

Original Article

The Effect of Aging and Silanization on the Mechanical Properties of Fumed Silica-based Dental Composite

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ARTICLE INFO

Article History:

Received 20 August 2015

Accepted 21 November 2015

Key words:

Flexural Strength

Flexural Modulus

Ageing

Cycling

Silanization

Hardness

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Abstract

Statement of Problem: Mechanical strength and durability of dental composites are the main topics studied in this field of science today. This study examined fumed silica-based composite as a strong and durable restorative material through flexural and cycling test methods.

Objectives: The purpose of this study was to evaluate the effect of silanization, ageing, cycling and hybridizing on mechanical properties of fumed silica-based resin composite.

Materials and Methods: 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 fumed silica filler. For each composite sample, 5 specimen bars were made using Teflon mould (2 x 2 x 25 mm³). The samples with 12 wt% fumed silica (FS) were considered as a base line group. The samples were exposed to cyclic cold water (FS-CCW) and hot water (FS-CHW). The effect of silanization and adding more filler was studied together with samples containing 12 wt% (FS-S (12)), 16 wt% (FS-S (16)) and 20 wt% (FS-S (20)) fumed silica filler. The filler was silanized with (γ -MPS). The degree of conversion was assessed with Fourier Transform Infra-Red spectroscopy. Flexural properties were evaluated with the Three-Point Bending test. Flexural data were analyzed with Excel software. Hardness was measured with an Atomic Force Microscope (AFM).

Results: The degree of conversion of the resin reached 74% within 24 hrs. Salinization allowed more filler to be wetted by resin. Addition of silanized particles from sample FS-S (12) to sample FS-S (20) improved the mechanical strength. Hybridizing fumed silica with nano-silica (FS-N) had no significant effect on the strength, but nano-hardness improved greatly. Ageing and cycling had adverse effects on the strength of the sample FS. The flexural strength of FS-CHW was 72% less than FS sample.

Conclusions: Sample FS-N with low diluent and filler percentage complied with the requirements of flexural strength was established by ISO 4049/2009 and may be cost benefit to be used as a dental composite for clinical application.

Cite this article as: Khaje S, Jamshidi M. The Effect of Aging and Silanization on the Mechanical Properties of Fumed Silica-based Dental Composit. J Dent Biomater, 2015;2(4):124-132.

Introduction

Nowadays, several filling dental materials such as amalgam, resin composites and glass ionomers are available in the market. Among these biomaterials, amalgam has the most strength. Amalgam is used in dentistry for more than 150 years, but because of its Mercury content and color, its application has been restricted in some countries [1-2]. Today, scientists believe that resin composite has the best features to replace amalgam as the most widely used dental restorative material [3].

Resin composite was introduced by Dr. Bowen in 1960s as a new tooth-colored restorative material [4]. Newly introduced resin-based material has been improved since 1960 and reached an appropriate strength and aesthetic for the last 2 decades. These improvements can be listed in three parts (i) improvement of filler phase (ii) adaptation of new monomer and (iii) improvement of the initiation system [4-5].

Nature, type, size distribution and surface properties of fillers have significant effects on the mechanical properties of resin composites [6]. Different kinds of fillers such as silica, alumina and hydroxyapatite are used as a dispersed phase [7-8]. It has been found that using more filler would result in more strength. Commercial dental composites have filler content around 80 w%. To have better bonding between organic and inorganic phases, silanization process is sometimes used. The size of the fillers plays an important role in mechanical characteristics, as well [9]. It has been reported that dispersing nano-sized fillers improves the mechanical properties such as flexural strength and wear resistance; however, high surface area of nanoparticles limits their presence in the resin to low loading levels [10].

In this study, fumed silica has been used as filler in the resin matrix to improve mechanical properties.

Fumed silica is used traditionally as filler, but because of its high surface area, the amount of added particles is so limited. Flexural properties of resin composites containing low amount of fumed silica filler was tested. The effect of Silanization of the particles on mechanical strength was also studied, because it was hypothesized that by silanization, more filler could be added to the resin. Therefore, mechanical properties could be improved. Flexural strength of the specimens aged and cycled in hot and cold water was investigated to show durability of the fumed silica-based dental composite in different temperatures. To improve the hardness of the composites, fumed silica was hybridized with nanosilica. Nano-indentation analysis was conducted to measure the effect of adding nanoparticles on the hardness of the samples.

Materials and Methods

Materials

The used resin system was based on triethyleneglycol dimethacrylate (TEGDMA) and 2, 2-Bis-[4-(metha-cryloxypropoxy)-phenyl]-propane (Bis-GMA) which were prepared from Sigma-Aldrich company (Germany). Photo initiation system which consisted of Camphorquinone (CQ) and Ethy 14-(dimethylamino) benzoate (4EDMAB) was also obtained from Sigma-Aldrich. Silanization process was conducted by N-propylamine and (3-Mercaptopropyl) trimethoxy silane (γ -MPS) which were purchased from Merck and Sigma-Aldrich companies, respectively.

Fumed silica and nano-silica particles were provided by Sigma-Aldrich and Nutrino (China). Properties of the used fillers are shown in Table 1. Sample codes are provided in Table 2.

Silanization of silica nanoparticles

Fumed silica particles were silanized with MPS

Table 1: Fillers' properties

Filler	Shape	Size (nm)	Specific surface area (m ² /g)	Purity (%)	Company
Fumed Silica	Agglomerated	200-300	175-225	99.99	SigmaAldrich
Nano Silica	Spherical	10-15	180-270	99.999	Nutrino

Table 2: Sample code, filler type and content

Sample Code	Sample Description
FS	Bis-GMA/TEGDMA(50:50) containing 12wt% fumed silica (un-Silanized)
FS-CW	Bis-GMA/TEGDMA(50:50) containing 12wt% fumed silica exposed to cold water
FS-CCW	Bis-GMA/TEGDMA(50:50) containing 12wt% fumed silica exposed cyclic to cold water
FS-CHW	Bis-GMA/TEGDMA(50:50) containing 12wt% fumed silica exposed cyclic to hot water
FS-S(12)	Bis-GMA/TEGDMA(50:50) containing 12wt% silanized fumed silica
FS-S(16)	Bis-GMA/TEGDMA(50:50) containing 16wt% silanized fumed silica
FS-S(20)	Bis-GMA/TEGDMA(50:50) containing 20wt% silanized fumed silica
FS(70:30)	Bis-GMA/TEGDMA(70:30) containing 12wt% fumed silica
FS-N	Bis-GMA/TEGDMA(50:50) containing 12wt% fumed silica and 10wt% nanosilica

following the method of Karabella and Sideridou [11]. For this purpose, at first the fumed silica (5 ± 0.05 g), the silane (0.5 ± 0.01 g), 100ml cyclohexane and n-propylamine (0.1 ± 0.01 g) were stirred at room temperature for 30 min. Then, the mixture was stirred at 60°C at atmospheric pressure for another 30 min. To achieve the silanized powder and removal byproducts, the mixture was placed in a rotary evaporator at 60°C for 30 min. The powder was then heated at 95 ± 50 °C for 1 hr in a rotary evaporator. At the end, it was dried at 80°C by a vacuum oven for 24 hrs.

Preparation of composites

The resin was composed of Bis-GMA/TEGDMA mixture (i.e. 50:50 by weight) which contained CQ (0.2 wt%) and 4EDMAB (0.8 wt%) as the photo initiating system. At first, TEGDMA was added to viscose Bis-GMA to dilute the polymer, causing incorporation of more filler. Then, the fumed silica particles were added and mixed by spatula well till the color of the paste changed into semi-transparent to assure well dispersion of particles in the paste. Because of high specific surface area of these particles, it was not possible to wet more than 12 wt% of the particles in the resin. Then, photo initiating system was added and the composite was casted into moulds. Finally, the paste was light-cured with the light curing device.

The Photo curing unit consisted of a LED lamp, which emitted radiation between 420 and 500 nm with a maximum peak of 470 nm. The LED Intensity was 550 mWcm^{-2} (Panaloux, China). Samples were casted into $25\text{mm} \times 2\text{mm} \times 2\text{mm}$ moulds based on ISO 4049:2009 for dental polymers [12]. The moulds were made of Teflon, because stainless steel was not appropriate for separating the specimen from the mould. Samples were light-cured by overlapping irradiations for a total of 40s on both sides. In the case of hybrid composite, nano-silica particles were mixed with fumed silica in advance. Then, the powder was added to the resin and the process continued.

Degree of Conversion

The FT-IR analysis was conducted to find out the degree of conversion of the matrix. Spectra were obtained over $600\text{--}4000 \text{ cm}^{-1}$ region by a Perkin-Elmer Spectrometer. First, a small amount of the matrix of the composite before curing was placed between two Mylar strips. The FT-IR spectrum was recorded at zero time, immediately after exposure to visible light for 40 seconds. The spectrum of the cured resin was recorded. For each spectrum, we determined the height of aliphatic C = C peak absorption at 1637 cm^{-1} , and the aromatic C = C peak absorption at 1580 cm^{-1} was measured using a baseline technique which proved the best fit to the

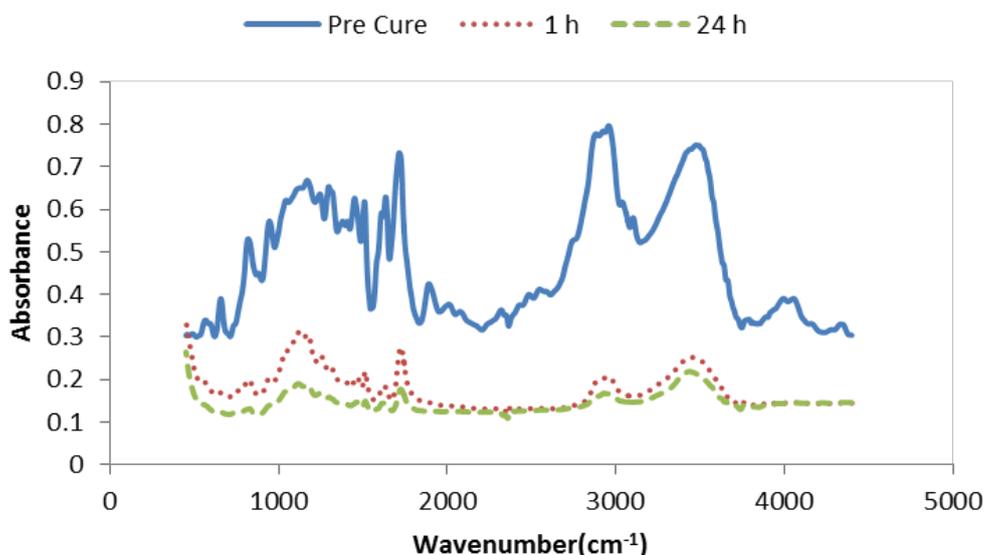


Figure 1: FTIR analysis for FS sample before and after curing

Beer–Lambert law. The aromatic C = C vibration was used as an internal standard. The degree of conversion was calculated by the following equation [13]:

$$\text{Degree of Conversion(\%)} = 100[1 - ((A_{1637}/A_{1580}) \times \text{Polymer}) / ((A_{1637}/A_{1580}) \times \text{monomer})] \quad (1)$$

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 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) [13]:

$$E_s = Fl^3 / 4bh^3d \quad (2)$$

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 [14]:

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

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). Diametral tensile strength was measured according to ADA Standard No.27. The mould’s diameter and thickness were 6 mm and 3 mm, respectively. The samples were loaded at a speed rate of 10mm/min with 100 KN load until fracture occurred. Diametral tensile strength was calculated as follows [15]:

$$DTS = 2F / \pi dt$$

where F is the maximum load at the point of

Table 3: Degree of conversion of the matrix at different times of exposure to day light			
Time	1h	24h	1 Month
Degree of Conversion (%)	60	74	80

fracture, d is diameter of the specimen, and t is thickness of the specimen.

Nano-hardness test

To measure the hardness of the surface of the specimens, nano-indentation technique was applied using an Atomic Force Microscope (AFM) (TriboScope®, Hysitron Inc. Germany), a Nanomechanical Test Instrument.

Evaluating the aging of the samples

The sample containing 12 wt% un-silanized fumed silica was stored in water to determine the effect of ageing on mechanical properties of the composite. Three different ageing mechanisms were defined. *A)* Continuous exposure to cold water: The sample was placed in cold water at 40C for 360 hrs. *B)* Cyclic exposure to cold water: The sample was placed for 2 hrs in cold water at 4 0C and then removed and placed for 2 hrs at room temperature. 60 Cycles were continued on the basis of this procedure. *C)* Cyclic exposure to hot water: The sample was placed for 2 hrs in hot water at 70 ± 5 0C then was kept for 2 hrs at room temperature. The cycle was repeated for 60 times.

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 \pm standard deviation were removed. Average and standard deviation of the remaining data were calculated and approved as a reliable data in the paper.

Results

Result of the FTIR analysis is shown in Figure 1.

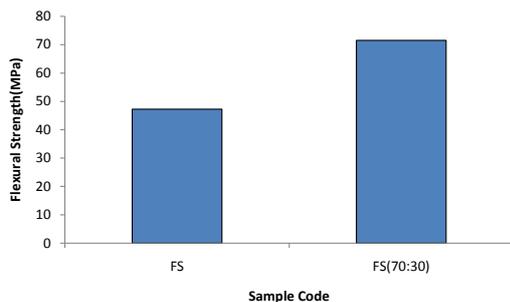


Figure 2: Flexural strength value of FS and FS (70:30)

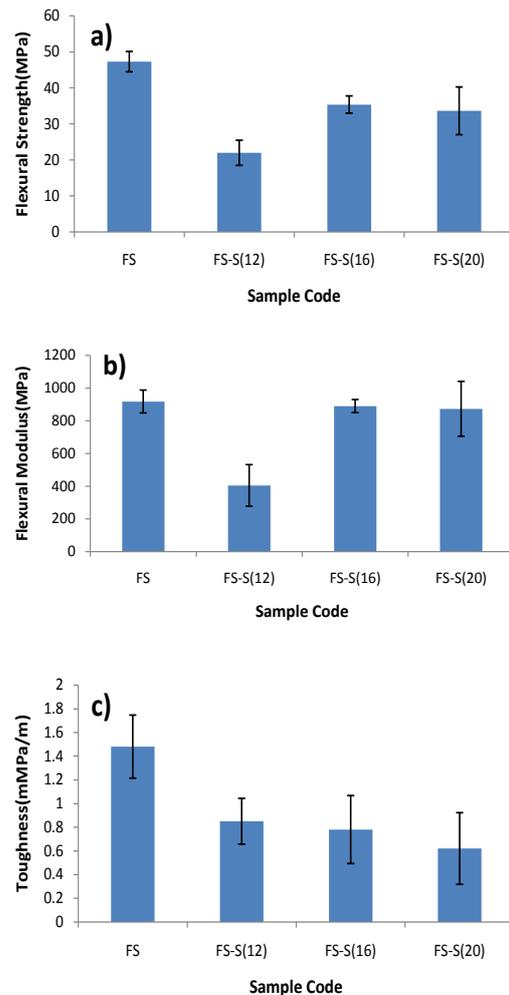


Figure 3: Flexural properties of silanized samples a) Flexural strength b) Flexural modulus and c) Toughness

Degree of conversion was measured and shown in Table 3. The conversion here is defined as the number of double bonds of monomer methacrylate groups which react. Usually, most of the conversion happens in the first hours. Based on the results, conversion increases rapidly in the first hour up to 60%. Then, the rate of increment declines significantly and it almost stops at 80% which shows high rate of conversion at the first day of exposure.

Figure 2 is presenting the results of the flexural strength values for FS and FS (70:30), showing a difference between the samples. The FS (70:30) sample had higher flexural properties, but there was a big problem in this sample. Here, dispersion of the fillers to the resin was done manually. Because of the highly specific area of the fumed silica and higher content of Bis-GMA, the workability of the created paste was so low in a way that it was not applicable in dentistry. Therefore, to improve workability, we increased diluent in resin content and tried to mix the filler as much as possible. On the other hand,

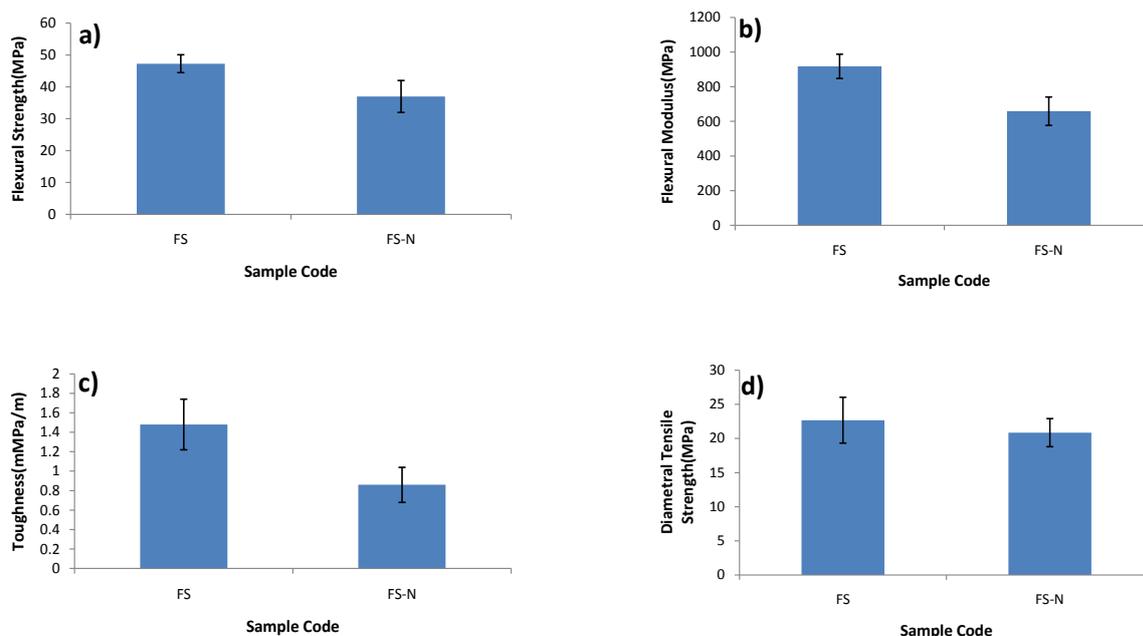


Figure 4: Mechanical properties of fumed silica composite with the hybrid fillers; a) Flexural strength b) Flexural modulus c) Toughness d) Diametral tensile strength

FS sample had an acceptable workability which can be more economical with low content of Bis-GMA.

A silane coupling agent was used to bridge between organic and inorganic materials in the resin and also to disperse the fumed silica particles uniformly to the resin. As we expected, silanization gave us the ability to disperse more filler into the resin, from 12 wt% in FS-S (12) to 20wt% in FS-S (20) sample. Flexural strength, flexural modulus and toughness of silanized samples are shown in Figure 3.

By increasing the filler content from 12 to 16 wt%, the flexural strength improved significantly from 21.95 MPa in FS-S (12) to 35.35 MPa in FS-S (16). Flexural strength of the sample FS-S (20) almost had no changed in comparison to FS-S (16). Flexural modulus also followed the same trend. Toughness decreased from FS-S (12) to FS-S (20).

Hybrid composites have been reported to have good mechanical properties [16]. Fumed silica particles were hybridized with nano-silica particles. Results for mechanical properties are shown in Figure 4.

Due to the environment of the mouth and its contact with different liquids and foods, longevity and durability of restorative materials are so important for the application in dentistry. As mentioned before, we defined three different processes to study the effect of ageing and cycling on the strength of the sample FS. Mechanical properties

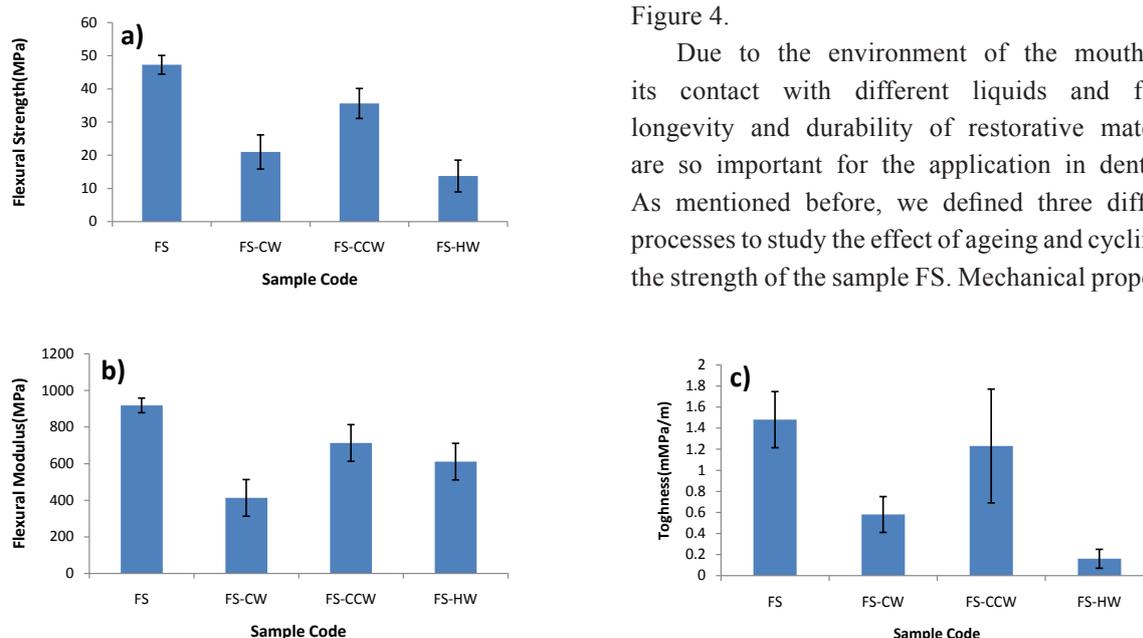


Figure 5: Flexural properties of FS aged samples a) Flexural Strength b) Flexural Modulus and c) Toughness

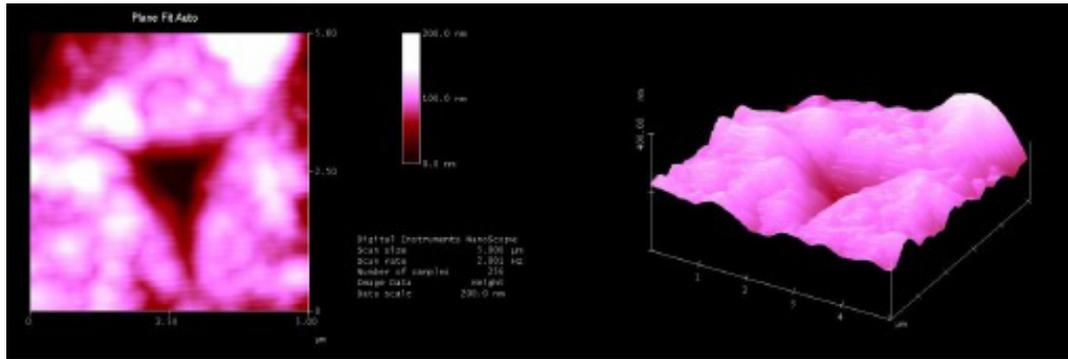


Figure 6: AFM photo related to Nano-indentation of the sample FS-N

of the different tested groups after all procedures are summarized in Figure 5.

Surface hardness is clinically the most relevant for mechanical performance of restorative materials. Surface hardness of the samples FS and FS-N was measured by a nano-indentation instrument. These two samples had the best mechanical properties with respect to the previous test results. AFM photo of the Berkovic tip on the surface of the FS-N is shown in Figure 6. Nano-hardness measurements of the samples are shown in Figure 7.

Discussion

Degree of Conversion

When particle size of the filler is about half of the wavelength of the photo curing device, the maximum conversion is achieved [5]. In this study, the visible light wavelength range was 420–500 nm for photo curing the matrix resin and average filler particle size of the filler was 200-300 nm; therefore, the increased light scatterings during photo curing caused an increase in the degree of conversion. Besides, the high percentage of TEGDMA in the resin caused easy mobility of the monomers; therefore, the rate of reaction increased.

Mechanical Properties

The main objective of this research was to investigate the mechanical properties of dental composite in which fumed silica was the filler. Usually by adding more filler to the resin, the strength increases.

Effect of Silanization

Increment of the flexural strength and modulus by adding more filler can be attributable to the reduced mobility of the macromolecules. The

decrease which happened in FS-S (20) was the result of poor links between the filler and matrix. Interfacial interaction plays an important role in the strength of the composite and as the result of adding more filler, the coherence between the resin and filler diminished. Toughness showed the strength of the material toward crack propagation. By adding more filler, the continuity of resin composite lowered; therefore, the toughness decreased.

Figure 3 also shows that silanization of fumed silica caused a decrease in the strength of the composite. This result is not in the same line with that of previous studies. We used n-propylamine as a stabilizer of silane connections and cyclohexane as solvent. Based on Chen and Brauer, although the silanization process would be more efficient using that method, the strength of the resulting composite would decrease greatly [9]. We found that the tests have been performed after a long time and this may be the reason for the weak result of silanization on mechanical properties of the sample.

Effect of Hybridizing fumed silica with nano-silica particles

The flexural strength, flexural modulus and toughness of the sample FS-N are significantly lower than FS. Nano-silica particles agglomeration

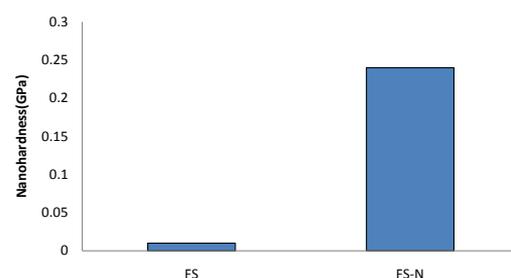


Figure 7: Nanohardness of FS and FS-N

and intervention between fumed silica particles and the matrix caused discontinuity in the composite; therefore, the strength was lowered. The amounts of diametral tensile strength of both samples are almost equal and similar to commercial restoratives [17].

Effect of Thermal Ageing

All the processes had a significant deteriorating effect on mechanical properties of the sample. Ageing in cold water had worse effects than cycling in cold water. Ageing in cold water caused 55% fall in the flexural strength but cycling in cold water decreased it about 25%. The same trend was seen for flexural modulus. Cycling in hot water had a tremendous effect on mechanical properties. The flexural strength of FS-CHW was 72% less than FS sample. Flexural modulus decreased, too. Although flexural strength of the sample aged in cold water (FS-CW) was more than FS-CHW sample, its flexural modulus was less than all the other samples. It was attributed to the low temperature of refrigerator in which FS-CW was aged. The low temperature didn't allow the molecules to have enough mobility, so the flexural modulus which showed elasticity decreased more than even FS-CHW which was exposed to hot water. Toughness, like flexural strength, was more inspired by hot water and hot water tremendously reduced the resistance of the sample toward cracks.

Nano-hardness

Light nature of fumed silica as a filler gives the resulting composite a low surface hardness property. Hybridizing improved the hardness 24 times based on Figure 7. This can be attributed to hard nano-silica particles which were presented in the surface of FS-N.

Conclusions

The effect of fumed silica particles as a filler on mechanical properties of dental resin composite composed of Bis-GMA/TEGDMA was studied.

- Maximum amount of 12 wt% fumed silica relative to resin matrix composed of Bis-GMA/TEGDMA (50:50) could be mixed manually into the matrix. Increment of Bis-GMA content improved the flexural strength significantly, but workability of the paste was not applicable.
- Silanization of the particles enhanced the capacity of the composite to accept more

filler, but mechanical properties decreased significantly. The silanization method was not efficient enough and the bonds which were created by coupling agent between organic resin and inorganic filler were so weak.

- Thermal cycling in both cold and hot water had negative effect on flexural strength and modulus. Cyclic ageing in hot water deteriorated the polymer matrix greatly.
- Hybridization of fumed silica composite with nan-osilica improved the surface hardness by 24 times. The mechanical properties decreased to some extent.
- Due to using lower contents of fumed silica (i.e. 10 wt%) and polymer to diluent proportions (i.e. 50:50) in comparison to traditional competes, the prepared samples can be considered as an economic dental retrofitting material. In this study, by attention to low weight percentage of fumed silica in the composite and high amounts of diluent in the resin, this dental resin composite is economical in comparison to other products.

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