

The Effect of Zirconium Silicate Nanopowder Reinforcement on Some Mechanical and Physical Properties of Heat Cured Poly (Methyl Methacrylate) Denture Base Materials

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ABSTRACT

Background: Polymethylmethacrylate (PMMA) has relatively unsatisfactory mechanical properties such as low flexural strength and impact strength also dimensional instability.

Material and method: Zirconium silicate nanoparticles were coated with a layer of trimethoxysilylpropylmethacrylate (TMSPM) before sonication in monomer (MMA) with the percentages 1% and 1.5% by weight then mixed with powder using conventional procedure, (150) samples were prepared and divided into three groups, each group consisted of (50) samples, the first group prepared from PMMA without addition (control), another group with the addition of 1% wt ZrSiO₄ nanoparticles (experimental) and the third one with 1.5% wt ZrSiO₄ nanoparticles (experimental). Each group was divided into 5 sub-groups according to the test performed. The tests conducted impact strength, transverse strength, indentation hardness (shore D), surface roughness, water sorption and solubility. The size, shape and distribution of nanofiller were estimated using scanning electron microscope (SEM). The results were statistically analyzed using ANOVA and LSD test.

Result: Highly significant increase in impact strength, transverse strength and surface hardness occurred with the incorporation of 1.5% wt Zirconium silicate nanofiller but non-significant increase in impact strength, significant increase in transverse strength and highly significant increase in surface hardness occurred with the incorporation of 1% wt ZrSiO₄ nanofiller. Non-significant increase in surface roughness with both 1% and 1.5% wt ZrSiO₄. Highly significant decrease in water sorption and solubility with 1.5% wt ZrSiO₄ nanofiller and non-significant decrease in water sorption and solubility with 1% wt ZrSiO₄ compared with control group.

Conclusion: The maximum increase in impact strength, transverse strength, and surface hardness was observed in denture base nano composite containing 1.5% ZrSiO₄. In addition, highly significant decrease in water sorption and solubility and non-significant increase in surface roughness was also noticed.

Key words: poly (methyl methacrylate), nano composite. (J Bagh Coll Dentistry 2015; 27(4):37-43).

INTRODUCTION

The most widely used material for construction of complete dentures is poly (methyl methacrylate) resins, because of satisfactory appearance, uncomplicated curing procedure and successful repairing ⁽¹⁻³⁾. However, clinician still encounter that artificial acrylic prosthesis may fracture as a result of sudden fall or continuous flexing by occlusal forces ⁽⁴⁻⁶⁾.

Water sorption and solubility of denture base PMMA have detrimental effects on color stability of the denture base and have negative effects on physical properties and may lead to harmful tissue reaction ⁽⁷⁻⁹⁾. The incorporation of nano reinforcements considerably enhances their mechanical and thermal barrier properties in conjunction with noticeable enhancements in adhesion, rheological and processing behavior.

In addition, improved dispersion of the fillers within the matrix gives high performance nano composites and furthermore the properties of the nano scale filler are significantly higher than those of the base matrix.

Currently, polymer nanocomposite materials are approaching with the incorporation of nanofiller like nanoclays, nano particles, nanotubes, nanofibers, etc ^(10,11).

Silane coupling agent might be used to improve better adhesion of nano particles with a resin matrix ^(12,13), his study was conducted to use zirconium silicate nanoparticles that were treated with 3-Trimethoxypropylsilylmethacrylate (TMPSM) and were added to heat cured PMMA to get PMMA/Zirconium silicate nanocomposite and study the effects of this addition on some mechanical and physical properties over pure heat cured PMMA.

MATERIALS AND METHODS

Surface Modification of ZrSiO₄ Nano Fillers:

Modification of nanofiller was done by the reaction of trimethoxysilyl propyl methacrylate TMSPM with zirconium silicate nanopowder.

Silanation Process was as follows:

Pure Toluene solvent in the amount of (175ml) and ZrSiO₄ in the amount of (25gm) were placed into glass beaker of capacity (250ml) and sonicated by ultrasonic probe (*hielcher, UP200S, Germany*) for 20 min. as seen in (figure 1). Then the beaker was placed on magnetic stirrer (*model SH-3, heating power 500 W, stirring speed*

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0-1600 R/min, made in England). Then 1.25 gm (5% wt to nano filler) of silane was added drop wisely by using sterile syringe under rapid stirrer. The slurry was left for two days and the beaker was covered after that the slurry was placed in rotary evaporator (*Heidolph LABORATA – 4000, Germany*) under vacuum of (60⁰C), rotation of (150 rpm) for (30 min.) as seen in figure (2).

Finally, the silanated Nano particles were moisture free by placing in vacuum oven (*vaucell, Germany*) for (20 hours at 60⁰C), and then stored at room temperature before use⁽¹⁴⁾. The infrared (IR) spectra were performed (Shimadzu, FTIR, Japan) to determine whether or not functional groups of the TMSPM have been attached to the nanofiller by analyzing the characteristic vibrations of functional groups⁽¹⁵⁾.



Figure (1): Ultrasonic Probe



Figure (2): Rotary Evaporator

Addition of Fillers:

Addition of modified Zirconium silicate nano fillers was done in two groups of 1% and 1.5% by weight. An electronic balance with accuracy of (0.0001g) was used; the fillers were dispersed with monomer by using a probe sonication apparatus (200 W, amplitude of the oscillatory system had adjusted on 70%) for 2 minutes to break them into individual nano crystals. The liquid monomer and ZrSiO₄ nanofiller were mixed at once with (PMMA) powder. The mixed ratio used for (PMMA), was (2.2g: 1ml) P/ L, following manufacturer instructions.

Selection of Proper Percentage of Zirconium Silicate Nano Fillers:

According to the pilot study the addition of 1% and 1.5% nano fillers to PMMA had the greatest amount of transverse and impact strength therefore, a decision was made to choose 1% and 1.5% of silanized Nano ZrSiO₄ filler, in addition to control group to complete the main study.

Pattern Preparation:

Three different plastic patterns were constructed by cutting plastic plate in desired shape and dimension by using laser cutting machine according to the required test. Transverse strength, Surface roughness and Shore D. hardness tests: bar shaped specimen with dimensions of (65mm x 10 mm x 2.5 ± 0.1 mm)⁽¹⁶⁾ length, width, thickness respectively, While water sorption and solubility tests: disc with dimensions of 50mm in diameter and 0.5mm in thickness⁽¹⁶⁾. Impact strength test: bar shaped specimen with dimensions of (80 mm x 10 mm x 4 mm) length, width and thickness respectively⁽¹⁶⁾.

Mould Preparation:

The conventional flasking technique for complete denture was followed.

Proportioning and Mixing of the Acrylic:

Table (1): Percentages and Amounts of Polymer, Monomer and Zirconium Silicate Nanofiller Powder.

ZrSiO ₄ conc. percentages	Amount of ZrSiO ₄ (g)	Amount of polymer (g)	Amount of monomer (ml)
0%	0g	44g	20 ml
1%	0.44g	43.56g	20 ml
1.5%	0.66g	43.34g	20 ml

Mechanical and Physical Tests Used to Examine Properties:

1. Impact Strength:

The test sample was supported as a beam on both sides and struck in the midpoint with a pendulum of charpy impact tester of two joules capability⁽¹⁷⁾. Unnotched sample was used and the energy absorbed by the specimen was recorded in KJ/m^2 , according to this equation:

$E/B.D \times 10^3$ (E: impact energy, B: specimen width, D: specimen thickness)⁽¹⁸⁾.

2. Transverse Strength:

The test was performed using a universal Instron testing machine, a load was applied in the middle of the testing sample that is supported at each ends separated by a distance of 50mm. The maximum stress was 50 Kg, and the load utilized directed in the midpoint of the sample until breakage occur. The speed of the load was 1mm/min, and calculation of transverse strength follows this equation:

$3PL/2bd^2$ (p: peak load, L: span length, b: sample width, d: sample thickness)⁽¹⁸⁾.

3. Surface Roughness:

Each specimen was tested for surface roughness using a portable surface roughness tester (Profilometer) which can measure small surface variation. This device has a diamond stylus which moves in contact with surface for 11mm. Three measurements were done at 3 positions across each specimen surface which was divided into 3 equal thirds and the mean of the 3 readings were recorded, as a roughness measurement.

4. Surface Hardness:

Shore D hardness tester was used according to (ANSI/ADA specification No.12, 1999). The device comprise of a dull end marker of 0.8mm which presents in a container of 1.6mm. The marker (indenter) is connected to a measuring device calibrated from (0-100 unit). Generally the indenter is compressed with rapid movement on the sample to record the maximum reading displayed from digital screen. The specimen was divided into 5 equal parts, and shore D was measured in these areas. Finally the average of the five readings was recorded.

5. Water Sorption and Solubility:

A dissector was used to dry the samples in which fresh silica gel was added, after that they were kept in an incubator at $37^\circ\text{C} \pm 2^\circ\text{C}$ for one day. Then the samples were transferred to room temp for 60 min, and then a digital balance was used to weigh the samples precisely to (0.000g). The same cycle repeated again every day at the same time until a constant mass "conditioned mass" (M1) was reached after 5 days which means

that not greater loss than 0.2mg in 24 hours (ADA Specification No. 12).

After that immersion of the samples in distilled water were continued up to seven days at $37^\circ\text{C} \pm 2^\circ\text{C}$, then each specimen carried from water with tweezers and rubbed for 30 seconds by clean dry hand towel, left in air for 15 second then weighed, this value represent M2. In order to gain the amount of solubility, the discs were again placed in the desiccator at $37^\circ\text{C} \pm 2^\circ\text{C}$ as mentioned before in sorption experiment and the reconditioned mass was known as M3. The whole group was reached to M3 within 5 days. The calculation of water sorption and solubility was according to the following equations⁽¹⁹⁾:

$$W_s = (M_2 - M_1) / S$$

$$W_{SL} = (M_1 - M_3) / S$$

RESULTS

FTIR test was done to samples of zirconium silicate nanofiller before and after Silanation to evaluate the differences in active groups, as seen in figure (3). Another FTIR was done to PMMA/ZrSiO₄ nano composite before and after Silanation of nano filler to evaluate the adhesion of nano particles with polymer matrix as seen in figure (4).

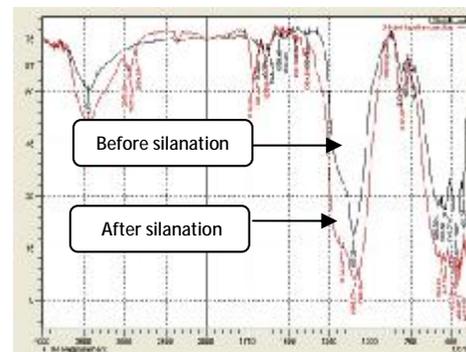


Figure (3): FTIR of Zrsio4 before and after Silanation

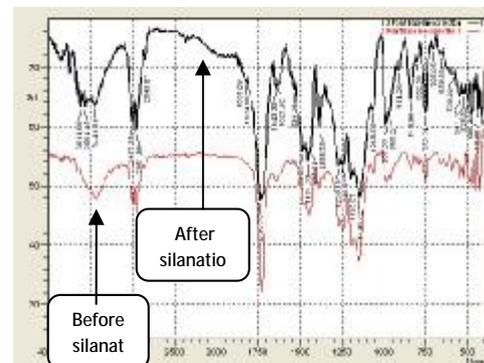


Figure (4): Polymer Nano Composite before and after Silanation

Impact Strength Test:

Descriptive data of mean, standard deviation, standard error, minimum and maximum and also

the ANOVA test and LSD test are listed in Table (2).

Table (2): Descriptive Data and LSD Test of Impact Strength Test.

	A 0%	B 1%	C 1.5%	ANOVA F-test	Sig.	Groups	P-value	Sig.
N	10	10	10	27.811	0.000 H.S	A&B	0.08	N.S
Mean	7.0740	7.5254	8.8884			A&C	0.00	H.S
SD	0.54461	0.52802	0.62216			B&C	0.00	H.S
SE	0.17222	0.16697	0.19674					
Min.	6.20	6.84	7.95					
Max.	7.90	8.71	9.78					

Transverse Flexural Strength:

Descriptive data of mean, standard deviation, standard error, minimum and maximum and also

the ANOVA test and LSD test are listed in Table (3).

Table (3): Descriptive Data and LSD Test of Transverse Flexural Strength Test

	A 0%	B 1%	C 1.5%	ANOVA F- test	Sig.	groups	P-value	Sig.
N	10	10	10	5.740	0.008 H.S	A&B	0.03	S
Mean	111.5800	120.9400	125.3630			B&C	0.00	H.S
SD	10.24053	10.05454	7.11225			A&C	0.31	N.S
SE	3.23834	3.17952	2.24909					
Min.	96.30	105.80	110.40					
Max.	127.20	135.00	135.20					

Hardness Test:

Descriptive data of mean, standard deviation, standard error, minimum and maximum and also

the ANOVA test and LSD test are listed in Table (4).

Table (4): Descriptive Data and LSD Test of Indentation Hardness Test

	A 0%	B 1%	C 1.5%	ANOVA F- test	Sig.	groups	P-value	Sig.
N	10	10	10	26.970	0.000 H.S	A&B	0.00	H.S
Mean	82.4800	84.8450	86.0050			A&C	0.00	H.S
SD	1.24793	1.10967	0.89519			B&C	0.02	S
SE	0.39463	0.35091	0.28308					
min	80.80	83.40	84.40					
max	85.10	86.30	87.30					

Surface Roughness Test:

Descriptive data of mean, standard deviation, standard error, minimum and maximum and also

the ANOVA test and LSD test are listed in table (5).

Table (5): Descriptive Data and LSD Test of Surface Roughness Test

	A 0%	B 1%	C 1.5%	ANOVA F-test	Sig.	groups	P-value	Sig.
N	10	10	10	2.122	0.139 N.S	A&B	0.64	N.S
Mean	1.5435	1.6181	1.8621			A&C	0.59	N.S
SD	0.27362	0.33790	0.45109			B&C	0.14	N.S
SE	0.08653	0.10685	0.14265					
min	1.19	1.02	1.08					
max	2.01	1.97	2.53					

Water Sorption Test:

Descriptive data of mean, standard deviation, standard error, minimum and maximum and also

the ANOVA test and LSD test are listed in table (6).

Table (6): Descriptive Data of Water Sorption Test (gm/cm²) and LSD Test

	A 0%	B 1%	C 1.5%	ANOVA F- test	Sig.	groups	P- value	Sig.
N	10	10	10	4.414	0.022 S	A&B A&C B&C	0.12 0.00 0.18	N.S H.S N.S
Mean	0.3888	0.3550	0.3262					
SD	0.02919	0.04926	0.05503					
SE	0.00923	0.01558	0.01659					
min	0.34	0.23	0.23					
max	0.43	0.40	0.40					

Water Solubility Test

Descriptive data of mean, standard deviation, standard error, minimum and maximum and also

the ANOVA test and LSD test are listed in table (7).

Table (7): Descriptive Data of Water Solubility Test (gm/cm²) and LSD Test

	A 0%	B 1%	C 1.5%	ANOVA F-test	Sig.	groups	P-value	Sig.
N	10	10	10	4.648	0.018 S	A&B A&C B&C	0.077 0.005 0.245	N.S H.S N.S
Mean	0.0138	0.0095	0.0076					
SD	0.00285	0.00617	0.00337					
SE	0.00090	0.00195	0.00106					
min	0.01	0.00	0.00					
max	0.02	0.02	0.01					

Scanning Electron Microscope Test (SEM) Test:

Particle size of nano particles was evaluated by SEM test, the results showed that the nanoparticles have spherical shape and with particles size < 100 nano as seen in figure (5). The

fracture surface of 1.5%wt sample of impact strength test specimen was examined by SEM with different magnifications power to evaluate dispersions of nanoparticles in the resin matrix as seen in figure (6).

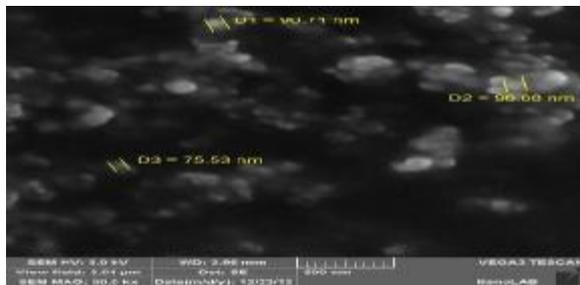


Figure (5): SEM of Nano ZrSiO₄ to Determine Dispersion of the Particle size

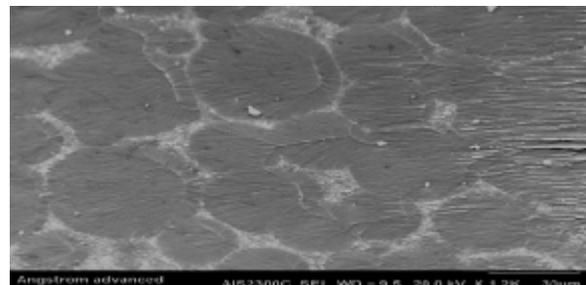


Figure (6): SEM of PMMA/ZrSiO₄ Nanofiller

DISCUSSION

The results of the present study indicate that there was highly significant increased in impact strength when zirconium silicate nano was added to PMMA. This is because the new compound (ZrSiO₄+PMMA), potentiate the internal resistance due to force exchange between filler and matrix. Moreover, particle size and bonding interaction significantly affect the compound stress-strain behavior. Also forces applied are moved to the nanoparticles which increases the impact strength^(20,21), This result was in agreement with Safi⁽²²⁾ who incorporated ZrO₂ nano fillers into heat cured (PMMA).

The increase in transverse strength after addition of nanoparticles lead to reduce free space distance between polymer chains and lead to filling free spaces between chains and attract resin molecules and hence polymer chains during curing process creating more complicated network chains^(23,24). This result was in accord with Jasim⁽²⁵⁾ who incorporated silanized alumina nanofiller into conventional heat cured (PMMA). The increased in hardness of nano composite can be explained with several factors; it may be attributed to the inherent hardness characteristic of the ZrSiO₄ Nano particles, the Zirconium silicate has tetragonal crystal structure seems like

small prism shaped structure separated or may appear as double pyramids connected from the bottom given the very hard and heavy properties⁽²⁶⁾. Another factor of increase in hardness may be due to good distribution in the resin matrix⁽²⁷⁾. This result was in agreement with Alamel⁽²⁸⁾ who found that there was a highly significant increase in surface hardness when SiO₂ was added to heat cure acrylic resin with different percentages (3%, 5% and 7%). The results showed non-significant increase in surface roughness when different percentages (1% wt and 1.5% wt) of silanized ZrSiO₄ nanoparticles were added, this may be due to that the surface roughness test is concerned with outer surface and not with inner surface of composite and because of using zirconium silicate Nanoparticles which is very small size <100 nano and well dispersed in the resin matrix moreover, because of small percentage of nano-Zrsio₄ particles were added to acrylic resin so only very small amount of nanoparticles concerned on the surface⁽²⁹⁾. The result was in agreement with Jasim, (2014), who concluded that the surface roughness was not changed when silanized Al₂O₃ nanoparticles added to PMMA.

ZrSiO₄ nano filler has the property of insoluble in water⁽³⁰⁾. When it was incorporated into PMMA resin matrix lead to decreasing in diffusivity of the water molecule which reduces water sorption and decrease in water uptake⁽³¹⁾. The decreasing in water solubility can be explained by that micro voids or pores can be formed during curing of acrylic resin. Therefore, when the amount of pores found in polymer are increases may result in more fluid gain through it which causes molecules to be separated that leads to more absorption of fluids. Zirconium silicate nanofiller which is insoluble material might decrease the total amount of polymer absorption⁽³⁰⁾. The results of water sorption and solubility were coincides with Mohammed⁽³²⁾, who found noticeable reduction in water sorption and solubility when ZrO₂ nano fillers were incorporated into conventional heat cured (PMMA).

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