The Effect of Silanized Alumina Nano-Fillers Addition on Some Physical and Mechanical Properties of Heat Cured Polymethyl Methacrylate Denture Base Material

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Abstract: ***Background**: aluminanano particales is commenly added material to PMMA to improve the physical and mechanical properties of polymer. Alumina was inorganic material and should silanized for good interaction with organic PMMA by using silane coupling agent. **Materials and methods**: the addition of silane coupling agent was done in three percentages and to louen and ethanol as a solvent. The three percentages was: group A 5% percent of coupling agent used for silanization and talouen as a solvent, group B was 25% of silane coupling agent was used , group C 50% percent of coupling agent and group D 75% of coupling agent and ethanol as a solvent. **Results**: A seen in FTIR of nanoalumina there was no change in active group of AL_2O_3 when silane coupling agent was added in 5%, 25% and 50%. When silane coupling agent was added to nanoalumina in percentage 75% there were changes in FTIR of alumina molecules and the active groups of silane coupling agent was seen on alumina nanopartical. **Conclusion**: The AL_2O_3 nanoparticles have greater surface area than microparticles so need larger percentage of silane coupling agent so the active groups of silane coupling agent can be seen on nanoparticales.***

Keywords: Silane, alumina nanoparticales.

1. Introduction

PMMA is the most commonly used material due to its satisfactory mechanical and physical properties, compatibility with oral tissue, aesthetics, ease of repair and low cost **(1)**. Recently, much attention has been directed toward the incorporation 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 **(10)**. PMMA has low thermal conductivity approximately 0.2 w/m.c**(7)**compared with gold or cobalt alloy denture base material and this can present problems during denture processing as heat produced cannot escape, leading to a temperature rise and this may lead to porosityduring fabrication **(8)**. In order to overcome these problems, several attempts were made to modify thethermal properties of the PMMA. These attempts included the filler particles alumina to resin **(9)**. Nanoparticles were undergone surface treatment with silane coupling agent and embedded into PMMA **(21)**. Alumina nanoparticles were treated with 3-(methacryloyloxy) propyltrimethoxysilane (MPS) to getPMMA/alumina nanocomposite with improved propertiesover pure PMMA. There are various types of silane coupling agents available; however, MPS 3-(Methacryloyloxy) propyltrimethoxysilane was selected based on its solubility parameters for methylmethacrylate (MMA) and PMMA bonding **(11)**. MPS (3-(Methacryloyloxy) propyltrimethoxysilane) is a bi-functional monomer, with the hydroxymethyl groups substituted by hydroxyl groups for attachment to the alumina nanoparticles. MPS also contained C=C bonds which reacted with the PMMA matrix during the curing process. Therefore, the silane coupling agent acted as a “molecular bridge” to establish chemical bonding between alumina nanoparticles and the PMMA matrix **(12)**. During the filler treatment process, the methoxy groups hydrolyze to generate hydroxyl groups through an acid or base catalyzed reaction. These hydroxyl groups then undergo condensation with the hydroxyl groups on the surface of the filler and become attached by covalent bonds. Condensation is also possible with the adjacent −OH groups of the hydrolyzed silanes or with water absorbed on the surface of the filler. This results in the formation of a very thin mono- or multilayer polymeric film on the surface of the filler with unreacted double bonds. During the curing of the composite, the double bond of the methacryloxy groups of the treated surface co-reacts with the monomer resins **(13)**.

2. Material and Methods

Surface modification of alumina nanofillers (ALR2ROR3R)

To improve bonding between alumina nanoparticles and PMMA matrix, the alumina nanoparticles were surface-treated with a silane coupling agent. The silanization technique used in the present study followed the previous studies **(14)**.Alumina nanoparticles treated with 3-(trimethacryloylpropyl) trimethoxysilane in order to introduce functional groups (reactive groups)into alumina nanofillers surfaces, through the reaction of alumina nanofillers with the silane coupling agent **(15)**.

A. Surface modification using 5% silane and toluene as a solvent

30g of nano filler and 200ml pure toluene were placed into a flask then sonicated at ambient temperature for 20minuts. After that, the nano filler and toluene were placed into a flask equipped with a magnetic stirrer 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 60P°PC at rotary 150 rpm for 30 min. After that the modified nanofillers was dried in vaccum oven at 60P°PC for 20 hours. Then nano filler stored at room temperature before use(15), (16).

*For charecterization of intering any functional groups, the (FTIR) spectrum (on Shimadzu FTIR-8400S infrared spectro photometer) where done (16)

B. Surface modification using 25wt%, 50%, 75% silane

One hundred milliliter of ethanol aqueous solution (70 vol%) was prepared using 99.8 vol% ethanol and deionized water, and adjusted to pH of 4.5 by titrating with 99.9% acetic acid using a pH meter. Then, 25wt%, 50wt%, 75wt% g of MPS was added respectively into each ethanol aqueous solution, and stirred. These MPS solutions were stored in a 100 mL polyethylene cup with a cover, and allowed 5 min for hydrolysis and silanol formation.

Then, 100 g of alumina nanoparticles were added into each MPS solutions. The mixture was stirred with magnatic stirrer for 30 minutes as in fig.(1)a, then the mixture was sonicated with probsonication apparatus for 30 minutes as in fig.(1)b, then the solution left dried at room temperature for 14 days (17) as in fig (2). The (FTIR) spectrophotometer where done to determine whether or not functional group of the MPS have been attached to nanofiller by analyzing characteristic vibrations of functional groups (16).

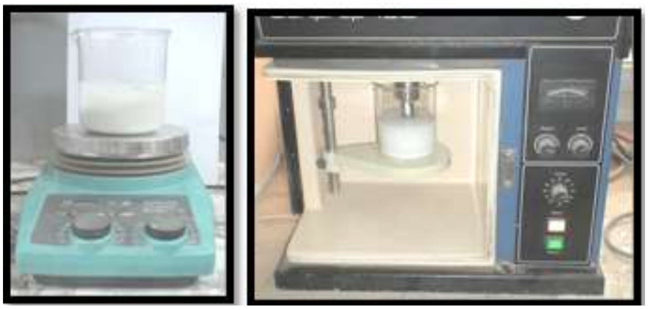

Figure 1: Show the equipments used for surface modification of nanofillers A: prob sonication apparatus; B: magnatic stirrer

Figure 2: Show modified nanoparticles before and after drynesssilanol containing nanoparticles; nanoparticles after 14 days

3. Results

Characterization of silanized alumina nanofillers (AL_2O_3)

Characterization of absorption bands of the material indicated by using FTIR. The absorption bands of MPS can be assigned to the presence of the functional groups, which are two promeninte peaks at 2945cmP -1 P and 2841cmP -1 P can be attributed to the (C-H) stretching, and the charcteristic (C=O) stretching occurs at 1720cmP -1 P, and the charcteristic for (C=C) stretching occurs at 1637cmP -1 P, for (CHR2R- andCHR3R) occurs at 1413cmP -1 P, and groups of peaks between 1296cmP -1 P and 1166cmP -1 Pcan be attributed (C-O-C) stretching, the charecteristic (Si-O-CHR3R) stretching occurs between (400 -470)cmP -1 P, figure (3). IR spectra of nano-AlR2ROR3R fillers, showed absorption at (550.82) cmP -1 P(Al-O), figure(4).

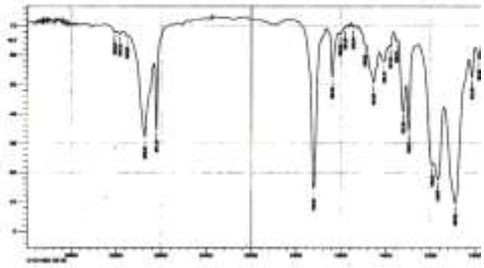

Figure 3: FTIR spectrum of MPS 3-(methacryloyloxypropyl) trimethoxysilane :A(2941)cmP-1 P; B(1637)cmP-1 P; C (1296)cmP-1 P ; D (400-470)cm P -1 P

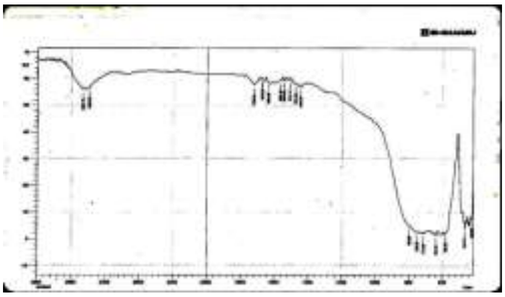

Figure 4: FTIR spectrum of alumina nanoparticles: A(550)cmP^{-1}

While the FTIR of the alumina nanofillers after surface modification of the nanofillers with 5wt% silane using ethanol and toluene as a solvent showed no change in the absorption bands as shown in the figure (5).

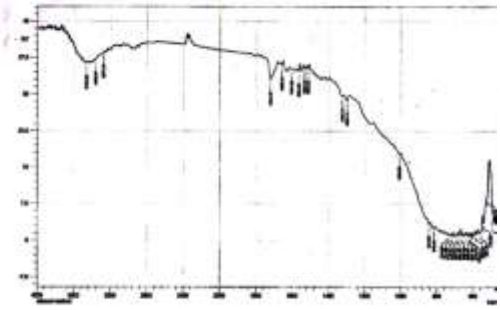

Figure 5: FTIR spectrum of alumina nanoparticles after modification with 5% silane and different solvents: A(550)cm^{-1}

The same results were obtained using 25wt% and50wt% figure (6).

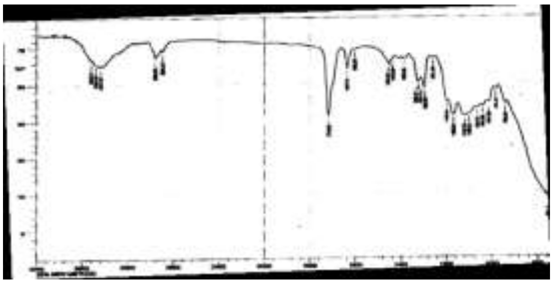

Figure 6: FTIR spectrum of alumina nanoparticles after silanization with 25wt% 50wt% of silane: A(2950)cm^{-1}; B(1637)cm^{-1}

The absorption band of silanized alumina nanoparticles has almost all the absorption peaks present in MPS (3-(Methacryloyloxy)propyltrimethoxysilane), in addition to the peaks present in the alumina nanoparticles. Figure (7) showed absorption at 2913cm^{-1} (C-H), 1720cm^{-1} (C=O), 1170cm^{-1} (C-O), this indicated the existence of chemically bonded MPS on Al_2O_3 nanofillers

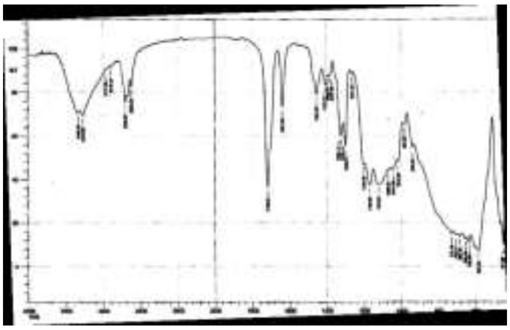

Figure 7: FTIR spectrum of alumina nanoparticles after silanization with 75wt% silane.

4. Discussion

As shown from the figure(5) no change in functional groups vibration after using different solvent and 5% silane coupling agent, this due to that the amount of coupling agent is too little that the active group could not be absorbed on alumina nanoparticle.

In figure (6) after addition of silane coupling in 25%, 50% also there are no change in functional groups 0f nanofillers for the same reasone, therefore the amount of coupling agent should be increased.

The method impart to increase the amount of silane coupling agent according to the equation of **(18)**, which indicate that amount of coupling agent should be increased as the surface areas of fillers increased for a given amount, the nanofillers have surface area greatly larger than micro fillers for a given amount (19)**.** According to Arkle's equation the minimum amount of silane that required to create monolayer of silane coating on the filler surface based on Arkle's equation as follows:

Amount of silane (g)= Amount of filler (g) × Surface area (mP2P/g) / Minimum coating area of silane coupling agent (mP2P/g) (18)

The percentage that had a change in the vibration or absorption of functional group was75% as in fig.(7). From this eqation the minimum amount of silane to create chemisorbed monolayer on single alumina nanoparticle was obtained. In the equation there is direct proportionality between the amount of silane and the surface area of particles in each gram, the surface area of nanoparticles in a given weight is much higher than surface area of micropaticles in the same weight (19)**.**In figure (5) the alumina nanoparticles where surface treated with 5 wt% of silane coupling agent MPS but as shown in the figure there was no reaction (no functional groups appeared), this could be due to insuficient amount of silane coupling agent that required to create monolayer on the surfaces of nanoparticles(17).

From the equation nearly 75 wt% MPS could produce monolayer of silane on alumina nano particles. **FTIR** results in figure(7) showed that 75wt% MPS was indeed successfully surface-grafted on alumina nanoparticles. The amount less than 75 wt% found to produce functional groups of MPS on alumina nanoparticles but very weak and the peaks were shallow as shown in figure(7).

References

[1] Meng TR, Latta MA. Physical properties of fouracrylic denture base resins. J Contemp Dent Pract2005; 6: 93-100.
[2] Manappallil JJ. Basic dental materials. 2nd ed. NewDelhi: 2007. p: 99-142, 346-377.
[3] Winkler S, Monasky GE, Kwok J. Laboratory wearinvestigation of resin posterior denture teeth. JProsthet Dent 1992; 67: 812-814.
[4] Darbar UR, Huggett R, Harrison A. Denture fracture –a survey. Br Dent 1994; 176: 342-345.
[5] Chaijareenont P, Takahashi H, Nishiyama N, Arcsorrnukit M. Effect of different amounts of 3-methacryloxypropyltrimethoxysilane on the flexuralproperties and wear resistance of alumina reinforcedPMMA. Dental Materials J 2012; 31(4): 623–8.
[6] Alhareb AO, Ahmad ZA. Effect of Al2O3/ZrO2reinforcement on the mechanical properties of PMMAdenture base. J ReinfPlast Compos 2011; 30: 83-5.
[7] Mc Cabe JF, Walls AWG: Applied dental materials.9th ed. Mosby; 2008.
[8] Noort RV, Murphy. Introduction to dental material. 2nded. Else view Science Limited: Mosby; 2002. p. 211-7.
[9] Messermith PB, Giannelis EP. Synthesis andCharacterization of Layered Silicate EpoxyNanocomposites. Chem Mater 1994; 6: 1719-25.
[10] Jordan J, Jacob KL, Tannenbaum R, Shart MA, JasiukI. Experimental trends in polymer Nan composites-Areview. Mater Sci Eng 2005; 393(1) 1-11.
[11] *Choi YS, Chung IJ, 2003* "Poly(*n*-butyl acrylate-*co*-methylmethacrylate) and poly(*n*-butyl acrylate-*co*-

styrene)/silicatenanocomposites prepared by emulsion polymerization". Macromol Res *2003*; 11: 425-430.

[12] *Yu DM.; Wu JS.; Zhou LM.; Xie DR.; Wu SZ.* "The dielectric and mechanical properties of a potassium-titanatewhiskerreinforced PP/PA blend". Compos. Sci.Technol.2000; 60: 499-508.

[13] *Powers M.John, and. Ronald L. Sakaguchi. 2012* -- 13th ed. p. ; cm. Craigs Restorative dental materials: 2012; p: 163-176., 192-194.

[14] *Arksornnukit M, Takahashi H, Nishiyama N. 2004*" Effects of silane coupling agent amount on mechanical properties and hydrolytic durability of composite resin after hot water storage". Dent Mater J 2004; 23: 31-36.

[15] *Ayad NM; Mand Badawi, Abdou A Fatah,* "Effect of reinforcement of high-impact acrylic resin with zirconia on some physical and mechanical properties", Rev. clinical. Dental, 4(3), (2008), p145-151.

[16] *Shi J.; Bao Y.; Huang Z. and Weng Z. (2004):* "preparation of PMMA-Nanomater calcium carbonate composites by in-situ emulsion polymerization" J. of zhejiang University Sci. 5(6) 709-713.

[17] *PisaisitChaijareenont ; Hidekazutakahashi ; Norihironishiyama and Mansuangarcsorrnukit*: "Effect of different amounts of 3-methacryloxypropyltrimethoxysilane on the flexural properties and wear resistance of alumina reinforced PMMA". Dental Materials Journal 2012; 31(4): 623–628, 627.

[18] *Arkles B. 1987* Silane coupling agent chemistry. Pennsylvania: Petrarch Systems Catalogue; 1987, p. 59.

[19] *Katsikis N., Franz Z., Anne H., Helmut M., and Andri V. (2007):* "Thermal stability of PMMA/ Silica nano- and micro composites as investigated by dynamic-mechanical experiments" Polym. Degra. And stability, 22: 1966-1976.