Effect of modified zirconium oxide nano-fillers addition on some properties of heat cure acrylic denture base material

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ABSTRACT

Background: Polymer nano composite attracted great attention especially because of their unexpected hybrid properties that are synergistically derived from the two components. The aim of this study was to evaluate the effect of addition of modified nano-zirconium oxide on some properties of heat cured acrylic denture base material.

Materials and methods: Zirconium oxide nano fillers modified by a silane coupling agent Tri (methoxysilyl) propyl methacrylate before dispersed and sonicated in monomer (MMA)in different percentage 2%,3%and 5%by weight. Three hundreds and twenty specimens were prepared for these studies were divided into five main groups according to the test used. The tests were abrasive wear, water sorption and solubility, porosity, tensile and fatigue strength test. For each test four sub groups (one control and three for different weight percentage of nano-ZrO_2). Scanning electron microscope techniques used to analyze the fracture surface of fatigue test and estimate the dispersion and distribution of the nano-ZrO_2 particles.

Results: Highly significant increase in abrasive wear resistance with 3wt% and 5wt% of nano fillers with all groups of denture cleansers. highly significant decrease in water sorption and solubility. Significant decrease in porosity in 3wt% and 5wt%. Highly significant increase in both tensile and fatigue strength in all groups but slightly decreased in 5wt% as compared with 3wt% but still high significant as compared with control group.

Conclusion: incorporating the modified nano-ZrO_2 into acrylic resin results in improvement in abrasive wear resistance, tensile and fatigue strength in addition decrease in water sorption, solubility and porosity of heat cure denture base resin.

Key words: Nano composite, SEM analysis, abrasive wear. (J Bagh Coll Dentistry 2012; 24(4):1-7).

INTRODUCTION

To date, up to 95% dental prostheses are composed of poly (methyl meth acrylate), due to its advantages including itsbiocompatibility, adequate strength and aesthetic [1]. However, few but important disadvantages are inherent in this resin such as poor strength particularly under fatigue failure inside the mouth and low abrasion resistance [2]. Polymer nanotechnology represents a new field in nano science, polymer nano composite attracted great attention especially because of their unexpected hybrid properties that are synergistically derived from the two components[3].

Zirconia(ZrO_2) nano filler is one of the nano materials incorporated with polymer because it is excellent biocompatible material also because of being white is less likely to alter esthetic. The nano-sized zirconia has been used to fabricate nano composite with high hardness, high refractive index and improved scratch resistance [4].In the light of the proceeding, the present study was designed to evaluate and test the addition of modified zirconium nanomaterials in different percentage (2wt%, 3wt%, 5wt%) to heat cured acrylic resin PMMA materials. It is intended to evaluate abrasive wear resistance, water sorption, solubility, porosity, tensile and fatigue strength of heat cured acrylic resin denture base materials before and after the addition of (ZrO_2).

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MATERIALS AND METHODS

Surface modification of nanofillers (ZrO2)

The introduction of reactive groups onto fillers surface was achieved by reaction of 3- tri (methoxysilyl) propylmethacrylate with zirconium oxide nano fillers [5].

Pattern Preparation:

Four different plastic patterns were constructed by cutting plastic plate into desired shape & dimension by laser cutting machine.

For abrasive wear test, specimens with (60mm, 30mm and 3mm) as length width and height respectively [6]. For porosity test 30mm in diameter and 3mm in thickness [7]. For tensile strength flat dumbbell shaped with (16mm in length, 3mm in width and 2mm in thickness) at the parallel segment [8].For fatigue test (70mm, 10mm and 2.5mm) length, width and thickness respectively. Except for water sorption and solubility metal pattern were constructed by cutting stainless steel plate with 50mm in diameter and 0.5mm in thickness [9]. Figure (1)

Figure 1: Plastic patterns (A,C,D,E) and metal pattern(B)

Table 1: Percentages and amounts of polymer, monomer and modified zirconium oxide nano fillers powder used in this study.

ZrO_2 Percentage	Amount of ZrO_2	Amount of polymer	Amount of Monomer
0%	-	10 g	4.4ml
2%	0.2 g	9.8 g	4.4 ml
3%	0.3 g	9.7 g	4.4 ml
5%	0.5 g	9.5 g	4.4 ml

Proportion and mixing of the acrylic resin:

Addition of fillers

Addition of modified Zirconium oxide nanofiller powder (ZrO2) was done by weight in three groups, includes 2%, 3%, 5% and to monomer. An electronic balance with accuracy of (0.0001g) was used (Sartorius BP 30155, Germany). After the addition of ZrO2 nano filler to monomer, the fillers were well dispersed in the monomer by ultra sonication, using a probe sonication apparatus (Soniprep-150, England) at 120 W, 60 KHz (Figure 2) for 3 minutes to break them into individual nano crystals[(9)]. The suspension of the monomer with ZrO2 nanofiller was immediately mixed with acrylic powder. The proportion for mixing for acrylic resin was (2.2g: 1g) P/L. All materials were mixed and manipulated according to manufacturer's instruction.

Figure 2: Probe sonication apparatus

Mechanical and physical tests utilized to examine properties

1. Abrasive wear test

Abrasive wear test was conducted following the procedure given by ISO 14569-1:2007. The specimen cleaned for one minute in an ultrasonic bath with de-ionized water containing 1% of detergent (Sodium lauryl sulfate). Then dried and weighted to an accuracy of 0, 1 mg (mass m1).The density was determined in accordance with ISO 1183-1:2004 to an accuracy of two decimal places. The density was measured by a gas helium pycnometer machine (Figure 3). Evaluation was made by measuring abrasive wear by volume loss after brushing the specimens with different mechanical denture base cleansers (water, denti-pur gel and colgate).

The brushing device manufactured from the apparatus described in the British standard Institution, 1974[(10)](Figure 4)**.**The specimen was subjected to a linear tooth brush abrasion movement with a rate of 350 brush strokes (forth & back) per minute, totalizing 35,000 brush strokes for each specimen, which is representative of 2 years of denture cleansing [(11)]**.** The machine was set to provide 250g vertical load over each specimen and the temperature of the denture cleaning material was kept at (23±3)°C. During the stroke the brush covered the entire length of the specimen, care being taken to ensure that no brush ran off the end of any specimen. After the wear test, the specimen was removed from the machine and subjected to the same cleaning and drying as mentioned above .The specimen weighted one minute after removal from the water to accuracy of 0.1mg (mass m_2).

Figure 3: Gas helium pycnometer machine

Figure 4: Brushing device

2. water sorption and solubility

The specimens were dried in desiccators containing freshly dried silica, the desiccators was stored in an incubator. The specimens were

weighed every 24hr at the same time by analytical balance of accuracy 0.0001 g. This cycle of desiccation before weighing, was continued until a constant mass (m1) (conditioned mass) was obtained which mean the weight loss from each disc was not more than 0.2 mg in 24 hours.

The specimens immersed in distilled water for 7 day, after this period of time; each disc was removed from the water with tweezers, then weighed, this value represent (m2). After this weighing, recondition the specimens to constant weight, by returning back to the desiccators and each of them were weighed every 24 hrs until a constant weight as changes was not more than 0.2 mg in 24 hours. The reconditioned mass was recorded and represents (m3).

Calculation for the volume (v) of the specimen from diameter and the mean of five thickness measurements, one taken at the center and four at equally spaced locations around the circumference. The measurements were made using vernier.

The value for the water sorption and solubility, calculated for each disc, expressed in microgram / cubic millimeter, from equation.

Sorption Wsp ((µg)/(mm^3))=(m2-m3)/V (ISO No.1567:2005).

Solubility Wsl ((µg)/(mm^3))=(m1-m3)/V (ISO No.1567:2005).

3.Porosity test:

The specimens were immersed in a solution of permanent black ink for 30 minutes, washed for 10 seconds & dried with absorbent paper. A surface area of 1cm^2 was limited in the center of each specimen & observed under 40X in a light microscope. The numbers of pores per area was determined for each group**.**

4.Tensile strength test:

The test was measured using Tinins Olsen testing machine for measuring tensile strength at a cross head speed of 5mm / min and with a 50 mm grip – to – grip distance and the force at the failure was recorded in Newton (N) and the tensile strength values were calculated from the following equation:

$$Tensile\ strength = \frac{F}{A}\ (ASTM, 1986)$$

F= force at failure (Newton).

A: Minimum cross sectional area (mm^2)

5.Fatigue strength test:

The Fatigue testing used was by an alternating-bending fatigue testing machine with the specification of (fatigue testing machine HSM20, 1400 rpm,Normal power 0.4 Kw), and performed at room temperature. The elementary bending stress can be estimated using the following equation:

D =M L^2/3EI

Where:

D: deflection (mm).

E: modulus of elasticity

L: length of the specimen (mm).

$$s = \frac{M \ . y}{I}$$

Where:

M: moment of inertia (N.mm).

Y: position of neutral axis (mm).

I : moment of inertia (mm^4).

Microscopic test:

The fracture surface of the fatigue strength test specimens selected randomly, one from each group of fatigue test, examined and photographed with scanning electron microscope (SEM).The specimens were sputter-coated with uniform 2µm layer of gold in a vacuum evaporator for 2min at 25Ma to enhance image resolution. Fracture surface was examined in the back scattered electron mode with an operating voltage of 2KV.

RESULTS

Mean values, standard deviation; standard error, maximums and minimums of the tests result are presented in Table 2-9.

Table 2: Descriptive data of volume loss in (mm^3) after brushing with water

No.	Control	2%	3%	5%
Mean	11.71	11.30	10.89	10.35
SD	0.997	0.976	0.921	0.746
SE	0.315	0.308	0.291	0.236
Min	10.50	9.52	9.81	9.10
Max	13.01	12.93	12.90	11.51

Table 3: Descriptive data of volume loss in (mm^3) after brushing with denti-pur gel

No.	Control	2%	3%	5%
Mean	13.22	12.29	11.74	11.44
SD	1.150	1.180	1.198	1.125
SE	0.363	0.373	0.379	0.355
Min	11.63	10.31	10.07	9.78
Max	15.29	13.98	13.81	13.59

Table 4: Descriptive data of volume loss in (mm^3) after brushing with colgate

No.	Control	2%	3%	5%
Mean	37.07	34.20	32.73	30.48
SD	1.881	1.260	1.010	1.310
SE	0.594	0.398	0.319	0.414
Min	34.56	32.20	30.90	29.15
Max	39.56	36.37	34.01	33.30

Table 5: Descriptive data of water sorption

No.	Control	2%	3%	5%
Mean	24.411	23.125	21.644	20.351
SD	0.901	0.901	0.629	0.713
SE	0.285	0.284	0.199	0.225
Min	22.98	21.57	20.93	19.56
Max	25.79	24.56	22.87	21.57

Table 6: Descriptive data of water solubility

No.	Control	2%	3%	5%
Mean	1.587	1.463	1.433	1.328
SD	0.081	0.107	0.079	0.085
SE	0.025	0.034	0.025	0.027
Min	1.42	1.32	1.32	1.22
Max	1.71	1.62	1.56	1.49

Table 7: Descriptive data of porosity test

No.	Control	2%	3%	5%
Mean	10.9	10.8	10.5	9.2
SD	1.523	1.032	0.977	1.475
SE	0.481	0.326	0.307	0.466
Min	8	9	9	7
Max	13	12	12	12

Table 8: Descriptive data of tensile strength test

No.	Control	2%	3%	5%
Mean	43.261	44.538	46.765	45.877
SD	1.759	1.698	1.953	1.369
SE	0.556	0.537	0.618	0.441
Min	39.86	41.24	43.53	42.63
Max	45.06	46.52	50.11	46.93

Table 9: Descriptive data of fatigue strength (load cycle) test

No.	Control	2%	3%	5%
Mean	621687	649603	909215	811509
SD	2588.02	2877.82	1101.61	2297.4
SE	818.82	910.66	348.07	7266.1
Min	580900	610500	890950	782920
Max	656930	703400	925400	840230

The results of LSD test, among groups were presented in tables (10-16).

Table 10: LSD test between groups of abrasive wear test

	P-value	Sig
Controls&2%	0.326	NS
Controls&3%	0.074	NS
Control&5%	0.002	HS
2%&3%	0.404	NS
2%&5%	0.026	S
3%&5%	0.149	NS

Table 11: Descriptive data of volume loss after brushing with dent-pur gel

	P-value	Sig
Controls&2%	0.113	NS
Controls&3%	0.005	HS
Control&5%	0.000	HS
2%&3%	0.175	NS
2%&5%	0.004	HS
3%&5%	0.106	NS

Table 12: LSD test between groups of abrasive wear after brushing with colgate

	P-value	Sig
Controls&2%	0.000	HS
Controls&3%	0.000	HS
Control&5%	0.000	HS
2%&3%	0.024	S
2%&5%	0.000	HS
3%&5%	0.001	HS

Table 13: LSD test between groups of water sorption test

	P-value	Sig
Controls&2%	0.001	HS
Controls&3%	0.000	HS
Control&5%	0.000	HS
2%&3%	0.000	HS
2%&5%	0.000	HS
3%&5%	0.001	HS

Table 14: LSD between groups of the water solubility test

	P-value	Sig
Controls&2%	0.004	HS
Controls&3%	0.002	HS
Control&5%	0.000	HS
2%&3%	0.828	NS
2%&5%	0.001	HS
3%&5%	0.002	HS

Table 15: LSD test between groups of porosity test

	P-value	Sig
Controls&2%	0.343	NS
Controls&3%	0.042	S
Control&5%	0.006	S
2%&3%	0.602	NS
2%&5%	0.008	HS
3%&5%	0.029	S

Table 16: LSD test between groups of tensile strength test

	P-value	Sig
Controls&2%	0.048	S
Controls&3%	0.000	HS
Control&5%	0.005	HS
2%&3%	0.006	HS
2%&5%	0.41	NS
3%&5%	0.045	S

SEM examination of specimens reinforced by 2%wt, 3%wt a nano zirconia shown well dispersion and homogeneous distribution of nano-ZrO_2 (individual single particles of nano ZrO_2), resulted in improve mechanical properties respectively (Figure 6,7). Although there was proper dispersion but there was poor distribution (heterogeneous distribution) in 5wt% ZrO_2 nano fillers within the matrix (Figure 10).

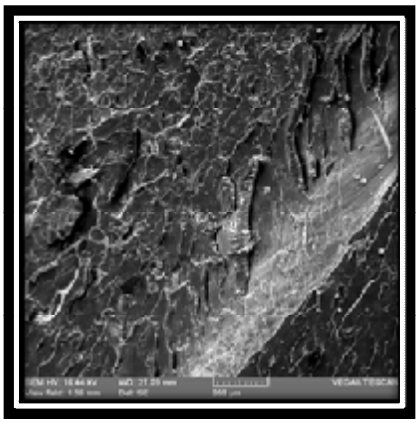

Figure 6: Surface fracture of the fatigue test specimen reinforced with 2wt% nano-fillers

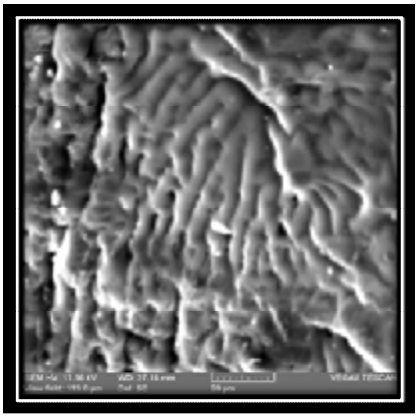

Figure 7: Surface fracture of the fatigue test specimen reinforced with 3wt% nano-fillers

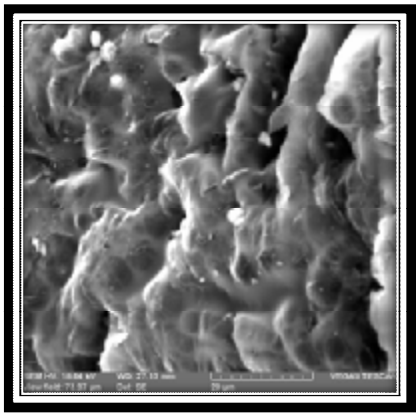

Figure 8: Surface fracture of the fatigue test specimen reinforced with 5wt% nano-fillers

DISCUSSION

Abrasive wear resistance

From the results of abrasive wear test by mechanical brushing with different denture cleaning materials (water, denti-pur gel and colgate). They show that decreased in volume loss is proportional with the increasing of modified nano-ZrO_2 concentration which mean increased in abrasive wear resistance , statistically this increase was not significant at 2wt% nano ZrO_2 but high significance presented in 3wt% and 5wt% nano-ZrO_2 concentration. The reduction in abrasive wear can be explained mainly by the physical properties of nano filler particles (ZrO_2), namely hardness and density (Vickers hardness of approximately 1200kg/mm^2 and a density of 5.68 g/cm^3) these apparent high physical properties as compared with neat polymer matrix will allowed them to retain their surface integrity and maintain their highly smooth surface during the entire wear test**,** thus the wear mechanism change from sever abrasion to mild sliding wear This explanation is in agreement with Fredrick et al [(12)] who found that various kind of micrometer sized particles, e.g. TiO_2, ZrO_2, SiC, and copper compounds were incorporated into different polymer matrices, the improvements of the wear resistance were due to mechanical properties (enhanced hardness).

Water sorption

These results mainly related to polar nature of resin molecules, PMMA which lead to absorb water, while reaction of this resin with the TMSPM-modified nano fillers which certainly lead to replace hydrophilic resin, result in a decrease in water uptake due to decrease this polarity since it utilized most of active sites in the molecules so diffusivity of water molecules through this material is greatly lower than that through matrix

This study is in agreement with Panyayang et al [(13)] who evaluated the addition of mixtures of

modified titania (Titanium dioxide TiO_2) powder and zirconium dioxide ZrO_2 powder in to PMMA powder in different concentration in which there is decreased in water sorption

Water solubility test

this decrease could be attributed to the fact that ZrO_2nanofillers is insoluble in water so that the addition of ZrO_2 to the mass of the specimens which their presence lead to reduction in the solubility of acrylic resin.These results were in agreement with the findings of study by Noori [14] which showed reduction in solubility when added AL_2O_3 filler to acrylic resin in different percentage.

Porosity test

Increased the ratio of ZrO_2nanofiller will lead to increase in density values that are higher than the density values of the control. The presence of inorganic fillers incorporated within the material lead to increase the density and make it bulkier and heavier. There is adverse relationship between density and porosity which was approved by Keller and Lautenschlag [15] that correlated between density and porosity and found that when density increased, porosity was decreased.

This study is in agreement with Laura et al [16] who added TiO_2 and Fe_2O_3 Nano particles, for simultaneously coloring and/or improving the antimicrobial properties of PMMA resins, the result showed a strong reduction of porosity with the introduction of nano sized metal – oxide pigments.

Tensile strength

Well-dispersion nanofillers can improve the modulus and strength and maintain or even improve ductility because their small size does not create large stress concentration. In addition the large interfacial area of nano composites provides an opportunity for altering the matrix properties in unique way [17]. The result of this study agreed with Hong et al[18] when methyacryloxy propyl trimethoxysilane (MPS)-modified colloidal silica nanoparticles where added to PMMA caused increase in tensile strength and tensile modulus.

Fatigue strength test

The increase in fatigue strength due to the interfacial shear strength between nano filler and matrix is high due to formation of cross links or supra molecular bonding which cover or shield the nano fillers which in turn prevent propagation of crack. Also the crack propagation can be changed by good bonding between nanofiller and resin matrix. Lingyu et al in [19] concluded The van de Waals forces in CNT/Polymer or polymer chain in PVA/MMT interact strongly with two or three fillers, which increase the interfacial strength and the energy required to form cracks.

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