A Study the Effect of Addition of Silanized Zirconium Oxide Nanoparticles on Some Properties of High-Impact Heat-Cured Acrylic Resin

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ABSTRACT

Background: The incorporation of rubber has not been entirely successful because it can have detrimental effects on the transverse Strength and hence the rigidity of the denture base.

Materials and methods: Zirconium oxide nanoparticales were coated with a layer of trimethoxysilylpropylmethacrylate (TMSPM) before sonication in monomer (MMA) with the percentages 3% by weight then mixed with powder using conventional procedure.(100) samples were prepared and divided into five groups according to the test performed ,Each group consisted of 20 specimens and these were subdivided into 2 groupsGroup (A): control group (10 specimens of high impact acrylic resin without zirconium oxide) and Group (B):zirconium oxide group(10 specimens of high impact acrylic resin with 3% wt zirconium oxide).The tests conducted were impact strength, transverse strength, indentation hardness(shore D), surface roughness, water sorption and solubility. The results were statistically analyzed using Dunntt t-test.

Results: Highly significant increase in impact strength and transverse strength occurred with the incorporation of 3% wt Zirconium oxide nanofiller. A highly significant increase in surface hardness, but the water sorption and solubility were significantly decreased with the addition of silanized (ZrO_2) Nano particles compared with the control group.no significant statistical difference in surface roughness.

Conclusions: The addition of silanized ZrO_2 Nano particles to high impact heat cure acrylic resin material improves the impact strength, transverse strength and surface hardness of high-impact heat-cure acrylic resin at the same time this addition decreases water sorption and solubility. On the other hand there was no change in surface roughness with the addition of 3% wt of silanized ZrO_2Nano particles.

Key words: High impact heat cured acrylic resin, Zirconium oxide nanoparticales, nano composite. (J Bagh Coll Dentistry 2016; 28(2):19-25).

INTRODUCTION

Poly(methylmethacrylate) (PMMA) is the most commonly used material in construction of denture base since 1930 (1).However, inadequate mechanical properties make them non-ideal (2). This occurs when the denture is accidentally dropped on a hard surface or fractures when subjected to high mastication forces (3-4).

In order to overcome these problems, several attempts were made to modify and improve the impact strength, flexural strength and hardness of the PMMA. One of these attempts is a Modification of chemical structure of acrylic resin by copolymerization with rubber. The incorporation of rubber phase in in the form of butadiene-styrene co-polymer has improved the impact strength but result in increased cost and lowered transverse strength (5-7).

Recently, much attention has been directed toward the incorporation of inorganic nanoparticles into PMMA to improve its properties.The properties of polymer nanocomposites depend on the type of incorporating nanoparticles,their size and shape,as well as the concentration and interaction with the polymer matrix (8).

Nano particles might be surface treated with saline coupling agent and embedded into PMMA to improve the bond between the matrix and filler (9).

This study was conducted to use zirconium oxide nanoparticles that were treated with3-Trimethoxypropylsilylmethacrylate (TMPSM) and were added to high impact heat cured PMMA to get high impact PMMA/Zirconium oxide nanocomposite and study the effects of this addition on some mechanical and physical properties over pure high impact heat cured PMMA.

MATERIALS AND METHODS

Surface modification of Zro_2nano fillers:

Modification of nanofillers was done by the reaction of trimethoxysilylprpoyl methacrylate TMSPM with zirconium oxide nanopowder.

Typical process as followed:

1)30g of nano filler and 200ml pure toluene were placed into a flask then sonicated at ambient temperature for 20min (figure.1).

2) The nano filler and toluene were placed into a flask equipped with a magnetic stirrer at room temperature.

3) 1.5g of silane (5% wt to nano filler) was added dropwisely by sterile syringe under rapid stirrer.

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4)The flask was covered by parafilm and the slurry was left standing in flask for 2 days.

5)The solvent (toluene) was removed by rotary evaporator under vacuum at 60°C at rotary 150 rpm for 30 min. (Figure2).

6) The modified nano filler was dried in vaccum oven at 60°C for 20 hours. Then nano filler stored at room temperature before use (9,10) .

Fig.1: Aprobe sonication apparatus.

Fig.2: Rotary evaporator

Selection of proper percentage of zirconium oxide nanofiller (ZrO_2):

According to the pilot study, addition of 3% by weight of silanized zirconium oxide nanofillers had the greatest values of flexural strength, impact strength and hardness, therefore the decision was made to choose 3% of silanized Nano Zro_2 filler, as a percentage of modified zirconia nanofiller, that added to the polymer.

Addition of silanized zirconium oxide nanofillers:

To prepare the dough, the measured ingredients were added to the monomer, the fillers were well dispersed in the monomer by ultra sonication, by using a probe sonication apparatus (120 W, 60 KHz) for 3 minutes to break them into individual nano crystals (Mohammad et al, 2009).The monomer with nano powder was immediately mixed with acrylic powder to reduce the possibility of particle aggregation and phase separation.

Pattern Preparation

Three different plastic patterns were constructed as shown in figure 3 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) length, width, thickness respectively, While water sorption and solubility tests: disc with dimensions of 50 mm in diameter and 0.5 mm in thickness(11). Impact strength test: bar shaped specimen with dimensions of (80 mm x10 mm x 4 mm) length, width and thickness respectively (12).

Fig. 3: Plastic patterns

Mould preparation:

The conventional flasking technique for complete denture was followed.

Proportioning and mixing of acrylic:

Amounts of polymer, monomer and silanized zirconium oxide nanofillers with percentages used in the study where present in table (1) by using an electronic balance with accuracy of (0.0001g).

Table 1: Mixing ratio of high impact-acrylic resin with ZrO2

ZrO2 percentage %	Amount of ZrO2 (g)	Amount of polymer(g)	Amount of monomer(ml)
0%	0 g	21g	10ml
3%	0.63 g	20.37 g	10ml

Mechanical and physical tests used to examine properties:

1. **Impact strength:**

Impact strength test was conducted following the procedure given by the ***ISO 179,*** charpy type impact testing instrument. The specimen was supported horizontally at it's ends and struck by a free swinging pendulum that released from a fixed height in the middle. A pendulum of 2 joules testing capacity was used. The charpy impact strength of un notched specimen was calculated in KJ/m^2, according to the following:

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

2. **Transverse strength:**

Test was performed using a universal Instron testing machine, each specimen was positioned on the bending fixture which consists of two parallel supports (50) mm apart, the full scale was 50 Kg ,and the load was applied with a cross head speed of 1mm/min by a rod placed centrally between the supports making deflection until fracture occurs, according to the following:

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

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 11 mm. Three measurements were done at 3 positions across each specimen surface which was divided in to 3 equal thirds and the mean of the 3 readings were recorded, as a roughness measurement.

4. **Surface hardness:**

Test was performed using durometer hardness tester (shore D hardness) according to ***(*****ANSI/ADA specification No.12, 1999*****)***.

The instrument consists of a blunt pointed indenter (0.8 mm in diameter) that present in a cylinder (1.6mm in diameter) .The indenter was attached to a digital scale that is graduated from 0 to 100 unit. The usual method was to press down firmly and quickly on the indenter and to record the maximum reading as the shore D hardness, measurements were taken directly from the digital scale reading. Five readings were recorded on different areas of each specimen by dividing the specimen in to five equal parts and the measure shore D hardness and the average of the five readings was recorded.

5. **Water sorption and solubility:**

The specimens were dried in dissecator containing freshly dried silica gel. Then they were stored in an incubator at a 37°C ±2 °C for 24 hours after that the specimens were removed to room temperature for one hour then weighed with a digital balance with an accuracy of (0.000lg). This cycle was repeated every day at the same time until a constant mass "conditioned mass"(M1) was reached after 5 days which means the weight loss from each disc was not more than 0.2mg in 24 hours **(ADA Specification NO.12, 2000).** The specimens were then immersed in distilled water for 7 days at 37^0C ± 2 ^{0}C , after this period of time, each disc was removed from the water with tweezers and wiped for 30 seconds by clean dry hand towel, left in air for 15 second then weighed ,this value represent M2. In order to obtain the value of solubility, the discs were again reconditioned to a constant mass in the desiccators at 37°C ±2 °C as done in the first time for sorption test and the reconditioned mass was recorded 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:

$Ws= (M2 – M1) / S$

$WSL= (M1- M3)/ S$

RESULTS

FTIR test was done to samples of zirconium oxide nanofiller and trimethoxysilylprpoyl methacrylate (TMSPM)before Silanation to evaluate active groups, as seen in Figure 4 and Figure 5. Also other FTIR was done tozirconium oxide nanofiller after Silanation to evaluate the differences in active groups, as seen in Figure6.

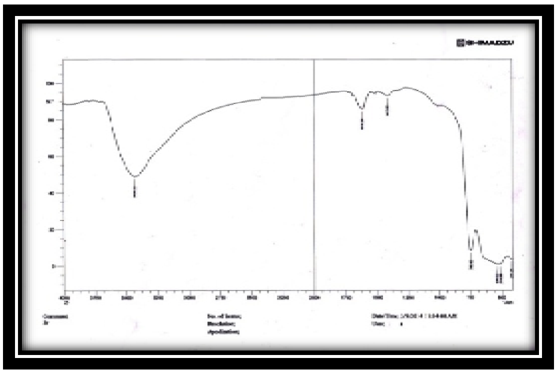

Fig.4: FTIR spectrum of non-silanized zirconium oxide nanoparticles.

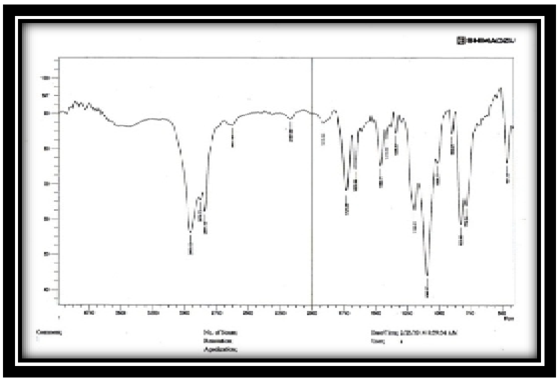

Fig. 5: FTIR spectrum of TMSPM

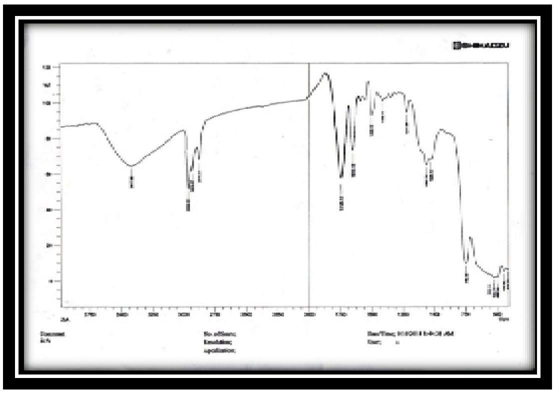

Fig. 6: FTIR spectrum of zirconia nanoparticles after silanization

Impact strength test:

Descriptive data of mean, standard deviation, standard error, minimum and maximum and also the t- test are listed in Table 2

Table 2: Descriptive statistics and groups' difference for the Impact strength (Kj/m^2)

Groups	Descriptive statistics						Groups' difference (d.f.=18)		
	N	Mean	S.D.	S.E.	Min.	Max.	Mean difference	t-test	p-value
Control	10	11.900	0.070	0.022	11.78	11.99	-0.723	-6.541	0.000 (HS)
Study	10	12.623	0.343	0.108	12.07	13.14			

The group B (Study group) exhibited the highest impact strength mean value (12.623Kj/m^2),while group A (Control group) exhibited the lowest one (11.900Kj/m^2).t-test revealed a P-value of 0.000 suggested a highly significant statistical differences (6%) between the two groups

Transverse flexural strength:

Descriptive data of mean, standard deviation, standard error, minimum and maximum and also the t- test are listed in Table 3

Table 3: Descriptive statistics and groups' difference for the Transverse strength (N/mm^2)

Groups	Descriptive statistics						Groups' difference (d.f.=18)		
	N	Mean	S.D.	S.E.	Min.	Max.	Mean difference	t-test	p-value
Control	10	154.680	2.912	0.921	150.100	160	-28.960	-13.767	0.000 (HS)
Study	10	183.640	5.981	1.891	164.500	199.700			

As shown in table (3), Group B had higher mean value (183.640N/mm^2) than group A which was (154.680N/mm^2). T-test showed highly significant with a p-value of 0.000 suggested significant statistical differences (19%)between the two groups.

Hardness test:

Descriptive data of mean, standard deviation, standard error, minimum and maximum and also the t- test are listed in Table 4.

Table 4: Descriptive statistics and groups' difference for the Hardness

Groups	Descriptive statistics						Groups' difference (d.f.=18)		
	N	Mean	S.D.	S.E.	Min.	Max.	Mean difference	t-test	p-value
Control	10	83.717	0.162	0.051	83.360	83.900	-1.603	-7.172	0.000 (HS)
Study	10	85.320	0.688	0.218	84.080	85.900			

As shown in table (4), Group B had higher mean value (85.320) than group A which was (83.717).T-test was highly significant with a P-value (0.000) suggested a highly significant statistical difference (2%) between the two groups.

Surface Roughness test:

Descriptive data of mean, standard deviation, standard error, minimum and maximum and also the t-test are listed in Table5**.**

Table5: Descriptive statistics and groups' difference for the Surface roughness (µm)

Groups	Descriptive statistics						Groups' difference (d.f.=18)		
	N	Mean	S.D.	S.E.	Min.	Max.	Mean difference	t-test	p-value
Control	10	1.463	0.174	0.055	1.260	1.820	-0.071	-0.767	0.453 (NS)
Study	10	1.534	0.235	0.074	1.120	1.880			

As shown in table (5), Group B had higher mean value (**1.534um**) than group A which was (**1.463um**). t-test was non-significant with a P-value (0.453) suggested no significant statistical difference(5%) between the two groups.

Water sorption test:

Descriptive data of mean, standard deviation, standard error, minimum and maximum and also the t-test are listed in Table 6.

Table 6: Descriptive statistics and groups' difference for the Water sorption (mg/cm^2)

Groups	Descriptive statistics						Groups' difference (d.f.=18)		
	N	Mean	S.D.	S.E.	Min.	Max.	Mean difference	t-test	p-value
Control	10	0.468	0.019	0.006	0.433	0.502	0.280	32.155	0.000 (HS)
Study	10	0.188	0.020	0.006	0.156	0.231			

Water sorption seems to be decreased in group B with mean value (**0.188** mg/cm^2) when it was compared with group A which was (**0.468** mg/cm^2).t-test was highly significant with a P-value of (**0.000**) suggested a highly significant statistical differences (60%) between the two groups.

Water solubility test

Descriptive data of mean, standard deviation, standard error, minimum and maximum and also the t-test are listed in Table 7.

Water solubility seems to be decreased in group B with mean value (0.025mg/cm^2) when it was compared with group A which was (0.039 mg/cm^2).T-test was highly significant with a P-value of (0.000) suggested a highly significant statistical difference (36%) between the two groups.

Table 7: Descriptive statistics and groups' difference for the Water solubility (mg/cm^2)

Groups	Descriptive statistics						Groups' difference (d.f.=18)		
	N	Mean	S.D.	S.E.	Min.	Max.	Mean difference	t-test	p-value
Control	10	0.039	0.005	0.002	0.031	0.046	0.014	5.625	0.000 (HS)
Study	10	0.025	0.006	0.002	0.015	0.031			

DISCUSSION

The results of the present study indicate that there was highly significant increased in impact strength when zirconium oxide nano fillers was added to high impact heat cured PMMA.

The increase in impact strength due to that the interfacial shear strength between nanofiller and matrix is high because of formation of cross-links or supra molecular bonding which cover or shield the nanofillers which in turn prevent crack propagation. Also the crack propagation can be changed by good bonding between nanofiller and resin matrix(13).Also may be when the particle size decrease, the total particle/ matrix interfacial surface area available for energy dissipation increase, the critical stress for particle/ matrix de-bonding also increase, this may be a reason for improved impact strength(14) .This study agreed with Alwan (15) who incorporating 3wt% concentration of silanized Nano TiO_2 fillers into conventional heat-cured denture base resin.

The increase in transverse strength that occur with the addition of 3wt% ZrO2 nanoparticles was due to good distribution of the very fine nanoparticles that enable them to enter between linear macromoleculars chains of the polymer and fill spaces between chains, segmental motions of the macromolecules are restricted lead to increase strength and rigidity of the resin, so cause improvement in fracture resistance and lead to improvement transverse strength (16).

Jasim (17) found incorporating silanized alumina nanofillers into conventional heat-cured denture base resin results in significant increase in transverse strength.

The increase in hardness may be attributed to most likely two factors: the accumulation of particles of a hard material (ZrO2) into acrylic matrix(relatively higher filler content) (18)andthe use of silane coupling agents and the new more homogeneous surface between dental resins and the adding ZrO_2 nanoparticles. The more filler added, the greater the improvement.

The surface properties of resin composites are therefore strongly related to the characteristics of their inorganic fillers (19). Similar finding were reported by Nabil (20) when he added zerconia nanoparticles into conventional heat-cured denture base resin.

Surface roughness of high impact heat cured acrylic denture base was not significantly change when 3wt% of addition of silanized nano-ZrO2 fillers was compared with the control. this result may be due to that the nano-ZrO2 particles have very small size and well dispersion, also surface roughness test is concerned with outer surface and not with innersurface of composite so when small percentage of nano-ZrO2 particles were added to acrylic resinonly few particles will be involved with the surface of the specimen (21).The result of this study coincide with the result of AbdulAmeer (22) when titanium and zinc oxide powder added to the acrylic resin. The reduction in water sorption could be due to the fact that zirconia nano particles replace hydrophilic resin, result in a decrease in water uptake since diffusion property of water molecules through this material is greatly lower than that through PMMA matrix(23).

The result of this study was agreed with Mohammed (24) who stated that the increase in percentage of ZrO_2nanofillers decreased water sorption.ZrO_2Nano particles used are insoluble in water and could reduce the overall volume of absorbing polymer(23,25).This decreasing in water solubility could be due to the fact that ZrO_2 is insoluble in water so that the addition of silanized ZrO_2 to the mass of the specimens would act as additives and their presence will lead to reduction in the overall solubility of acrylic resin. However, the results were within the limitation of ADAspecification No. 12, 1999.

The result of this study was in agreement with Gurbuz et al. (26) when milled glass fiber fillers where added to acrylic resin, they found that there was reduction in solubility. Also the study agreed with Mohammed(24) who stated that the increase in percentage of ZrO_2 nanofillers decreased water solubility.

REFERENCES

1. Manappallil JJ. Basic dental materials. 2nd ed. New Delhi: JAYPEE Brothers Medical publisher; 2007. pp. 100- 42.
2. Seo RS, Murata H, Hong G, Vergani CE, Hamada T. Influence of thermal and mechanical stresses on the strength of intact and relined denture bases. J Prosthet Dent 2006; 96: 59–67.
3. Manley TR, Bowman AJ, Cook M. Denture bases reinforced with carbon fibers. Br Dent J 1979; 146(1): 25-5.
4. Kim SH, Watts DC. The effect of reinforcement with woven E-glass fibers on the impact strength of complete dentures fabricated with high-impact acrylic resin. J Prosthet Dent 2004;91(3):274-80.
5. Matsukawa S, Hayakawa T, Nemoto K.Development of high-toughness resin for dental application. Dent Mater 1994; 10(6):343-6.
6. Jagger DC, Harrison A, Jandt K. The reinforcement of dentures. J Oral Rehabil 1999; 26: 185-94.
7. Jagger DC, Jagger RG, Allen SM, Harrison A. An investigation into the transverse and impact strength of "high strength" denture base acrylic resins. J Oral Rehabil 2002; 29: 263-7.
8. Jordan J, Jacob KL, Tannenbaum R, Shart MA, Jasiuk I. Experimental trends in polymer Nan composites-A review. Mater Sci Eng 2005; 393(1) 1-11.
9. Shi J, Bao Y, Huang Z, Weng Z. Preparation of PMMA Nanometer-calcium carbonate composites by

in-situ emulsion polymerization. J Zhejiang University Sci 2004; 5(6): 709-13.

10. Ayad NM, Badawi MF, Fatah AA. Effect of reinforcement of high impact acrylic resin with micro-Zirconia on some physical and mechanical properties. Rev Clín Pesq Odontol 2008; 4(3):145-51.
11. American dental association specification No. 12 for denture base polymer guide to dental materials and devices,7th edition, Chicago Illinois, 1999.
12. ISO 179-1:2000: Plastics -- Determination of Charpy impact properties -- Part 1: Non-instrumented impact test.
13. Sun L, Ronald FG,Suhr J,Grodanine JF. Energy absorption capability of nano composites: A review. Composites Science and Technology 2009; 69: 2392-2409.
14. Chen J, Huang Z, Zhu J. Size effect of particles on the damage dissipation in nanocomposites. Compos SciTechnol 2007; 67(14): 2990-6.
15. Alwan SA. The effect of addition of silanized Nanotitania fillers on some physical and mechanical properties of heat cured acrylic denture base material. A master thesis, College of dentistry/University of Baghdad, 2014.
16. Katsikis N, Franz Z, Anne H, Helmut M, Andri V. Thermal stability of PMMA/ Silica nano- and micro composites as investigated by dynamic-mechanical experiments. Polym Degra and Stability 2007; 22: 1966-76.
17. Jasim BS. The effect of silanized alumina nano-fillers addition on some physical and mechanical properties of heat cured polymethyl methacrylate denture base material. A master thesis, College of dentistry/University of Baghdad, 2013.
18. Keith HL, Chanakya M, Perrotta AJ, Karl W, Williams. Aluminum Oxide in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim. 2002
19. Xia Y, Zhang F, NingGu HX. Nanoparticle-reinforced resin-based dental composites. J Dentistry 2008; 36: 450-5.
20. Nabil E. evaluation the effect of modified nanofillers addition on some properties of heat cured acrylic resin denture base materials. A master thesis, University of Baghdad, College of Dentistry, 2011.
21. Al-Momen MM. Effect of reinforcement on strength and radioopacity of acrylic denture base materials. A master thesis, University of Baghdad / College of Dentistry, 2009.
22. Abdul- Ameer AS. Evaluation of changes in some properties of acrylic denture base material due to addition of radio- opaque fillers. A master thesis, College of Dentistry/ University of Baghdad, 2006.
23. Ferracane JL. Hygroscopic and hydrolytic effects in dental polymer networks. Dent Mater 2006; 22: 211–22.
24. Mohammed D. Effect of modified zirconium oxide nano-fillers addition on some properties of heat cure acrylic denture base material. J Bagh Coll Dentistry 2012; 24(4): 1-7.
25. Panyayong W, Oshida Y, Andress CJ, Borco TM, Hovijitra S. Reinforcement of acrylic resin for provisional fixed restoration. Part III: effect of addition of titrant and zirconia mixtures on some mechanical and physical properties. Biomed Mater Eng 2002; 12(4): 353-66.
26. Gurbuz O, Pinarkursoglu F. Water sorption and solubility of denture teeth acrylic resin reinforced with milled glass fiber. OHDMBSC 2005; 4: 57-62.