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RESEARCH ARTICLE

Determination of Residual Monomer in Heat Cured of Acrylic Resin Denture Base Material after strengthening it with Titanium Nanotubes

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Abstract

Objectives: The objective of this introductory study was to investigate, for the first time, the impacts of incorporation of titanium nanotubes to polymethyl methacrylate (PMMA) on the remaining monomer content of the of PMMA denture base. Methods: Forty-five specimens of heat polymerizing acrylic resin were prepared according to ISO 20795-1:2013. Divided into three groups (n=15) Methyl methacrylate was mixed with 0% (control), 2.5 weight %, and 5 weight % titanium dioxide nanotubes. TiO_2 nanotubes were prepared using alkaline hydrothermal process. Gas Chromatography analyses GC-MS was used as an analytical monitoring method to quantify the remaining monomer in the cured samples. Data were analyzed using ANOVA and Tukey's test ($p < 0.05$). Results: residual monomer content significantly reduced in both modified groups with TiO_2 nanotubes 2.5and 5w% (0.0783,0.1407, %) respectively) compared with the unmodified group (0.1567%). Conclusion: supporting of acrylic cured acrylic denture base with TiO_2 nanotubes reduces the residual monomer content significantly, which improves the physical, chemical and biological properties of the acrylic denture base material.

Keywords: *Acrylic resin; GC-MS; Methyl methacrylate; Residual monomer; TiO_2 Nanotubes.*

Introduction

Traditional heat-cured acrylic resins are the most closely used base material in the dental prosthesis until the present time. Acrylic resins are commonly used due to its easy handling, easy in polishing and finishing, chemical reliability, lightweight, color matching, and stability in the oral environment, good appearance, as well as it does not need costly equipment. Regardless of these positive characteristics, the denture base resin did not achieve all the desirable mechanical quality [1].

The heat polymerization of PMMA can be influenced by a set of time and temperature variables, and different quantities of the non-reactive methyl methacrylate monomer remain after the treatment cycle. All acrylic resins have different residual monomer amounts based on surround conditions and heat transfer capacity [2]. Many studies have shown that residual monomer content varies greatly with treatment conditions, and the level of residual monomer was one of the fundamental factors influencing the characteristics of the denture base materials produced by different treatment cycles [3]. The residual monomer may spread from acrylic, leading to irritation or allergic side effects,convenient treatment techniques reduce the residual monomer content in dental bases and maintain a residual monomer in a range of 1-3% that most individuals tolerate it well [4].The proper acrylic polymerization procedure is the one that can obtain the best characteristics of acrylic resins, for example, flexural strength, monomer release, fracture toughness, and hardness.

One of the characteristics of acrylate is the releasing of a monomer, which causes dimensional imbalance, thus exposing the material to internal stresses that may lead to crack formation, and ultimately, fracture of the prosthesis [5]. When a denture user is shown signs and the symptoms as above, always consider the probability of an allergic reaction, and conduct a thorough investigation essential to achieve an accurate diagnosis. Cytotoxic influences resulted by denture base resins are produced from substances that leaching out of these resins. The major substance which is leached out through the diffusion action from these materials is the unreactive remaining monomer [6]. Expansion of the openings present between the polymer chains caused by continuous contact of saliva with the material and thus causing the non-reacting monomer to diffuse out. consequently, saliva transfers the substances that are leached out from the dental bases to the oral structures, causing allergic symptoms [7]. The ratio of the liquid to the powder should be considered as one of the important factors when fabricated the denture base resin.

It has been discovered that when resins are prepared in vitro using higher levels of polymer content (found in the powder), with a ratio of 5: 3, fewer monomers were found remaining. The little the content of residual monomer, the less cytotoxic influences will be [8]. One more agent that act as a critical role and is accountable for different degrees of cytotoxic effects is the temperature of the polymerization. When the polymerization period is prolonged, the level of the non-reactant monomer is considerably minimized and thus reduced the probability of cytotoxic impacts. It has been recommended that curing for 7 h in water at 70 °C followed by a 1 h curing in water at 100 ° C leads the maximum transformation of the monomer[9].

It has been suggested that boiling through the polymerization phase should be done for at least 30 minutes at maximal temperatures and that the resin denture bases must be submerged in water for a period of 1-2 days before use by the patient [10].The mouth is liable to wide alteration in the pH and inconstancy in the temperature. The degradation of the metal may happen during the effect of atmospheric acid, moisture, and alkaline other chemical agents.

Moreover, it has been notified that water, chloride, sulfur, oxygen corrodes different minerals found in dental alloys [11]. Titania nanotubes are deemed to be the most important biological materials because they are resistant to the influences of body fluids, major tensile strength, and flexibility and height corrosion resistance. This incorporation of strength and biocompatibility makes it appropriate for medical requests [12].The nanotubes can show an incremented surface area in comparing to nanoparticles among the various nanotubes, TiO_2 (TNT) nanotubes have been taken in account of due to high particular surface area, photocatalytic characteristic and ion fungibility. The tubular form of titania contains a surface area of 250 m^2/g about five times the size of nanoparticles. The great high surface area of the interior and exterior surfaces and the surfaces between the layers of walls [13].

Various studies notified reinforcement mechanical features of polymers moderated with titanate nanotubes[14]. The ISO-1567standards[15] and ADA Specification No. 12 [16] standardized the upper limit (greatest) for the remaining monomer standard to be $35.37_{mg}\ g^{-1}$ (2.2 % cluster portion) of the content of the specimen for the acrylic resins.

Materials and Methods

Synthesis of TiO_2 nanotubes

The materials utilized were traditionally heat-cured acrylic resin (Acrostone, WHN, England). The precursor utilized for the output of nanotubes was a commercial TiO_2 powder (SkySpring Nanotbarticals,Inc., Houston, TX, USA) with a crystalline structure of ca.99.5% anatase and particle size of 10 - 30 nm. TiO_2 nanotubes were prepared using an alkaline hydrothermal process [17].

Samples Grouping

There were a total of 45 disc-shaped specimens were fabricated, 15 specimens from each group. The dimension of specimens was 50 mm diameter and 3 mm thickness and all specimens tested for monomer release, as stated by the ISO 20795-1:2013 [18]. Disc-shaped stainless steel molds were invested in flasks with dental stone (Type lll, Hydrocal dental stone, Moldano, Bayer Lerekusen, Germany).

After the setting of the stone, the flasks were opened, and the stainless steel molds were removed, leaving disc-shaped cavities in the stone, used as templates for the fabrication of heat-polymerized acrylic resins specimens. Titanium dioxide (TiO_2) nanotubes were mixed thoroughly to the acrylic powder by hand before mixing with the acrylic monomer.

The monomer and polymer of the heat-polymerized acrylic resin were proportioned, mixed, packed, and pressed into the mold following manufacturer' instructions [19].

Three groups were prepared as follows:

Group I: Control unmodified group (prepared for the conventional heat-cured acrylic resin).

Group II: Titanium dioxide nanotubes modified group (acrylic resin powder mixed with (TiO2) 2.5% w.

Group III: Titanium dioxide nanotubes modified group (acrylic resin powder mixed with (TiO2) 5% w.

Gas Chromatography

An Agilent Technologies GC-MS (Santa Clara, CA, USA) consisted of a 7890A GC system coupled with a 5975C network mass selective detector and equipped with a HP5-MS capillary fused silica column: Rtx 5MS (length, 30 m; internal diameter, 0.25 mm; film thicknesses, 0.25 μm; and stationary phase, (5% phenol-methyl polysiloxane) was used to achieve the chromatography analyses.

The initial temperature of the GC program was adjusted at 45 °C and keep going for 1 min, then was scheduled at 30 °C /min to 250 °C for 5 min. The temperature of the injection port 200 °C and the split ratio was 25. Other operating circumstances were: carrier gas, He (99.999%). Data collection and processing were performed by using an improved Chemstation G1701 DA version D.00.01.27.Mass spectra were taken at 70 EV ionization energy and full scan mode.

The inspected mass range was adjusted at 50-800 m/z. A standard for the calibration curve was obtained by plotting peak area of 4 standard solutions containing a known concentration (0.0005, 0.001, 0.01 and 0.025%) of the monomer in methanol. Samples were prepared the same as the procedure of Ohyama and Imai [19], 50 mg of powdered sample was solved in 1 ml of acetone, then 10 ml of methanol was added to the solution to precipitate the polymer.

Then 1 μL of supernatant was injected to (GC-MS). Peak identity was confirmed with CO- chromatogram of standards and mass spectrum. The quantification of monomer was computed from the GC- MSC peak areas and using a standard curve. To ensure the reliability of the results, 2 g of sample drill cuttings was used in the second test. All the procedures were repeated the same as the first procedures. The extracted monomer of samples was calculated by measuring their peak area. One-way analysis of variance (ANOVA), followed by a post hoc Tukey's test at a level of significance $p < 0.05$ were performed to analyze the data, using SPSS 23.0 (IBM, Armonk, NY, USA).

Results

Table.1 shows the average 4 readings for each sample of the three groups. Statistical calculations appeared a wider variety of the RM concentrations ranged between the smallest percent for control specimens (0.1567 %) to the greatest values for modified group 5% TiO_2 nanotubes (0.0783 %). While the RM concentration for modified group 2.5% TiO_2 nanotubes (0.1407 %) with a significant difference at $P \leq 0.05$ among all groups.

Table. 1: Average data of RM for the three groups

Sample name	Peak area	Average percent (w/w) of monomer in denture base	P-Value
Control	404711	0.1567	0.000
TiO_2 Nanotube (2.5%)	359438	0.14 07	0.000
TiO_2 Nanotube (5%)	222161	0.0783	0.000

The results of the residual MMA quantities in the cured acrylic resin specimens of the three groups [control, TiO_2 Nanotube (2.5%), TiO_2 Nanotube (5%)], expressed as a percentage of the residual monomer (RM) mass fraction are shown in the Figures(1, 2, 3).

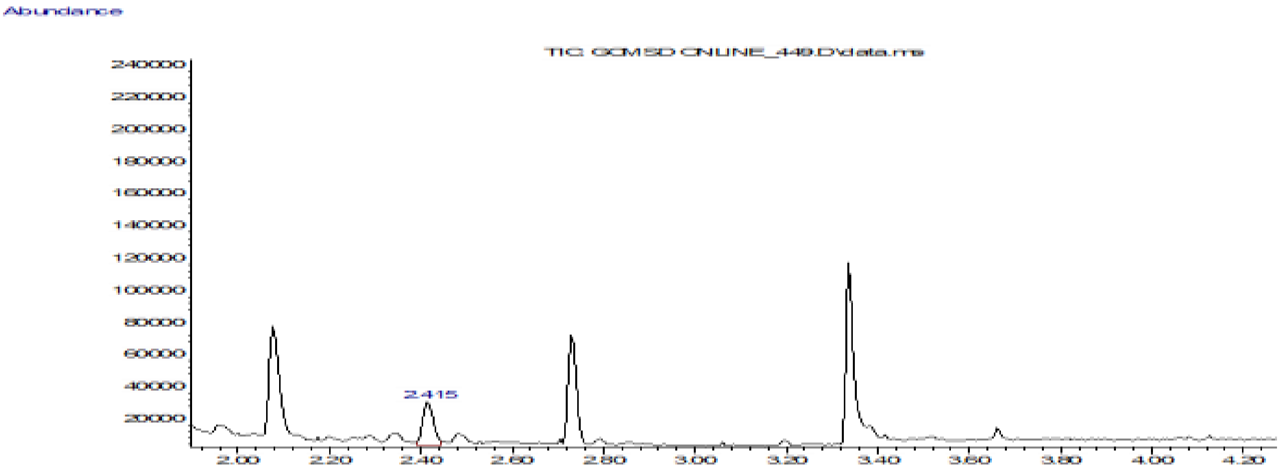

Fig. 1: Chromatogram of extracting monomer from denture base (Control)

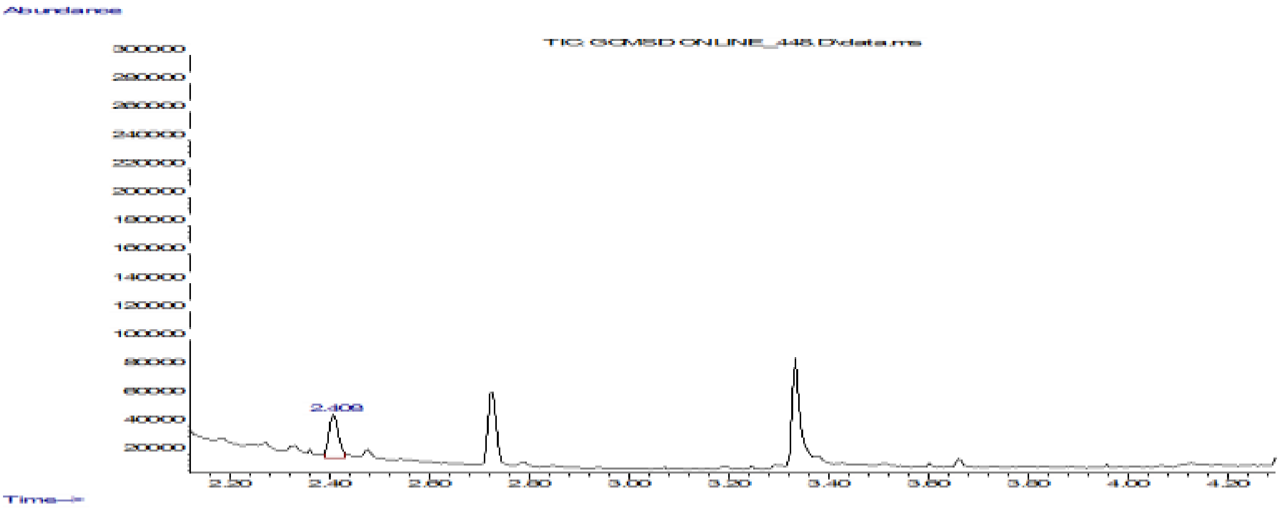

Fig. 2: Chromatogram of extracting monomer from denture base (2.5% Tio_2 nanotube)

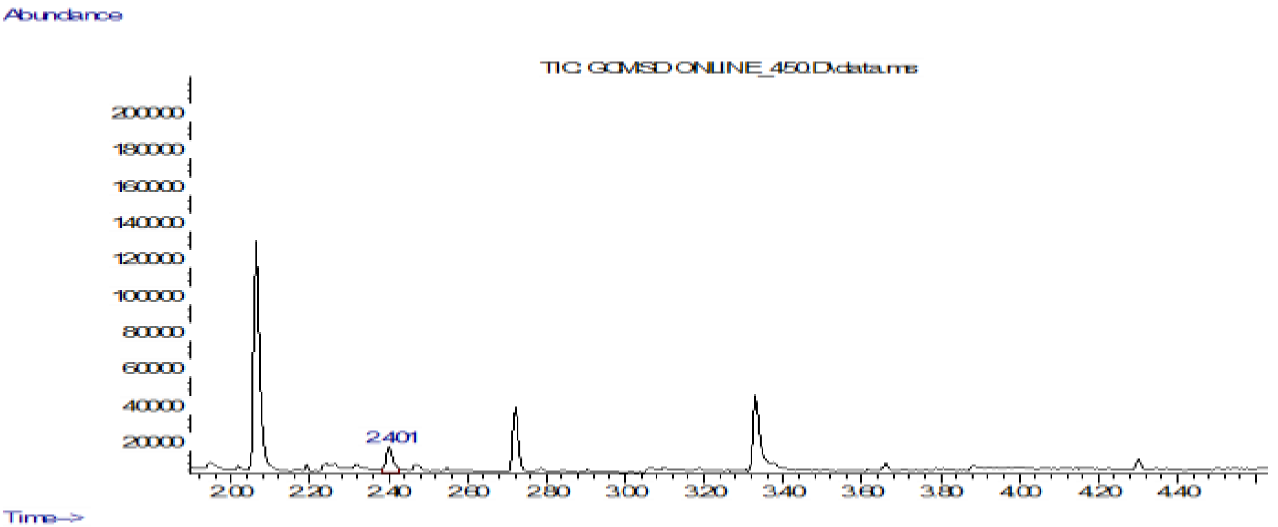

Fig. 3: Chromatogram of extracting monomer from denture base (5% Tio_2 nanotube)

Discussion

Acrylic resin obsess many eligible characteristics, unfortunately, it is recognized that the acrylic denture base incloses residual monomer which may a source of significant side effects such as hypersensitivity of oral tissue, color instability and physical, mechanical and biological characteristics of the denture base[21].

Different surveys exhibited that resins used in the fabrication of denture bases have varied levels of toxicity in vitro and at the same time showed in vivo an allergic response [21]. The reduction in mechanical characteristics is due to the loss of residual monomer, which leaches out into either water or saliva and to the absorption of water which results in plasticization of the resin, which makes it more flexible and soft. The residual monomer quantity in the cured resin does not reliant on only the processing method but as well, on the period of water immersion of dentures, specimens thickness, drill speed, the surface condition of the dentures, usage period of dentures and measuring method [22].

Various methods have been proceeded by investigators in an attempt to minimize the amount of residual monomers in acrylic specimens. The impact of different polymerization durations and temperature on the residual monomer amount of denture base materials has been investigated, and these studies demonstrated that high temperatures and prolonged polymerization times were associated by the reduction in the residual monomer amount.

The specimens manufactured by a short curing cycle contain 7 times the residual monomer amount of the specimens cured by a long cycle. Hence, the high temperature and long cycle have become a means to improve the properties of acrylic resins[9].It was indicated that the residual monomer amount of the denture base materials is reduced to a quarter of the former value if the denture is immersed in water for 1 h at 50 °C after the curing process. Same results are obtained when the samples immersed in water at 37 °C for 24 h, also, it is observed a considerable amount of monomer has been eliminated if the samples are flooded in water at 22 ° C, so a group of researchers recommended that the denture base should be immersed in water at 37 ° C for a full day before use by the patient [23].

It is indicated that thinning areas have a tendency to have an excessive amount of residual monomer compared to thick areas for each curing cycles [30].This influence can be ascribed to the growing heat during the polymerization process. During the curing process, this self-generated heat would cause the thicker section to reach higher temperatures resulting in a greater degree of polymerization and a corresponding reduction in the amount of an unconsumed monomer [18].One of the most promising attempts that contribute to depleting the residual monomer content is the reinforcement the acrylic denture base with TiO_2 nanotubes. This study, which is the first study of its kind, was based on adding TiO_2 nanotubes to the acrylic denture base in different ratios (2.5% and 5% titanium nanotubes) and then investigating the quantities of residual monomer after the polymerization process.

Our study revealed that the residual monomer content in the control samples was 1.567 % while the modified samples with 2.5 % and 5% TiO_2 nanotubes were 1.407 % and 0.0783% respectively, with a significant difference among all the three groups. The results distinctly indicate the role of TiO_2 nanotubes in reducing residual monomer content after polymerization, where samples modified with a higher ratio of TiO_2 nanotubes(5% w) showed lower residual monomer content compared to samples modified by a low ratio of TiO_2 nanotubes(2.5% w) and the unmodified control group.

Evidently, the analyzed residual monomer quantities of all polymerized sample groups did not show any obvious sign of approaching the upper limit of a residual monomer of the heat-cured denture base polymers according to ADA requirements no.12 (2.2% mass fraction). This hopeful results may be attributed to that the 24 hours immersion of the cured sample in distilled water at 23°C before their preparation for GC analysis may be accountable for residual monomer lowering. The attempt to reduce the residual monomer by strengthening the acrylic resin with TiO_2 nanotubes as mentioned above has not been studied before. the results obtained from this study are of great scientific importance.

We noticed that the decrease in the amount of monomer is proportional to the increase in the amount of TiO_2 nanotubes added in the percentages used during this study. These results certainly require a scientific explanation of the mechanisms that have resulted in reducing the amount of monomers. Of course, this study will open a gate for researchers who interested in this aspect and will start a profound discussion about the results of this study and subsequent studies. Titania nanotubes have attracted broad interest and have been vastly utilized in biomedicine, given their large surface area, good corrosion resistance, excellent biocompatibility, and enhanced biological activity [24].

In our previous study[13], we studied the effects of the addition of TiO_2 nanotubes to polymethyl methacrylate (PMMA) on some mechanical properties of PMMA denture base, and we noticed obviously from the SEM image the tubular shapes of synthesized TiO_2 nanotubes.

It is believed that some Ti-O bonds are decomposed and TiO_2 sheets are formed. Under autoclaving and high concentration of NaOH, these sheets peel into nanosheets, then they can roll or fold in tubal morphology [25,26]. Disparity in the width of various layers of multi-walled nanosheets may lead to the tendency of the layers to move inside the walls to decrease growing surface energy.

In terms of high surface area, nanotubes consist of long cylinders with a hollow cavity at their center. The tubular shape and multilayer structure of n-TiO_2 work on increasing the ratio of surface area to volume, which better the interfacial interaction and its specified features. Also it is proposed that in non-clustered nanotubes, improved mechanical characteristics of strengthened PMMA can be fulfilled with longer nanotubes[27].

We think that the high length of synthesized n-TiO_2 utilized in this study might help better the mechanical characteristics of reinforced acrylic base resin , this perception is consistent with other studies which indicated the impact of the length of nanotubes on the mechanical features , they reported better mechanical properties obtained with nanotubes with higher interfacial regions[28].

Otherwise, the tubular, open-ended structure of n-TiO_2 may allow the PMMA monomer to enter the tubes by capillary action and polymerize there. This mechanical entanglement may increase by involving polymers with the inner surface of the n-TiO_2. Thus, the added nanotubes and polymer chains may establish an enhanced network with higher degree of cross-linking, leading to increased load transfer within the acrylic[24].

Conclusion

Strengthening poly(methyl methacrylate)-based material by the addition of 2.5% and 5% weight portion of TNTs powder significantly decreases the amounts of residual MMA ($p \leq 0.05$), The analyzed residual MMA quantities of all polymerized samples were lesser than ADA standards (2.2% mass fraction). Although the results of this study are of significance, however, as we mentioned earlier that this study is considered preliminary and need more supplement studies, which can support the results of this study and provide explanations for the mechanisms, what is important that we opened the door to researchers for research, investigation, and interpretation.

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