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# MECHANICAL PROPERTIES OF DENTAL COMPOSITE MATERIALS REINFORCED WITH MICRO AND NANO-SIZE $Al_2O_3$ FILLER PARTICLES

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***Abstract:*** *Composite specimens were prepared by dispersion of various amounts of nano-sized $Al_2O_3$ fillers in a monomer system containing 60% Bis-GMA and 40% TEGDMA. For comparative purposes, composite samples containing micrometer size $Al_2O_3$ fillers were also prepared following the same procedure. The mechanical properties of the light- cured samples were assessed by three-point flexural strength, diametral tensile strength, and microhardness tests. The results indicated a more than hundred percent increase in the flexural strength and nearly an eighty percent increase in the diametral tensile strength values in the samples containing nano-size $Al_2O_3$ filler particles. It is interesting to note that, this improvement was observed at a much lower nano-size filler content. Fracture surfaces analyzed by scanning electron microscopy, indicated a brittle type of fracture in both sets of specimens.*

***Keywords:*** *Composites, Polymers, Ceramics, Mechanical Properties*

## 1. INTRODUCTION

A dental composite material typically consists of a resin-based matrix, a photo initiator system, and a high percentage of inorganic filler. Dimethacrylate (DMA) monomer such as the visible light cured 2, 2'-bis- [4-(methacryloxy propoxy) -phenyl] -propane (Bis-GMA) is used as photo activated monomer in most common dental composites [1-2]. Usually, a low molecular weight diluent monomer such as tri (ethylene glycol) dimethacrylate (TEGDMA) is added to thin the highly viscous Bis-GMA monomer and to achieve a consistency suitable for the incorporation of fillers [3-4]. The ideal restorative material should be identical to the natural tooth structure, both in appearance, and strength. Although the composite materials based on Bis-GMA have become vital for dental restorations due to their superior aesthetic quality, they experience a considerable mechanical challenge during function. Thus, improving the mechanical properties is one of the most important research tasks in this field. In recent years, the use of reinforcing inorganic fillers in various forms has been a major approach towards the development of improved dental composites [5,6]. In general, the size, shape, amount, and hardness of the filler material, the nature and quality of the bond between the filler and the polymer matrix, and the distribution of filler particles in the polymer matrix all have an influence on the wear and mechanical properties of the composite resins [7-14]. Perhaps one of the most noticeable advances in composite filler technology has been the incorporation of fillers in the nanometer scale [15-19]. One potential advantage of nanoparticles is the improvement in the optical properties of the epoxy resin composite because their diameter is a fraction of the wavelength of visible light resulting in the inability of the human eye to detect the particles. In addition, the high surface area associated with nanoparticles provides more interfacial interactions and improved properties in the composite samples [16-17, 20]. The positive effect of nano-sized silica and silicate-based fillers on flexural strength, surface hardness, fracture toughness, and optical properties has already been reported in the literature [15,17,19,21]. In view of the importance of the size of the fillers, the main purpose of this study was to determine the effect of nano-sized $Al_2O_3$ particles as reinforcing filler, on the mechanical properties of dental composite samples.

## 2. EXPERIMENTAL METHODS

### 2. 1. Sample Preparation

$Al_2O_3$ particles in the nano (25 - 40 nm) and micrometer (< 10μm) size ranges were purchased from Alfa Aesar Laboratory Chemical Supplier (Ward Hill, MA, USA). The resinous matrix used in this study was a commercially available (Enamel Bonding SDI Group, Australia) enamel bonding system made of 60 wt.% Bis-GMA , 40 wt% diluent monomer, TEGDMA, along with an activating agent. Two series of composites were prepared using Bis-GMA/TEGDMA in a w/w of 60/40 as the base resin for both series. For the first series of composites micrometer size $Al_2O_3$ particles were incorporated in the monomer matrix in different proportions. Various amounts of nano-sized filler particles were used in the second set of composite samples. Filler particles underwent an ultrasonic treatment (SonoPlus-UW 2200, Germany) in acetone for 10 minutes prior to mixing with the resin. In initial mixing attempts it was noticed that micro-sized filler particles were easily dispersed in the resin matrix to a rather high proportion of 60 wt.%. On the other hand, maximum amount of nano-sized $Al_2O_3$ admitted by the matrix was around 30 wt.%. Inserting larger amounts increased the viscosity of the composites beyond the handling capabilities. Table 1 lists the compositions of the samples investigated in this study, along with their codes. A typical composite sample was prepared by mixing the desired proportions of components (based on the composition given in Table 1.

**Table 1.** The composition of the samples. Sample code filler type - content (wt. %)

| Sample Code | Filler Type - Content (WT. %) |
|---|---|
| M1 | μm size α- $Al_2O_3$ (45) |
| M2 | μm size α- $Al_2O_3$ (50) |
| M3 | μm size α- $Al_2O_3$ (55) |
| M4 | μm size α- $Al_2O_3$ (60) |
| N1 | nm size α- $Al_2O_3$ (10) |
| N2 | nm size α- $Al_2O_3$ (20) |
| N3 | nm size α- $Al_2O_3$ (30) |

To prevent polymerization, the mixing process was done in the absence of light. After the mixing process, the composite samples were vacuum ($10^{-3}$ atm) dried for 8 h to remove the final traces of acetone from the mixture.

### 2. 2. Characterization

The resin composites were tested with respect to flexural strength, modulus of elasticity, diametral tensile strength (DTS), and microhardness. Flexural strength and flexural modulus were determined by conducting a three - point loading test using a universal testing machine (SANTAM-SMT20), according to the guidelines of ISO- 4049 [22]. Rectangular-shaped specimens were prepared by filling the unpolymerized composite material in metal molds of internal dimensions 2 mm x 2 mm x 25 mm. For each test conducted six samples of the same compositions were used. Polymerization was initiated with a visible light-curing unit (Demetron LC-Kerr, USA). To assure complete polymerization, the samples were irradiated on both sides for 40 s. All specimens were stored for 24 h in distilled water at 37 °C prior to testing. The flexural strength ( $\sigma$ ) was obtained using the following relation:

$$\sigma = \frac{3Fl}{2bh^2} \tag{1}$$

Where F is the maximum load at the point of fracture, l is the distance between the supports; b and h are the width and height of the sample respectively. The average tensile strength of the nanocomposites was evaluated by performing a diametral compression test. Specimens for this test were prepared by pouring unpolymerized samples into a cylindrical metal mold of 3mm height and 6mm diameter. The samples of the diametral tensile test were cured under the same condition as before. The test was conducted following the ADA 27 standard [22], using a universal testing machine (SANTAM-SMT20). The formula used for determining the diametral tensile strength (DTS) was:

$$DTS = 2F/DT \tag{2}$$

Where F is the maximum applied load, D is the sample diameter, and T is the sample thickness. The Vickers hardness number (VHN) was measured using disc-shaped specimens (thickness = 2mm and diameter = 8mm). A load of 200 g was applied for 30 s on their surface. The hardness values were obtained using the following equation:

$$H = 1854.4 \times F/d^2 \quad (3)$$

Where H is Vickers hardness in $kg/mm^2$, F is the load in kilograms, and d is the length of the diagonal in mm. The hardness values were determined by measuring the diagonal of at least six square indentations produced by the applied load. The mechanical test results were analyzed by one-way ANOVA. A statistical significance was considered if $P < 0.05$. Scanning electron microscope (SEM, Model Cam Scan MV2250) was employed to examine the size and morphology of the $Al_2O_3$ particles as well as representative fracture surfaces of the dental composite samples. Samples were sputter coated with gold prior to the SEM study.

## 3. RESULTS & DISCUSSION

The main objective in this study was to study and compare the mechanical behavior of dental composite materials containing nano and micrometer size $Al_2O_3$ filler particles. The flexural strengths of the composite samples containing various mass fractions of micro- sized $Al_2O_3$ fillers are displayed in Fig. 1. Each data point is the mean value of six measurements with error bar representing standard deviations. As shown in this figure, there is an initial increase in the flexural strength of the micro-particle filled composites as the filler content is increased from 45 to 50wt.%. However, a decrease in strength values is observed at higher values of filler addition. Prior to giving an explanation for this behavior, it should be mentioned that no coupling agent was used in the preparation of the samples shown in Fig. 1.

Going back to the results obtained for the flexural strength, it should be reminded that, one of the major factors affecting the mechanical properties of the composite samples is the extent of interfacial interaction. In other words, a poor interfacial interaction prevents an efficient stress transfer between the components. In such cases, the addition of filler particles is expected to increase the number of weak links and therefore have a negative effect on the strength. Therefore, we believe that the increase in the strength shown in Fig. 1 is due to the reduced macromolecular mobility in the matrix and the drop in the strength

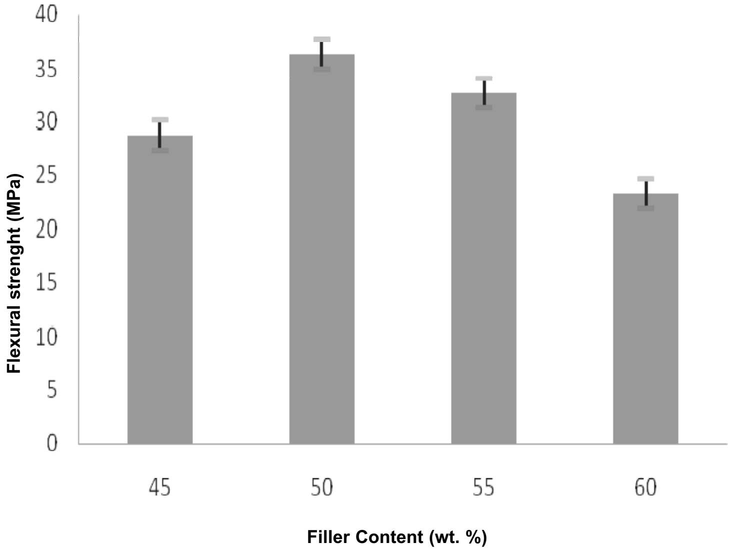


**Fig.1.** Flexural strength of the composite samples containing various amounts of μm-size $Al_2O_3$ filler particles.

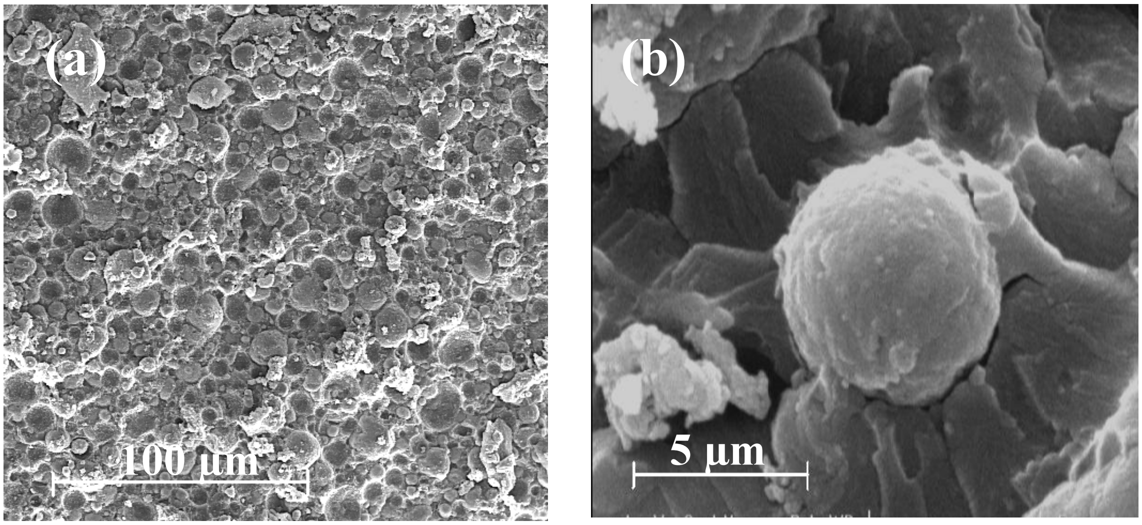


**Fig. 2.** (a) SEM image of the fracture surface of a composite sample containing 55 wt.% µm-size filler particles. (b) Same as in (a) but magnified.

values is most likely attributable to the overcoming effect of poor filler/matrix coherence at higher values of the filler content. To further investigate this point, as a representative case the fracture surface of a sample containing 55 wt.% microfiller was examined by SEM, the result of which are presented in Figs. 2a-b.

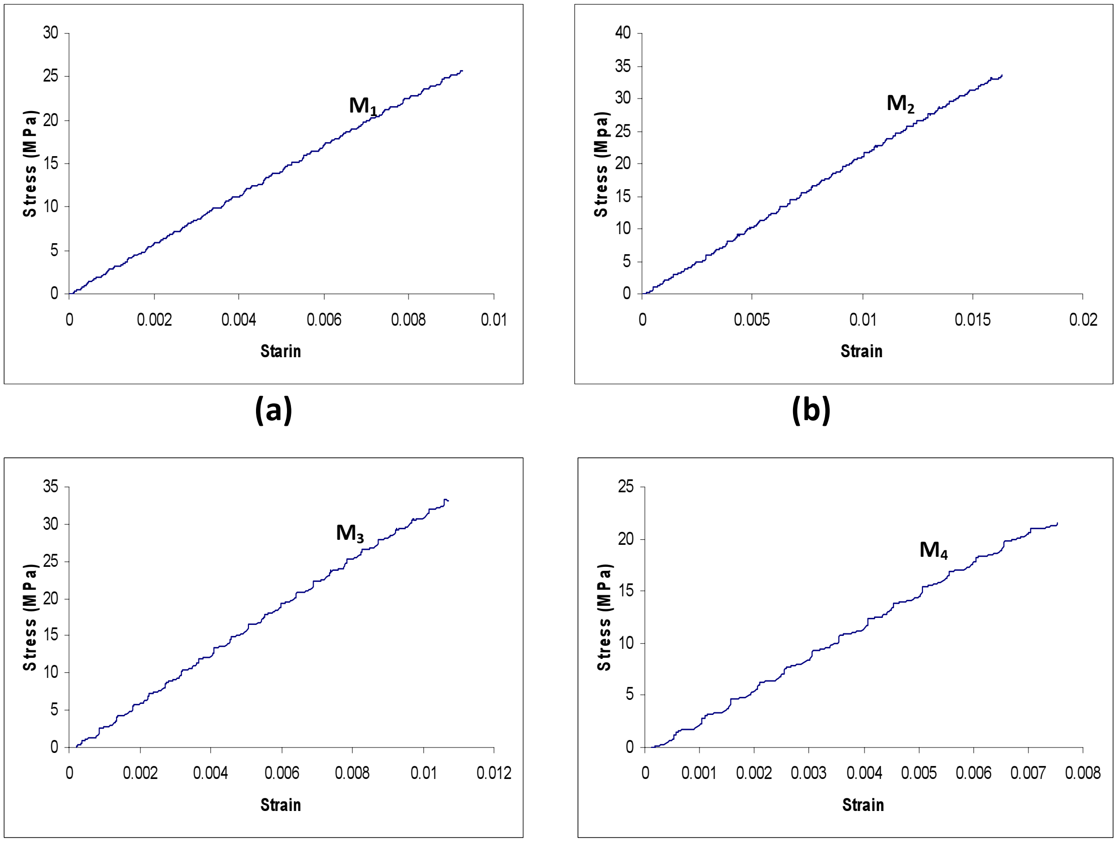
Spherical and evenly distributed micrometer size filler particles can be observed in Fig. 2a. A closer examination of this micrograph indicates that, as a result of a weak interfacial bond between the filler and resin, some filler particles have been effectively forced out of the matrix during the mechanical testing. The presence of a weak interface can be seen more clearly in the magnified image shown in Fig. 2b. Figs. 3a-3d show stress-strain curves for the samples M1-M4 respectively.

The modulus of elasticity values were calculated from these data and are presented in Table 2.

As indicated in this table, except for the case of the sample containing 60 wt.% micro-$Al_2O_3$ the increase in filler content is accompanied by an increase in elastic modulus value. A possible explanation for the increase in the modulus of elasticity value is the more restricted motion of Bis-GMA matrix with an increase in the filler content [24]. Once again, at some critical value of the filler content the sample behavior is dominated by the poor bonding at the interface causing a decrease in modulus value. The rather low modulus values observed in this study may be due to the lower weight percent (max. 60 wt.%) filler values used compared to most commercial dental composites (80-90 wt.%). An exponential dependence of modulus of elasticity on filler content has already been reported in the literature [25]. Another point which can be concluded from the data shown in Fig. 3, is that there is no sign of plastic deformation prior to fracture in these samples. In Fig.4, we show the mean values and standard deviations of the diametral tensile strength for the microfilled

**Table 2.** The modulus of elasticity values for the samples containing µm-size $Al_2O_3$ filler particles.

| Sample Code | Flexural Modulus (MPa) |
|---|---|
| M1 | 2159.32 ± 107.9 |
| M2 | 2346.93 ± 117.3 |
| M3 | 3164.68 ± 158.2 |
| M4 | 2986.47 ± 149.3 |



**(a)** **(b)**

**(c)** **(d)**

**Fig. 3.** Stress-strain curves for the composite samples containing various amounts of µm-size $Al_2O_3$ filler particles.

composite samples.

The diametral tensile strength provides an indication of a restorative’s resistance to the lateral forces generated during function [26]. As indicated in Fig. 4, the DTS data follow a trend similar to the results for flexural strengths (Fig.1), and thus, the data may be explained in a similar manner. The results of the Vickers hardness tests on the samples containing various amounts of micrometer size filler particles are presented in Table. 3.

It may be seen that the increase in the microfiller content has increased the hardness values in the samples. The results from the three-point fracture tests on the nanometer size $Al_2O_3$ filler particles containing samples are presented in Fig. 5.

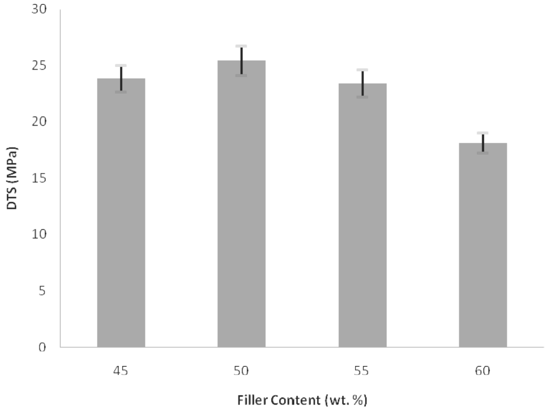


**Fig. 4.** Diametral tensile strength of the composite samples containing various amounts of µm-size $Al_2O_3$ filler particles.

**Table 3.** The Vickers micro-hardness values for the samples containing µm-size $Al_2O_3$ filler particles.

| Sample Code | VHN |
|---|---|
| M1 | 22.5 ± 1.1 |
| M2 | 26.9 ± 1.3 |
| M3 | 34.1 ± 1.7 |
| M4 | 35.2 ± 1.8 |

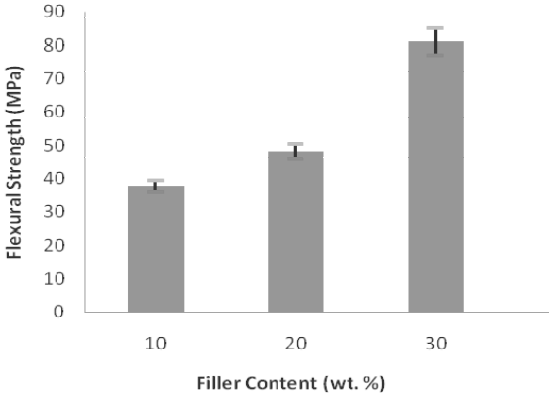


**Fig. 5.** Flexural strength of the composite samples containing various amounts of nm-size Al2O3 filler particles

These results show that all nanoparticulate containing samples have significantly higher mean strength than those of the microfilled composite samples (compare the results with Fig. 1. This implies an effective stress transfer as a result of good bonding between the nano-sized particles and the matrix. It is also important to take into account that the filler fraction values were lower in the nano-size filler containing composites compared to the microfilledcomposite samples prepared in this study. In Figs. 6a-c, we show the stress-strain curves for the composite samples containing nanofiller particulates.

Comparing the results shown in Fig.6 with those shown in Fig.3 indicates that the strain at failure values are higher for all the nanocomposite samples investigated in this study. In Fig.6, it is also observed that, the nanocomposite sample containing 30 wt.% nanofiller particles (sample designated as N3) shows the highest maximum load and therefore the biggest area under the stress-strain curve; indicating that the greater the nanofiller content, the higher is the fracture toughness of the nanocomposite sample. A positive effect of the presence of nano-silica filler particles on flexural strength, surface hardness, and fracture toughness has also been reported by others in the literature [19,27]. The flexural modulus values of the nano-$Al_2O_3$ composite samples are given in Table 4.

The trend shows that the addition of the nanofiller particles increases the elastic modulus values in the composite samples. A similar behavior is also observed on the DTS data (Fig.7) and micro-hardness values shown in Table 5.

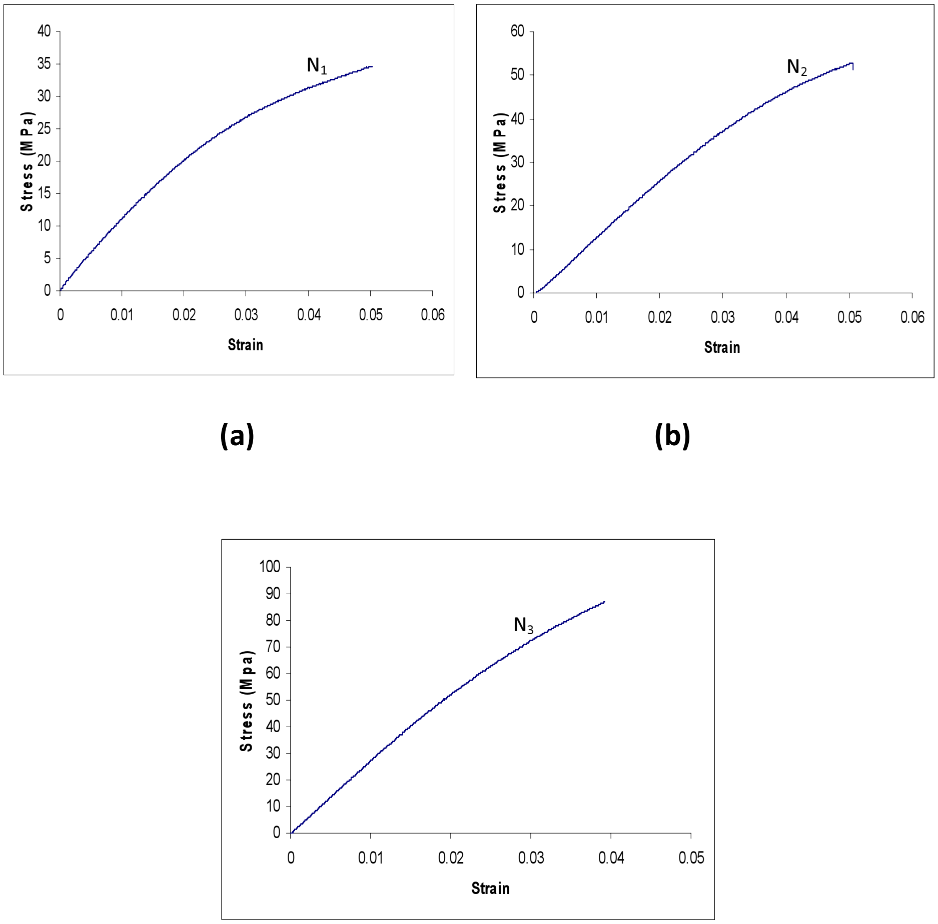
In summary, the data presented in this paper on the mechanical properties of the nano-sized filler containing samples, indicates that in spite of the

**Table 4.** The modulus of elasticity values for the samples containing nm-size $Al_2O_3$ filler particles.

| Sample Code | Flexural Modulus (MPa) |
|---|---|
| N1 | 1157.23 ± 57.8 |
| N2 | 2221.57 ± 110 |
| N3 | 2894.76 ± 144 |

**Table 5.** The Vickers micro-hardness values for the samples containing nm-size $Al_2O_3$ filler particles.

| Sample Code | VHN |
|---|---|
| N1 | 18.3 ± 0.9 |
| N2 | 23.8 ± 1.2 |
| N3 | 34.3 ± 1.7 |



**(a)** **(b)**

**(c)**

**Fig. 6.** Stress-strain curves for the composite samples containing various amounts of nm-size Al2O3 filler particles.

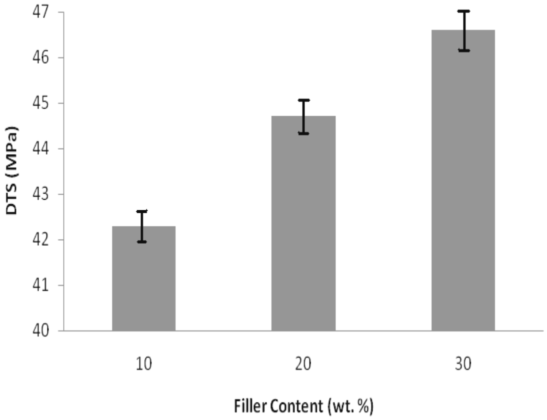


**Fig. 7.** Diametral tensile strength of the composite samples containing various amounts of nm-size Al2O3 filler particles.

lower weight fraction, the use of nano-size $Al_2O_3$ filler particles has led to a significant improvement in the mechanical properties of the dental restorative composite samples. Obviously, several factors are at play, but we believe that maybe the most important is the favorable adhesion between the nano-size filler and the polymetric matrix.

## 4. CONCLUSION

The mechanical properties of dental restorative samples containing nano and micro-sized $Al_2O_3$ filler particles were compared. Nano and micrometersize filler containing dental restorative samples have been compared. The use of nano-sized $Al_2O_3$ filler particles proved to be quite effective in improving the mechanical properties. One other advantage of nano-size reinforcing agents compared to micro-sized particles was the lower loading requirements. The improved mechanical properties exhibited by nanoparticle containing composites is most likely due to better filler/polymer interaction. A more efficient nanoparticle dispersion combined with higher loadings may lead to an even more improved composite dental restorative materials. Further investigations is needed to improve the interaction between the nano-sized fillers and the matrix phase and also to increase the loading capacity of nanofiller particles into the polymer matrix.

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