Effect of modified nanohydroxyapatite fillers addition on some properties of heat cured acrylic denture base materials

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ABSTRACT

Background: Poly (methylmethacrylate) is not ideal in every aspect and has disadvantages such as insufficient surface hardness, increase water sorption and poor impact resistance and the latter being the primary cause of fracture of denture base resins. The aim of this study was to evaluate the effect of addition of silanized nano-hydroxyapatite (HA) on some properties of heat cured acrylic denture base material.

Materials and methods: HA nano particles were first silanized with γMPS (tri methacryloxypropyletrimethoxy silane coupling agent) then ultrasonicated with methylmethacrylate (monomer) to disperse agglomerated nano particles and mixed with polymer. 2% by wt of HA nano particles was selected as the best concentration that added to the denture base material according to the pilot study.(100) specimens were prepared by conventional water bath processing technique and divided to two groups: 50 specimens for control group or 0% HA and 50 for experimental group or 2% HA then each group was subdivided to five groups with 10 specimens for each test: impact strength, transverse strength, surface hardness, surface roughness, water sorption and water solubility.

Results: highly significant increase in impact strength and surface hardness after addition of 2% HA nano particles but not significant decrease in water sorption whereas solubility was significantly decreased. Surface roughness was significantly increased as compared with control group but remained within the acceptable limit less than 2µm. HA nanoparticles addition highly decreased the transverse strength value.

Conclusion The addition of 2% HA nano particles considerably improved the impact strength, surface hardness and had positive effect on water sorption and solubility. Whereas the same concentration tend to highly decreased transverse strength and increase surface roughness.

Keywords: poly methylmethacrylate, HA nanoparticles, γMPS (tri methacryloxypropyletrimethoxy. **(J Bagh Coll Dentistry 2017; 29(2):49-54)**

INTRODUCTION

Since first polymerized by Walter Bauer in 1936, acrylic resin denture base gradually took the place of traditional metal base and became most commonly used denture base material in clinical fabrication (1). It is a combination of advantages rather than one excellent aspect that accounts for its wide usage, including its popularity in satisfying aesthetic demands and clearly defined processing method in dentistry application. This material is not ideal in every aspect, especially when meeting with mechanical requirements of prosthesis (2).

The primary problem of PMMA is its poor strength characteristics, low impact strength and fatigue resistance (3). Thus, there is a need to improve the performance of PMMA in denture base application. Several methods have been used to modify the properties of PMMA denture base materials. Among these methods is strengthening the acrylic resin prosthesis by modifying or reinforcing the resin with fiber, and graft copolymerization with high-impact resins (4,5). However, fabrication of properly oriented fibers added in the resin is technically difficult and random dispersion would even result some defects (6).

The introduction of nano dentistry in the last years as well as the great advantages of nanofiller in reinforcing the mechanical properties of denture base materials led to introduction of Polymer nanocomposites, which are materials contain nanoscopic inorganic particles, typically 10-100 nanometer in at least one dimension, are dispersed in an organic polymer matrix in order to dramatically improve the performance properties of the polymer (7). Also clinical application of denture base not only requires excellent mechanical performance, but also expects good biocompatibility and biosafety, while some inorganic materials may cause irritation or even damage to gingival tissue and mouth mucosa (8,9). It was reported that hydroxyapatite nanopowder had been used in dental material as an effective biocompatible filler to reinforce self-cured polymer matrix (10). HA is natural biosafety material and widely used in ceramic for its excellent biocompatibility with tissues and skin (9). As any inorganic filler the mechanical properties of PMMA/HA composites could be limited by the incompatibility between the PMMA and HA. It was found that the silane coupling agent [3-methacryloxypropyltrimethoxy silane (γ-MPS)] can improve the mechanical and physical properties of PMMA/nano HA significantly owing to the better adhesion (11). A novel kind of acrylic resin studied in this research by incorporating of hydroxyapatite (HA)

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$Ca_{10}(PO_4)_6(OH)_2$ to improve the mechanical properties of heat cured denture base materials.

MATERIALS AND METHODS

Materials

The most important component used in this study were heat cured acrylic powder and liquid (Vertex, Netherlands).Hydroxy apatite nanoparticles with 20nm for diameter and 97% purity (MK nano ,Canada) , γMPS , methanol and glacial acetic acid (Sigma Aldrich Germany)

Method

-Silanation of hydroxyapatite nano particles

HA nanoparticles were silanized using 3-methacryloxypropyltrimethoxy silane (γ-MPS) in 90/10 methanol/distilled water solution .(11,12) about 30 gm of HA nano particles were mixed by prob sonicator (soniprep-150, England) for 2 hours. PH of the result solution was adjusted with glacial acetic acid until PH meter(Eutech instrument, Germany) recorded 3.5-4 then 3 ml of γMPS was added under vigorous magnetic stirring (Hanna instrument HI300, China) for 12 hours. Methanol and distilled water were evaporated by air and heat drying then the silanized HA powder was tested by Fourier transformes infrared machine (shimadzue,FTIR-8400S,Japan) to check for functional groups.

- Preparation of acrylic specimens

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. To test the impact strength :abar shaped specimen with dimensions of (80 mm x10 mm x 4 mm) length, width and thickness respectively(13) (ISO.179-1, 2000 for un notched specimens). A bar shaped specimen with dimensions of (65mm x 10 mm x 2.5 ± 0.1 mm) length, width, thickness respectively was used to test transverse strength(14) (ADA No. 12, 1999). Same specimen's measurements were used to prepare samples to test surface roughness and hardness of the tested materials. Water sorption and solubility tests: disc with dimensions of 50 mm in diameter and 0.5 mm in thickness (14) (ADA No. 12, 1999) was prepared.

-Mold preparation

Conventional water bath flasking technique for complete dentures construction was followed during the mold preparation and processing

-Proportioning and mixing

A pilot study was conducted to estimate the most suitable HA nanoparticles concentration .2% showed the best results regarding impact and transverse strength test.

Addition of hydroxyapatite nano particles

2% of modified HA Nano filler powder was added by weight to monomer to prepare the experimental group specimens. An electronic balance with accuracy of 0.0001g (Sartorius. Germany) was used to determine the exact PMMA and HA nano powder weight. The appropriate weight of HA nano filler was added to the selected monomer volume following manufacturer instruction regarding P/L ratio, the filler was dispersed very well in the monomer by probe sonicater apparatus (120W, 60KHz) for three minutes(15). The suspension of monomer with HA Nano filler was immediately mixed with acrylic powder to reduce the possibility of particle agglomeration and phase separation. The mixing was carried out in a clean and dry mixing vessel by a clean wax knife for 30 second. The mixture was then covered and left to stand until a dough stage was reached approximately 30 min according to manufacturer's instruction.

Mechanical and physical tests

Impact strength test

Impact strength test was conducted following the procedure recommended by the ISO 179 with Charpy type impact testing instrument (N 43-1, New York, USA). Ten specimens were constructed for control and experimental groups. Each one was supported horizontally at its ends and struck by a free swinging pendulum of 2 joules testing capacity was used). The charpy impact strength of unnotched specimen was calculated in KJ/mm^2 according to this equation

Impact strength = $\frac{E}{B.D}$ X10^3 (16)***(Anusavice, 2008)***

E: is the impact absorbed energy in joules.
B: is the width in millimeters of the specimens.
D: is the thickness in millimeters of the specimens.

Transverse strength test

Ten specimens were constructed for each group and tested for transverse strength by the use of instron testing machine (Instron corporation, 1122, canton mass). The specimen was horizontally positioned on bending fixture, consisting of 2 parallel supports (50) mm apart, load was applied with cross head speed of 1mm/min by rod placed centrally between the supports making deflection until fracture occurred. Calculation of transverse strength in N/mm² according to this equation .

Transverse strength = $3PL/2BD^2$,where

P: is the peak load.
L: is the span length in millimeter.
B: is the sample width in millimeter.
D: is the sample thickness in millimeter.(16)

Surface hardness test

The shore D hardness (210 time group Italy)was used in this test which consists of spring loaded metal indenter point (0.8mm diameter) with a screen from which the hardness value was read directly on a digital scale. Each one of the ten specimens was divided in to five equal area and five measurements were recorded from the center of each area. The average of five reading was calculated representing the hardness value of the specimens.

Surface roughness test

A portable surface roughness tester or Profilometer(SRT-6210 ,England) were used to test ten specimen for both control and experimental groups .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 reading were recorded, as a roughness measurement.

Water sorption and solubility test

Ten specimens were prepared for each group and dried by placing them in a desiccator containing silica gel. The desiccator stored in an incubator at 37°C ± 2 for 24 hours, and then the specimens were removed from the incubator and remained at room temperature for 1 hour after that the specimens weighed with digital balance. This procedure was repeated until a constant mass "conditioned mass"(M_1) was reached.Then all discs of two groups were immersed separately in distilled water inside incubator for 7 days at 37°C ± 2°C (14). Then, the discs were removed from the water and weighed one minute after removal from the water; this mass was recorded as (M_2) (The mass of the disc after conditioning). water sorption was calculated in mg/cm² and calculated according to this equation.

$WSP = M_2 - M_1 / S$

WSP: water sorption in (mg/cm^2)

M_2: The mass of the disc after immersion in distilled water (mg)

M_1: The mass before immersion in distilled water (conditioned mass) (mg)

S: Surface area of the disc (cm^2)

In order to measure solubility of the material, the specimens were placed in the desiccators containing silica gel incubated at 37°C ±2 °C. The specimens were weighed every 24 hours until a constant weight (M_3) was reached. Water solubility was calculated in mg/cm² according to this equation.

$WSL = M_1 - M_3 / S$

WSL: Solubility (mg/cm^2)

M_1: The conditioned mass (mg)

M_3: The reconditioned mass (mg)

S: The surface area of the disc (cm^2)

RESULTS

FTIR spectrum for sample of nano hydroxyapatite before silanization presented in fig (1) bands at 560,640,963 and 1028 to 1110cm^{-1} correspond to phosphate group and band at 3572cm^{-1} to structural OH^-. Modified hydroxyapatite has the same spectrum but with the presence of extra peaks of vinyl C=C, carbonyl C=O and methyl group detected at 1638cm^{-1} , 1718cm^{-1}and 1455 cm^{-1} which are the required functional groups as shown in fig (2)

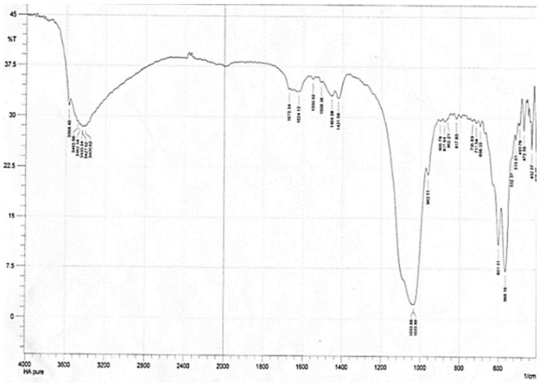

Figure 1: FTIR of pure HA

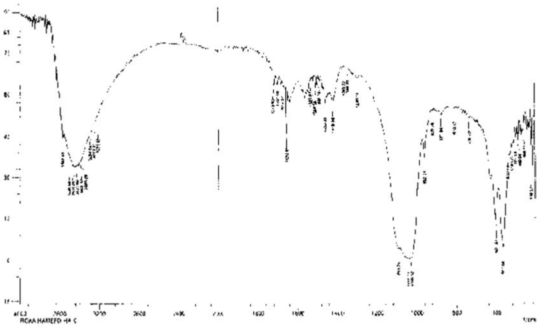

Figure 2: FTIR of silanized HA

The results were analyzed using SPSS. Version 19and t- test was used to determine the difference at a level of significance 0.05 in which P-value more than 0.05 considered as statistically non-significant, less than 0.05 accepted as significant and less than 0.01 accepted as highly significant.

Mean values, standard deviation, standard error and independent t tests results for all the tests conducted in this study are presented in tables 1-5. Regarding impact strength the higher mean value appeared in experimental group as compared with control group. High significant difference resulted at P value of 0.000 as shown in table (1)

Table 1: impact strength in (KJ/mm²).

	control group (0% nano filler)	experimental group2% nanofiller
No.of specimens	10	10
mean	8.1723	11.1419
SD	0.47119	0.62091
SE	0.14900	0.19635
T value	-12.048	
P value	0.000	
Significance	HS	

For transverse strength test mean value of control and experimental groups are 105.3738 and 94.02 N/mm^2 respectively. Independent t test showed high significant difference between them as shown in table (2)

Table 2: Transverse strength test results in (N/mm^2)

	control group) 0% nano filler	(experimental group)2% nanofiller
No.of specimens	10	10
mean	105.3738	94.0200
SD	5.75066	8.76685
SE	1.81852	2.77232
T value	3.424	
P value	0.003	
Significance	HS	

The experimental group of surface hardness test showed higher mean value as compared with control group. Highly significant improvement in surface hardness was seen with P value 0.000 as shown in table (3)

Table 3: Surface hardness test results

	control group 0% nano filler	experimental group 2% nanofiller
No.of specimens	10	10
mean	83.3840	86.8310
SD	0.49214	0.95823
SE	0.15563	0.30302
T value	-10.199	
P value	0.000	
Significance	HS	

As shown in table (4) surface roughness increased in experimental group. Independent t test shows highly significant difference with P value 0.002

Table 4: surface roughness test results

	control group 0% nano filler	experimental group 2% nanofiller
No.of specimens	10	10
mean	1.8300	1.8360
SD	0.0000	0.00516
SE	0.0000	0.00163
T value	-3.674	
P value	0.002	
Significance	HS	

Anon significant reduction in water sorption was seen between control and experimental groups, table (5)

Table 5: water sorption test results in (mg/cm^2)

	(control group) 0% nano filler	(experimental group) 2% nanofiller
No.of specimens	10	10
mean	0.35632	0.34483
SD	0.065351	0.021334
SE	0.02067	0.00675
T value	0.529	
P value	0.060	
Significance	NS	

Water solubility mean value decreased in experimental group as compared with control group. Independent t test with a P value of 0.000 show high significant reduction between them as shown in table (6)

Table 6: water solubility test results in (mg/cm^2)

	control group 0% nano filler	experimental group 2% nanofiller
No.of specimens	10	10
mean	0.0657	0.0492
SD	0.00815	0.00729
SE	0.00258	0.00230
T value	4.656	
P value	0.000	
Significance	HS	

DISCUSSION

3-methacryloxy propyltrimethoxy silane (γMPS) was used to silanized hydroxyapatite nano particles in which methoxy group in Si-O-CH_3 readily hydrolyze and react with hydroxy apatite nano particles to form stable Si-O-HA. On the other side vinyl group C=C can react with vinyl group of PMMA during polymerization reaction and this allow better dispersion of HA and high interfacial bonding with PMMA as demonstrated in fig (3).

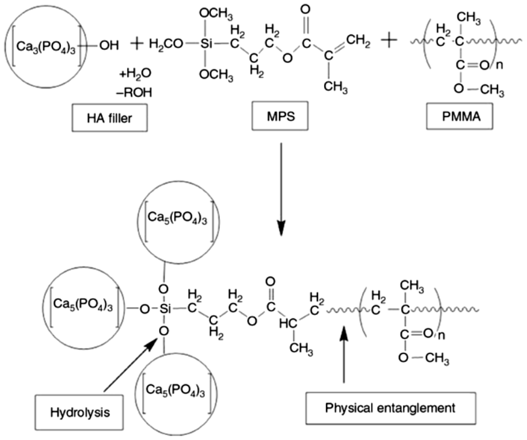

Figure 3: Inter action of Hydroxyapatite γ MPS and PMMA. (11)

The addition of 2% nano hydroxyapatite to PMMA resulted in highly significant increase in impact strength and this may be due to treating particles with coupling agents which improve inter facial bonding between them. On the other hand the small size and low concentration of HA nanoparticles helped in well dispersion and embedding in polymer matrix and this positively affected the impact strength. In this study transverse strength was adversely effected by the addition of HA nanoparticles and this may be due to the plasticizing effect of (γMPS) coupling agent (17) (18) .Shore D hardness tester was used to test hardness properties in this study and showed significant increase in surface hardness of 2% acrylic specimens and this may be explained on the basis of two reasons: one of them might be high inter facial bonding between nano particles with polymer matrix, good dispersion, equal distribution of particles in the polymer matrix and these improved by silanation of HA particles and the other reason might be the incorporation of HA which represent the main mineral component of hard dental tissues that responsible for their hardness and other mechanical properties (19). Highly significant increase in surface roughness of unpolished surface after addition of 2% nano hydroxyapatite to PMMA as compared with 0% or unfilled PMMA was observed.This change can be considered uninfluential since significant surface bacterial colonization occurs when the roughness is more than 2µm(20).Any how regular cleaning and disinfecting the denture can solve the problem. Therefore the significant increase in surface roughness may be statistical and clinically uninfluential. It was found that water sorption of experimental group decreased but statistically not significant at the same time there was highly significant decrease in water solubility after addition of 2% of HA which is the result of γMPS modified HA nanoparticles and the ability of γMPS to react with hydroxyl groups in the HA filler converting it from hydrophilic to hydrophobic molecule(21).

CONCLUSION

γ MPS treated hydroxyapatite nanoparticles successfully enhanced dispersion and interfacial bonding with polymer matrix.

The addition of 2% hydroxyapatite nano particles considerably improved the impact strength, surface hardness and had positive effect on water sorption and solubility. Whereas the same concentration tend to highly decreased transverse strength and increase surface roughness

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المستخلص

مادة البولي مثيل ميثاكريليت ليست متكامله من كل النواحي ولها ميزات غير مرغوبه مثل قلة الصلاده وكثرة امتصاص الماء بالاضافه لاخفاقها في تحمل الصدمه وهي السبب الرئيسي لكسر قواعد الاطقم .

الهدف من هذه الدراسه هو تقييم تأثير اضافة الهايدروكسي اباتايت النانويه والمعامله كيميائيا الى مادة البولي مثيل ميثاكريليت على بعض الخواص مثل قوة الصدمه ،القوة المستعرضه،الصلاده، خشونة السطح، قابلية الامتصاص والذوبان في الماء .

المواد وطريقة البحث:تمت معاملة جزيئات الهايدروكسي اباتايت النانويه بالمادة الرابطه ثم تحريكها مع المثيل ميثاكريليت او المونومير باستخدام الموجات فوق الصوتيه لغرض تفريق الجزيئات المتلاصقه ثم خلطها مع البولي مثيل ميثاكريليت او البوليمر.وفقا لنتائج الدراسه الاوليه تم اختيار نسبة 2% من الهيدروكسي اباتايت النانويه لاضافتها الى العينات التجريبيه .تم تحضير مئة عينه قسمت الى مجموعتين مجموعة السيطره والمجموعه التجريبيه كل منهما تحوي خمسين عينه تم تقسيمها الى خمس مجاميع كل منها تحوي عشر عينات موزعه حسب الاختبارات المستخدمه وهي قوة الصدمه، القوه المستعرضه، الصلاده، خشونة السطح، قابلية الامتصاص والذوبان في الماء .

النتائج : نتائج التحليل الاحصائي اظهرت زياده معنويه في قوة الصدمه والصلاده بعد اضافة الهايدروكسي اباتايت النانويه . كذلك نقصان في امتصاص الماء في نفس الوقت انخفاض معنوي في قابلية الذوبان في الماء وارتفاع معنوي في خشونة السطح ولكن ضمن الحد المقبول للخشونه وهو اقل من 2 مايكروميتر. من ناحيه اخرى هذه الاضافه سببت نقصان معنوي بالقوه المستعرضه.

المحصله :ان اضافة 2% من الهايدروكسي اباتايت النانويه الى البولي مثيل ميثاكريليت ادى الى زياده بقوة الصدمه والصلاده بالاضافه الى التاثير الايجابي على قابلية الامتصاص والذوبان بنفس الوقت اضافة هذه الماده ادى الى زيادة الخشونه وانخفاض القوه المستعرضه .