Journal of the Serbian Chemical Society

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*J. Serb. Chem. Soc.* *83* (1) 75–91 (2018)
*JSCS-5060*

UDC 661.183.8+678.744:620.3:543.57:616.314
*Original scientific paper*

# Effect of nano- and micro-alumina fillers on some properties of poly(methyl methacrylate) denture base composites

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(Received 18 January, revised 21 April, accepted 26 April 2017)

*Abstract*: This research investigated the effects of alumina ($Al_2O_3$) micro- and nano-particles on poly(methyl methacrylate) (PMMA) denture base. $Al_2O_3$ was surface treated using (3-methacryloxypropyl)trimethoxysilane ($\gamma$-MPS), added to methyl methacrylate (MMA), and mixed with PMMA powder. The filler volume fractions in the micro-composites were 0.5, 1, 2, 5 and 7 wt. %, whereas those in the nano-composites were 0.13, 0.25, 0.5, 1, 2 and 5 wt. %. The treated fillers were examined using Fourier transform infrared spectroscopy (FTIR). The influence of filler size and loading on mechanical properties was studied using fracture toughness and flexural tests. The thermal stability of the PMMA/$Al_2O_3$ composites was investigated using thermogravimetric analysis (TGA). In addition, the water absorption and solubility characteristic of the prepared composites was also investigated. The FTIR spectra showed new absorption bands, indicating the occurrence of surface modifications. Both micro- and nanoscale particles showed increased fracture toughness. The maximum value of 2.02 $MPa\cdot m^{1/2}$ was achieved with the addition of 0.5 wt. % nano-$Al_2O_3$, which accounts for a 39 % increase. In contrast to the flexural strength, the flexural modulus improved with increasing filler content. The micro-composites showed higher thermal stability than nano-composites. The water absorption and solubility of the prepared composites were slightly higher than those of the control. The use of low concentrations of $Al_2O_3$ nanoparticles may be of considerable interest in future studies to improve the mechanical properties of PMMA denture base.

*Keywords*: PMMA denture base; nano-particles; mechanical properties; water absorption; water solubility; toughening mechanisms.

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https://doi.org/10.2298/JSC170118056K

## INTRODUCTION

Poly(methyl methacrylate) (PMMA) is the most commonly used material for denture construction since its introduction in 1936 by Dr. Walter Wright.[1,2] PMMA features low cost,[1] optical properties,[3] biocompatibility, aesthetic appearance, favorable stability in the oral environment, and ease in processing, finishing, and polishing. PMMA also does not require expensive equipment[4] and is repairable,[5] free from toxicity, and easily pigmented.[6,7] Moreover, PMMA exhibits color and shape stability, it is odorless, and tasteless and does not cause irritation of tissues.[8] To date, the mechanical properties of pure PMMA denture base do not meet the required level for denture fabrication.[4,9,10] PMMA exhibits poor strength,[3,5,11] low resistance impact,[5,12] low flexural strength,[1,5,12] insufficient ductility,[13] crazing,[14] susceptibility to distortion,[10] tendency to aging,[15] insufficient surface hardness, and poor antibacterial property, which can lead to fracture.[1] Several attempts were made to improve the mechanical properties of PMMA dentures and solve denture fracture problem.[4,16–21] These attempts include addition of polyfunctional crosslinking agents, such as polyethylene glycol dimethacrylate[13] or incorporation of metal wires,[1,4,5,13] mesh[1] or plates,[4] metal powders[4,13] or rubber-toughening agents[4,5,13] or fillers; commonly applied fillers include fibers,[1,4,5,13] nanoparticles[1,11] and whiskers.[1]

Fillers play a significant role in production of composites with desired properties and can decrease processing costs. Inorganic fillers with size in the micrometer range are widely used to improve the mechanical properties of traditional polymer composites. The properties can be tailored by modifying the volume fraction, shape, and size of filler particles.[21] Antunes *et al.* determined the influence of particle volume fraction and size on the wear loss of polyester resin. The composite reinforced with silica, with average size of 6 μm, exhibited the highest wear resistance; moreover, the abrasion resistance of the composite increased with decreasing volume fraction of the filler particles.[20] PMMA denture base incorporated with $Al_2O_3$/$ZrO_2$ micro-particles possessed high fracture toughness and flexural properties.[17] Ellakwa *et al.* investigated the effect of $Al_2O_3$ powder addition on the flexural strength of PMMA denture base; the flexural strength of the composite significantly increased after incorporation of 10% $Al_2O_3$ which accounts for more than 30% increase.[18] Previous studies also demonstrated that incorporation of $Al_2O_3$ micro-particles into PMMA denture base led to improvements in flexural strength, wear resistance, and hardness.[7,16] The use of $Al_2O_3$ with small particle size can efficiently enhance the impact strength. In another study, the thermal conductivity and tensile strength of the composites increased with decreasing particle size.[19] The Vickers hardness and flexural modulus of the dental resin composites mixed with $Al_2O_3$ micro-particles increased to 63 and 280%, respectively.[22] The addition of $Al_2O_3$ particles with 18–23 μm diameter improved the mechanical properties of PMMA denture base composites. The experimental results showed about 24 % increase in flexural strength, and 76.3% decrease in wear volume loss of the composites.[16] Vojdani *et al.* evaluated the effects of adding $Al_2O_3$, with an average particle size of 3 μm, on the flexural strength, surface hardness, and roughness of PMMA denture base; the use of 2.5 wt. % $Al_2O_3$ resulted in 6.4 % increase in flexural strength, 15 % increase in hardness and did not adversely affect the surface roughness of the composites.[7]

Reinforcing polymers with nano-particle fillers can more effectively improve the mechanical properties of the composites[23–27] than incorporating microparticles.[24,27] Zhang *et al.* reported that the fracture toughness, microhardness, and modulus of epoxy increased upon the addition of $SiO_2$ nanoparticles.[28] The wear resistance can also be improved by adding nano-SiC particles.[29] Kim and Moon utilized $TiO_2$ with an average size of 20 nm to improve the properties of epoxy resin. The results showed an increase in tensile strength and modulus of the film-shaped nanocomposites.[30] Balos *et al.* investigated the effect of adding low amounts of nanosilica (7 nm) on the mechanical properties of PMMA denture base; incorporation of the lowest nanosilica content led to the maximum fracture toughness and microhardness values of the PMMA denture base.[11] Researchers also found that incorporation of $Al_2O_3$ nano-particles enhanced the mechanical properties of polymers.[31,32] Hassan *et al.* compared the effects of two differently shaped $Al_2O_3$ nano-particles (spherical and whisker) on the mechanical properties of PMMA denture base; both nano-particles improved the mechanical properties of the composites. In particular, the mechanical properties were significantly enhanced after the addition of whiskers at volume fraction of 3 wt. %.[33] Foroutan *et al.* reported that adding $Al_2O_3$ nano-particles increased the flexural and tensile strength of dental composite materials.[24] In addition, Yahya *et al.* stated that the application of $Al_2O_3$ and ZnO nano-particles as filler increased the hardness of dental amalgam.[34] Thorat *et al.* reported that ultra-rigid nano-particles, such as $Al_2O_3$ (and possibly $ZrO_2$ and diamond), can be potentially used to enhance the elastic properties of dental composite materials.[35] Patel *et al.* synthesized and investigated the thermal and mechanical properties of PC(polycarbonate)/PMMA–$Al_2O_3$ nano-composites using $Al_2O_3$ nano-particles (with size of 10–20 nm); the results showed an improvement in both mechanical and thermal properties.[32] Foroutan *et al.* compared the effects of using micro- and nano-sized $Al_2O_3$ particles as reinforcing fillers on the mechanical properties of dental composite samples. In general, the use of nano-sized $Al_2O_3$ considerably improved the mechanical properties of the composites.[24] Similarly, Thorat *et al.* studied the effect of two different classes of particle size (*i.e.*, nano- and micro-sized) on the mechanical properties of dental composites; the use of $Al_2O_3$ particles (60 nm) increased the Young's modulus of the composite.[35] Moreover, McElwain *et al.* reported that $Al_2O_3$ nano-composite is more abrasion resistant to the mating steel counter surfaces compared with $Al_2O_3$ micro-composite.[36] The use of $Al_2O_3$ particles (40 nm) as fillers improved the hardness, tensile modulus, tensile strength, and elongation of polyetherimide.[31] Safi investigated the changes in the glass transition temperature, *E* modulus, and coefficient of thermal expansion (CTE) of PMMA denture base after adding $Al_2O_3$, $TiO_2$ and $SiO_2$ nano-fillers; the results showed that the nano-composite is more thermally and mechanically stable than the neat PMMA denture base.[37] Saboktakin *et al.* incorporated $Al_2O_3$ nano-particles to PMMA denture base to investigate the effects of new surface modifier on some mechanical properties. The results of dynamic mechanical properties indicated that the addition of $Al_2O_3$ nano-particles increased the storage moduli.[38] In the present study, an attempt was made to improve the mechanical properties of the PMMA denture base. To this end, $Al_2O_3$ micro- and nano-particles fillers were chosen as the preferred additives to this material. Different ratios of silanized $Al_2O_3$ micro- and nano-particles fillers were employed, and the aim of this study was to evaluate their effects on the mechanical properties, water absorption, and solubility of PMMA denture base composites.

## EXPERIMENTAL

### *Materials*

The following materials were used in this study: PMMA with weight average molecular weight of $\bar{M}_w$ = 996,000 g $mol^{-1}$ (product No. 182265, Sigma–Aldrich) and 0.5 % benzoyl peroxide (BPO, product No. 513474, Sigma–Aldrich). The liquid consisted of methyl methacrylate (MMA, product No. M55909, Sigma–Aldrich) stabilized with ≤ 30 ppm hydroquinone monomethyl ether as inhibitor and ethylene glycol dimethacrylate (EGDMA, product No. 335681, Sigma–Aldrich). $Al_2O_3$ powder was supplied by Inframat Advanced Materials (USA): product No. 26R-0822AOFA, with an average particle size of 6 μm and a specific surface area of 0.5 $m^2$ $g^{-1}$, and product No. 26N-0801G with an average particle size of 7 nm; the mean diameter of the agglomerates was 65 nm, and a specific surface area of 2.1 $m^2$ $g^{-1}$. (3-Methacryloxypropyl)trimethoxysilane ($\gamma$-MPS, Sigma–Aldrich) was of ≥ 98 % purity.

### *Sample preparation*

*Treatment of filler particle surface*. The treatment solution was prepared by adding 10 wt. % $\gamma$-MPS relative to the filler to a solution of 70/30 wt. % acetone/water. The solution was added to $Al_2O_3$ filler and stirred for approximately 1 h using a magnetic stirrer (C-MAG HS 7, IKA, Malaysia). The mixture was filtered, washed with acetone, and dried in an oven at 80 °C for 24 h.[22]

*Addition of fillers to MMA*. Monomer was prepared by adding MMA to EGDMA at a weight ratio of 9:1. An electronic balance (Mettler Toledo, AL204, Switzerland), with accuracy of 0.0001 g, was used. Prior to mixing with the resin, the modified $Al_2O_3$ fillers were dispersed in the monomer. The mixture was stirred for 15 min using a magnetic stirrer (C-MAG HS 7, IKA, Malaysia) and treated in an ultrasonic bath (Wisd WUC-A03, DAIHAN Scientific, Korea) for 10 min. The suspension was stirred again for 10 min.

*Mixing of acrylic*. Powder was prepared by adding BPO to PMMA. The powder was immediately mixed with the suspension of MMA and $Al_2O_3$ to minimize the possibility of agglomeration and phase separation. The proportion of mixing powder/liquid was set at 2.5:1. The powder and liquid were mixed in accordance with the standard prescription of dental laboratory practice. Upon reaching the dough stage, the mixture was packed into a mold and placed under a dental flask press (hydraulic press 660, Silfradent, Italy) at 14 MPa for 20 min. The mold was immersed in water bath (Wisd WB-11, Daihan Scientific, Korea) at room temperature. The temperature was slowly increased to 75 °C and held for 90 min and then to 100 °C and held for 30 min. The mold was bench cooled to room temperature before opening. The acrylic specimens were carefully removed from the mold and finished using silicon carbide abrasive papers. A total of 120 samples were prepared and categorized into 12 groups. Table I lists the compositions of the PMMA denture base composites, where M represents the composites containing $Al_2O_3$ micro-particles (6 μm) and N denotes the composites containing $Al_2O_3$ nano-particles (7 nm).

TABLE I. Formulation of the PMMA denture base composites

| Group | Filler content, wt. % |
|---|---|
| PMMA | 0 |
| M0.5 | 0.5 |
| M1 | 1 |
| M2 | 2 |
| M5 | 5 |
| M7 | 7 |
| N0.13 | 0.13 |
| N0.25 | 0.25 |
| N0.5 | 0.5 |
| N1 | 1 |
| N2 | 2 |
| N5 | 5 |

*Examination of the samples*

*Morphology*. The size and morphology of $Al_2O_3$ particles, and their dispersion in the nano-composites were visualized either by transmission electron microscopy (TEM) (Philips-CM 12) or a field emission scanning electron microscope (FESEM, Zeiss SupraTM). For TEM investigations, the powder was suspended in ethanol, and then a droplet of the suspension was placed on a coated grid. The ethanol then subsequently evaporated at room temperature. For SEM, gold was deposited on the fillers and fractured surfaces of the samples.

*Fourier transform infrared spectroscopy (FTIR)*. To confirm the silanization procedure, the $Al_2O_3$ particles were analyzed by Fourier transformed infrared (FTIR) spectroscopy, conducted in a Perkin–Elmer Spectrum One. The FTIR spectra were obtained at room temperature, in the wavenumber region between 650 and 4000 $cm^{-1}$.

*Fracture toughness testing*. Fracture toughness was evaluated using single-edge notch bending (SENB) specimens according to ISO 13586:2000. A sharp pre-crack was introduced into the notch *via* tapping of a sharp razor blade. The specimens had 80 mm length, 20 mm width, 4 mm thickness and 4 mm notch length. The support span was set at 64 mm. The tests were performed under a constant displacement rate of 1.00 mm $min^{-1}$ at the loading point by using a universal testing machine (Instron, 3367, USA). At least five samples for each formulation were examined to determine the optimal loading (wt. %). The fracture toughness ($K_{IC}$) was calculated using the following equation:

$$K_{\mathrm{IC}} = \frac{3PSa^{1/2}y}{2tw^2} \tag{1}$$

where $P$ = load at peak, N; $S$ = span length, mm; $a$ = notch length, mm; $y$ = a geometrical correction factor; $t$ = specimen thickness, mm and $w$ = specimen width, mm.

*Flexural strength testing*. The flexural strength of the specimens was determined using a universal testing machine (Instron, 3367, USA) in accordance with ASTM D790-86. The support span was set at 50 mm, and the diameter of the loading nose and support was set at 20 and 10 mm, respectively. Tests were conducted at a crosshead speed of 2 mm min$^{-1}$. At least five samples for each formulation were examined. The flexural strength was calculated using the following equation:

$$S = \frac{3PI}{2bd^2} \tag{2}$$

where $S$ = flexural strength, N mm$^{-2}$; $P$ = load at fracture, N; $I$ = span length, mm; $b$ = specimen width, mm and $d$ = specimen thickness, mm.

### *Sample testing*

*Water absorption*. Water absorption tests were conducted according to ISO 1567-2000. Five specimens from the best composition of both groups (*i.e.*, M2 and N0.5) were dried in a vacuum oven at 37±1 °C for 24 h and kept in a desiccator containing silica gel for 24 h. When constant mass was reached ($W_0$), the samples were weighed using an electronic balance (Mettler Toledo, AL204, Switzerland), with a precision of 0.0001 mg. The specimens were immersed in distilled water at a temperature of 37±1 °C for 1, 7, 14, 21 and 28 days. After each period, the specimens were removed from the water, dried, and weighed again ($W_1$). Water absorption was calculated as follows:

$$\text{Change in weight, \%} = 100\frac{W_1 - W_0}{W_0} \tag{3}$$

*Thermogravimetric analysis (TGA)*. The thermal stability was determined by TGA using a Perkin Elmer TGA 6 instrument, at a heating rate of 10 °C min$^{-1}$ under a nitrogen atmosphere (50 mL/min) in the temperature range 30–600 °C.

*Water solubility*. The water solubility test was conducted in accordance with ISO 1567--2000. Five specimens from the best composition of both groups (*i.e.*, M2 and N0.5) were dried in a vacuum oven at 37±1 °C for 24 h and kept in a desiccator containing silica gel for 24 h. When a constant mass was reached ($W_0$), the samples were weighed using an electronic balance (Mettler Toledo, AL204, Switzerland), with a precision of 0.0001 mg. The specimens were immersed in distilled water at 37±1 °C for 28 days. All specimens were then removed from the water and dried. The specimens were reconditioned to a constant mass in a desiccator. The reconditioned mass was recorded as $W_1$. The change in weight was calculated as follows:

$$\text{Change in weight, \%} = 100\frac{W_0 - W_1}{W_0} \tag{4}$$

where $W_0$ is the weight of the specimen before immersion, and $W_1$ is the reconditioned mass.

### *Statistical analysis*

One-way ANOVA was performed to detect significant effects of the variables. The Tukey multiple comparison was used to compare data at a $p$ value of 0.05.

## RESULTS

FESEM micrographs of the $Al_2O_3$ micro-particles and TEM images of the $Al_2O_3$ nano-particles are presented in Fig. 1. Nano-particles dispersion in a PMMA resin is difficult due to the van der Waals forces between the nano-particles. Scanning electron microscopy (SEM) was conducted to verify the dispersion quality of the $Al_2O_3$ nano-particles within the PMMA matrix. As can be seen in Fig. 2, the $Al_2O_3$ nano-particles as received from the supplier were highly agglomerated, the mean diameter (65 μm) was measured using an image analysis tool. However, the particles were highly dispersed into the PMMA matrix. Hence, the indicated mixing technique was effective in breaking the agglomerate of the particles.

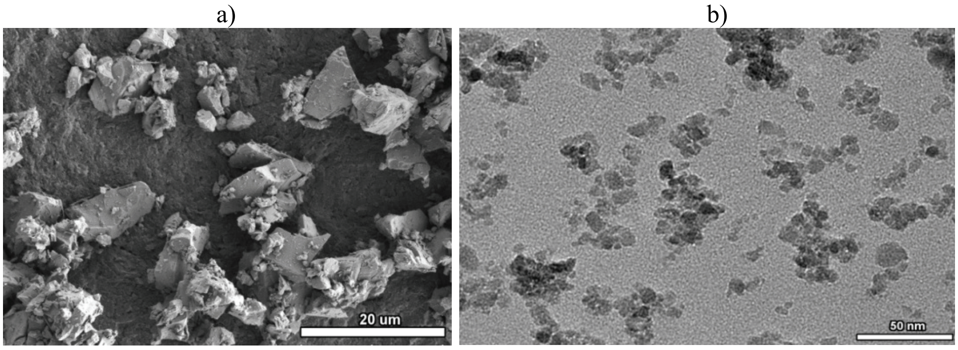

Fig. 1. The micrographs of $Al_2O_3$ particles: a) FESEM of $Al_2O_3$ micro-particles and b) TEM of $Al_2O_3$ nano-particles.

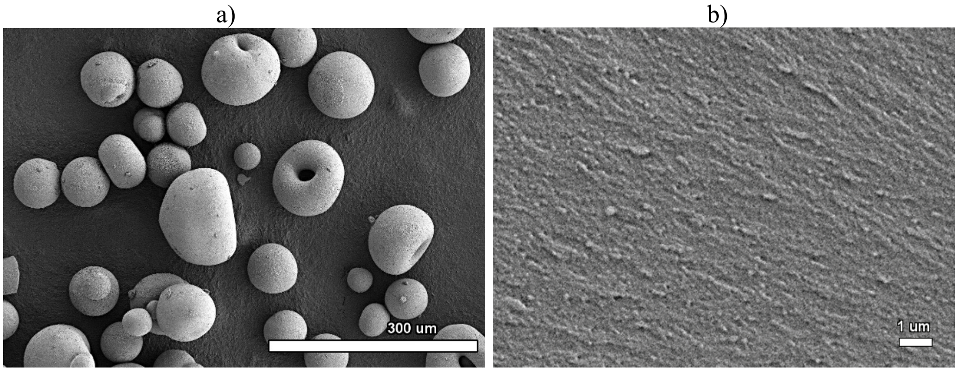

Fig. 2. FESEM micrographs of $Al_2O_3$ nano-particles before and after adding to PMMA: a) the spherical agglomerates of $Al_2O_3$ nano-particles and b) fracture surface of PMMA nano-composite.

The FTIR spectra of $Al_2O_3$ particles before and after treatment with $\gamma$-MPS are shown in Fig. 3. The spectra revealed the presence of numerous hydroxy groups as indicated by the large OH stretching band at 3547 and 751 cm$^{-1}$.[39,40] The bands at 3469, 3422 and 975 cm$^{-1}$ are due to silanol groups (Si/OH) present on the $Al_2O_3$ surface.[41,42] The absorption peak at 1702 cm$^{-1}$ indicates the stretching vibrations of C=O groups.[43] The peak at 1457 cm$^{-1}$ is due to the bending vibration of $CH_2$ group.[44] In addition, the band at 1409 cm$^{-1}$ is due to C=O stretching, indicating the presence of silane groups on the filler surface.[22] The characteristic peaks at 1024 and 1176 cm$^{-1}$, indicate the formation of Si–O–Si groups.[45–47] The Si–O peaks at 1058 and 1302 cm$^{-1}$ indicated the formation of Si–O–$Al_2O_3$ bonds.[42,48]

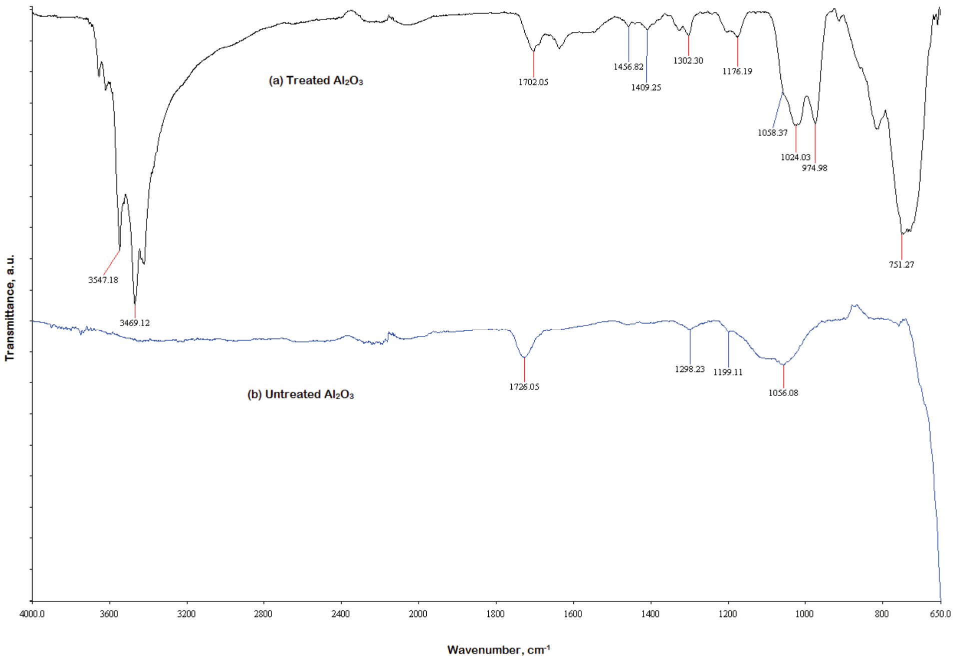

Fig. 3. FTIR spectra of $Al_2O_3$ particles before and after silane treatment.

The fracture toughness values of the micro- and nano-composites are shown in Fig. 4. All samples displayed increased fracture toughness. The Tukey test showed that the fracture toughness was significantly different ($p < 0.05$) between the tested groups, in particular between N0.5 and the control (2.02 and 1.63 MPa m$^{1/2}$, respectively, accounting for a 39 % increase), and N0.5 and M1. However, these improvements decreased with increasing filler loading.

The flexural test results are shown in Fig. 5. The flexural strength decreased with increasing content of $Al_2O_3$ particles in the acrylic resin. Based on the Tukey test, the flexural strength was significantly different ($p < 0.05$) among the tested groups, particularly between N5 and M0.5, and N5 and M1.

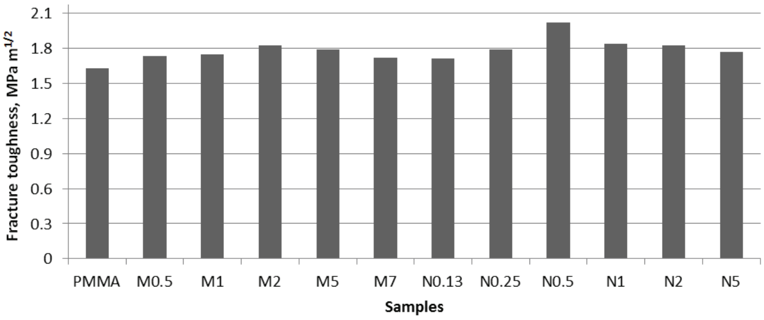

Fig. 4. Fracture toughness of $Al_2O_3$ micro- and nano-composites.

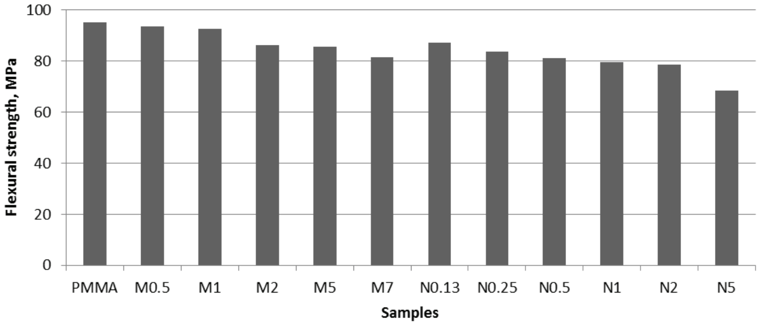

Fig. 5. Flexural strength of $Al_2O_3$ micro- and nano-composites.

Flexural modulus increased slightly with filler content. The Tukey test showed that the flexural modulus was significantly different ($p < 0.05$) between the tested groups. The results of the flexural modulus are displayed in Fig. 6.

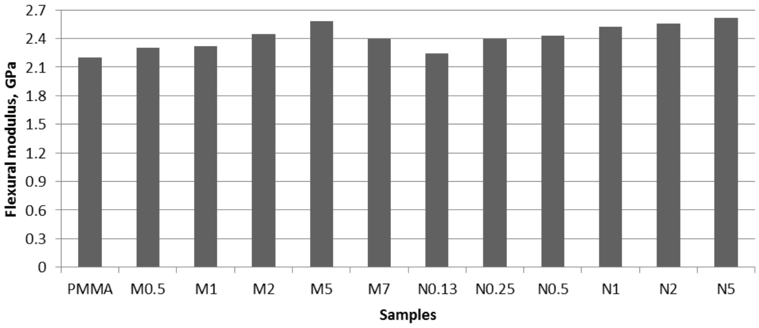

Fig. 6. Flexural modulus of $Al_2O_3$ micro- and nano-composites.

The TG curves of PMMA and its composites are shown in Fig. 7. The micro-composites had the highest degradation temperature followed by the nano-composites, whereas pure PMMA exhibited the lowest temperature. Compared to pure PMMA, the PMMA/$Al_2O_3$ composites were thermally more stable.

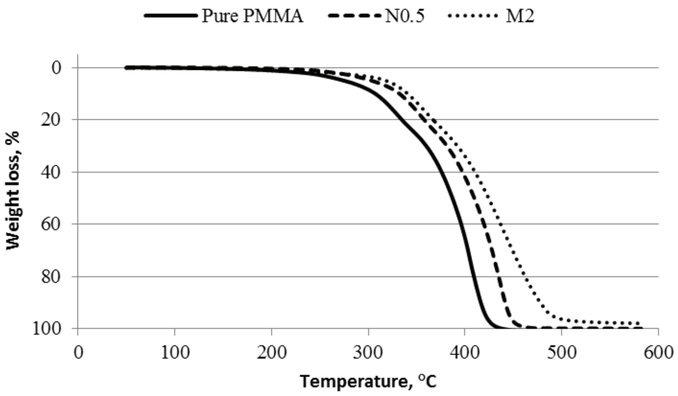

Fig. 7. TG curves of pure PMMA and the PMMA/$Al_2O_3$ composites.

The water absorption and solubility values were slightly higher for M2 and N0.5 than those in the control. Based on the Tukey test, water absorption and solubility did not significantly differ after storage in water for 4 weeks ($p > 0.05$). A statistical summary for the water absorption and solubility tests is presented in Table II.

TABLE II. Statistical summary for water absorption and solubility tests; ISO standard (1567-2000) value: the maximum increase in the volumic mass was 32 μg $mm^{-3}$ and the maximum loss in volumic mass was 1.6 μg $mm^{-3}$

| Group | Water sorption, μg $mm^{-3}$ | Water solubility, μg $mm^{-3}$ |
|---|---|---|
| PMMA | 14.3 | 1 |
| M2 | 15.6 | 1.1 |
| N0.5 | 15.8 | 1.1 |

## DISCUSSION

PMMA is the most widely used material for denture construction[4] because of its excellent properties, such as aesthetics,[10] biocompatibility, teeth adhesion, and low cost.[3] However, PMMA cannot satisfy the mechanical requirements of dentures.[10,13] PMMA is susceptible to fracture due to its poor strength,[5] low impact,[5,12,13] and inferior flexural strength.[1,5,13] The present study evaluated the effects of different loading of $Al_2O_3$ micro- and nano-particles on fracture toughness, flexural properties, and water absorption and solubility of PMMA denture base. The PMMA denture base could be reinforced by incorporating metal wires,[1,4,5] mesh[1] or plates,[4] metal powder[4] or rubber-toughening agents,[4,5] or fillers, such as fibers,[1,4,5] nanoparticles,[1,11] and whiskers.[1] Filler loading, type, size and morphology are important parameters that should be considered to enhance the mechanical properties of dental composites. In the present study, $Al_2O_3$ fillers, with particle sizes of 6 μm and 7 nm, were used at different loadings. The filler volume fraction was low to achieve dispersion levels. Eleven groups were prepared: five groups were filled with micro-particles, and six groups were filled with nano-particles. Inorganic fillers exhibit hydrophilicity,[49] large specific surface area, high surface energy, and active chemical properties, which lead to agglomeration.[9] The lack of chemical bonding between the filler particles and PMMA is another challenge in the incorporation of $Al_2O_3$ fillers into PMMA.[50] PMMA is hydrophobic,[51] and the added $Al_2O_3$ particles are hydrophilic;[52] as such, the filler surface should be modified with a silane coupling agent to convert the filler surface into a hydrophobic one,[53] reduce agglomeration, enhance filler dispersion, and improve interfacial adhesion properties between organic and inorganic phases.[54]

In the present study, the surface of the $Al_2O_3$ particles was modified using the silane coupling agent 3-(trimethoxysilyl)propyl methacrylate (TMSPMA). All composite samples showed higher fracture toughness values compared with the control samples. However, the flexural strength decreased, while flexural modulus increased as the filler loading was amplified.[55] High mechanical property, water absorption, and solubility are among the most important properties that should be considered to obtain a successful denture because it is subjected to various forces in the oral cavity, which is an aqueous environment. Control group possessed a fracture toughness value of 1.63 MPa $m^{1/2}$. The highest fracture toughness in the nanocomposites was observed for N0.5 (2.02 MPa $m^{1/2}$) and in the microcomposites M2 had the highest fracture toughness (1.82 MPa $m^{1/2}$). The fracture toughness of the composites increased to 39 % upon the addition of 0.5 wt. % nano-$Al_2O_3$ and to approximately 11 % after adding 2 wt. % micro--$Al_2O_3$. These values gradually decreased with increasing percentage of incorporated $Al_2O_3$. As reported by Topouzi *et al.*, this phenomenon (*i.e.*, decreasing fracture toughness) could be attributed to improper dispersion of the filler in the PMMA matrix, resulting in agglomeration and the formation of microcracks.[56] The improvement in fracture toughness could be attributed to incorporation of high-strength fillers[57] and silanization.[58] In addition, resistance to crack propagation increased as a result of toughening mechanisms, such as, crack deflection,[59–61] crack pinning/bowing,[59] matrix–filler interactions[59,62] and crack bridging.[60,63] The control showed higher flexural strength than the experimental groups (95.02 MPa). Increasing the amount of the micro- and nano-$Al_2O_3$ fillers decreased the flexural strength; this phenomenon could be explained by the presence of agglomerates and voids, which are initiating factors for failure.[64,65]

High filler fractions led to more filler–filler interaction than filler–matrix interaction; consequently, agglomeration serve as a points of stress concentration, which may lead to inappropriate stress distribution.[66] Under load, the agglomeration will constrain the movement of molecular deformation[67] and finally decrease the flexural strength.[65] Furthermore, the incorporation of fillers to PMMA could adversely affect the degree of conversion,[50] thereby increasing the residual monomer that acts as a plasticizer.[68] Moreover, the addition of additional fillers, such as $Al_2O_3$, to PMMA decreased flexural strength because they act as impurities.[50,69] Many researchers attempted to improve the mechanical properties of PMMA denture base. The present results are consistent with the experimental findings reported by Asar *et al.*, who added $Al_2O_3$ micro-sized filler (12.4 μm) to PMMA denture base; the fracture toughness increased at a volume fraction of 2 wt. %.[13] Ahmed and Ebrahim incorporated $ZrO_2$ nano-sized filler (5–15 nm) into PMMA denture base; the fracture toughness significantly increased with a loading of 7 wt. %.[70] A similar result was obtained by introducing nanodiamond filler (clusters 20–60 nm) into PMMA acrylic resin; samples added with 0.1 wt. % filler exhibited the highest fracture toughness.[71] Furthermore, the present results on flexural strength are in agreement with those obtained by Shyang *et al.*, who added hydroxyapatite (HA) filler (18.1 μm) at different loadings (5, 10, 15 and 20 wt. %) to PMMA denture base; the flexural strength values decreased with increasing filler content.[66] In addition, two studies showed that the flexural strength of neat resins was higher than that of nanocomposites. The first study was conducted by Sodagar *et al.*, who incorporated $TiO_2$ (21 nm), $SiO_2$ (20 nm), and $TiO_2$ with $SiO_2$ at two concentrations (1 and 0.5 wt. %) into PMMA denture base.[50] In the second study, $TiO_2$ (21 nm) was added to PMMA denture base at a volume fraction of 5 wt. %.[4]

The addition of $Al_2O_3$ fillers into dental composites leads to improvements in flexural modulus.[72] In the current study, the flexural modulus of the PMMA composites increased to 19 % by the addition of 5 wt. % nano-$Al_2O_3$ and to 17.3 % after the addition of 5 wt. % micro-$Al_2O_3$. However, the addition of 7 wt. % micro-$Al_2O_3$ caused a decrease in the modulus value. These results are consistent with those reported by Foroutan *et al.*, who added micro-$Al_2O_3$ (<10 μm) at different loadings (45, 50, 55 and 60 wt. %), and nano-$Al_2O_3$ (25–40 nm) at different volume fractions (10, 20 and 30 wt. %) to dental composite; the flexural modulus values increased with increasing filler content. However, a composite containing 60 wt. % micro-$Al_2O_3$ exhibited a decrease in the modulus values.[24] Hamizah *et al.* investigated the effect of the addition of 16 wt. % HA (5.46 μm) and glass–ceramic (12.64 μm) fillers on PMMA bone cement; the flexural modulus of the composite increased by 22 and 19.7 %, respectively.[55] The increase in flexural modulus is a consequence of the addition of an inorganic material with a stiff structure,[55] which allows the polymer matrix to transfer stress to the stiffer filler particles,[73] in addition to the restriction of polymer movement, due to matrix–filler interactions.[74] The increase in flexural modulus with the increasing filler loading arises because the matrix becomes more rigid and stiff,[75] and the restriction of polymer chain motion is increased.[24] In the present study, the nanocomposites exhibited higher flexural modulus than the microcomposites. This is attributed to the important role of dispersion and filler–polymer interaction, which lead to effective load transfer, thereby more uniform stress distribution.[76] In addition, Barghamadi *et al.* reported that the flexural modulus increased when smaller nano-particles were incorporated.[77] At specific filler content, the microcomposites showed a decrease in flexural modulus values. According to Žukas, a higher content of fillers decreased the flexural properties[78] due to the poor bonding at the interface.[24]

The TG curves showed no significant weight loss up to a temperature of 270 °C. However, with increasing temperature, a sharp decrease in weight was observed. Complete weight loss was observed at 400 °C. The samples displayed different thermal degradation behaviors. It could be seen that the degradation temperature of the nano- and micro-composites samples was slightly higher than that of the PMMA matrix. According to Liu *et al.*, this could be attributed to the formation of a strong chemical force between PMMA and $Al_2O_3$ particles,[79] which is consistent with the FTIR results. In addition, no residual material was observed for the PMMA sample at temperature up to 450 °C. This behavior is an indicator of the random chain scission processes that PMMA undergoes during degradation.[80] Nano- and micro-composites samples showed similar thermal behavior. However, some differences could be observed; the microcomposites showed slightly higher degradation temperatures than the nanocomposites, which indicate the high thermal stability of the microcomposites. The degradation ratio increased rapidly above 300 °C. Hu and Chen stated that vinyl end groups exist due to the chain transfer of end groups to monomer. Compared to the polymer chain structures, the end groups show weaker bonding chains, and started to degrade at about 220 °C. With increasing temperature above 300 °C, the PMMA degrades by random main chain scission, and the depolymerization rate increased. The entire polymer unzipped completely.[81]

An acrylic resin should exhibit excellent mechanical and physical properties, in addition to water absorption and solubility.[82] Water acts as a plasticizer that causes dimensional changes and decreases mechanical properties, such as hardness, transverse strength, and fatigue limit, of composites.[83,84] For denture base polymers, the water absorption value should be less than or equal to 32 μg $mm^{-3}$ after 7 days of storage, as recommended by ISO 1567-2000. The water absorption and solubility values of the composites were slightly higher than those of the control samples. The obtained water absorption values were lower than those reported by Kostić *et al.*,[82] who tested two PMMA denture base materials, and Akin *et al.*,[83] who employed 1 week of immersion; the results of which were 19.4, 20.7 and 25.5 μg $mm^{-3}$, respectively. Furthermore, the obtained values were lower than those recommended by ISO 1567-2000. The M2 and N0.5 samples exhibited the same water absorption (15.6 and 15.8 μg $mm^{-3}$, respectively) and water solubility values (1.1 μg $mm^{-3}$), which are lower than the ISO 1567-2000 standard for heat-polymerizable polymers (≤ 1.6 μg $mm^{-3}$). In the present study, the composites exhibited slightly higher water absorption and solubility values than those of the control group. This finding could be attributed to the dependence of water absorption and solubility on the presence of soluble impurities, filler particle size, filler distribution, interfacial properties between the filler and resin matrix,[51] and homogeneity of the composite.[85] Moreover, air voids may be introduced in the dental resin during mixing.[86] In addition, microvoids are formed during polymerization[87,88] and due to leaching of unreacted monomers, plasticizers, and initiators when these resins are immersed in water.[84] Most water molecules occupy the free volume between the chains and crosslinks, in addition to microvoids,[87] or accumulate at the filler––matrix interface.[51] Hence, water absorption can facilitate breakdown, leading to filler–matrix debonding; the plasticizing effect of water molecules also promotes the hydrolytic degradation of the matrix and filler–matrix interface, resulting in a decrease in mechanical properties.[51,89] The solubility of resin composites is affected by filler type, filler treatment, and presence of air voids, which decrease the material mass.[86] These results are supported by a study showing that the water absorption values of the composite groups were higher than those of the control group.[90] Sideridou *et al.* demonstrated that fillers slightly influenced water absorption.[91] Janda *et al.* reported no correlation between filler loading and solubility.[92]

## CONCLUSIONS

Composite samples were prepared by the addition of $Al_2O_3$ micro- and nano-particles to PMMA denture base resin. The filler surface was modified using $\gamma$-MPS. Fracture toughness and flexural strength tests were conducted to characterize the mechanical properties of the composites. Water absorption and solubility tests were also performed on the control group and two composite samples (*i.e.*, the optimal formulation from micro- and nano-composites). The FTIR spectra showed that $Al_2O_3$ micro- and nano-particles were successfully treated by the silane coupling agent. The fracture toughness increased in both groups but decreased when the optimum values were achieved. The optimum quantities of micro- and nano-$Al_2O_3$ particles were 2 and 0.5 wt. %, respectively. The flexural modulus increased with increasing filler content, whereas the flexural strength decreased with increasing filler loading. The water absorption and solubility values were higher in the composite samples than those in the control.

*Acknowledgement*. F. Kundie is grateful for his PhD scholarship from the Ministry of Higher Education and Scientific Research, Libya.

## ИЗВОД

# УТИЦАЈ НАНО- И МИКРО- АЛУМИНИЈУМ-ОКСИДНИХ ПУНИЛАЦА НА НЕКА СВОЈСТВА КОМПОЗИТА НА БАЗИ ПОЛИ(МЕТИЛ-МЕТАКРИЛАТА)

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У оквиру овог рада су приказана изучавања утицаја микро- и нано-честица алуминијум-оксида ($Al_2O_3$) на нека својства поли(метил-метакрилата) (PMMA) за денталну примену. Површина $Al_2O_3$ је третирана помоћу (3-метакрилоксипропил)триметоксисилана ($\gamma$-MPS), а затим су честице додате метил-метакрилату (MMA), и помешане са прахом PMMA. Запремински удели пуниоца у микрокомпозитима су били 0,5; 1; 2; 5 и 7 мас. %, док су у нанокомпозитима износили 0,13; 0,25; 0,5; 1; 2 и 5 мас. %. Хемијски третиране честице $Al_2O_3$ пунила су анализиране помоћу инфрацрвене спектроскопије (FTIR). Утицај величине и садржаја пунила на механичка својства композита је анализиран у огледима на удар и тестовима савијања. Термичка стабилност PMMA/$Al_2O_3$ композита је испитивана помоћу термогравиметријске анализе (TGA). Поред тога, анализирана је апсорпција воде и растворљивост припремљених композита. Присуство нових апсорпционих трака у FTIR спектрима је потврдило успешност површинске модификације честица алуминијум-оксида. Обе врсте честица, микро- и нано-димензија доприносе повећању отпорности на удар. Максимална вредност од 2,02 MPa m$^{-2}$ је остварена додатком 0,5 мас. % нано-$Al_2O_3$, што одговара повећању од 39 %. За разлику од чврстоће на савијање, модул савијања се повећава са повећањем садржаја пуниоца. Микрокомпозити су показивали већу термичку стабилност у односу на нанокомпозите. Апсорпција воде и растворљивост припремљених композита су биле мало више у односу на контролни узорак PMMA. Додатак $Al_2O_3$ наночестица у малим количинама може послужити за побољшање механичких својстава PMMA при изради зубних протеза.

(Примљено 18.јануара, ревидирано 21. априла, прихваћено 26. априла 2017)

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