Evaluation the effect of modified nano-fillers addition on some properties of heat cured acrylic denture base material

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ABSTRACT

Background: The poly(methylmethacrylate) (PMMA) shown to be lacking two properties which are strength and radio-opacity. The aim of this study was to evaluate the effect of addition of modified nano-zirconium oxide (ZrO_2)on some properties of heat cured acrylic denture base material.

Material and method: (ZrO_2) nanofillers were incorporated into (PMMA) denture base by free radical bulk polymerization. (PMMA) nanoparticales were coated with a layer of trimethoxysilypropylmethacrylate (TMSPM) before dispersed and sonicated in monomer (MMA) in different percentages 2%, 3%, 5% and 7% by weight. Then mixed with acrylic powder as general conventional method. Two hundred fifty five (255) specimens were prepared for this study they were divided into (6) groups according to the test used. The tests were impact strength, indentation hardness, surface roughness, transverse strength, radio-opacity and microscope test, for each test five subgroups (one control and four for nano-ZrO2). The size and shape distribution of nano-ZrO2 particles were estimated using scanning electron microscope (SEM) and atomic force microscope (AFM).

Result: Highly significant increase in impact and transverse strength occur in acrylic reinforced with 5wt%, but non significant increase was observed at 7wt% when compared to control group. Non-significant increases in indentation hardness and surface roughness appear with addition of modified nano-ZrO_2 at different percentages. For radio-opacity a highly significant increase had occurred with the addition of modified nano-ZrO2.

Conclusion: The maximum increase in impact strength, transverse strength and radio-opacity was observed in denture base nano composite containing 5wt% of nano-ZrO2.

Key words: poly (methylmethacrylate), nano composite. (J Bagh Coll Dentistry 2011;23(3): 23-29).

INTRODUCTION

Poly (methylmethacrylate) (PMMA) is the most commonly used material in construction of denture base since 1930 . This material is not ideal in every respect and it is the combination of various rather than one single desirable of properties that accounts for its popularity and usage.Despite its popularity which satisfy aesthetic, simple processing and easy repair, the main problems associated with PMMA as denture base material are poor strength particularly under fatigue failure inside the mouth, impact failure outside the mouth and lack of radio-opacity [1]. The PMMA used routinely today is radiolucent and cannot be imaged using standard radiographic techniques, so in cases of accidental ingestion, aspiration and traumatic impaction of dental appliance, their detection very difficult and require invasive procedures as advanced imaging techniques. Delay in localizing or removing the foreign body may be life threatening [2]. Recently, much attention have been directed toward the incorporation of in organic nanoparticles into PMMA to improve its properties.

The properties of polymer nanocomposites depend on the type of incorporated nanoparticles, their size and shape, as well as the concentration and interaction with the polymer matrix [3]. Nanoparticles were undergone surface treatment with saline coupling agent and embedded into PMMA [4]. Many attempts have been carried out to incorporate inorganic nanoparticles into PMMA. Alumina nanoparticles were coated with acryloxypropyldimethyl methoxysilane to get PMMA/alumina nanocomposite with increased mechanical properties over pure PMMA[5]. Calcium carbonate nanoparticles modified with stearic acid was incorporated into PMMA to improve the abrasion resistance of PMMA[6]**.** Barium sulphate nanoparticles was added to PMMA to enhance radiopacity [7] .This study was conducted to use inorganic nanofillers that are added to heat cure PMMA and test the effect of this addition on radio-opacity and some mechanical properties of heat cured acrylic denture base material

MATERIALS AND METHOD

Surface modification of fillers (ZrO_2, $BaTiO_3$)

The introduction of reactive groups onto fillers surface was achieved by reaction of 3-trimethoxysilyl propylmethacrylate TMSPM (meth acryloxy propyl trimethoxy saline) with zirconium oxide and barium titanate nano fillers.

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Table 1: Some of the materials that were used.

	Material	Trade	Manufacturer
1.	**Zirconium (IV) oxide ZrO_2 nanofiller**	544760	Sigma-Aldrich Germany
2.	**Barium titanate $BaTiO_3$ nano filler**	467634	Sigma-Aldrich Germany
3.	**Trimethoxysilylpropyl methacrylate 98%**	Silane .440159	Sigma-Aldrich Germany
4.	**Toluene**	solvents	GCC , U.K.
5.	**Heat-curing resin for denture .**	Superacryl plus	Spofa Dental Czechoslovakia

Typical process was as follows

30g of nano filler and 200ml pure toluene were placed into a flask then sonicated at ambient temperature for 20min (Figure 1.). After that, the nano filler and toluene were placed into a flask equipped with a magnetic stirrer(LABINCO, BV Model L-81) at room temperature. Then 1.5g of silane (5% wt to nano filler) was added dropwisely by sterile syringe under rapid stirrer. The flask was covered by parafilm and the slurry was left standing in flask for 2 days. The solvent (toluene) was removed by rotary evaporator under vacuum at 60°C at rotary 150 rpm for 30 min (RE 510, Yamato, Japan).

Figure 1: Probe sonication apparatus

After that the modified nano filler was dried in vaccum oven at 60°C for 20 hours (Gallen bamp, England). Then nano filler stored at room temperature before use[4,8] . The infrared (IR) spectra were performed (Shimadzu, FTIR-8400 S, 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[4] .

Pilot study

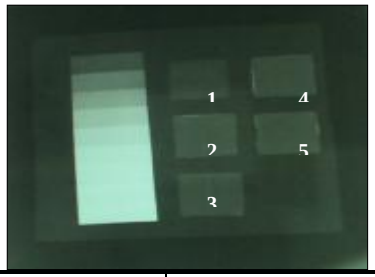
Selection of proper percentage of zirconia nanofiller (ZrO2)

Percentages of 1%, 2%, 3%, 4%, 5% and 7% by weight were used, percentages above 7% were not used due to change in the colour of acrylic. Transverse strength and impact strength tests were used.Form the result obtained 2%, 3%, 5% and 7% were selected as a percentages of modified zirconia nanofiller that added to the polymer by weight.

Selection of proper percentage of Barium titanate BaTiO3 nanofillers

Percentages of 1%, 2%, 3%, 4%, and 5% were added to acrylic by weight percentage above 5% were not used due to change in the colour of acrylic, the result showed a marked decrease in the transverse and impact strength at the percentage above 3%. Also the result showed that percentage below 5% did not give adequate radio-opacity (Figure 2.).Therefore, this material was neglected in this study.

Fracture surface of specimens were tested by scanning electron microscope (SEM) and atomic force microscope (AFM) show random distribution of nano- $BaTiO_3$ particles within the nano cluster (aggregation), non- uniformity of the particles, this lead to decrease in the mechanical properties.(Figure 3.



ZrO2 percentage	Amount of ZrO2	Amount of polymer	Amount of monomer
0%	0	12g	6ml
2%	0.240g	11.760g	6ml
3%	0.360g	11.640g	6ml
5%	0.600g	11.400g	6ml
7%	0.840g	11.160g	6ml

Figure 2: X-ray examination of specimens reinforced with $BaTiO_3$ nano fillers.

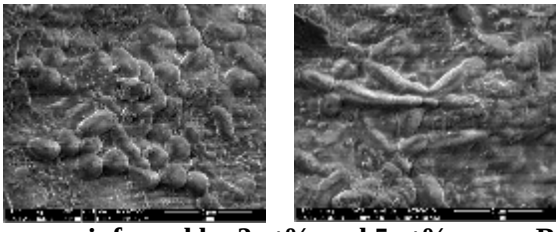


Figure 3A: Specimens reinforced by 3wt% and 5wt% nano- $BaTiO_3$ fillers (SEM).

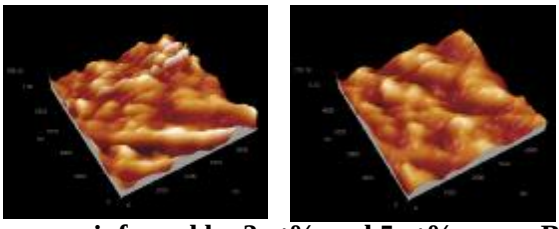


Figure 3B: Specimens reinforced by 3wt% and 5wt% nano- $BaTiO_3$ fillers (AFM)

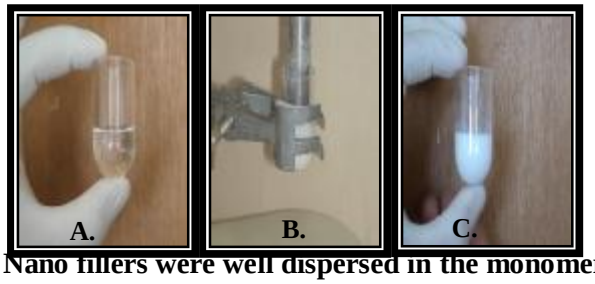


Figure 4.A, B, C: Nano fillers were well dispersed in the monomer by ultrasonication

General preparation of test specimens

Three different metal patterns were constructed by cutting stainless steel plate in desired shape and dimension by turning machine according to the required test. For impact strength test, a bar shaped specimen (80mm x 10mm X 4mm) length, width, thickness respectively [9] .For transverse strength test, hardness test, and surface roughness test: a bar shaped specimen (65mm X 10mm X 2.5mm) length, width, thickness respectively[10] .For radioopacity test: a square shaped specimen (30mmX30mmX3mm) length, width, thickness. [11]

Mould preparation

The conventional flasking technique for complete denture was followed.

Proportioning and mixing of the acrylic

Table 2: percentages and amounts of polymer, monomer and zirconium oxide nanofiller powder .

Addition of fillers

Addition of modified Zirconium oxide nanofiller powder (ZrO_2) was done by weight in four groups, includes 2%, 3%, 5% and 7% 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 for 3 minutes to break them into individual nano crystals[12] as shown in the (Figure 4.).

The suspension of the monomer with ZrO2 nano filler was immedatly mixed with acrylic powder to reduce the possibility of particle aggregation and phase separation. The proportion for mixing for acrylic resin was (2.5g:1g) P/L. All materials were mixed and manipulated according to manufacture's instructions. The mixing was carried out in a clean and dry mixing vessel and mixed by a clean wax knife for 30 second. The mixture was then covered and left to stand until a dough stage was reached.

Mechanical and physical tests utilized to examine properties

Evaluation of the mechanical and physical properties of the prepared nano composite denture base was compared with convensional denture base (heat cure acrylic resin).These tests are**:**

1-Impact strength test

Impact strength test was conducted following the procedure given by the ISO 179 with charpy type impact testing instrument (Impact tester N. 43-1, INC. USA.). The specimen was supported horizontally at it's ends ad struck by a free swinging pendulum which released from a fixed height in the middle. A pendulum of 2 joules testing capacity was used. The charpy impact strength of unnotched specimen was calculated in KJ/m^2.

2-Microscope test

The fractured surface of the impact test specimens were examined and photographed with 1-scanning

electron microscope (SEM). 2-Atomic force microscope(AFM). For SEM, five specimens were examined,one representing the control ,four representing 2wt%,3wt%, 5wt %,and 7wt% ZrO2 nanocomposite , they were sputter-coated with uniform 2µm layer of gold in a vacuum evaporator for 2 min at 25 mA to enhance image resolution. Fracture surface was examined in the back scattered electron mode with an operating voltage of 2KV. For AFM ,two specimens were examined, one representing 5wt%,and the other representing 7wt% of ZrO2 nanocomposite were examined.The thickness of the specimen should be 2 mm to be put under the probe of the scanning.

3-Transverse strength

The test was achieved using instron testing machine (instron corporation, 1122, canton mass), each specimen was positioned on bending fixture, consisting of 2parallel supports (50)mm apart, the full scale load was 50kg, and the load was applied with cross head speed of 1mm/min by rod placed centrally between the supports making deflection until fracture occurred .

4-Surface hardness test

Surface hardness was determined using durometer hardness tester from type shore D, (hardness tester-th 210, time group Inc. Italy) which is suitable for acrylic resin material. The instruments consist of blunt-pointed indenter 0.8mm in diameter that tapers to a cylinder 1.6mm. The indenter is attached to a digital scale that is graduated from 0 to 100 units; measurements were taken directly from the digital scale reading. Five measurements were done on different areas of each specimen (the same selected area of each specimen), and an average of five reading was calculated.

5- Surface roughness test

The profilometer device (Surface roughness tester SRT-6210, England) was used to study the effect of ZrO2 nano filler reinforcement on micro geometry of the test surface. This device is supplied with surface analyzer (sharp stylus) made from diamond. Maximum distance that can be move is 11mm .Two measurements were done on different areas of each specimen (the same selected area of each specimen), and an average of two readings was calculated.

6-Radio-opacity test

Aluminum step wedge was constructed by cutting pure Aluminum plate into desired shape and dimension which consist of 10 stepper beginning with 1mm thickness of aluminum with 1mm increment in each step reaching to 10mm at the 10^{th} steps [11] .The specimens of different concentration are arranged over a wax plate of 10mm thickness. The addition of wax to simulate the absorbing and scattering media of soft tissue. An aluminum step wedge was fixed beside the specimens for standardization of the density of the film.The wax plates, specimens and Aluminum step wedge were kept over the exposure side of a 35X43cm cassette type KODAK GREEN 400.A chest x-ray meachine (Siemens polydoros Lx and Sx 65/80 with videomed DI, Germany), 1 meter between the source of x-ray and specimens, machine was operated at 53 kv and 5m As, exposure time is 0.35 second, as it is used for normal chest radiography .The processing was done according to manufacture's instructions by using KODAK RPX-OMAT processor. A light transmission densitometer (Densonorm21i, pehamed,France) was used to measure the difference in the image density of all specimens which contain different concentration ZrO2 nano filler in comparison with standard acrylic resin and aluminum step wedge. (Figure 5). Five measures in different areas of each specimen was done, and the mean of them was calculate.

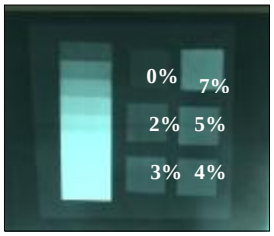


Figure.5: x-ray examination of specimens reinforced with ZrO_2 nanofiller

RESULTS

The results of infra red (IR) Spectra were obtained by analyzing the characteristic vibrations of functional groups in TMSPM, nano-ZrO2 , modified nano-ZrO2 ,PMMA and PMMA/ZrO2 nano composite help to clarify the interaction of nano-ZrO2 with TMSPM in one side, and between TMSPM with PMMA on other

side.Trimethoxy silypropylmethacrylate(TMSPM) can couple the ZrO_2 particle to the resin matrix (PMMA).The result of IR spectra,(Figure 6.) indicate of chemical bonded TMSPM on the ZrO2 surface[change the shape of adsorption peaks of (C=O, C-O)].The result of IR spectra, (Figure 7.) indicate of chemical bonded TMSPM with PMMA [change the shape of adsorption peak of (C=C)]

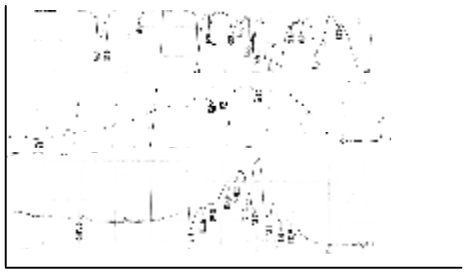


Figure 6: IR spectrum of TMSPM, ZrO_2, modified nano zirconia fillers.

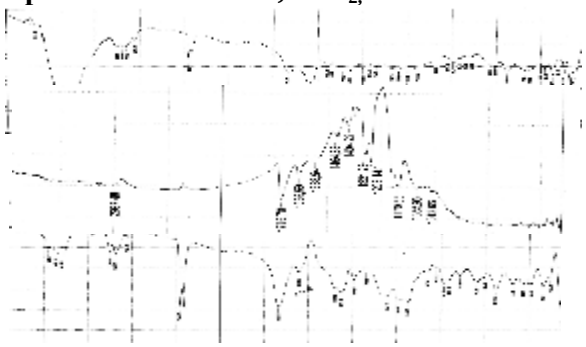


Figure 7: IR spectra of PMMA, modified nano-ZrO2 and PMMA/ZrO2 nanocomposite.

Mean values, standard deviation; standard error, maximums and minimums of the tests result are presented in Table 1-5.

Table 1: Descriptive data of impact strength.

	Control	2%	3%	5%	7%
Mean	8,9	9,25	9,3	9,7	8.775
SD	0,210	0,513	0,349	0,453	0.1419
SE	0,066	0,16	0,110	0,143	0.0449
Min	8,5	8,75	8,75	9	8.5
Max	9,25	10,25	9,75	10,25	9

Table2:Descriptive data of transverse strength test.

Table 3: Descriptive data of surface roughness

	Control	2%	3%	5%	7%
Mean	116	120	124	132	115
SD	2,429	4,383	7,598	6,97	1.78
SE	0,768	1,387	2,404	2,208	0.566
Min	112,8	111,6	115,2	117,6	112.8
Max	120	128	141	142	117
	Control	**2%**	**3%**	**5%**	**7%**
Mean	2,337	2,33	2,339	2,342	2,345
SD	0,235	0,268	0,256	0,190	0,079
SE	0,074	0,084	0,081	0,060	0,025
Min	1,84	1,74	1,96	2,04	2,24
Max	2,68	2,62	2,81	2,64	2,49

Table 4: Descriptive data of hardness test.

	Control	2%	3%	5%	7%
Mean	84,62	85,01	85,22	85,34	85,71
SD	0,875	1,249	0,785	1,113	0,872
SE	0,277	0,395	0,248	0,352	0,276
Min	82,8	82,9	84,1	83,1	84,4
Max	85,5	86,4	86,4	87,3	87,1

Table 5: Descriptive data of radio-density test.

	Control	2%	3%	5%	7%
Mean	1,471	1,311	1,26	1,14	0,972
SD	0,008	0,012	0,011	0,011	0,008
SE	0,002	0,004	0,003	0,003	0,002
Min	1,46	1,29	1,24	1,13	0,96
Max	1,48	1,33	1,27	1,16	0,98

SEM and AFM examination of specimens reinforced by 2wt%, 3wt% and 5wt% nano zirconia showed well dispersion of nano-ZrO_2.While examination of specimen reinforced by 7wt% nano zirconia showed aggregation of nano-ZrO2. (Figure 8).

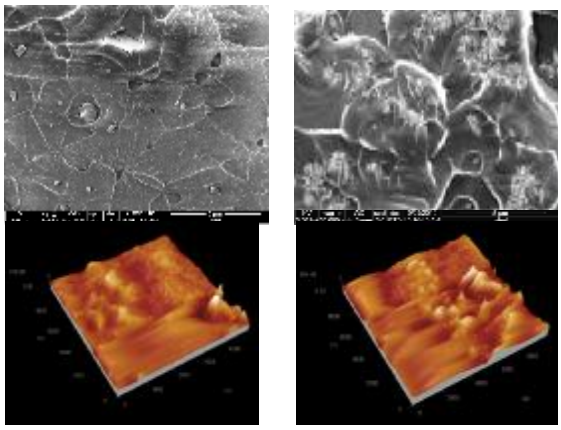


Figure 8: Specimens reinforced by 5wt% and 7% nanoZrO2 filler.(SEM)

DISCUSSION

The addition of modified nano-ZrO_2 to improve mechanical properties and to achieve maximum radio-opacity with minimum effect on mechanical properties. Zirconia (ZrO_2) was used because it is excellent biocompatible material also because of being white is less likely to alter esthetic. Silanization of the nano-filler particles yields a better dispersion, eliminate aggregation and improve its compatibility with organic polymer. the addition of modified nano-ZrO_2 powder increased the value of the impact strength and transverse strength compared to control group, 5wt% group has the highest impact strength and transverse strength, but increasing the percentage of modified nano-ZrO_2 to 7wt% lowered the impact strength and transverse strength due to agglomeration nano-ZrO_2 . The increase in impact strength at 5% due to the interfacial shear strength between nanofiller and matrix is high due to formation of cross-links or supra molecular bonding which cover or shield the nanofillers which in turn prevent propagation of crack. Also the crack propagation can be changed by good bonding between nanofiller and resin matrix [13] ,and the increase in transverse strength that occur with addition of 2-5wt% ZrO_2 nanoparticles due to good distribution of the very fine size of nanoparticles enable them to enter between linear macromoleculars chains of the polymer, segmental motions of the macromolecular chains are restrict lead to improve transverse strength[14] . In this study, shore (D) hardness tester was used which is suitable for measuring the hardness of acrylic resin .Shore durometer type (D) hardness tester eliminate problem with elastic recovery. It was found that hardness value increases, but statistically was not-significant. The surface roughness of acrylic denture base was not significantly change when different percentages of modified nano-ZrO2 fillers were added, this result may be due to that the nano-ZrO_2 particles have very small size and well dispersion, also surface roughness test is concerned with outer surface and not with inner surface of composite so when small percentage of nano-ZrO_2 particles were added to acrylic resin only few particles will be involved with the surface of the specimen. Many studies have been conducted on radio-opacity of denture base resins, decrease in radiographic densities mean increase in radio-opacity. Therefore, the transmission densitometer show reduction in radiographic density with increase in amount of added modified nano-ZrO_2 powder, while the control group shows the highest mean of radiographic density (low radio-opacity), the increase in radio-opacity is statistically highly significance, there was an increase in the relative radio opacity with the increasing of modified nano-ZrO_2 concentration. This is oboviously due to the presence of radio-opaque modified nano-ZrO_2 powder in the polymer matrix which absorbs more radiation than polymer matrix and appears more radio-opaque. The radio opacity that occurs due to the present of modified nano-ZrO_2 powder may be related to the high atomic number of Zr compared to the chemical constituent of acrylic which has low atomic number. The absorption of X-ray by an element is dependent chiefly on the cube of its atomic number.

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