Effect of addition ZrO_2 nanoparticles to dental composites on the physical and mechanical properties

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Abstract— The aim of the present has focused on effect of ZrO_2 nano particles with different concentration on the physical and mechanical properties of dental composites. Six dental composites test containing different amount of ZrO_2 nano particles 1,3,5,7,and 10wt% were mixed with a Bis-GMA/TEGDMA (70/30 wt%) matrix, and investigated using different tests The sorption, solubility and volumetric increase were measured after storage in water for 180 days. In addition, depth of cure and the flexural strength and modulus were measured using a three-point bending set-up according to the ISO-4049 and diametral tensile strength (DTS) were measured according to ANSI/ADA specification No.27 for cure resins. Measurements were taken and samples stored, immediately after curing, in water at 37°C for 24h. The results showed that the prepared composites containing ZrO_2/NPs exhibited significantly higher water sorption, solubility and volume increase when compared to control group. Water sorption and solubility increased with increasing the loading of ZrO_2 nano particles. Depth of cure of tested composites range from (2.94 to 2.3mm), 1%wt tested composite exhibited the highest flexural strength (118.98 MPa) and the lowest observed for 10wt 47.32MPa. 5wt% test composite revealed the highest flexural modulus value (11.95 GPa). The composite with the lowest amount of ZrO_2/NPs (1wt%) showed the highest flexural strength value, the higher DTS values and the lowest sorption value and solubility. The optimum concentration of ZrO_2/NPs seems to be that of 3wt%. Higher concentrations did improve the properties of composites.

Index Terms— Zirconia, Nanoparticles, Dental composite, Flexural strength, DTS, Sorption, Solubility, Depth of cure.

1 Introduction

A restorative dental material to the relevant dental structures can treat the restoration of decayed dental structures including caries, decayed dentin or decayed enamel. posterior class I or II restorations require composites that show high mechanical properties while anterior restorations need composites that have superior aesthetics [1]. The most traditional dental composites for restorative purposes are hybrid and microfill types. Recently nanoparticles have been used in the formulation of restorative composite systems, such as addition nano oxides materials. In addition, nanoparticles have also been incorporated into the dental adhesives [2, 3]. Furthermore, many studies reported that the dispersion of nanoparticles was the key factor for improving physical and mechanical properties of the composites.

The nanocomposites are developed part of composites contain filler particles in nanometric dimensions (between 20 to 75 nm) [4]. Because nanoparticles have a large surface area, leading to falling interfacial area for Nanocomposite [5, 6]. Nanocomposites are claimed to combine the low wear rate and the brightness retention is better [7, 8], good mechanical strength of the hybrids [4, 9] and the superior polish of the microfills [10], improved optical characteristics[4] and reduced polymerization shrinkage [11].

Zirconia is a strong transition metal its strong resistance corrosion and biomedical grade due to that bears a resemblance to titanium, also ZrO_2 biomedical grade was used to solve the problem of alumina brittleness and the consequent potential failure of implants [12], ZrO_2 have wide applications due to outstanding biocompatibility, increasing strength, and low wear cost. In other hand due to their smaller sizes, ZrO_2/NPs high chemical stability and ionic conductivity, biomedical applications and non-toxic [12, 13], also Zirconia nanoparticles (ZrO_2/NPs) have been applied in several areas of dentistry, as dental crown [14, 15], an implant biomaterial [16], femoral heads for total hip replacement [17], implantology [18], dental prostheses [19], and restorative dentistry [20]. Furthermore, ZrO_2/NPs could be recommended for applications in dental care and other relevant biomedical applications [12]. The aim of this study was to determine and to distinguish the unique physical properties (such as sorption and solubility of water and depth of cure) and mechanical properties (such as flexural strength, modulus, and DTS) of light cure composites modified with different ratio (1, 3, 5, 7 and 10 wt%) of ZrO_2 Nano particles.

2 Materials and Methods

2.1 Material

ZrO_2/NPs (particle size < 100nm coated and 99.8% purity) (American Elements, USA), Barium Borosilicate Glasses with particles size 9.5µm (Esstech Inc, USA) used as filler, γ-methacryloxy propyl trimethoxy silane (γ-MPS). Bis-GMA and Triethyleneglycol dimethacrylate (TEGDMA) from Sigma

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Aldrich (UK). Camphorquinone (CQ) and 2-(Dimethylamino) ethyl methacrylate from Aldrich (UK).

2.2 Preparation of specimens

Five experimental groups of composites containing ZrO_2/NPs in different concentrations of 1,3, 5, 7 and 10 wt% and one control group with no additive. The tested composites were prepared by the incorporation of the ZrO_2/NPs the nanoparticles were then dispersed into a dental resin Bis_GMA/TEDGMA and filler (after surface treated with 1.0 wt% of (γ-MPS)) [21]) filled to 76wt% (57.2%Vol). The compositions of the composites used in this study are given in Table 1.

TABLE 1: COMPOSITIONS OF THE COMPOSITES USED (WT %).

Materials	0%	1%	3%	5%	7%	10%
Bis-GMA/ TEGDMA (70/30wt%)	23	23	23	23	23	23
Barium Borosilicate Glasses	76	75	73	71	69	66
ZrO_2/NPs	-	1	3	5	7	10
CQ	0.5	0.5	0.5	0.5	0.5	0.5
Amin	0.5	0.5	0.5	0.5	0.5	0.5

2.3 Water sorption and solubility

Water sorption were performed according to the specification standard for composite dental resins (ISO 4049: 2008), 4 specimens for each ratio of ZrO_2/NPs were produced in stainless steel mold (15mm diameter and 1mm thickness), they were irradiated 40sec with a LED light source. After polymerization the specimens were placed in a desiccator containing silica gel to reach constant mass (M_0), then immersed in distilled water at 37°C for 180 days and mass was recorded until there was no significant change in weight (mass variation less than ±0.1 mg) (M_1). After this, the specimens discs were removed from water and placed in a desiccator containing silica gel after one week was weighed (M_2).

Water sorption (WA) and solubility (WS) values were obtained according to ISO 4049, using the following equation:

$$WA\ (\frac{\mu g}{mm^3}) = \frac{M_1 - M_2}{V} \qquad (1)$$

$$WS\ (\frac{\mu g}{mm^3}) = \frac{M_0 - M_2}{V} \qquad (2)$$

Volumetric changes of specimens were obtained by using Archimedes principle via accurate measurement for densities. Furthermore, the volume increase, VI (%), is calculated using the available data on densities of the dry (ρ_d) and densities after immersion (ρ_i):

$$Vl\ (\%) = \frac{(M_1/\rho_i - M_0/\rho_d)\rho_d}{M_0} \times 100 \qquad (3)$$

2.4 The depth of cure

The depth of cure was performed according to ISO standard 4049 with 4 mm in diameter and 10mm in depth. The stainless steel mold was placed on a glass slide and filled with one of tested composite, then the specimens polymerized 40sec with a LED light source from top of mold, after curing the specimens was pressed out from the mold, the part which had uncured was removed. Depth of cure defines, as 50 percent of the length of the composite specimen after the part of uncured material is removed spatula with a plastic [22].

2.5 Flexural strength and modulus

Flexural strength were measured according to ISO 4049 for resin. The specimens (2mm × 2mm × 25 mm) were prepared by filling stainless-steel rectangular mold with one of uncured tested composite, the upper and lower surfaces of the mold were covered with glass slides. An overlapping regime was applied to irradiate the specimens were irradiated for 40 sec on each sides. After polymerization the specimens were stored in distilled water at 37°C for 24hrs, the specimens were bent in a three-point bending rig with 20 mm between the two supports using universal testing machine (Zwick/roell BT1-FR2.5TN Germany) with a cross head speed of 1 mm/min. The flexural strength (FS) in MPa was calculated as [23]:

$$FS = \frac{3pL}{2bd^2} \qquad (4)$$

Where p the maximum load exerted on the sample at the point of fracture (N), L length, the distance between two supports (20 mm), and b the width (mm) and d thickness (mm). Flexural modulus E (MPa) was calculated using the following formula:

$$E = \frac{3PL^3}{4bd^3D} \qquad (5)$$

Where P load at fracture (N), L distance between the supporting wedges (mm), b width of the specimen (mm), d thickness of the specimen (mm) and D the deformation of the specimen at P, also the elastic modulus was determined from the slope of the initial linear part of stress–strain also curve.

2.5 Diametral tensile strength (DTS)

For DTS a cylindrical stainless-steel mold, 6mm internal diameter and 3mm height, specimens were prepared according to ANSI/ADA specification No.27 for cure resins. The uncured composites were inserted into mold and polymerized for 40sec, then stored in distilled water for 24hrs at 37°C. A universal testing machine (Zwick/roell BT1-FR2.5TN Germany) was used for the test at a cross head speed of 1mm/min. The DTS (MPa) was then calculated according to the following equation [21]:

$$DTS = \frac{2p}{\pi DL} \qquad (6)$$

Where p stands for load at fracture (N), D are diameter (mm) and L height (mm) of specimens.

3 Result

3.1 Water sorption and solubility

The Mean (Std. Deviation) results for water sorption and solubility (µg/mm^3) are showed in Figure 1 and tabulated in Table 2. Tested composite loading 1% of ZrO_2/NPs denoted lowest sorption 9.45±0.25 µg/mm^3 and the value increase when ratio of nanoparticles increase the highest sorption denoted at 10wt% tested composites 12.74±0.62µg/mm^3.

The slightly less hydrophilic tested composite, results showed an increasing solubility with increasing concentration of ZrO_2/NPs. The lowest value of solubility for control group 1.285±0.37 µg/mm^3 and increase when loading of nano particales increase the highest denoted at 10Wt% (4.77±0.44 µg/mm^3) Figure 1.

In Figure. 2 the volume increase (%) of tested composites after immersion in water (37°C) after 100 days the value ranged from 2.05±0.13 to 2.81±0.16%.

Table 2. Mean (standard deviations) for sorption, solubility (µg/mm^3) and Volume increase (%) of test composites containing 0-10 wt% ZrO_2/NPs

Concentration	Sorption (µg/mm3)	Solubility (µg/mm3)	Volume increase (%)
Control (0%)	9.67 (0.47)	1.28 (0.37)	2.05 (0.13)
ZrO2 (1%)	9.45 (0.25)	1.76 (0.48)	2.06 (0.077)
ZrO2 (3%)	10.10 (0.40)	2.26 (0.65)	2.03 (0.10)
ZrO2 (5%)	11.49 (1.04)	4.70 (0.64)	2.57 (0.28)
ZrO2 (7%)	11.77(0.20)	4.64 (0.68)	2.64 (0.31)
ZrO2 (10%)	12.74 (0.62)	4.77 (0.44)	2.81 (0.16)

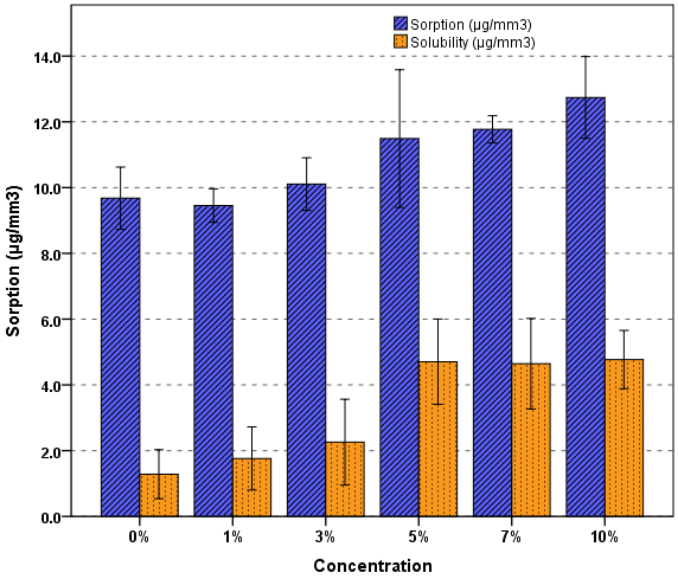

Fig. 1. Water sorption and solubility of tested composites containing ZrO_2/NPs.

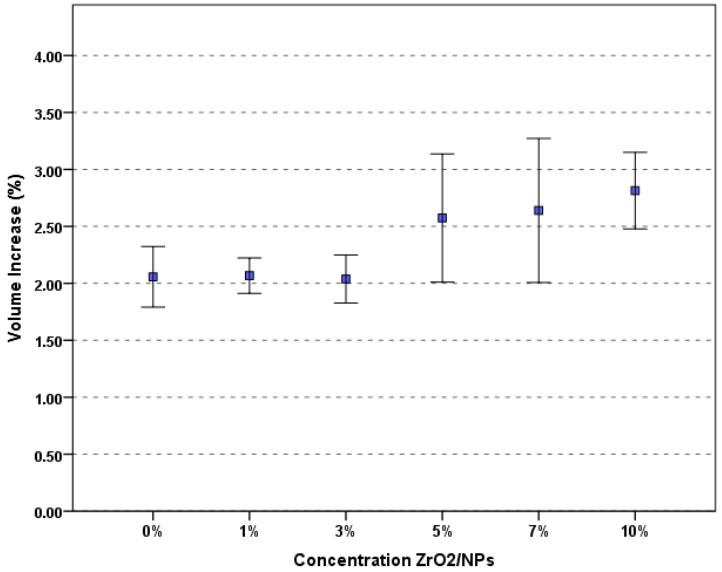

Fig. 2. Volume increase (%) of test composites containing 0-10 wt% ZrO_2/NPs.

2.2 Depth cure

The results of the depth of cure measurements are given in Figure 3. The larger mean depth of cure obtained with control 2.941±0.19mm, while tested composite loading 10wt% denoted lowest depth of cure 2.3mm. The value slightly decreases when increasing concentration of ZrO_2/NPs.

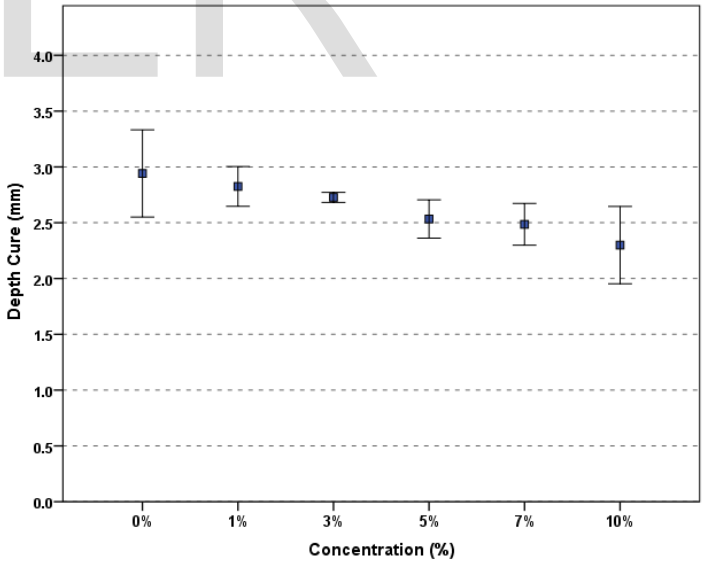

Fig. 3. Depth of cure (mm) of resin composites containing 0-10 wt% ZrO_2/NPs.

2.3 Flexural strength test (FS) and flexural modulus (FM)

The results for flexural strength are depicted in Figure 4 and tabulated in Table 3. Test Composite with 1wt% has significantly high flexural strength than control. the control denoted about 113.3554±8.22 MPa, while the value of 1% denoted 118.981±6.9 MPa ratio of increase ~5%, then for tested

composite loading upper to 1wt% the FS become decreases demonstrated the minimum mean FS for 10% 47.323±6.48 MPa. Figure 5 shown, incorporation of the ZrO_2/NPs into the resin composite resulted in an increase in FM of the tested composites with a maximum corresponding to 5wt% (11.95±0.58GPa) then become decrease of FM after 5wt% the lowest FM 9.86 ±0.62GPa observed for 10wt%.

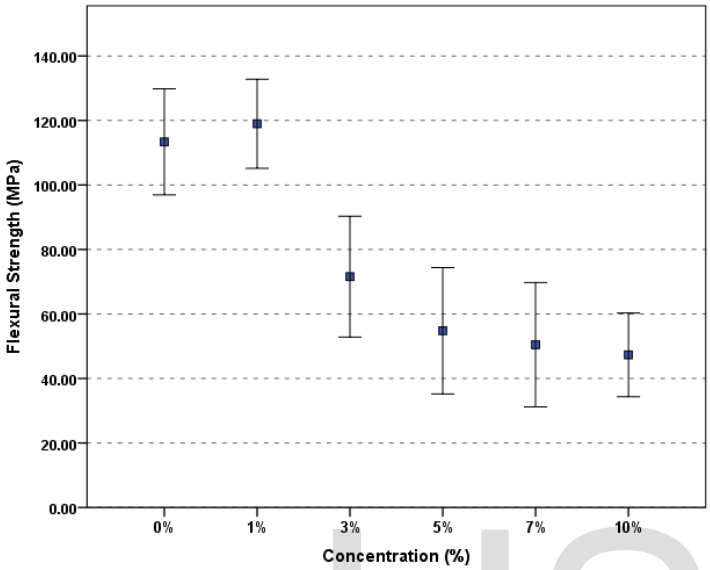

Fig. 4. Flexural strength (MPa) of test composites containing 0-10 wt% ZrO_2/NPs.

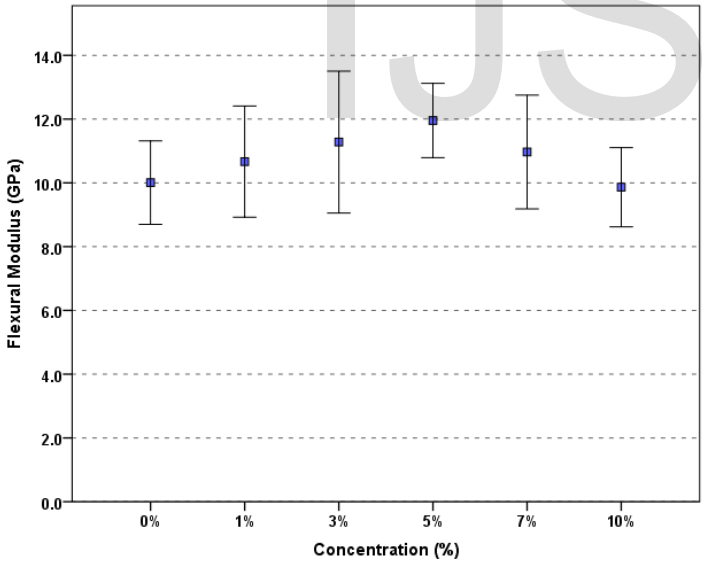

Fig. 5. Flexural modulus (GPa) of test composites containing 0-10 wt% ZrO_2/NPs.

TABLE 3. FLEXURAL STRENGTH, FLEXURAL MODULUS AND DTS OF TEST COMPOSITES (ENTRIES ARE MEAN VALUES WITH STANDARD DEVIATIONS).

Concentration (wt%)	FS (MPa)	Fm (GPa)	DTS (MPa)
Control (0%)	113.35 (8.22)	10.00 (0.65)	**52.39 (4.26)**
ZrO_2 (1%)	118.98 (6.90)	10.66 (0.87)	**63.16 (2.08)**
ZrO_2 (3%)	71.57 (9.37)	11.28 (1.11)	**51.38 (3.13)**
ZrO_2 (5%)	54.80 (9.80)	11.95 (0.58)	**49.42 (4.4)**
ZrO_2 (7%)	50.45 (9.63)	10.97 (0.89)	**40.70 (3.06)**
ZrO_2 (10%)	47.32 (6.48)	9.86 (0.62)	**39.71 (3.5)**

2.4 Diametral tensile strength (DTS)

The DTS of tested composites containing different amounts of ZrO_2/NPs are shown in Figure 6 and tableted in table 3. Tested composites contained 1% ZrO_2/NPs demonstrated higher values of DTS 63.16±2.08MPa compared with those contained Upper to 1%, the lowest value for DTS was observed for composite containing 10Wt% 39.71±3.5MPa .

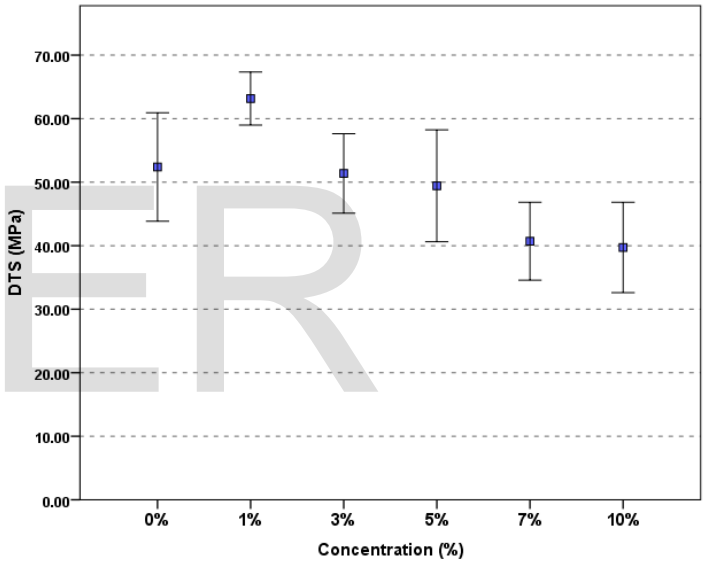

Fig. 6. DTS (MPa) of test composites containing 0-10 wt% ZrO_2/NPs.

4 DISCUSSION

The maintenance and improve of physical and mechanical properties of restorative materials is main to ensure the long-term clinical success of the restoration. Therefore, studies in this area may be useful for recommendations on their application and the modifications of the material. In this study, physical and mechanical properties of light cure composite modified with verses amount of ZrO_2/NPs were study.

Water has a significant role in the lifetime and degradation of dental composite. Sorption and solubility are affecting composite restorations by two different mechanisms; the first is the uptake of water producing an increased weight and the second is the dissolution of materials (fillers or monomers) in water, leading to a weight reduction of the final conditioned samples [24]. Water sorption in composite materials takes place because water molecules (less than 0.158 nm) are able to

diffuse through the inter chain spaces of the resin matrix, which are larger than water molecules [25].

As Figure. 1 shows, low value sorption for all tested composites ranged between 9.677µg/mm^3 for control group and 12.74µg/mm^3 for 10wt% tested composite, and results showed an increasing sorption with increasing concentration of ZrO_2. Therefore, a arising in the rate of water uptake is to be expected with increasing concentration of ZrO_2/NPs, because increasing in surface area of nanoparticles, connected with the polymer leading to the diffusion of water between them. In addition, table2 shown 1wt% test composites (9.45 µg/mm^3) less than the control group, It is expected due to large flexural strength which suggests an increase in the polymerization process.

The value of solubility in dental materials reflect that amount of unreacted monomer leachable by the water. Many factors influencing solubility may include the chemical composition of composite and coupling agent between filler- matrix , the solvents, immersion time periods and temperature [26]. All composites showed low solubility in water (Table 2), but solubility increases when concentration increases, because contains a higher level of ZrO_2/NPs, making a relatively large surface area of the fillers available for removing and non-polymerization fillers. In addition, figure 3 showed the increasing in volume for tested composite contain ZrO_2/NPs, a reason for volumetric change is a swelling of the material by increased absorption of water, results showed a slight increase in volume after sorption of upper 3wt% than lower 3wt%. Finally, the composites tested in this study showed low sorption, which denoted values varied from 9.67 to 12.74 µg/mm3 and were lower than those required by the ISO 4049 standard, which establishes that the maximum sorption value is 40 µg/mm3. On the other hand, the solubility mean values presented by the composite tested ranged from 1.28 to 4.77 µg/mm3, these values were lower than the maximum value established by the ISO 4049 standard (<7.5µg/mm3).

Depth of cure is a significant first step the test composites, the depth of cure measurements in this study denoted 2.9mm for control group and slightly decreases in 1% and 3% of ZrO_2/NPs (Figure 2). In other hand, specimens containing upper to 3 wt% ZrO_2/NPs concentration have very low depth of cure, the mean depths of cure obtained in 10wt% are ~2.3mm, therefore about 21% lower than those obtained with control group. Because the density of the ZrO_2/NPs diffusion within the test composites causes to be scattered and attenuate the light during attempting to penetrate composites in the polymerization process, since smaller filler particles scatter the light more than large filler particles and can promote areas of poor polymerization [27, 28] . The results of depth of cure were obtained for all tested composites contain of ZrO_2/NPs deeper than required by either the current ISO 4049 (lower limit 2 mm) [22].

In the present study, the flexural strength test was chosen to assess whether differences in mechanical properties were present in Nano composites when modified different loading of ZrO_2/NPs. Improvement in flexural strength of the nanocomposites was significant at concentrations of 1wt% ZrO_2/NPs which obtained 119MPa, ~5% higher than FS of the control group (Table 3 and Figure 3). This phenomenon can be attributed to the small sizes of the nanoparticles of ZrO_2 incorporated along with the filler into the composites, On the other hand, the FS values significantly decreased for nanocomposite containing upper to 1wt% ZrO_2/NPs concentration when a comparison of the control group. The FS values were 71.57, 54.8, 50.4 and 47.32 MPa for 3, 5, 7 and 10wt% concentrations respectively. It could be argued that, the finding show that because of the smaller particles size and greater surface area of ZrO_2/NPs compared to the filler, there may be insufficient matrix resin to bond to the increased amount of ZrO_2/NPs powders effectively and thus weaken the interfacial bonding between the particles and the matrix resin.

The fillers in the resin matrix have the responsibility of mechanical reinforcement and improvement of the modulus of matrix [29]. Ideally, the flexural modulus of a dental material should be comparable to the dental tissues that are claimed to be replaced. Dental Materials with much high flexural modulus may not be advantageous [30]. In this study showed that the flexural modulus (FM) of tested composites increases with increasing concentration of ZrO_2/NPs (Table 3 and Figure 4), control group denoted 10GPa and increasing slightly to the highest FM value of the tested composites 11.95GPa at ZrO_2/NPs loading of 5wt%. The increase in FM values in this study attributed to tested composites filler particles include both glass and ZrO_2/NPs, which predominately consisted of glass, whose silica (SiO4) structures have an amorphous (non-crystalline) [31].

DTS is an acceptable and common test for dental composites and more important than compressive strength, because this material will more likely be subjected to tensile or shears than in compression in clinical application [32]. Figure 5 shown increase in DTS of the tested composite was only significant at a concentration of 1wt%, while deterioration in DTS of the tested composites was significant at concentrations of upper 1wt% ZrO_2/NPs. This phenomenon can be resulted a conglomerate in ZrO_2/NPs because of its small size, which leading due to lack of crosslinking of these nanoparticles with matrix resin, which are likely to weaken the tested composite at concentration upper 1wt%. Generally, dental composites contain with nanoparticals has lower DTS than that contain with macro fillers only [33].

5 Conclusions

In light of the results obtained in this study, could be concluded that the physical and mechanical properties can be drawn:

1. Addition different amount of ZrO_2/NPs added to filler and mixture with Bis-GMA affect the physical and metical properties. Sorption and solubility of water increase with increasing concentration of nanoparticales, in addition to increasing volume, and decrease flexural strength and DTS when increase ZrO_2/NPs.

2. Incorporation of the ZrO_2/NPs in minute amounts of about 1 wt% would positively affect the physical and mechanical properties of the composite.
3. Incorporation of high percentage by weight of ZrO_2/NPs would adversely affect the physical and mechanical properties of Composite.

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