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Original Article

Mechanical properties of new denture base material modified with gold nanoparticles

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Abstract

Purpose: Poly(methyl methacrylate) (PMMA) is the most commonly used material in the production of dental prostheses, and its application is often accompanied by the formation of biofilm. The aim of this work was the preparation of a PMMA/gold nanoparticles (AuNps) composite to improve the antimicrobial properties of heat-polymerised PMMA. The AuNPs were synthesised from gold (III) acetate by Ultrasonic Spray Pyrolysis (USP). In the present study, flexural strength and elastic modulus were investigated, as well as thermal conductivity, density and hardness of the PMMA/AuNps` nanocomposite, with different concentrations of AuNps. Flexural strength and elastic modulus were measured using a three-point bending test, and surface hardness was evaluated using the Vickers hardness test. The thermal conductivity of the samples was measured using the Transient Plane Source (TPS) technique. Density was determined by the pycnometry procedure. Statistical analysis was conducted on the data obtained from the experiments.

Results: The flexural strength and elastic modulus of AuNps/PMMA nanocomposites decreased for all groups containing AuNps. Thermal conductivity and density increased in all groups containing AuNps compared to the control group, but it was not significant in all groups. Vickers hardness values increased significantly with an increase in AuNps` content, with the highest value 21.45 HV obtained at 0.74 wt% of AuNps. Statistical analysis was performed by means of the SPSS 19 software package.

Conclusions: Incorporation of AuNps into heat-polymerised PMMA resin led to decrease of the flexural strength and elastic modulus. At the same time, the density, thermal conductivity and hardness increased.

Keywords: *PMMA, Gold nanoparticles (AuNps), Ultrasonic Spray Pyrolysis (USP), Nanocomposite, Denture base*

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1. Introduction

The numerous advantages of poly(methyl methacrylate) (PMMA) make it the most dominant polymer used as a denture base material [1]. PMMA shows good performances in aesthetics, biocompatibility, and stability in the oral environment, it is easy to process and is a low-cost material [2, 3]. However, biofilm formation is occurring on these acrylic appliances, and it is one of the most often discussed practical problems [4, 5]. Hence, one of the major goals in the studies related to dental materials is their antimicrobial capability. Most authors relate the creation of biofilm on PMMA-based denture materials as a cause of denture stomatitis [6–8]. Although denture related stomatitis is not considered a serious condition, it is presented with chronic inflammation, which can seriously affect the patients' quality of life, especially among elderly and immune-compromised patients [6]. Therefore, the ultimate aim of this study will also be production of a biofilm-resistant PMMA nanocomposite. This goal is pursued by different methods, such as impregnation or incorporation of metal/metal oxide nanoparticles in a PMMA matrix [9–11]. The incorporation of gold nanoparticles (AuNps) was used in the present study. AuNps are a good choice for fillers in nanocomposites, because they have desirable properties, such as stability, non-toxicity, uniform particle size and antimicrobial properties [12–15]. In particular, they have shown antimicrobial effects on many microorganisms, such as Candida albicans,

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Staphylococcus aureus, Enterococcus faecalis, Escherichia coli and/or Pseudomonas aeruginosa [12, 14]. There are three typical approaches for mixing AuNps with the polymer material: (1) Mixing the nanoparticles with a polymer, (2) Generating the nanoparticles during polymerisation and (3) Adding the nanoparticles to the monomer (applied here as well) [16].

Although there is a number of studies in the literature which investigate the antimicrobialactivity of AuNps` solutions against several microorganisms, available data on the effect of these AuNps upon their incorporation in denture base polymer are limited [17, 18].In addition, the literature on the antimicrobial efficiency of AuNps incorporated in polymers is inconclusive. Some authors relate it to the release of gold ions or AuNps themselves, while others have reported that the inhibitory effect was probably due to the direct contact between the microorganisms and the composite material itself [19–22].

Several physicochemical factors (non-specific interaction forces) such as Lifshitz Van der Waals forces, electrostatic forces, hydrophobicity, acid-base interactions and Brownian motion forces, could influence the kinetics of microbial adhesion, or their behaviour on the surface of Au/PMMAnanocomposites [23–26]. It is presumed that, upon approach to the surface, organisms will be attracted or repelled by the surface, depending on the resultant of the different non-specific interaction forces [25]. The surface of various solid plastic materials generally has a negative net surface charge, just like most bacteria and fungi. Kiremitci-Gumustederelioglu reported that bacterial adhesion decreases on negatively charged PMMA, while it increases on positively charged PMMA [17, 26, 27].

As for the nanoparticles, Ultrasonic Spray Pyrolysis (USP) was used for the synthesis of AuNps from gold (III) acetate (Au(CH3COO)3), an emerging technique of choice. This method has recently been recommended for scale up production of AuNps, since it overcomes technological problems in other methods, and gives well-defined materials with narrow size distribution [28–31].

The problem with the literature is that the antimicrobial and mechanical properties of AuNps-doped denture base resins have rarely been reported together [17, 18]. However, the mechanical properties are as important as the antimicrobial properties, since, ultimately, the composite in the dental prosthesis will be subjected to high-pressure during mastication. The addition of AuNps studied here, might also affect the PMMA`s mechanical properties. Therefore, the properties studied here were: Flexural strength, elastic modulus, thermal conductivity, density and Vickers hardness. The most important contribution of the present study is that it evaluates the effects of various concentrations of AuNps produced by USP comparatively on the mechanical properties of the heat-polymerised acrylic resin.

2. Materials and methods

A precursor solution was prepared by the already reported method [30]. First, the gold (III) acetate (Au(CH3COO)3) (Alfa Aesar, Germany) was dissolved in deionised water (D.I.) (99.99 % ultrahigh pure). The aqueous solution consisted of 480 mL D.I., 20 mL HCl and 2 g of Au (III) acetate, which represented in this stage the initial concentration of [Au] = 2 g/L. The solution was then stirred for 1 hour using a magnetic stirrer at 250 rpm. A clear yellow solution was obtained, and neutralised by solid sodium hydroxide (granules). After that, 500 mL of D.I. was added to the solution, and its pH value was adjusted in the range of 6-7, while the final concentration of [Au] in the precursor solution was 1 g/L. The used USP device consists of an ultrasonic atomizer, a tubular reactor furnace, a quartz tube and a quartz connector with attached thermostat, and two bottles with suspensions for collection of nanoparticles. The frequency of the atomizer which produced the aerosol droplets was 2.5 MHz. The droplets were transported into the reactor by nitrogen gas at a flow rate of 1.5 L/min. The reduction was accomplished by hydrogen gas at a flow rate of 1.5 L/min at 250 °C (the temperature of the reactor). During the displacement of droplets into the reactor, they were exposed to drying, droplet shrinkage, solute precipitation, thermal decomposition, hydrogen reduction, and densification, after which they were collected into two bottles with collection medium. The D.I., stabilised with 0.1 wt% of polyvinylpyrrolidone (PVP) was used as the collection medium to prevent possible agglomeration of the synthesised AuNps. The concentrated AuNps were then filtered through centrifugal filter membranes "Amicon Ultra-15 with 100,000 NMWL" (MiliporeSigma, USA) in order to remove the PVP stabiliser. The filtered solution was used to prepare the nanocomposite.

As for the basic concept of the nanocomposite, a conventional heat-polymerised PMMA (ProBase Hot, Ivoclar Vivadent, Liechtenstein) was used as a matrix component, and the above described AuNps as a reinforcing agent. 24 samples were prepared for the purpose of the present laboratory study. The specimens were categorised into four groups (n=6), coded A to D. Group A was the control group, consisting of unmodified heat-polymerised PMMA, while the AuNps were added in groups B, C and D. Optimal concentrations of the different nanometals to the acrylic resin with the purpose of enhancing the antimicrobial and mechanical quality of the dental resin are still the subject of discussions. Preliminary investigations were undertaken to determine the most appropriate weight percentages of AuNps for the current study. In the preceding study [17], significant colour changes occurred with the addition of large amounts of AuNps in the PMMA. Based on this experience, it was decided to reduce the amount of AuNps in the PMMA/AuNps nanocomposite. Therefore, specimens of the groups (B-D) were modified with the addition of 0.12, 0.43 and 0.74 wt. % of the USP-synthesised AuNps to the methyl-methacrylate (MMA) and, consequently, sonicated for 15 min. In order to suppress the agglomeration, the AuNps` solutions were previously dispersed in the liquid MMA at the desired ratio and then mixed with the PMMA powder. This procedure was done according to the manufacturer's recommendation related to the polymer/monomer ratio, and they were mixed by hand using a stainless-steel spatula to obtain a homogenous mixture. The resin was left in a closed mixing jar until it reached the dough stage, and then the mixture was kneaded thoroughly to a homogeneous dough. The dough was packed into metal moulds to create specimens with square shapes (dimensions: 80 mm × 10 mm × 4 mm), suitable as specimens for the flexural strength and hardness tests. The mould lid was closed and placed under 80 bars pressure in a bench press to compress the material within the mould. Polymerisation was carried out by heating the mould from Room Temperature (RT) in a water bath, up to 100 °C, where it was kept for 45 minutes. The heat was then turned off and the metal moulds were left in the water bath to cool naturally to RT, after which the specimens were removed from the moulds. The specimens were polished with 800-, 1000- and 1200-grit abrasive paper to obtain smooth surfaces, and stored in distilled water at 37°C for 50 ± 2 h before testing.

The flexural properties of the A-D samples were measured according to the ISO 178:2001 Standard [32]. The flexural strength and the elastic modulus of the specimens were tested. Each specimen was placed on a 50 mm-long support for three-point flexural testing. A vertical load was applied at the mid-point of the specimen, at a crosshead speed of 5 mm/min on a load testing machine (Zwick/Roell-Z010 Zwick Roell Group, Ulm, Germany). The flexural strength (σf) of the experimental samples (A-D) was determined by using the following Equation (1):

$$\sigma f = \frac{3Fl}{2bh^2} \text{ [MPa]}$$

where F is the breaking force in Newton, l is the support distance (span length = 50 mm), b is the specimen width (10 mm), h is the specimen thickness (4 mm).

The elastic modulus (E) of the samples (A-D) was determined by using the following Equation (2):

$$E = \frac{Fl^3}{4bh^3d} [MPa] \quad (2)$$

where d is the deflection (mm) at load F.

Fractured surfaces were then examined by Scanning Electron Microscopy (SEM-Sirion 400 NC and Quanta 200 3D). After breaking, the samples were sprayed with an Au (Jeol JSM 8310 appliance) in order to enable the observation of this non-conductive surface with an electron beam (Fig.1). The observations were performed with the SEM accelerating voltage of 10 kV.

The effective thermal conductivities of PMMA/AuNPs` nanocomposites were determined using the Transient Plane Source (TPS) technique with the Hot Disk TPS 2200 apparatus (Hot Disk®, Sweden). A TPS sensor consists of an electrically conducting pattern of thin nickel foil (10 μm) in the form of a double spiral embedded in an insulating layer made of Kapton® (50 μm). The sensor is sandwiched between the two pieces of the samples having a perfectly smooth surface so as to ensure perfect thermal contact. Data obtained during the analysis were collected using the software available with the Hot Disk TPS 2200.

Density was determined by the standard pycnometry procedure. Weighing was carried out at a temperature of 20 °C. Determination of the density was carried out by first weighing the mass of the empty pycnometer, then the mass of the pycnometer with water (water density 1g /mL), after which the nanocomposite sample was plunged inside the pycnometer. The density of the samples in experimental groups (A-D) was determined by using the following Equation (3):

$$\rho vz = mvz \times \rho t / m_{(\rho + t)} + mvz - m_{(\rho + t + vz)}$$

ρ_{vz} = sample density
ρ_{vz} = sample density
ρ_t = density of the liquid
m_{vz} = sample mass
$m_{(\rho + t)}$ = mass of pycnometer and liquid
$m_{(\rho + t + vz)}$ = mass of the pycnometer, liquid and sample

The hardness of the composites was measured by the Vickers Hardness Test, which has the widest scale among the hardness tests and uses the hardness unit "Vickers pyramid number" (HV) [33, 34]. Surface hardness was determined using a Vickers microhardness tester (The ZwickRoell ZHV10 hardness tester, USA). The test specimens were fabricated using dimensions of 80 × 10 × 4 mm. The microhardness tester was adjusted to a load of 0.49 N for 5 s indentation time. A total of three indentations were taken at different points on one side of each specimen. The diagonal length of the indentations was measured on a microscopic scale, and surface microhardness was calculated automatically.

For Transmission Electron Microscopy (TEM) thin slices were ground into a fine powder using a grinding tool. The powdered samples were sonicated in ethanol for around 60 min to disperse the nanoparticles in methanol. The dispersion was dropped onto a carbon coated copper grid (200 mesh) for TEM observation and dried at room temperature. The TEM images of nanoparticles were taken using a JEM-2010 (JEOL) equipped with an LaB6 electron source operated with an accelerating voltage at 200 kV. The images were acquired using a CCD camera (Gatan, Ultra scan 1000). Statistical analysis was performed by one-way ANOVA using the SPSS 19 software package (IBM Company, New York, U.S.). Tamhane's test was applied as a post hoc test to compare the results of each tested group, with $p < 0.05$ being considered statistically significant, because the hypothesis of equal variances was rejected by a Levene test.

3. Results

Four study groups (one control group with pristine polymer and three composites with different concentrations of nanoparticles) each contained 6 specimens, giving a total number of 24 results. The mean value, Standard Deviation, minimum and maximum values for flexural strength and elastic modulus of each test group are shown in Table 1 and Table 2. In comparison with the control (A), the flexural strength and elastic modulus in all groups containing AuNps (B-D) no statistically significant decreased ($p < 0.05$). The lowest values were observed for group D, which had the highest concentrations of AuNps. The SEM images after the flexural strength tests are shown in (Fig. 1). Fractured surfaces in groups B, C, D exhibited similar surface texture to that of control group A, with slightly increased cracking observed. The values of flexural strength and elastic modulus of all groups showed a slight decrease, although the values were within the recommendations given by the ISO 20795-1: (2013). In particular, they were higher than the standard level of 65 MPa for flexural strength and 2000 MPa for elastic modulus [35].

Table 3 shows a comparison of the mean thermal conductivity values of all experimental groups (B-D) with the control group (A). Results showed that the effective thermal conductivity of the prepared nanocomposites was higher than the pure material. A statistically significant increase in thermal conductivity can be observed only in the first experimental group (B).

Table 4 shows a comparison of the mean density values of all experimental groups (B-D) with the control group (A). Statistically significant increase is notable in the groups (C) and (D) ($p < 0.05$).

An increase in the mean value of microhardness by Vickers was observed in all experimental groups (B-D) compared to the control group (A). A statistically significant increase can be observed only in the group (C) (Table 5). According to the results obtained by SEM (Vickers pyramidal number), the microhardness value increased proportionally to the concentration of the AuNps in the PMMA from the control sample to the sample with the highest concentration (D) (Table 4).

The morphology and distribution of the AuNps in the reinforced PMMA denture base are shown in the TEM images (Fig. 2). These images revealed that AuNps are of similar size and have mainly ellipsoidal shapes with low aggregation and agglomeration.

4. Discussion

Overall, the investigation of the effects of AuNps produced by USP on the mechanical properties of heat-polymerised dental acrylic resin have shown promising results. Flexural strength, elastic modulus, thermal conductivity, density and hardness were dependent on the amount of nanoparticles incorporated in the PMMA. Flexural strength reflects the ability of the material to resist the initiation of a crack during the action of the bending force that occurs during the act of mastication [36]. For this reason, the denture base should have sufficient flexural strength, and also elastic modulus, to resist the formation of the fracture [37]. High elastic modulus improves the ability of denture base material to resist significant deformation by mastication [37]. The present results were in accordance with the ISO 20795-1:(2013) International Standard, which demands 65 MPa as the minimum flexural strength, and 2000 MPa for the elastic modulus required for heat-polymerised acrylic resins used for denture bases [35]. It was confirmed that addition of AuNps did not affect the mechanical properties of acrylic materials dramatically, nor had it caused any flexural strength and elastic modulus decrease below the standard recommended levels.

Previous studies reported that different percentages of nanoparticles can lead to positive and/or negative effects on the flexural strength and elastic modulus of acrylic resins. The results of this study have shown that there is a statistically significant decrease in the flexural strengthand elastic modulus of all three experimental groups compared to the control group.

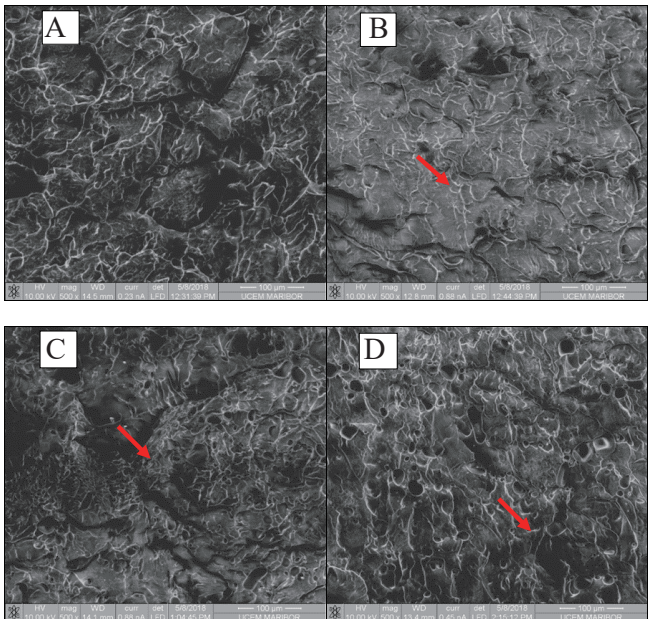

Fig. 1. Scanning Electron Microscope images of samples from groups A, B, C and D. SEM images of groups B, C and D reveal similar surface texture, with slightly increasing surface cracking as compared to the control group (A)(x500). The arrows point to the AuNps in the PMMA.

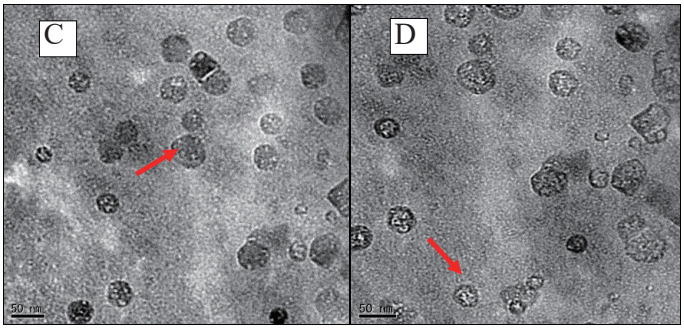

Fig. 2. TEM images of samples from groups C and D. The arrows point to the AuNps in the PMMA.

The highest reduction in flexural strength and elastic modulus can be observed in group D (82.5 MPa). This group had the highest concentration of AuNps in PMMA (0.73 wt%), and the presented results agreed with those of other authors [38, 39]. Akkus et al. added 1% and 3% of 40 to 50 nm Al2O3 and 15 nm SiO2 nanoparticles to heat-polymerised acrylic resin, and they observed the highest flexural strength values in the control group. Ahmed et al. added 1% and 5% 40 nm TiO2 nanoparticles to traditional heat-polymerised and high resistance heat-polymerised acrylic resin powder, and they observed a decrease in flexural strength values. Nazirkar et al. investigated the flexural strength of heat-polymerised acrylic resin in which 0.5% and 1% 7 nm TiO2 nanoparticles were added, and indicated that flexural strength decreased with the addition of the nanoparticles. The study of Shibata et al. indicated that, by adding nanoparticles, the unreacted monomer quantity may be increased, and it acted like a plasticiser [40]. Taken together, decreasing the degree of conversion of acrylic resin and an increase in the residual monomer amount, would cause lesser mechanical properties of the material. Chaldek et al. reported that the mechanical properties of the final polymer are affected adversely by increasing nanoparticles` concentration [41]. The nanoparticles within the polymer matrix can act as impurities, which change the physicochemical properties in polymers, along with varied chemical interactions of the C=O groups, which then

Table 1. The results of the flexural strength for the tested groups.

Groups	Mean±SD(MPa)	Minimum	Maximum	P value
Group A [a]	101,85±9,96	92,05	116,18	
Group B [b]	97,77±3,05	94,87	102,16	0,963
Group C [c]	85,92±2,49	82,15	88,06	0,120
Group D [d]	83,14±1,49	80,92	84,51	0,075

* Significance p<0.05, SD=Standard Deviation, [a] without AuNPs, [b] 0.12 wt% AuNPs, [c] 0.43 wt% AuNPs, [c] 0.74 wt% AuNPs.

Table 2. The results of elastic modulus for the tested groups.

Groups	Mean±SD(MPa)	Minimum	Maximum	P value
Group A [a]	2703,94±431,66	2347,33	3442,57	
Group B [b]	2657,73±84,08	2538,60	2774,79	0,989
Group C [c]	2503,19±118,35	2368,15	2663,95	0,546
Group D [d]	2477,89±115,00	2352,88	2623,77	0,448

* Significance p<0.05, SD=Standard Deviation, [a] without AuNPs, [b] 0.12 wt% AuNPs, [c] 0.43 wt% AuNPs, [c] 0.74 wt% AuNPs.

Table 3. The results of the thermal conductivity for the tested groups.

Groups	Mean±SD(MPa)	Minimum	Maximum	P value
Group A [a]	2703,94±431,66	2347,33	3442,57	
Group B [b]	2657,73±84,08	2538,60	2774,79	0,989
Group C [c]	2503,19±118,35	2368,15	2663,95	0,546
Group D [d]	2477,89±115,00	2352,88	2623,77	0,448

* Significance p<0.05, SD=Standard Deviation, [a] without AuNPs, [b] 0.12 wt% AuNPs, [c] 0.43 wt% AuNPs, [c] 0.74 wt% AuNPs.

Table 4. The results of the density for the tested groups.

Groups	Mean±SD(MPa)	Minimum	Maximum	P value
Group A [a]	1,117±0,0057	1,1125	1,128	
Group B [b]	1,144±0,0575	1,0653	1,1964	0,897
Group C [c]	1,154±0,0077	1,1473	1,1683	0,000*
Group D [d]	1,198±0,0313	1,1624	1,2402	0,007*

* Significance p<0.05, SD=Standard Deviation, [a] without AuNPs, [b] 0.12 wt% AuNPs, [c] 0.43 wt% AuNPs, [c] 0.74 wt% AuNPs.

Table 5. The results of the Vickers micro hardness for the tested groups.

Groups	Mean±SD(MPa)	Minimum	Maximum	P value
Group A [a]	17,08±0,27	17,5	18,1	
Group B [b]	17,96±1,54	17,9	21,5	0,110
Group C [c]	20,08±1,89	21	25,2	0,012*
Group D [d]	23,86±0,92	16,4	16,9	0,348

* Significance p<0.05, SD=Standard Deviation, [a] without AuNPs, [b] 0.12 wt% AuNPs, [c] 0.43 wt% AuNPs, [c] 0.74 wt% AuNPs.

lead to the weakening of the mechanical properties of the material. As a result, the final material became more brittle than the pure resin itself [17, 42]. Decreasing values of flexural strength in the present study can be explained by the formation of smaller areas of agglomerations, which can be seen in the TEM images (Fig. 2). The agglomerated nanoparticles resulting from increasing filler concentration can act as stress concentrating centres in the matrix, and affect the flexural strength of the polymerised material adversely [33, 42, 43]. There are indications that decreasing elastic modulus can also be explained by the same reason. In other words, reduction in the cross-section of the load-bearing polymer matrix occurs with increase in the amount of filler particles, which allow formation of voids containing moisture or air [34]. In summary, the important contribution of the present study is that it shows that the values of flexural strength and elastic modulus in doped materials, although reduced if compared to the control group, are still in accordance with the

values prescribed by ISO 20795-1: (2013) Standard [35]. The benefits of their antimicrobial properties, which will be investigated in the next study, should by far outweigh the slight decrease in mechanical properties which remained with the Standard demands here.

In particular, the method shown here (an incorporation of the fillers which will enhance self-sterilisation) is often recommended [44]. This subject is attractive, since very often denture wearers do not use the denture cleansers/antibacterial denture creams routinely properly. This leads to microbial adhesion to the denture base acrylic resin of many microorganisms, able to form biofilms and aid the development of oral infections [45]. Obviously, incomplete disinfection of the surface leads to the rapid microbial recolonization of microorganisms like the Candida species, especially Candida albicans [44].

The present study also investigated the effect of the addition of low weight percentages of AuNps on the thermal conductivity of PMMA. In contrast to plenty of data on overall mechanical properties, there is a lack of literature on the effect of various filler materials in improvement of thermal conductivity of acrylic resin. In particular, in the internationally recognised literature there are no reports on gold addition, while only reports on the addition of silver nanoparticles and some other metallic nanoparticles could be found [43, 46–49]. Therefore, the idea of the present research was to use AuNps, because of their high thermal conductivity, which should be able to improve the low thermal conductivity of PMMA. Namely, improved thermal conductivity in polymers may be achieved either by molecular orientation, or by the addition of highly heat conductive fillers, as gold is [50]. Results in this study have shown that addition of AuNps increased thermal conductivity of PMMA significantly (Table 2). The tendency of results is in agreement with those of previous ones [47, 51, 52]. The study of Agarwal et al. explained this behaviour on the basis of the compact structure of the composite. If we take into consideration that the mechanism of thermal conductivity by non-metallic materials such as polymer is completely different from that of metals, then is necessary to predict some facts by the nanocomposite PMMA/AuNps. It is known that in metals the heat is transmitted by free electrons, while, in the case of polymers, heat is transmitted by phonons or waves, which are generated by the vibration of atoms. Transmission of heat is much faster by metals than in the case of polymers. Based on this, it could be assumed that, for PMMA/AuNps, thermal conductivity should be influenced by incorporation of metallic AuNps into the polymer PMMA (concentration, size, etc.), where the mechanical contact between the polymer PMMA and the AuNps is the most important property. Tight contact between the PMMA matrix and AuNps could represent some artificial bond, and probably provides a better phonon-phonon pathway and better thermal conductivity in comparison to the pure PMMA [47]. This could explain some of the reasons for the increased thermal conductivity of nanocomposite PMMA/AuNps. At room temperature, the heat-conducting phonons have large wave vectors and a mean free path in the nanometer range. Based on these dimensions, nanoparticles become comparable to the mean free paths, which would lead to significant improvement in phonon heat transport within nanocomposites. The AuNps have a thermal conductivity in water of 0.60 W/mK and, due to their nanodimension, they can easily approach to the cross-linking centres in the polymer network [53]. Thus, the present study results are promising, since better thermal conductivity of a denture base enhances the enjoyment of eating by denture wearers, and reduces the sensation of the denture as a foreign body [47, 49, 54].

Most probably, well-dispersed AuNPs serve as a phonon-phonon pathway which conducts heat in the polymer network. This should be the explanation for increase in thermal conductivity, achieved even with small amounts of AuNps in the nanocomposite [55]. Also, nanoparticles added to the polymer matrix and well dispersed, tend to fill the cavities filled with air, reducing the free volume, which gives a more compact structure of nanocomposite. As the concentration of nanofillers increases, the free volume decreases further, and makes the nanocomposite more compact than the pure PMMA. With increasing compactness of nanocomposite the contact between polymer and filler improves, and enables phonons to conduct heat through the nanocomposite [47].

The results of density measurement obtained in this study showed that the density of all groups (B, C, D) compared with the control group (A) increased significantly increased with the incorporation of AuNps into the acrylate. A statistically significant increase in the value of density was recorded only in group B (Table 3). Increase in density was expected, since the density of AuNps is greater than the PMMA density (1.22 g/mL) [56]. According to Sonavana et al. the density of AuNps ranges from 2.022 to 2.337 g/mL, depending on the size of AuNps [57]. Therefore, it was expected that, upon blending, the density of the composite would increase to a certain level between the densities of blending components. Attention should be paid to the demand that the materials for denture bases should have lower specific gravities in order to be as light as possible. Therefore, an increased denture base material density is considered undesirable. Especially in the case of upper denture bases, a heavier base would be unstable in the patient's mouth, and would drop down during use.

Microhardness by Vickers of all sample groups (B, C, D) compared with the control group (A) increased significantly with the incorporation of AuNps into the acrylate. A statistically significant increase was recorded in groups B and D (Table 4). The largest increase was achieved in group D (21.45 HV), which also had the largest amount of AuNps incorporated into PMMA. This result shows that there is a strong correlation between the amounts of AuNps in the PMMA matrix and the microhardness by Vickers. In other words, depending on the quantity of added nanoparticles, it should be possible to control the increase of decrease in microhardness. The control of microhardness, i.e the resistance of a material to permanent surface indentation or penetration, is valuable, since dental material with a higher surface hardness could better withstand excessive wear by a denture cleanser, toothbrush or food [58]. Available literature on this subject shows that increase of the filler amount in a polymer matrix often improves the hardness of the resulting composites [57, 59, 60]. The presented study results, showing an increase of hardness values with increasing the AuNps` content, are in agreement with these reports. However, the experimental conditions should be planned carefully in order to avoid saturation. The mechanical properties of the composite material began to decline after that point, due to the weakening of the mechanical connection between the filler and the matrix [61]. Related to the microhardness, the most similar to the present study is the study of Aoyagi et al., who added nanoclusters of gold, which is a slightly different system than the dispersed AuNps shown here. They demonstrated that addition of gold nanoclusters caused an increase in the Vickers microhardness of their composite with PMMA [62]. It is reasonable to assume that the results obtained here for microhardness and flexural strength are in correlation. In particular, AuNps have likely reduced the size of the defects which originally existed in the PMMA matrix, thus leading to an increase in microhardness and a decrease in flexural strength. Similarly, lower values of modulus of elasticity can also be explained with the increased density of the Au-embedded PMMA.

5. Conclusion

Within the frame of this study, it could be concluded that the incorporation of AuNps decreases the flexural strength and elastic modulus of the used denture base materials. However, the results of this study are still in accordance with the ISO 20795-1: (2013) Standard for these properties. Thermal conductivity and microhardness by Vickers of PMMA/Au nanocomposites were improved gradually by increasing the volume fraction of the AuNPs. Therefore, since the physic-mechanical properties are satisfactory, the effect of AuNPs` addition to PMMA on antimicrobial activity would be beneficial. Expectations are that the antimicrobial properties of PMMA should be improved if it is in the form of its composite with gold nanoparticles, a known antimicrobial agent. Further

studies are, however, required, to address the antimicrobial issues and also the biocompatibility of these composite denture base materials. The current study is dealing only with in vitro conditions and one brand of heat-polymerised PMMA, and should be studied on multiple types of the material. Next, the experiments are on course on the antimicrobial properties, biocompatibility, and, ultimately, they should result in clinical studies.

Conflict of interest statement

There are no financial and personal relationships with other people or organisations that could influence (bias) this work inappropriately.

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