

Comparative Evaluation of Water Sorption of Heat-Polymerized Polymethyl Methacrylate Denture Base Resin Reinforced with Different Concentrations of Silanized Titanium Dioxide Nanoparticles: An *In vitro* Study

Abstract

Statement of Problem: Polymethyl methacrylate (PMMA) is the most regularly used material in denture fabrication. Water sorption of denture base PMMA denture base resin has negative effects on physical properties, may lead to harmful tissue reactions in patients, and also has detrimental effects on color stability of the denture base. **Purpose:** The purpose of this study was to evaluate the effect on water sorption of heat-cured PMMA denture base material after incorporation of 1%, 3%, and 5% by weight of silanized titanium dioxide (TiO₂) nanoparticles. **Materials and Methods:** For preparation of test samples, TiO₂ nanoparticles (PCode: 700339, Sigma-Aldrich, USA) were coated with a layer of trimethoxysilylpropylmethacrylate (PCode: 440159, Sigma-Aldrich, USA) before sonicated in monomer (MMA) (DPI Heat Cure) with the percentages 1%, 3%, and 5% by weight; after sonication, it was mixed with PMMA powder using conventional denture fabrication procedure. Then, we prepared total 40 samples for study; 10 samples for each four groups, i.e. that is one control group and three experimental groups. The first group was prepared from PMMA without addition of TiO₂ nanoparticles (control group), the second group with the addition of 1 wt% TiO₂ nanoparticles, the third group with 3 wt% TiO₂ nanoparticles, and the fourth one with 5 wt% TiO₂ nanoparticles (experimental groups). Water sorption test was then conducted on each sample. **Results:** Each group was evaluated for water sorption test, and it was found that increasing the wt% of nanoparticles, there was a significant decrease in water sorption of denture base resin from 1.74 to 1.46 mean wt%. *P* value suggested that the difference of mean percent increase across all groups was statistically significant with *P* = 0.034. **Conclusion:** The maximum decrease in water sorption was observed in denture base resin incorporated with 5 wt% TiO₂ nanoparticles.

Keywords: Fourier-transform infrared, nanoparticles, polymethyl methacrylate, silanization, titanium dioxide, water sorption

Introduction

Polymethyl methacrylate (PMMA) is one of the most widely used materials in prosthetic dentistry because of its ease of processing, low cost, light weight, and color-matching ability, but it also has the tendency to absorb water; this water absorbed by the acrylic resin can act as a plasticizer and cause softening, discoloration, and loss of mechanical properties of acrylic resin such as hardness, transverse strength, and fatigue limit.^[1,2] However, water sorption has detrimental effects on color stability of the denture base.^[3,4] three-dimensional expansion and can cause the dimensional changes in denture base resin.^[5]

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Titanium dioxide (TiO₂) is a biocompatible material (nontoxic), esthetically acceptable,^[6,7] corrosion resistant and has the highest flexural and impact strength among all metal oxides. It also has antimicrobial properties, and incorporation of silanized TiO₂ nanoparticles into PMMA has been done in the past for reducing water sorption and to improve the mechanical properties of PMMA resin.^[8,9]

Silanes have the ability to bond inorganic materials such as metal and metal oxides to organic resins, resulting in improved mixing, better bonding, and increased matrix strength.^[10] Silanated nanoparticles may be the material of choice for reinforcing denture base resin because

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of their well-documented enhancement in physical and esthetic properties.^[11] Hence, the purpose of this study was to compare the effect of silanized TiO₂ nanoparticles on water sorption of PMMA denture base resin at different concentrations. The hypothesis of the present study was that incorporation of silanized TiO₂ nanoparticles into PMMA denture base resin could reduce the water sorption of PMMA denture base resin.

Materials and Methods

Sample grouping

Forty samples were prepared and divided into four groups, one control group and three experimental groups, and each group consisted of 10 samples as seen in Table 1.

Mold preparation

According to the American Dental Association specification No. 12 and ISO No. 20795, for water sorption test, disc-shaped metal dies of 50 ± 1 mm in diameter and 1 ± 0.1 mm in thickness as seen in Figure 1 were used to create uniform mold spaces in gypsum and replica blocks of the samples were produced as seen in Figure 2.

Surface modification of titanium dioxide nanoparticles by silanization process

According to the Arkle's equation, the minimum amount of silane required to create monolayer of silane coating on the fillers is as follows:

Amount of silane (g) = amount of filler (g) × surface area of fillers (m²/g)/minimum coating area of silane coupling agent (m²/g).^[11]

One hundred milliliter of ethanol aqueous solution (70 vol%) was prepared by mixing 99.8 vol% ethanol and deionized water (30 vol%) and adjusted to pH of 4.5 using a pH meter

by titrating with 99.9% acetic acid, then silane coupling agent trimethoxysilylpropylmethacrylate (TMSPM) was added, respectively, into each ethanol aqueous solution and stirred.

One hundred gram of TiO₂ nanoparticles was added into each TMSPM solution. The mixture was stirred for 20 min by using a magnetic stirrer, and then the mixture was kept for sonication in Probe Sonicator for 30 min. Then, the solution was dried by keeping it for 14 days at room temperature.^[6] The (Fourier-transform infrared [FTIR]) spectrophotometer (SHIMIDZU, IR-AFFINITY-1) was used to check whether functional group of the TMSPM has been attached to TiO₂ nanoparticles by evaluating the characteristic vibrations of functional groups as seen in Figures 3 and 4.^[12]

Fabrication of the test samples

For sample fabrication of samples for experimental Group-B, Group-C, and Group-D, weight percent of polymer and silanized TiO₂ nanoparticles was measured in proportion as seen in Table 2, using high-accuracy digital weighing scale. The measured silanized nanoparticles are then directly mixed in monomer with the help of ultrasonicator until a homogenous mix is obtained as seen in Figure 5.

The samples were fabricated by mixing heat-polymerized PMMA powder, and respective modified monomer and processing was done as per the manufacturer's instruction.

Test used to examine water sorption

After fabrication of all samples, they were immersed in distilled water and then kept in an incubator at 37 ± 2°C for 7 days to simulate the intraoral condition. Then, samples were removed from the water and wiped with a tissue and with the help of high-accuracy digital weighing scale (Model no. AUW220D, SHIMADZU) seen in Figure 6, and the mass of each sample was measured 60 s after removal from the water (*m*₁). After weighing all samples, they were kept in desiccator containing fresh silica gel (PCode GRM151, HIMEDIA) for desiccation at 37 ± 2°C for

Table 1: Sample grouping

Control group	Experimental groups		
Group-A	Group-B	Group-C	Group-D
PMMA without nanoparticles	PMMA + 1 wt% silanized TiO ₂ nanoparticles	PMMA + 3 wt% silanized TiO ₂ nanoparticles	PMMA + 5 wt% silanized TiO ₂ nanoparticles
10 samples	10 samples	10 samples	10 samples
Total - 40 samples			

PMMA: Polymethyl methacrylate; TiO₂: Titanium dioxide

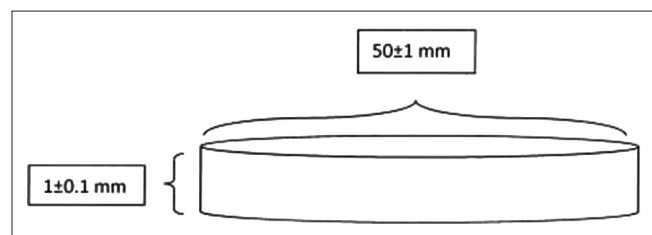


Figure 1: Dimensions of metal dies used for water sorption testing



Figure 2: Mold space created with the help of metal die

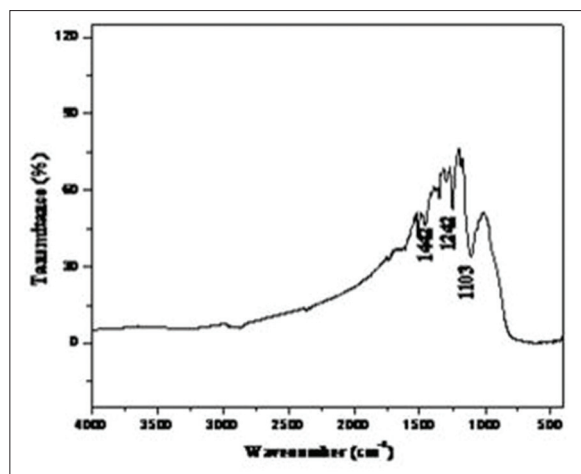


Figure 3: Infra-red spectra of nano-titanium dioxide before silanization

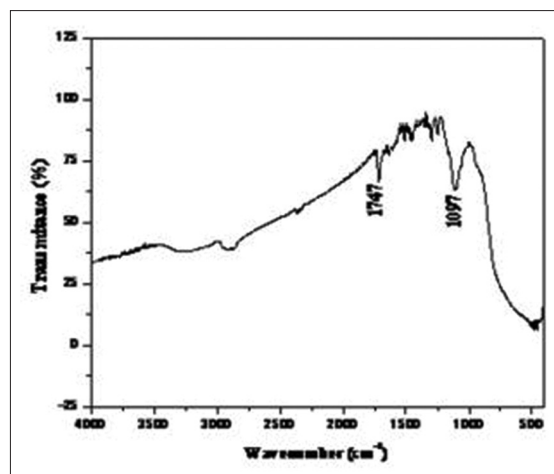


Figure 4: Infra-red spectra of nano-titanium dioxide after silanization

Table 2: Proportioning of nanoparticles and acrylic resin for mixing to fabricate samples

TiO ₂ concentration	Amount of TiO ₂	Amount of polymer	Amount of monomer
Group-A (0 wt%)	0 mg	5000 mg	2 ml
Group-B (1 wt%)	50 mg	4950 mg	2 ml
Group-C (3 wt%)	150 mg	4850 mg	2 ml
Group-D (5 wt%)	250 mg	4150 mg	2 ml

TiO₂: Titanium dioxide

4 days and then the dry weight of each desiccated sample was measured (*m*2) as seen in Figure 6.

The water sorption of the samples was calculated using the formula:

$$W_{sp} = (m1 - m2)/V$$

where

*W*sp: water sorption (µg/mm³)

V: volume (mm³)

*m*1: mass of each sample after removal from the water.

*m*2: dry weight of each desiccated sample was measured.

Results

The results of infra-red (IR) spectra were obtained by analyzing the characteristic vibrations of functional groups in nano-TiO₂, and modified nano-TiO₂ helped to clarify the interaction of nano-TiO₂ with silane coupling agent (TMSPM) using FTIR spectrometer (model-SHIMIDZU, IR-AFF INITY-1). FTIR spectrum was used to measure the different functional groups present in the TiO₂ nanoparticles; Figure 3 represents FTIR spectra of bare TiO₂ nanoparticles in the range of 400–4000 cm⁻¹. The peaks at 1103, 1242, and 1442 cm⁻¹ are due to bonding between stretching vibration of –OH group, Ti-O-Ti, and Ti-O. After silanization, the bond position shifted from 1442 to 1747 cm⁻¹ which is

due to the silanization, and 1747 cm⁻¹ stretching indicates the presence of “acrylates” which is a component of silane coupling agent TMSPM as seen in Figure 4.

Fourier-transform infrared of titanium dioxide before and after silanization

After statistical analysis of data obtained from water sorption test, it was found that with increase in the wt% of nanoparticles, there was a consistent decrease in water sorption of denture base resin from 1.74 to 1.46 mean wt%. Water sorption was maximum with control group (Group-A) and minimum with 5 wt% (Group-D) as seen in Table 3.

The mean percent increase for 0 wt% group was maximum, that is, 1.7407 ± 0.048, followed by 1.5735 ± 0.113 for 1 wt%, 1.4948 ± 0.168 for 3 wt%, and 1.4605 ± 0.4123 for 5 wt%. The difference in decrease in water sorption was tested for statistical significance across four groups using the Kruskal–Wallis test. The resulting value for Kruskal–Wallis Chi-square was 8.6707 and the corresponding *P* = 0.034. *P* value suggested that the difference of mean percent increase across groups was statistically significant (*P* < 0.05).

Discussion

PMMA is the most commonly used material in dentistry. However, it shows weak physical and mechanical properties, and water sorption by PMMA is one of the major factors responsible for reduced physical and mechanical properties. Many experiments have been undertaken to reduce water sorption of PMMA to prevent clinical failure. The results in this study show that there was a significant decrease in water sorption when silanized TiO₂ nanoparticles were added to PMMA. This might be because of the physical presence of nano-sized TiO₂ particles in the free spaces between polymer chains of polymerized PMMA resin, and it also might have attracted resin molecules creating more complicated network chains during curing process, further eliminating space for water sorption.^[13,14] Decrease

Table 3: Descriptive statistics for percent increase in water sorption for four study groups

Statistical parameters	0 wt%	1 wt%	3 wt%	5 wt%
Mean±SD	1.7407±0.048	1.5735±0.1128	1.4948±0.1680	1.4605±0.4123
Median	1.7337	1.5583	1.4880	1.6696
Minimum	1.6614	1.4372	1.2689	0.9121
Maximum	1.8101	1.7654	1.7679	1.9022

SD: Standard deviation

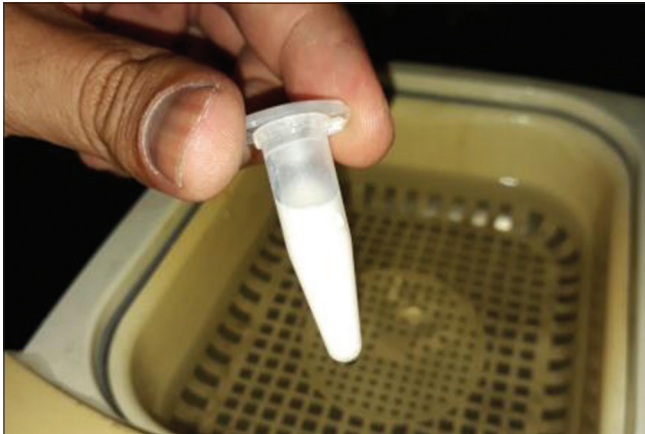


Figure 5: Silanized titanium dioxide nanoparticles were directly mixed in monomer using ultrasonicator

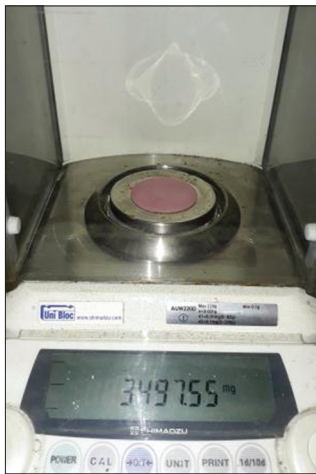


Figure 6: Weighing of samples using high-accuracy digital weighing scale

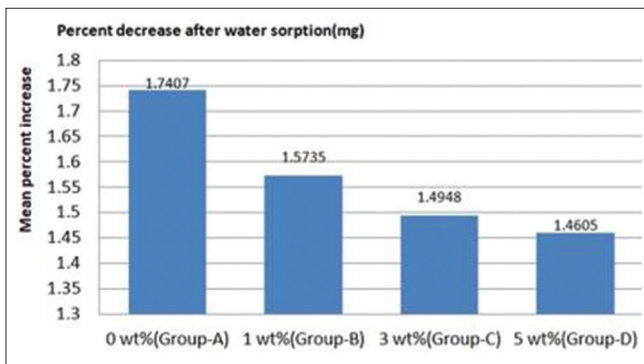


Figure 7: Bar chart showing mean percent decrease in water sorption in four study groups

in water sorption might also be because of the new compound (TiO₂ + PMMA), potentiating the internal resistance due to force exchange between filler and PMMA matrix.

Before incorporating TiO₂ nanoparticles, we did silanization of TiO₂ nanoparticles using silane coupling agent, TMSPM, and compatibility of TMSPM with TiO₂ particles was confirmed by FTIR spectroscopy which indicated the presence of functional group of silane on the surface of particle, and this surface modification of TiO₂ was done for better bonding with resin molecules.

The result of this study is in acceptance with the result of the study by Sama A Alwan in 2015 who found a decrease in water sorption after incorporation of 3 wt% silanized TiO₂ nanoparticles.^[9]

Limitation of study is that after incorporation of silanized TiO₂ nanoparticles into PMMA in increasing wt%, there is a consistent decrease in water sorption; therefore, further study is required to find out the optimum concentration of TiO₂ nanoparticles for water sorption by increasing the wt% of silanized TiO₂ >5 wt%.

Conclusion

The addition of silanized TiO₂ nanoparticles to heat-cured PMMA denture base resin reduces water sorption and a decrease in the water sorption was maximum with 5wt% [Figure 7].

Clinical implications

As the complete denture has to be used for a longer time by patient in intraoral moist condition, water sorption by PMMA results in dimensional changes in the denture which, in turn, can change the adaptability of denture, and decrease in the water sorption by the addition of silanized TiO₂ nanoparticles can enhance the clinical success of complete denture in long-term use.

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Nil.

Conflicts of interest

There are no conflicts of interest.

References

1. John J, Gangadhar SA, Shah I. Flexural strength of heatpolymerized polymethyl methacrylate denture resin

- reinforced with glass, aramid, or nylon fibers. *J Prosthet Dent* 2001;86:4247.
2. Saritha MK, Shadakshari S, Nandeeshwar DB, Tewary S. An *in vitro* study to investigate the flexural strength of conventional heat polymerised denture base resin with addition of different percentage of aluminium oxide powder. *Asian J Med Clin Sci* 2012;1:805.
 3. Latief A. Sorption and Solubility of a Denture Base Acrylic. A Master Thesis of Dental Technology, Cape Peninsula University of Technology; 2012. p. 467.
 4. Jorge JH, Giampaolo ET, Vergani CE, Machado AL, Pavarina AC, Carlos IZ, *et al.* Cytotoxicity of denture base resins: Effect of water bath and microwave postpolymerization heat treatments. *Int J Prosthodont* 2004;17:3404.
 5. Hemmati MA, Vafae F, Allahbakhshi H. Water sorption and flexural strength of thermoplastic and conventional heat-polymerized acrylic resins. *J Dent (Tehran)* 2015;12:478-84.
 6. Emsley J. Titanium Nature Building Blocks. An A to Z Guide to the Elements. Oxford, England, UK: Oxford University Press; 2001. p. 452.
 7. Gao L, Sun J, Liu YQ. The Dispersion and Surface Modification of Nanoparticles. Beijing: Publishing House of Chemical Industry; 2003.
 8. Donachie J, Mathew JR. Titanium a Technical Guide. 2nd ed. Metal Park, Ohio 44073-0002, ASM International; 2000.
 9. Alwan SA, Alameer SS. The effect of the addition of silanized Nano titania fillers on some physical and mechanical properties of heat cured acrylic denture base materials. *J Baghdad Coll Dent* 2015;27:86-91.
 10. Goyal S. Silanes: Chemistry and applications. *J Indian Prosthodont Soc* 2006;6:14.
 11. Hasanen A. Alnamel. The effect of silicon di oxide nano – Fillers reinforcement on some properties of heat cure polymethyl methacrylate denture base material. *J Baghdad Coll Dent* 2014;26:32-6.
 12. Chaijareenont P, Takahashi H, Nishiyama N, Arksornnukit M. Effect of different amounts of 3-methacryloxypropyltrimethoxysilane on the flexural properties and wear resistance of alumina reinforced PMMA. *Dent Mater J* 2012;31:623-8.
 13. Ke YC, Stroeve P. Polymer-Layered Silicate and Silica Nanocomposites. St. Louis: Elsevier B.V.; 2005. p. 120-201.
 14. 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 Degrad Stab* 2007;22:1966-76.