDMA(50:50) containing 10 wt%, un-silanized nanosilica
n (20)	Bis-GMA/TEGDMA(50:50) containing 20 wt%, un-silanized nanosilica
n (30)	Bis-GMA/TEGDMA(50:50) containing 30 wt%, un-silanized nanosilica
n-s (10)	Bis-GMA/TEGDMA(50:50) containing 10 wt%, silanized nanosilica
n-s (20)	Bis-GMA/TEGDMA(50:50) containing 20 wt%, silanized nanosilica
n-s (30)	Bis-GMA/TEGDMA(50:50) containing 30 wt%, silanized nanosilica
SG5 (10)	Bis-GMA/TEGDMA(50:50) containing 10 wt%, 5 micrometer silica glass
SG5 (30)	Bis-GMA/TEGDMA(50:50) containing 30 wt%, 5 micrometer silica glass
SG14 (10)	Bis-GMA/TEGDMA(50:50) containing 10 wt%, 14 micrometer silica glass
SG14 (30)	Bis-GMA/TEGDMA(50:50) containing 10 wt%, 14 micrometer silica glass

rate of 0.75 mm/min until fracture occurred. The load and the corresponding deflection were recorded and used to calculate the flexural modulus (GPa) and the strength (MPa) (10):

$$E_s = Fl^3/4bh^3d$$

where F, l, b and h are maximum load, length span, sample width and sample height, respectively. d is deflection corresponding to the load F. The flexural strength was calculated using the following equation (11):

$$\text{Flexural Strength} = 3.F.l./2b.h^2$$

Where F is maximum load at the point of fracture, l is length span, b is the width of the sample and h its height.

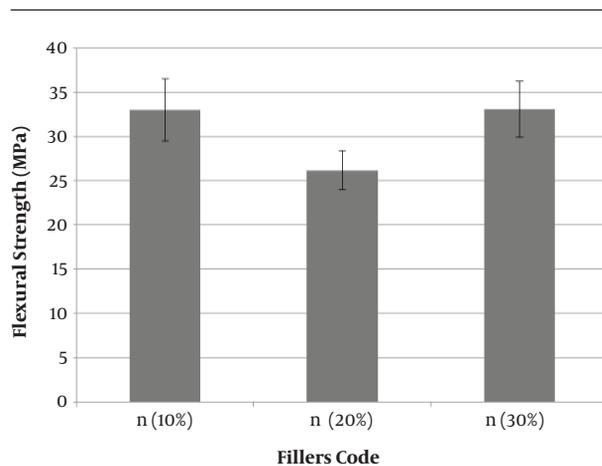
Fracture strength is the resistance of a material to fracture and toughness is an indication of the amount of energy necessary to cause fracture. The total area under the elastic and plastic portions of a stress-strain curve represents the toughness of a material. Stress/Strain curve was already provided by three point bending test results (i.e. load deflection curve).

### 2.5. Data Analysis

Mechanical properties were analyzed to find outliers. Each sample consisted of 5 specimens. Average and standard deviation of these specimens were calculated. Then the numbers out of average ± standard deviation were removed. Average and standard deviation of the remaining data were calculated and approved as a reliable data in the paper.

### 3. Results

Figures 2 and 3 presents flexural strength and flexural modulus of composites containing 10, 20 and 30 wt% nanosilica respectively. Flexural strength decreased when filler amount increased from 10 to 20 wt%. Contrarily, it increased when weight fraction increased from 20 to 30 wt%. Flexural modulus had the same trend.



**Figure 2.** Flexural Strength of Un-Silanized Silica Nanocomposite

Figure 4 shows toughness of the un-silanized samples. By addition of the filler from 10 to 20 wt% the toughness didn't change, but for the sample n (30) it decreased significantly from 1.8 kJ/m<sup>2</sup> to 1 kJ/m<sup>2</sup>.

γ-MPS was used as silane coupling agent to bridge between the matrix and inorganic nanosilica in the resin and also to disperse the silica particles uniformly. Flexural strength, flexural modulus and toughness of silanized samples are shown in Figures 5 - 7.

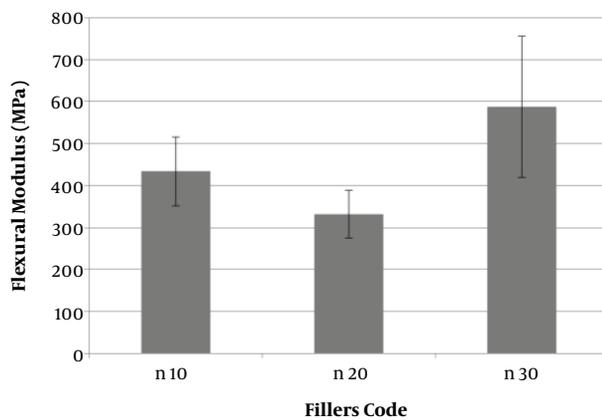


Figure 3. Flexural Modulus of Un-Silanzed Silica Nanocomposi

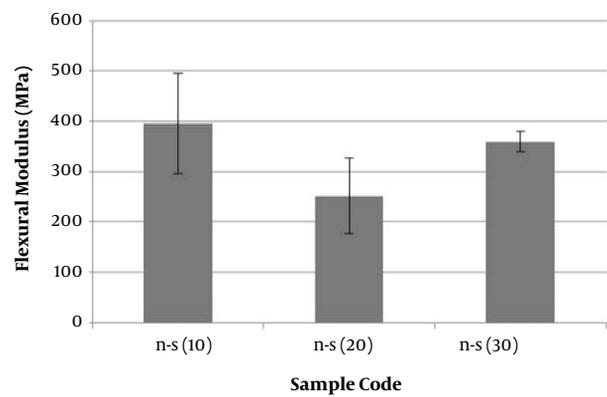


Figure 6. Flexural Modulus of Silanzed Silica Nanocomposite

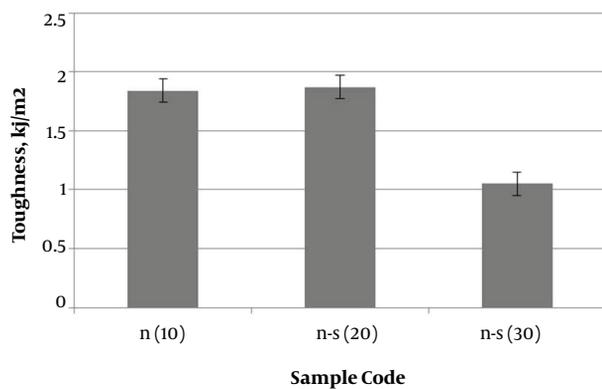


Figure 4. Toughness Un-Silanzed Silica Nanocomposite

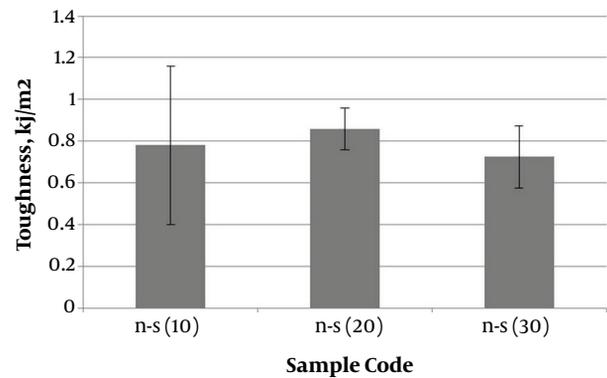


Figure 7. Toughness of Silanzed Silica Nanocomposite

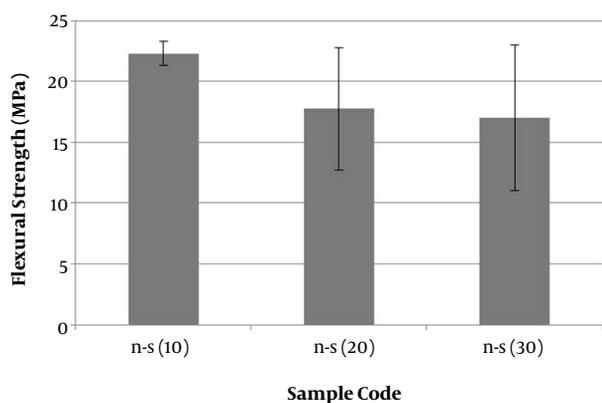


Figure 5. Flexural Strength of Silanzed Silica Nanocomposite

By increasing the filler content from 10 to 20 wt%, the flexural strength decreased from 22.3 MPa in the sample n

(10) to 17.73 MPa in the sample n (20). Flexural strength of the sample n (30) almost had no change in comparison to n (20).

Flexural modulus of the sample n-s (20) had lowest number in comparison to the other samples, though it had better toughness than the other two samples. Toughness of all the silanzed samples was almost in the same order.

Figure 8 summarizes all the measured flexural properties of the silanzed and un-silanzed samples in one figure. Silanzation had negative effect on all the properties. It is further explained in the Discussion section.

Figures 9 and 10 shows effect of size on flexural strength of the composite. Strength of the sample n (10) is 2 to 3 times more than glass silica samples and it shows increase in the strength by reduction in the size of the fillers. For the composite containing 30 wt% filler, based on Figure 11, the sample filled with nanosilica had better strength again, but the difference was not significant like the samples with 10 wt% filler. Silica glass samples with different

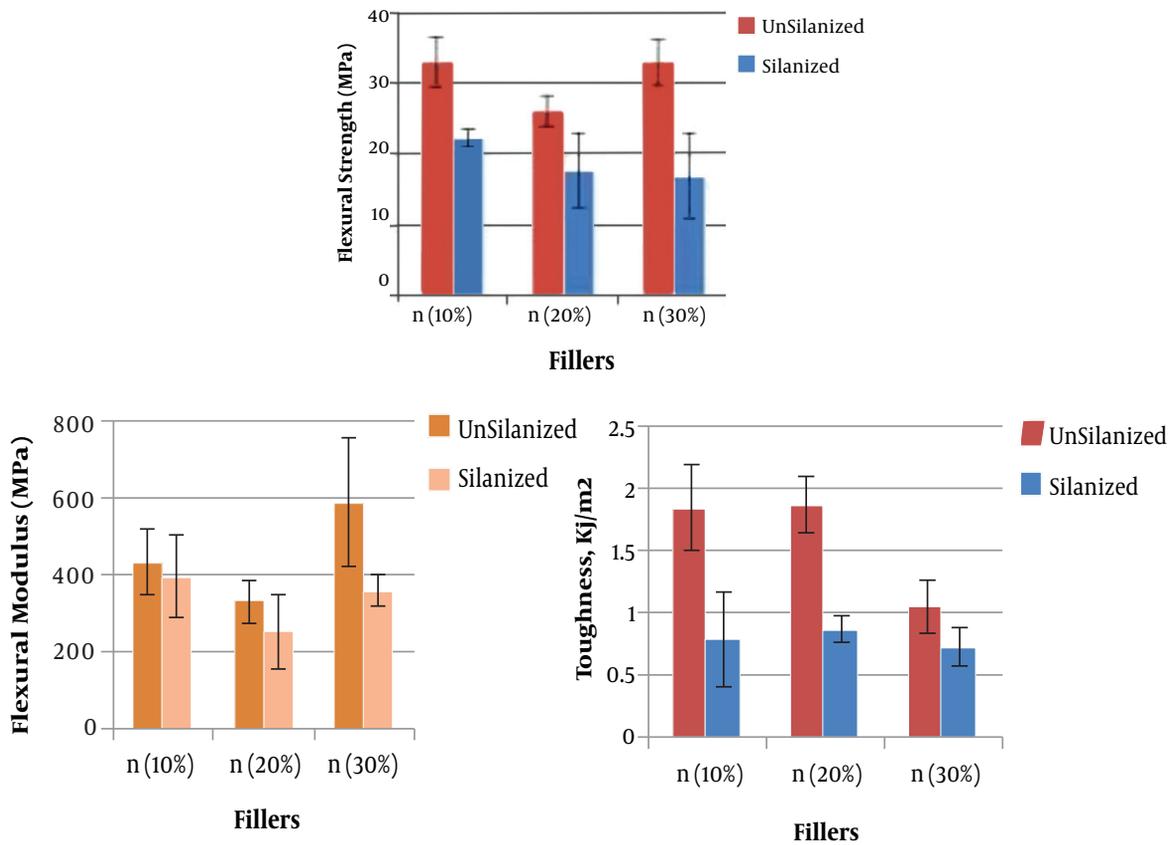


Figure 8. Comparison Between Mechanical Properties of Silanized and Un-Silanized Nanocomposite Containing 10, 20 and 30 wt% Nanosilica

micro size fillers (14 and 5 micrometer) had closed strength relative to each other.

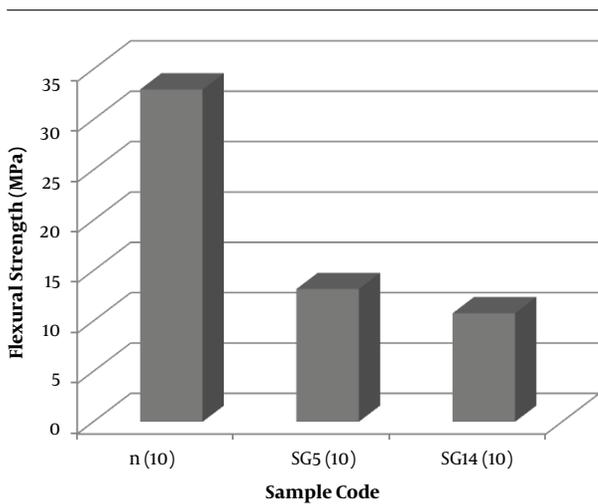


Figure 9. Comparison Between Flexural Strength of the Samples Containing 10 wt% Filler

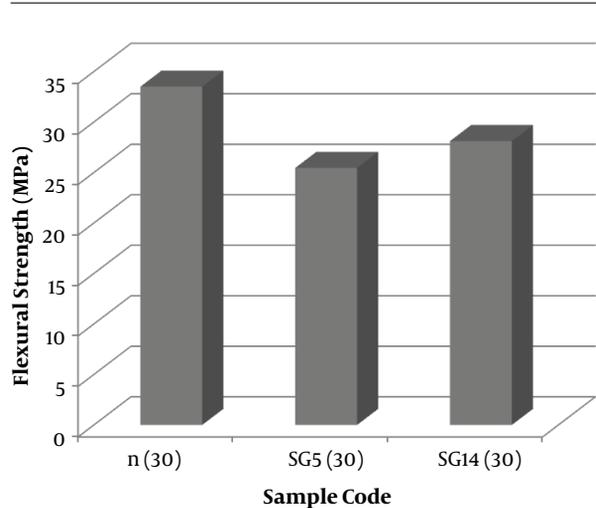
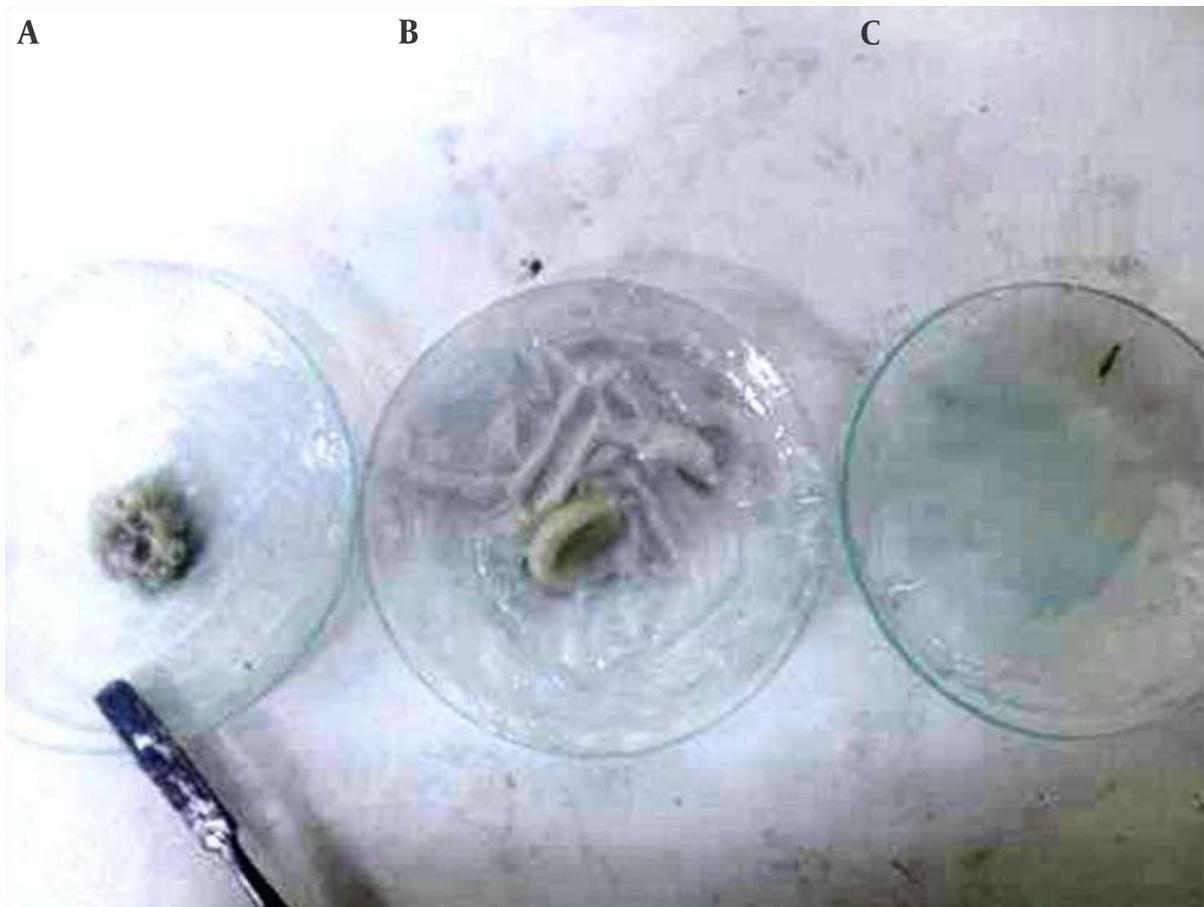


Figure 10. Comparison Between Flexural Strength of the Samples Containing 30 wt% Filler



**Figure 11.** A, Nanocomposite containing 30 wt% nanosilica; B, Nanocomposite containing 20 wt% nanosilica ;C, Nanocomposite containing 10wt% nanosilica

## 4. Discussion

### 4.1. Mechanical Properties

The main objective of this research was to investigate the mechanical properties of dental composite in which nanosilica was as the filler.

The content of nanofiller and good dispersion of nanoparticles are the key parameters for improving the mechanical properties of the dental composite (12). [Figure 11](#) shows the physical state of the composites containing 10, 20 and 30 wt% un-silanized nanosilica. When the addition of filler was 10 wt%, due to semiliquid state of the composite, the nano particles dispersed properly in the resin matrix and it was helpful for stress transfer between the regions. Besides, the free volume was reduced and the good interaction between the nanofiller and matrix resulted in high mechanical properties. Decrease in flexural strength of the sample n (20) was probably due to inappropriate dispersion, thus agglomeration of nanoparticles

and resulted concentration of forces caused lower flexural strength than the sample n(10). Increase in the mechanical properties of the sample n(30) can be attributed to higher amount of filler. Flexural strength of the sample n(30) was only slightly more than n(10), but the semiliquid state of the sample n(10) makes it inapplicable in dentistry practice.

Flexural modulus had the same trend as flexural strength. Modulus is proportional to crosslinking density (8). Lower modulus of the sample n(20) shows lower plasticity resulted from concentration of agglomerated nanoparticles.

Toughness of the sample n(10) and n(20) are almost equal, but the number decreased significantly for the sample n(30). High amount of nanoparticles caused insufficient resin to wet the particles as it can be seen in [Figure 11](#). This lead to discontinuity in the matrix, thus crack grew easier and toughness decreased significantly from 1.8 to 1  $\text{kJ/m}^2$ .

#### 4.2. Effect of Silanization

For the silanized samples, flexural strength of the n- (10) was more than other samples. It shows better stress transfer between filler and the matrix in this sample. Modulus had the same trend as the un-silanized ones. There was not considerable difference between toughness of the silanized samples. It shows filler amount doesn't play a role in the toughness here. Silanization caused same dispersion of particles in the sample.

Figure 8 compares un-silanized and silanized mechanical properties of the samples. Silanization did not afford logical and applicable outcome. Flexural properties of all the silanized samples are significantly lower than un-silanized ones. This result is not in the same line with many of previous studies. We used n-propylamine as a stabilizer of silane connections and cyclohexane as solvent. Chen and Brauer, in their research on effect of different solvents on silanization concluded that although the silanization process would be more efficient using that method, but the strength of the resulting composite would decrease rapidly (13). Performing the tests on the samples after a long time, might be the reason for the weak result of silanization on mechanical properties of the sample.

The flexural strength, flexural modulus and toughness of the sample FS-N are significantly lower than FS. Nanosilica particles agglomeration and intervention between fumed silica particles and the matrix caused discontinuity in the composite; therefore, the strength was lowered (14).

Based on Figures 9 and 10, the nanocomposite samples with 10 and 30 wt% filler both had better flexural strength than their micro glass silica counterparts. As the size of the particles reduces, the specific surface area increases, thus higher surface energy at the interphase is expectable and the stress concentration at the interphase of filler and matrix decreases and this resulted stronger flexural properties in the sample n (10) and n (30) in comparison to the other micro silica glass samples (8).

#### 4.3. Conclusions

The effect of nanosilica particles as a filler on mechanical properties of dental resin composite composed of Bis-GMA/TEGDMA (50:50) was studied.

Adding low amount of nanosilica improved mechanical properties of the resin composite.

Good dispersion plays central role in the flexural properties of resin composites, thus higher filler amount doesn't always guarantee better flexural strength.

Silanization of the particles enhanced workability of the paste, but mechanical properties decreased significantly. The silanization method was not efficient enough and the bonds between the matrix and filler were so weak.

Reduction in the size of the filler to nano scale caused better flexural strength in comparison to micro glass silica composites. It shows less concentration of stress in nanocomposites, therefore better mechanical features.

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