Gold nanoparticles-PMMA composite for denture base: Synthesis, mechanical and thermal characteristics

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Abstract

Acrylic resin and rubber-reinforced acrylic polymers represent approximately 95% of the denture base materials used in prosthodontics today. The synthesis of highly dispersed gold nano-particle (AuNP) in polymethyl methacrylate (MMA) as monomer phase transferring agent followed by the formation of polymer composite is described. The resulting nanocomposites undergo various pertaining physicochemical analysis, especially the thermal diffusivity measurements and dynamic mechanical analysis (DMA), to evaluate their basic functional properties. Cylindrical test specimens containing an embedded Pt-wire were used to determine heat conductivity and thermal diffusivity of the investigated samples over a physiologic temperature range (0 to70 oC) based on the in-stationary heat-wire method. The DMA has been conducted on the basis of the Young's Modulus' approximation to investigate the viscoelasticity of rectangular samples of these materials using the three point bending test as well as the compression plats. The results indicated that   the modified PMMA resin with gold nanoparticles fillers have potential as added components in denture bases to provide increased thermal diffusivity and well enhanced viscoelastic responses, which could lead to more patient satisfaction

1. Introduction

Resistance to impact fracture, high flexural strength, and proper thermal diffusivity are desirable properties of denture base acrylics. New materials such as polystyrene and lightactivated urethane dimethacrylate have been developed, but PMMA remains the preferred material   for complete and partial removable prostheses [1]. The popularity of PMMA materials is based on its low cost, relative ease of use, reliance on simple   processing equipment, lightweight, and color matching ability [2]. However, acrylic resin denture base materials are low in strength, brittle, and low in thermal conductivity [3,4]. Therefore, many research efforts were performed to produce significant differences in the chemistry among denture materials based on PMMA chemistry. Some materials rely on high levels of crosslink resin and heat activated initiators to maximize the physical properties of the processed materials, i.e., Sledgehammer Maxipak and ProBase Hot. Other formulations like Lucitone 199 and Fricke Hi-Impact employ a PMMA polymer modified by adding a rubber compound to improve shock resistance and improve strength properties.

The ideal denture base material should possess several key physical attributes [5-9].Some of these properties include biocompatibility, good esthetics, high bond strength with available denture teeth, radiopacity, ease of repair, and should possess adequate physical and mechanical properties [10]. Therefore, many have incorporated an ample variety of additive materials into the PMMA polymer, including glass fibers, long carbon fibers, and metal wires, among others to improve it physical and mechanical properties. Success has been limited [11,12], for example, approaches to strengthening acrylic resin polymer have included the incorporation of metal powder fillers. Silver, copper, and aluminum particles were added to PMMA. In addition, the heat transfer characteristic of the denture base material is another important factor in determining patient satisfaction. For example, it has been established that food temperature significantly affects the perception of taste [13-16]. Because the process of

eating consists of frequent and abrupt changes in the temperature of food, thermal characteristics of the denture base material can become important factors affecting the gustatory response, for example, chemical perception of taste, smell, textural perception, and temperature [17-19]. Recently, our research team investigated the effect of adding aluminum oxide powder on flexural strength and thermal diffusivity of heatpolymerized acrylic resin [20].

In this study, the work focuses on the development and characterization of new denture base material with adequate thermal properties and mechanical characteristics. The study involves the synthesis of gold nano-particle (AuNP) dispersions that is initially fractionated into smaller size distributions (~ 10 nm). The phase transferred to monomer solutions using polymethyl methacrylate (MMA) monomer phase transfer agents followed by the formation of polymer composite was conducted. The resulting nano-composites undergo various impact fracture strength, flexural strength, flexural modulus, and the yield distance of PMMA-AuNP composite impact and conventional denture base resins. Consecutively, other samples undergo the thermal diffusivity were evaluated.

2. Experimental

2.1 Materials.

All chemicals were of ACS analytical grade or better. Oleylamine (C19H37NH2; tech.,70%), the hydrogen tetrachloroaurate (III) hydrate (HAuCl4•xH2O), and all solvents (ACS Reagents), such as methanol, toluene and acetone, HPLC grade, were purchased from Aldrich (Milwaukee, WI) and were used as received without further purification. The MMA (>99%) was also purchased from Aldrich while the denture base was purchased from MAJOR Prodotti Dentari S.P.A., Italy, in the form of powder and liquid.

2.2 Samples Preparation.

The gold nanoparticles (AuNP) were synthesized as follows: 10 ml of 0.66 mmol of oleylamine was quickly injected into 100 ml of 1 mM boiling HAuCl4 solution in toluene.The solution quickly

changed color from pale yellow to burgundy. The heating was continued for 120 min. The obtained gold nanoparticles have the absorption maximum at 520 nm in toluene and 560 nm in MMA representing an average particle size of about 10 nm as shown in Figure 1.
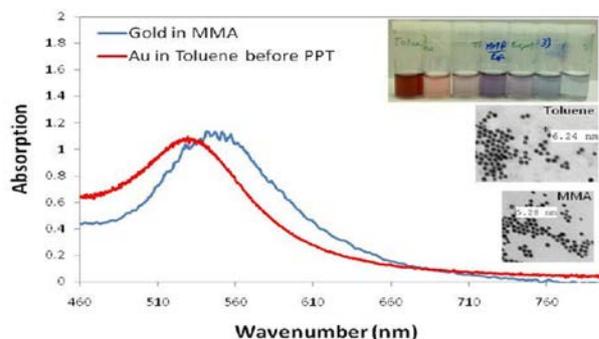

Figure 1. Absorption spectra of diluted solutions of the gold nanoparticles (AuNP) in Toluene (red) and in MMA (blue) and their TEM images confirm its distribution in a mono-disperse form.

The cross-linked PMMA samples were prepared by mixing 15g of PMMA polymer powder with 5ml (4.5g) of MMA monomer liquid; empirically, 4 powder parts to one of liquid in volume. Three different series of these materials were prepared for thermal diffusivity, for the tension stress tests to evaluate the flexural strength and flexural modulus and for the tension/compression tests to determine the glass transition (Tg) of the denture base polymer materials.

2.3 Thermal Diffusivity Measurement.

Thethermal conductivity of the fluidand the AuNP-PMMAcomposite materials were measured by Measuring System Lambdafrom PSL Systemtechnik GmbH (Pfeiffer SystemUnd Labortechnik). Cylindrical tested specimens with an embedded Pt-wirewereused to determine heat conductivity and thermal diffusivity of the investigated system over a physiologic temperature range (0 to 65°C) based on the in-stationary heat-wire method based on ASTM D2717 [31]. The samples were regulated to very homogeneous temperature allocations by performed all the measurements in aqueous media and by using thermostat unit LabTemp 30190 to exclude any convention influences (See Figure 2).
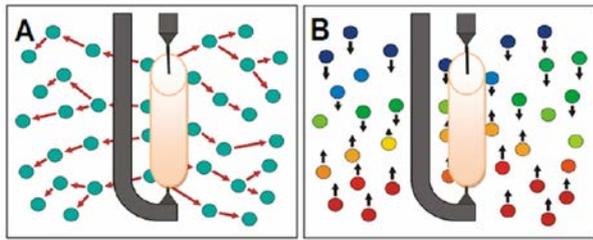
Figure 2. Temperature allocation. In A-homogeneous: The temperature is equal in the whole sample, so almost no convection takes place, while in B-inhomogeneous:The temperature is cool above and warmer on the bottom in which the temperature differences lead toconvention

2.4 Dynamic Mechanical Analysis (DMA)

The flexural and compression characteristics of the PMMA and AuNP-PMMA composite samples were measured by Dynamic Mechanical Analyzer (DMA), DMA25, from 01dB-MetraviB, France. The three-points bending and compression plates' specimen holders were used to investigated the tension stresses and glass transition temperature (Tg) of the samples.

3. Results And Dıscussıon

3.1 Synthesis and characterization of the AuNP-new composite materials

Solution of the suspended AuNP in methyl methacrylate has been added in a controlled manner to the PMMA resin where auto-polymerization of the MMA monomer was carried by traditional self-curing method to afford the composite resin. Figure 3 shows the AFM topography of the AuNPs immobilized PMMA films. The results indicted highly aggregated particles were obtained in the polymer films of a size ranging from 10 nm to about 40 nm. This aggregation could be due to the improper re-dispersed in the methyl methacrylate monomer solution.
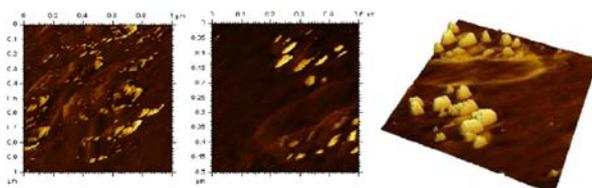

Figure 3. AFM micrographs of AuNPs in PMMA thin films. 3-D AFM images of AuNPs at different magnitude are shown.

While a proper re-dispersed AuNP in the methyl methacrylate monomer solution using long time ultrasonic. AFM micrographs confirmed that the morphology of AuNPs was retained by such ultrasonic action as shown in the following Figure.4.
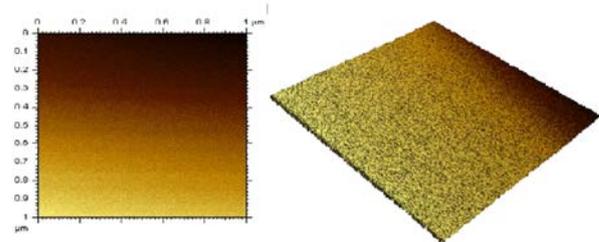

Figure 4. AFM micrographs of well re-dispresed AuNPs in PMMA thin films.

3.2 Sample preparation for Thermal Diffusion and Testing

The powder and liquid components of the resin was mixed into a pliable mass and then was loaded into the stone molds and pressed at 200 psi to form the resin cylinders. All specimens were conditioned at room temperature in distilled water for 24 hours before measurement. These specimens were carefully drilled with 1 mm drilling unit and then a platinum wire (0.1 mm wire diameter) was inserted at the center of these cylinders. Thermal diffusivity (Δ) was measured over a physiologic temperature range (0 to65 $^{\circ}$C) that corresponds to the temperatures of food and drink likely to be ingested in a typical meal based on the in-stationary heat-wire method. All the measurements were performed in aqueous media for composite materials as well as the pure denture base materials (See Figure 5). The results indicated thatthe addition of the gold nano-particles almost double the thermal conductivity of the pure PMMA resin materials.
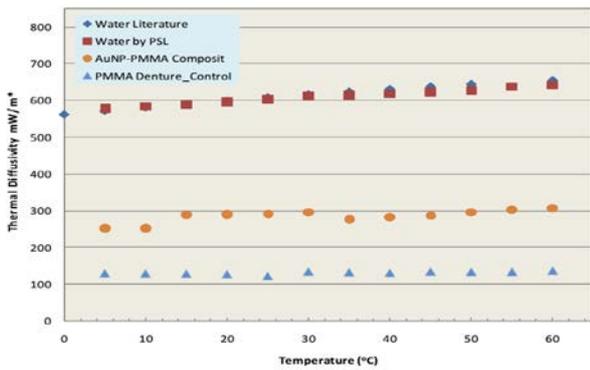
Figure 5. Thermal diffusivity of double distilled water, PMMA denture base control sample without any additives, and AuNP-PMMA composite with high loaded gold nano-particles.

3.3 Sample preparation for Dynamic Mechanical Analysis (DMA) and Testing

Different shapes of the testing specimens were prepared for the DMA testing by mixing of about 3 g of PMMA polymer powder and 1ml (~ 1 g) MMA monomer. The mixing time was 20 seconds. After 2 minutes from the start of mix, the material reached the dough stage for packing into the different specimen s' moulds. Polymerization took place at room temperature for about 9 min. in either a rectangular and cylindrical shape. The rectangular specimens were prepared and then hand-finished using a sanding Wheel and a polishing wheel to the final dimensions of ~1.8×20×50 mm. All specimens were prepared and stored in a water bath for 7 days to attain saturation. These specimens were divided into groups according to the loading of the AuNP per specimen; each group comprised 15 specimens of dimension ~1.8×3×50 mm. The fracture testing is then performed for specimen lies between the span and the load beams where the load is applied to the center by the loading nose producing three points bending at a rate 0.2 N/s and displacement variation of 1×10^{-6} m. The test is stopped when the specimen breaks. If the specimen does not break, the test is continued as far as possible and the stress at 5% (conventional deflection) is reported. The static force, displacement and stress, Stat F, Stat D and Stat C, respectively, of the blank and one of the AuNP loaded polymer samples are shown in Figure 6.
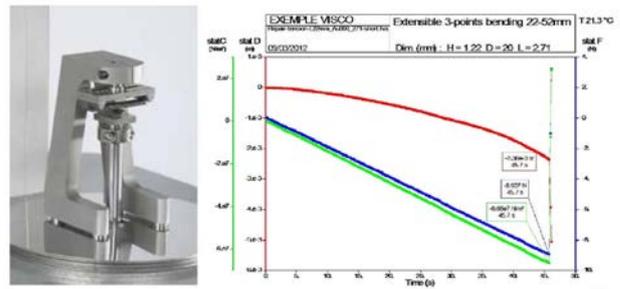

Figure 6. Specimens' holder of the rectangular samples for the three points bending tests (left) and the static force, displacement and stress of a blank PMMA polymer sample (right).

The results indicated that the mean flexural strength values of the self-polymerized acrylic resin were increases from about 50 MPa to 100 MPa by introducing the AuNP as shown in Table 1. These results were analyzed by one-way analysis of variance (ANOVA) and posthoc Tukey paired group comparison tests (P < 0.05).

Table 1. The fracture stress and elastic modulus of pure PMMA (Blank) and the loaded PMMA with a solution of high AuNP content approach 500 ppm in MMA.

Sample	Fracture Stress (10^{-6} N/m²)	Elastic Modulus (10^{-6} N/m²)
Pure PMMA	59.9 ± 2.8	1549 ± 276
AuNP- PMMA	91.1 ± 7.8	2080 ± 262

The cylindrical samples were prepared by backing the material after reaching its dough stage into a disposable syringe of an internal diameter 4.5 mm. After the polymerization is completed, groups each contains 15 specimens of a similar dimension of about 4.5×8 mm were fitted to the compression specimen holder. The loss factor, tan ⬜⬜ is the used to identify the peak for tangent delta as a function of temperature and the other related modulus, E' and E", storage and loss, respectively. These specimens were analyzed in the shear mode where they were subjected to frequency/temperature sweeps from 0.1 to 10 Hz at 0.1% strain under a nitrogen purge using a pre-defined temperature range from 26 to 190 oC. The E', tan tanδ and Tg of the Blank PMMA and one of the AuNP-PMMA composite are shown in Figure 7.
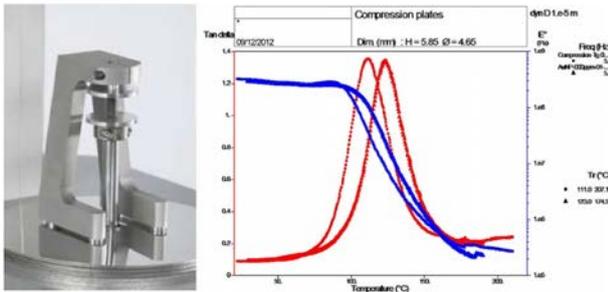
Figure 7. Specimens' holder of the cylinder samples for the tension/compression tests (left) and the storage modulus, tan samples (right) of a blank (square symbol) and a high concentration PMMA-AuNP (triangle symbol) samples using a 3-points bending

After mounting the sample in tension mode, the furnace was sealed off, scanned over a temperature range from 26°C to +190 °C at fixed frequency 1 Hz. The heating/ramp rate was 2 °C/min and strain amplitude 0.01mm within the linear viscoelastic region for all temperature scan tests. The mechanical loss factor (Tan δ) has been determined during the test as a function of increasing temperature to estimate the Tg-values as shown in Figure 8. The Tg-values were found to be significantly lower by the introduction of the AuNP than the unmodified acrylic resin by about 15°C. This decrease was found in proportion to the weight percentage of AuNP filler. This confirmed the proper distribution of AuNP through the PMMA polymer matrix as they play the main role as a pathway for heat conduction.

4. Conclusıon

In this approach, the efficient impregnation of Au nanoparticles to the PMMA resin is presented. The AFM images confirmed the uniform dispersion of AuNPs in PMMA polymer, which was further supported by a UV absorption band obtained at 540 nm and the TEM spectroscopy. Moreover, the results indicated that the addition of the gold nanoparticles almost doubles the thermal conductivity and the flexural stresses of the pure PMMA resin materials. The results also indicated that the remarkable reduction in the glass transition of the highest loaded AuNP specimens to about 15°C. Thus, increasing the flexural strength and heat transfer characteristics of the acrylic resin base material could lead to more satisfaction of the patients

5. Ackowledgement

6. References

Brady, A. P.; Lee, H.; Orlowski, J. A. "Thermal conductivity studies of composite dental restorative materials." J. Biomed. Mater. Res. 1974; 8: 471-85.

Craig, R. G. "Restorative dental materials." St Louis: Mosby C. V.; 1993.

Diwan, R. "Materials Prescribed in the Management of Edentulous Patients". In: ZarbG., Bolander C. L. (ed): "Prosthodontic Treatment for Edentulous Patients." 12th edn St. Louis, Mosby C. V., 2004: 190-207.

Ellakwa, A. E.; Morsy , M. A.; El-Sheikh, A. M. "Effect of aluminum oxide addition on the flexural strength and thermal diffusivity of heat-polymerized acrylic resin." J. Prosthodont. 2008; 17(6): 439-44.

Green, B. G.; Frankmann, S. P. "The effect of cooling on the perception of carbohydrate and intensive sweeteners." Physiol. Behav. 1988; 43: 515-9.

Hisada, K.; Takeshita, T. "Poly(methyl methacrylate) (PMMA)-based denture base materials with good biocompatibility" Jpn. Kokai Tokkyo Koho 2007, JP 2007332044 A 20071227.

Ishida, H.; Nakagaki, N. "Resin composites as dental materials" Jpn. Kokai Tokkyo Koho 2006, JP 2006069924 A 20060316.

Jinno, S.; Suzuki, T.; Ishikawa, A.; Hayashi, T.; Deguchi, M.; Ito, M.; Nakano, K.;Kawai, T.; Noguchi, T. "Influence of newly developed resin and MMA resin on Mouse fibroblasts cellular viability" Key Engineering Materials 2006, 309-311(Pt. 2,Bioceramics), 817-820.

Kurata, S.; Nihei, T.; Umemoto, K. "Study on the development of antibacterial dental resin using silver methacrylate as an antibacterial substance. Part 1. Solubility of silver methacrylate in MMA and the mechanical strength of the resin with silver methacrylate" Shika Zairyo, Kikai 2005, 24(6), 466-470.

Nakamura, M.; Kurihara, K. "Temperature dependence of amiloride-sensitive and insensitive components of rat taste nerve response to NaCl." Brain Res. 1988; 15:159-64.

Nakamura, M.; Kurihara, K. Differential temperature dependence of taste nevre responses to various taste stimuli in dogs and rats." Am. J. Physiol. 1991; 261 (6 Pt2): R1402-8.

Narva, K. K.; Lassila, L. V. J.; Vallittu, P. K. "Flexural fatigue of denture base polymer with fiber-reinforced composite reinforcement Composites" Part A: Applied Science and Manufacturing 2005, 36A(9), 1275-1281.

Narva, K. K.; Lassila, L. V. J.; Vallittu, P. K. "Flexural fatigue of denture base polymer with fiber-reinforced composite reinforcement Composites" Part A: Applied Science and Manufacturing 2005, 36A(9), 1275-1281.

Narva KK, Lassila LV, Vallittu PK. The static strength and modulus of fiber reinforced denture base polymer. Dent Mater 2005;21(5):421-8

Ogawa, T.; Hasegawa, A. "Effect of curing environment on mechanical properties and polymerizing behaviour of methyl methacrylate autopolymerizing resin" Journal of Oral Rehabilitation 2005, 32(3), 221-226.

Phoenix, R. D. "Denture Base Materials." Dent. Clin. North Am. 1996; 40: 113-120.

Ren, Y.; Chen, H.; Li, B.; Li, G. "Antimicrobial activity of polymethyl methacrylate denture base with Ag-nano-TiO2 in vitro" Zhejiang Yixue 2007, 29(10), 1045-1047.

Shklar, G.; Chernin, D. (ed). Chapter 22, "Dental Science and Practice in the Twentieth Century, Part 2. A Sourcebook of Dental Medicine." Wabam, Maro Publications, 2002.

Zappini G, Kammann A, Wachter W. Comparison of fracture tests of denture base materials. J Prosthetic Dent 2003;90(6):578-85

Zellner, D. A.; Stewart, W. F. "Rozin P, Brown JM. Effect of temperature and expectations on liking for beverages." Physiol. Behav. 1988; 44: 61-8.