



Effect of Zirconia and Alumina Nanofillers on the Microstructure and Some Properties of Flowable Composite

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ABSTRACT

PURPOSE: This study was conducted to evaluate the effect of reinforcing flowable composite with different concentrations of zirconia and alumina nanofillers on its microstructure, complex viscosity, colour changes, flexural strength and degree of conversion. **MATERIALS AND METHODS:** 200 samples were divided according to nanofillers type into two groups (n=100), each group was subdivided into five subgroups according to concentration of fillers (0%, 2%, 4%, 8% and 16%) (n=20). Each subgroup was subdivided into 4 subdivisions according to type of test performed (n=5). Samples were characterized by SEM, viscosity was measured by oscillatory rheometer, colour changes was measured using spectrophotometer, flexural strength was measured by three point bending test and degree of conversion was measured by FTIR. **RESULTS:** SEM showed homogenous distribution of zirconia and alumina np at 2&4wt%, some agglomeration for both types of fillers at 8wt%. For complex viscosity, zirconia np at 16wt% at 25°C had higher median value compared to 37°C (6.17), Alumina np at 2wt% and 4wt% at 25°C had higher median value compared to 37°C (5.665), (8.516) respectively. For colour changes, zr& al np at 4wt% showed the highest mean values (10.2±1.5, 11.1±1.4) respectively. In flexural strength, zirconia filler at 4wt% had higher mean value (137.8±18.1MPa) compared to alumina filler (94.4±16.9MPa). For DC, 4wt% for both zr& al np showed the highest mean values compared to other groups (66.4±2.4, 64.3±0.82) respectively. **CONCLUSION:** Viscosity increased as the concentration of nanofillers increased. Incorporation of nanofillers affected the colour of the flowable composite. Flexural strength was improved with increasing the concentration of zirconia nanofillers, while it decreased with alumina nanofillers. DC increased as the filler concentration increased till 4 wt.% then decreased.

KEYWORDS

Nanozirconia, nanoalumina, composite, reinforcement

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INTRODUCTION

Different types of aesthetic restorative materials are used nowadays as they are highly accepted by patients, bond to tooth structure, have excellent esthetic properties, have low cost and applied in both anterior and posterior teeth ⁽¹⁾.

For clinicians, the use of a composite with a variable consistency in restorative treatment is attractive because the viscosity affects the application and manipulation of the material. Flowable composites are characterized by low modulus of elasticity, low viscosity, and high wettability of the tooth structure. Accordingly, in clinical situations, flowable composites have been reported to adapt well to the cavity wall ⁽²⁾.

Flowable composites have been proposed as liners, fissure sealants and restorative materials for small cavities⁽³⁾. Their usage is indicated in non-stress bearing areas, because of their low mechanical properties. It was shown that the mechanical properties of flowable composites, such as diametral tensile strength, compressive strength, and fracture toughness, are generally about 60–90%

of those of conventional composites. Furthermore, flowable composite wear resistance is lower compared to conventional composites and especially highly filled composites⁽⁴⁾.

As flowable composites exhibit a relatively low mechanical properties due to low filler content, one notable way of improving it is adding nanoparticles. The addition of nanoparticles might improve its strength, abrasion resistance, decrease the polymerization shrinkage as there is a correlation between physical and mechanical properties and filler content weight and size in composite resins ⁽⁵⁾.

Considering the previous pathways to improve the strength by modifying the composition of the materials, the aim of this study was to evaluate the influence of the addition of zirconia and alumina nanofillers on the physical, rheological and mechanical properties of flowable composite.

MATERIALS AND METHODS

The materials used in this study, their specification, composition and manufactures are summarized in table (1).

Table (1): The trade name, type, composition and manufacturers of the materials used in this study:

Material	Type (specification)	Composition	Manufacturer
Light-curing composite	T-econom flowable composite, shade A3	-Bis-GMA, UDMA, Decandioldimethacrylat (37.6 %) -Barium glass filler, Yettebrium fluoride, Mixed oxide, Highly dispered silica (41.1 %) -Prepolymers (20.4%) -Additives, Catalysts and Stabilizers (0.9%) Pigments (< 0.01%)	Ivoclar vivadent
Zirconia nanofillers	Spheroidal in shape, Particle size 20 nm	Zirconium oxide	Nanotech company, 6 th october city, Egypt
Alumina nanofillers	Spheroidal in shape, Particle size 25 nm	Aluminum oxide	Nanotech company, 6 th october city, Egypt

METHODS:

Preparation of the formulated flowable composite:

Zirconia and alumina nanofillers were incorporated separately into the flowable composite (T-econom flow) at various concentrations (2,4,8 & 16 wt %). A digital sonicator (Sh80- 2L, MTI Corporation, USA) was used for 1 hour to ensure homogenous distribution of the zirconia and alumina nanofillers into the flowable composite and preparing the formulated flowable composite ⁽⁶⁾.

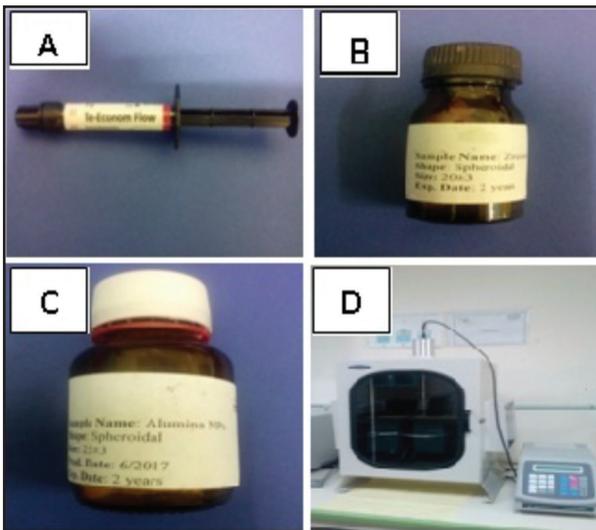


Figure (1) **A:** Te-economflowable composite, **B:**zirconia nanofillers, **C:**alumina nanofillers, **D:**digital sonicator

Testing Methods:

I- Characterization of the experimental flowable composite by Scanning electron microscope:

Scanning electron microscope (Quanta, FEG 250, Japan) was used to determine the homogenous distribution of zirconia and alumina nanofillers in the composite. Scanning Electron Microscopy (SEM) provides high resolution and high depth of field images of the sample surface and near surface. It is one of the most widely used analytical tools due to the extremely detailed images it can quickly provide.

II- Rheological properties testing:

An oscillatory rheometer (PhysicaMCR301, Anton par Austria) was used to measure the dynamic viscoelastic behavior of the resin composite. A rheometer has a compartment consisting of two halves enclosing two round plates. The movable upper plate was connected eccentrically to a driving wheel by a rod and a lower plate upon which the sample was placed. Each plate was 10 mm in diameter and made of stainless steel. The samples were placed on the lower plate and then the upper plate was brought down. The excess material was removed using tissue paper. Finally two halves of the outer compartment of the rheometer were closed and the temperature was adapted by the computer software at 25°C. After relieving the residual normal stress, a frequency sweep was completed over the angular frequency range. The range of shear-rate results obtained by each material was dependent upon its viscosity. The specimens were directed to high torque frequencies (synonymous with increasing shear rates) while the resulting shear stress developed in the resin was measured. The obtained shear stress to shear strain values enabled the calculation of the materials instantaneous viscosities. Since the viscosity varied with shear rate, viscosities over the measured shear rate range were averaged and tabulated for each concentration of the formulated flowable composite and temperature. Then the temperature was elevated for the same sample by the computer software to 37°C.

The viscosity was measured according to the equation ⁽⁷⁾:

$$\eta^* = \tau/\dot{\gamma}$$

Where η^* is the complex viscosity, τ is the shear stress and $\dot{\gamma}$ is the shear rate.

III- Colour changes measurements:

A split Teflon mould with central cavity (7 mm in diameter and 2 mm thick) was fabricated for sample preparation. The mould was placed on a glass slab and filled with the flowable composite

using plastic instrument, then covered with celluloid strip and compressed with another glass slab to remove the excess, then light cured with the intensity of 1200mw/cm² with a distance of 1 mm for 20 seconds according to the manufacturer instructions. All specimens were removed from the mould and polished using a 600grit SiC paper to remove excess material. The specimens were then stored in distilled water at 37°C for 24 h. The specimens' colours were measured using a reflective spectrophotometer (X-Rite, model RM200 QC, Neu-Isenburg, Germany). The aperture size was set to 4 mm and the specimens were exactly aligned with the device. A white background was selected and measurements were made according to the CIE L*a*b colour space relative to the CIE standard illuminant D65. The colour changes (ΔE) of the specimens were evaluated using the following formula⁽⁸⁾:

$$\Delta E_{\text{CIELAB}} = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \text{ where,}$$

L* = Lightness (0-100),

a* = change the colour of the axis (red/green)

b* = colour variation axis (yellow/blue)

IV-Flexural strength testing:

A split Teflon mould was prepared which was a bar shaped (l= 25mm, h= 2mm, w= 2mm). Five bar shaped specimens were prepared, the flowable composite was placed into the teflon mould (l= 25mm, h= 2mm, w= 2mm) positioned on a glass slab and covered with celluloid strip. Another glass slab was positioned on the mould containing the material to remove the excess composite which was light cured for 20 s at each third of the upper and lower surfaces of the specimen with intensity of 1200 mw/cm² with a distance of 1mm. All specimens were removed from the mould and polished using a 600grit SiC paper to remove excess material. The specimens were then stored in distilled water at 37°C for 24 h. All samples were individually and horizontally mounted in a custom made loading fixture (three-point bending test assembly; two parallel stainless steel rods with span length 13 mm supporting the specimen, with the damage

site centrally located on the tensile side) on a computer controlled materials testing machine (model 3345; Instron Industrial products, Norwood, MA, USA) with a load cell of 5 KN and data were recorded using computer software (Instron® Bluehill Lite Software), then the samples were statically compression loaded at a crosshead speed of 0.5 mm/min until fracture. The stress strain curves were recorded with computer software (Instron® Bluehill Lite Software). FS represents the limiting stress at which failure or instability is imminent. The value of FS was calculated by the following equation⁽⁹⁾:

$$FS(\sigma) = 3Fl/2wh^2 \text{ where:}$$

F: the maximum load at the point of fracture

l: distance between the supporting rollers (20mm),

w: specimen width (2 mm),

h: specimen height (2 mm).

V- Degree of conversion testing:

Fourier Transform Infrared Spectrophotometer (model Jasco FTIR- 4600) was used for measurement. A sample of uncured paste of composite was smeared onto a potassium bromide disc and the absorbance peaks were obtained before curing by transmission mode of FTIR. To cure each material, the paste was placed into a split Teflon mould (6 mm diameter, 2.2 mm high) and the surfaces were covered by celluloid strip. Light curing was performed from the top surface for 60 s with light intensity of 1200 mW/cm². The absorbance peaks were recorded using the diffusion mode of FTIR. The percentage of unreacted carbon=carbon double bonds (% C=C) was determined from the absorbance intensities ratio of aliphatic C=C (peak at 1637 cm⁻¹) against internal standard before and after curing of the specimen. The aromatic C=C (peak at 1608 cm⁻¹). The DC was determined by subtracting the % C=C from 100%⁽¹⁰⁾

$$DC = 1 - \frac{\text{abs}(\text{aliphatic} = \text{c } 1637 \text{ abs}) / (\text{aromatic} = \text{c polymer } 1608)}{\text{abs}(\text{aliphatic} = \text{c } 1637 \text{ abs}) / (\text{aromatic} = \text{c polymer } 1608)} \times 100$$

RESULTS

I- Characterization of the experimental flowable composite by Scanning electron microscope:

Scanning electron microscope of 2%, 4% and 8% concentration by weight revealed homogenous distribution of spherical shaped zirconia nanofillers into the matrix of the flowable composite while with increasing the percentage to 16%, some agglomeration and inadequate distribution of the fillers appeared within the composite matrix as shown in figure (2). For the alumina nanofillers, Scanning electron microscope of 2% and 4% concentration by weight revealed homogenous distribution into the matrix of the flowable composite while with increasing the percentage to 8%, some agglomeration and inadequate distribution of the fillers appeared within the composite matrix and with incorporation of 16wt% of alumina nanofillers into the matrix, failure in mixing was detected as a high percentage of agglomeration occurred as shown in figure (3).

II- Rheological measurements:

There was an increase in the viscosity with the increase in the concentration of both zirconia and alumina nanofillers, while it decreased with increasing the temperature. Table (2) showed statistically non-significant differences between all groups of Zirconia fillers at (0%, 2%, 4% and 8% concentrations) at (25°C and 37°C) in complex viscosity ($P > .05$). In contrast, (at 16% concentration) Zirconia filler at 25°C had statistically significant higher complex viscosity compared to 37°C ($P < .05$).

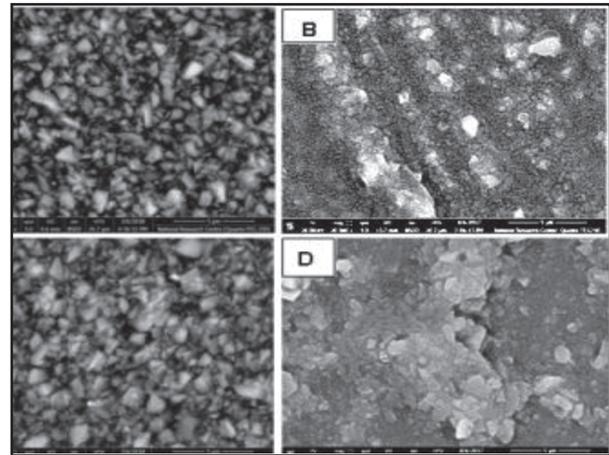


Figure (2) **A:** zirconia fillers with 2%conc. **B:** zirconia fillers with 4%conc. **C:**zirconia fillers with 8%conc. **D:** zirconia fillers with 16%conc.

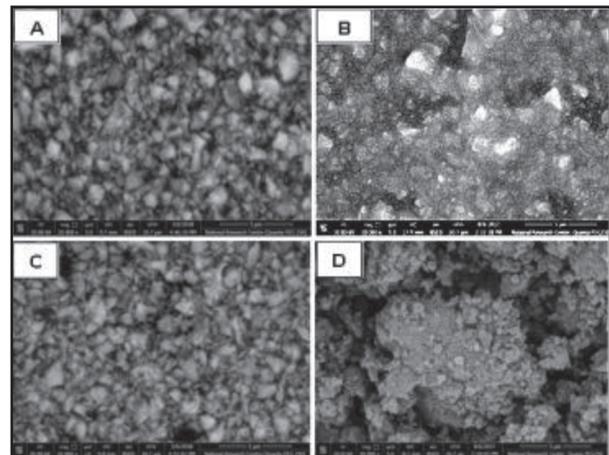


Figure (3) **A:** alumina fillers with 2%conc. **B:**alumina fillers with 4%conc**C:**alumina fillers with 8%conc. **D:**alumina fillers with 16%conc.

Table (2) Comparison between zirconia fillers at the same concentrations (250 C and 370 C) regarding complex viscosity

Complex viscosity [Pa·s]	Zirconia filler at 25°C	Zirconia filler at 37°C	Wilcoxon Signed-Rank Test	P-value
Concentration				
Control (0%)				
Median (Range)	1.840(1.12-2.8)	1.35(1-9.8)	$z=0.47$.64
At 2%				
Median (Range)	2.47 (2.27-4.15)	1.9(0.12-8)	$z=1.3$.18
At 4%				
Median (Range)	3.12(2.42-3.75)	2.54(0.105-4.4)	$z=0.63$.53
At 8%				
Median (Range)	2.045(1.94-4.89)	3.11(1.1-4.86)	$z=0.94$	0.35
At 16%				
Median (Range)	6.17(5.73-9)	4.54(1.8-7.5)	$z=3.1$.002**

Table (3) showed comparison between Alumina fillers at the same concentrations (25°C and 37°C) regarding complex viscosity. The table showed statistically non-significant differences between Control and Alumina fillers (at 8% concentration) at (25°C and 37°C) in complex viscosity ($P>.05$). In contrast, (at 2% and 4% concentration) Alumina fillers at 25°C had statistically significant higher complex viscosity compared to 37°C ($P<.05$).

III- Optical properties:

The results showed colour changes with incorporation of both zirconia and alumina nanofillers and higher value of colour changes with alumina nanofillers. Table (4) showed statistically non-significant differences in mean colour changes between Zirconia filler and Alumina filler at (2%, 4% and 8%) concentrations ($P>.05$).

Table 3: Comparison between Alumina fillers at the same concentrations (25^o C and 37^o C) regarding complex viscosity

Complex viscosity [Pa·s]	Alumina filler at 25°C	Alumina filler at 37°C	Wilcoxon Signed-Rank Test	P-value
Concentration				
Control (0%) Median (Range)	1.85(1.12-2.8)	1.350(1.07-9.84)	$z=0.47$.64
At 2% Median (Range)	5.665(3.63-20.3)	2.14(1.1-5.04)	$z=3.1$.002**
At 4% Median (Range)	8.516(1.36-70)	7.902(1.209-754.2)	$z=2.4$.015*
At 8% Median (Range)	46.29(6.62-282.5)	28.73(2.668-1772)	$z=1.7$.084

Table 4: Comparison between Zirconia and Alumina fillers at the same concentrations regarding colour changes

Colour changes (ΔE)	Zirconia filler	Alumina filler	Independent sample-t test	P-value
Concentration				
At 2% Mean±SD	5.1±2.2	6.3±3	$t=-.97$.35
At 4% Mean±SD	10.2±1.5	11.1±1.4	$t=-1.4$.19
At 8% Mean±SD	7.1±1.8	8.7±3.7	$t=-1.2$.27

IV- Flexural strength:

Zirconia nanofillers with conc. of 16% showed the highest value of flexural strength, while 8% conc. of alumina nanofillers showed the highest value of flexural strength. Table (5) showed statistically non-significant differences in mean flexural strength between Zirconia filler and Alumina filler at (2% and 8%) concentrations, but Zirconia filler at 4% concentration had a statistically significant elevation in mean flexural strength compared to Alumina

filler ($P < 0.039$).

V-Degree of conversion:

With incorporation of both zirconia and alumina nanofillers at 4% concentration by wt, the highest value of degree of conversion resulted. Table (6) showed statistically non-significant differences in mean degree of conversion between Zirconia filler and Alumina filler at (2%, 4% and 8%) concentrations ($P > .05$).

Table (5) Comparison between Zirconia and Alumina fillers at the same concentrations regarding flexural strength

Flexural strength (MPa)	Zirconia filler	Alumina filler	Independent sample-t test	P-value
Concentration				
At 2%				
Mean±SD	68.3±35.3	113.9±22.5	t=-1.9	.13
At 4%				
Mean±SD	137.8±18.1	94.4±16.9	t=3	.039*
At 8%				
Mean±SD	84.1±2.9	58.9±19.7	t=2.2	.15

Table (6) Comparison between Zirconia and Alumina fillers at the same concentrations regarding degree of conversion

Degree of conversion (%)	Zirconia filler	Alumina filler	Independent sample-t test	P-value
Concentration				
At 2%				
Mean±SD	61.6±3.1	63.9±3.5	t=-0.84	.45
At 4%				
Mean±SD	66.4±2.4	64.3±0.82	t=1.5	.22
At 8%				
Mean±SD	59.3±2.4	45.5±4.1	t=1.4	.23

DISCUSSION

In the present study, the incorporation of zirconia nanofillers into the flowable composite with concentrations of 2&4% showed homogenous distribution within the matrix which enhanced the handling properties and mechanical properties of flowable composite, while adding Zr. nanoparticles with 8 &16% concentration showed some agglomeration which affected the handling properties and mechanical properties of the flowable composite. The incorporation of alumina nanofillers into the flowable composite with concentrations of 2&4 % showed homogenous distribution within the matrix which enhanced the handling properties and mechanical properties of flowable composite, while adding Al. nanoparticles with 8% concentration showed some agglomeration. The concentration of 16% wt. didn't mixed before sonication which was the cause to reject this concentration in the present study.

The addition of the nanofillers to the flowable composite greatly affect the handling properties of the composite including viscosity⁽¹¹⁾. In the present study, the effects of different percentages of filler loading and effect of temperature at both (25°C) and (37°C) on the viscosity of flowable composite were investigated. For both zirconia and alumina nanofillers, as the concentration of the fillers increased, the viscosity also increased. It was found that 16 % conc. of zirconia nanofillers had the highest median value of complex viscosity compared to other concentrations at both 25°C and 37°C.

For alumina nanofillers, there was a significant increase with increasing the concentration of incorporated fillers. The 8% conc. showed higher median values of complex viscosity than other groups at both 25°C and 37°C. The results were consistent with previous studies which showed an increase in viscosity with loading which was more pronounced with small particles. As the smaller the particle size, the greater their number would be which increased the degree of interactions between them⁽¹²⁾.

Another factor which affected the viscosity of the flowable composite was the temperature. This finding came in agreement with another study which showed decrease in viscosity with increasing the temperature. This was attributed to the excitement and movement of the molecules. The energy generated from this movement was enough to overcome the forces that bind the molecules together⁽¹³⁾.

The present study revealed that the incorporation of zirconia and alumina nanofillers with different concentrations affected the colour of the flowable composite. The results were inconsistent with previous studies which concluded that ΔE_{ab} values greater than or equal to 3.3 were considered visually not acceptable⁽¹⁴⁾.

As investigated in this study that the colour of the flowable composite was affected by the difference in filler loading, this came in agreement with another study in which the effect of filler on colour parameters was evaluated. It was found that the amount of fillers significantly influenced the lightness of composite resins as increasing the filler content had an impact on the ability for light transmission through the layers of the composite⁽¹⁵⁾.

In the present study, flexural strength was affected by the amount of fillers incorporated into the flowable composite which come in agreement with others who concluded that reinforcement of dental composite resins with nanofillers causes an improvement in their mechanical properties due to good bonding between nanofillers and resin matrix⁽¹⁶⁾.

The results of the present study was in agreement with another study which revealed that increasing the amount of nano-alumina fillers decreased the flexural strength due to presence of agglomerates and voids, which were initiating factors for failure. Moreover, the high percentage of alumina fillers within the matrix of composite resin decreased flexural strength as they act as impurities⁽¹⁷⁾.

The DC of the composites was assessed using FTIR spectroscopy. A certain degree of conversion (DC %) in dental composite resins must be achieved for the material to develop adequate physical and mechanical properties to withstand masticatory forces and attain adequate biocompatibility. The optimal value of degree of conversion of composite resins ranging from 43 to 73%⁽¹⁸⁾.

In the present study, zirconia and alumina nanofillers at 4% concentration had greater mean degree of conversion compared to other groups. These results were consistent with other results which reported that filler size, weight, volume, and filler-to-matrix ratio of composite resin had a significant effect on its degree of conversion⁽¹⁹⁾.

The results were also in accordance with another study which showed lower conversion with high percentage of untreated fillers, while various fillers had been shown to inhibit free radical polymerization through electron transfer from constituent oxides⁽²⁰⁾.

CONCLUSIONS

Under the limitations of this study, it was found that:

- 1- For both types of nanofillers used, the complex viscosity showed a direct proportionality with the filler concentration and inverse proportionality with the temperature.
- 2- The nanofillers affected the colour changes which became noticeable and unaccepted as the filler concentration increased greatly.
- 3- For the nanozirconia reinforcement, the flexural strength was improved as the filler concentration increased. On the contrary, the increase in the nanoalumina filler concentration had a negative impact on the flexural strength.
- 4- The degree of conversion increased as the filler concentration increased till 4 wt. % conc. where higher concentrations led to decrease in the DC.

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