

## Evaluation of resin composites modified with nanogold and nanosilver

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Silver and gold have been used for centuries as antimicrobial agents. The aim of the study was to investigate diametral tensile strength, microhardness, ion release and light transmission of experimental resin composites. Flowable dental composite SDR (Dentsply, United Kingdom) was modified by nanogold, nanosilver and silica addition. The metal ion release, light transmission study, microhardness, Diametral Tensile Strength were evaluated. The experimental nanosilver-containing composites released significant amounts of Al, Si, Sr and Ba ions up to 30 days, and negligible silver ion amounts. Significant Ag ion release occurred in nanosilver- and nanogold-modified composite. Resin composites modified with nanogold and nanosilver deposited on silica carrier exhibit lower light transmission and have opaque appearance. All experimental composites exhibited higher microhardness in comparison to non-modified resin composites. Diametral Tensile Strength of the experimental composites was comparable to the control group.

*Key words: anogold, nanosilver, composite, diametral tensile strength, microhardness, ion release, light transmission*

### 1. Introduction

Dental caries continues to be an important public health concern. Caries is defined as transmissible, infectious illness in which diverse pathological factors, including the presence of acidogenic bacteria, have been identified [1]. Therefore, bacteria elimination seems to be the best way of secondary caries prevention. Unfortunately, resin composites exhibit no long-lasting antibacterial properties. The introduction of antibacterial restorative material may possibly help to overcome the limitations of contemporary restorative materials. Silver-containing orthodontic adhesives, resin composite, denture soft lin-

ing material have been investigated recently [2]–[10].

Silver and gold have been used for centuries as bactericidal and bacteriostatic agents. Silver has found versatile application in human health care [11]. Its long history includes water purification, wound care, bone prostheses, reconstructive orthopedic surgery, cardiac devices, catheters and surgical appliances. Several studies have demonstrated that silver ions are selectively toxic for prokaryotic microorganisms with little effect on eukaryotic cells [12], [13]. The antibacterial, antifungal and antiviral action of silver or silver compounds is proportional to the amount of released bioactive silver ions ( $\text{Ag}^+$ ) and its availability to interact with microbial cell membranes [3], [14]–

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[18]. Silver can inhibit enzymatic systems of the respiratory chain and alter DNA synthesis in bacteria [19]–[21]. Ag in nanoparticulate form (AgNP) may release Ag ions more effectively and due to its high surface area-to-volume ratio has better bactericidal activity [21]. It has been shown that Ag can attach to the outer membrane affecting its permeability and inducing structural changes in the cell, causing cell death. In addition, Ag does not lead to the development of resistant bacterial strains.

Gold has shown a weak or no antimicrobial effect against many microorganisms [22], [23]. Some research groups have reported that mixtures of gold nanoparticles with antibiotics result in materials with enhanced bactericide properties [24], [25]. The effect has been compared with such antibiotics as mupirocin [26], [27]. Hernandez-Sierra et al. [23] proved that nanoparticles of silver, as compared with those of gold and zinc oxide, required a lower concentration to inhibit development of the *S. mutans* strains.

However, few studies have tested the mechanical, optical properties and ion release of the nanometal-containing composites [3], [28]. Therefore, in-depth investigation of diametral tensile strength, microhardness, ion release and light transmission of resin composites modified with nanogold and nanosilver deposited on silica carrier will complement this gap in scientific knowledge.

## 2. Materials and methods

Dispersion of gold nanoparticles was obtained by citrate synthesis using chloroauric acid (0,21% HAuCl<sub>4</sub>, puriss p.a., POCH, Poland) and trisodium citrate dihydrate (C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub>O<sub>7</sub>, puriss p.a., POCH, Poland) as substrates. Silver nanoparticles were synthesized applying silver nitrate (AgNO<sub>3</sub>) as reactant. Fillers: precipitated silica (Arsil, Z.Ch. Rudniki, Poland) and pyrogenic silica (Aerosil 380, Evonik Degussa, Poland) were also employed in the study. Silver nanoparticles were deposited electrochemically on the surface of silica carriers (Ame-pox, Poland).

Dispersion of silver nanoparticles was prepared by chemical reduction of AgNO<sub>3</sub> using NaBH<sub>4</sub> as a reducing agent, and polyvinylpyrrolidone (PVP) as a stabilizer of the suspension.

Gold nanoparticles were obtained by chemical reduction of chloroauric acid using trisodium citrate dihydrate as a reducing agent and a stabilizer of the suspension. Gold nanoparticles suspension in triso-

dium citrate dihydrate solution of 50 ppm concentration was prepared.

Flowable dental composite SDR (Dentsply, United Kingdom) was modified by nanogold, nanosilver and silica addition (Table 1). Each sample made of experimental and control composite was light-cured (Elipar S10 LED Curing Light, 3M ESPE, light intensity >450 mW/cm<sup>2</sup>) in three layers for 60 seconds.

Table 1. Experimental and control group composition

Group	Composition
1	24 µg Arsil + 14 µg Areosil + 2 g SDR
2	20 µL nano Ag 2000 ppm + 2 g SDR
3	20 µL nano Ag 5000 ppm + 2 g SDR
4	15 µL nano Ag 5000 ppm + 5 µL nanoAu 50 ppm + 2 g SDR
Control	SDR

Light transmission study samples were prepared according to the following protocol. Discs of 1 mm in height were prepared on silicone matrix and light-cured. Light transmission was measured with Cure Rite (Caulk Dentsply, USA) visible light meter (400–500 nm band), keeping the optical fiber tip in direct contact with the sample surface. The measurement was performed three times. The results, expressed in mW/cm<sup>2</sup>, were referred to the measurement of lamp power made without material samples, keeping the distance of 1 mm between optical fiber tip and radiometer sensor.

The metal ion release from experimental and control composites into the artificial saliva solution (0.9% NaCl) was investigated. In order to assess the short and long-term corrosion resistance, the samples (5 mm in diameter and 3 mm in height) were stored at 37 °C for 7 and 30 days. The amount of the metal ions released into the 0.9% NaCl solution was determined using the inductively coupled plasma mass spectrometer with the time-of-flight analyzer, ICP-ToF-MS (OptiMass 8000, GBC, Australia). The mass spectra were compared using multi-element spectral finger printing OptiMass 9500 software application. The data were normalized against signal for <sup>115</sup>In added to the samples in the same amount before analysis and used as an internal standard. Therefore, any daily sensitivity drift was taken into account.

Microhardness of the cured composite samples was determined with a digital ZHV2-m Hardness Tester (Zwick/Roell, Germany). The instrument was fitted with a Vickers diamond and a 1 N load was used to make indentations in the composite surface. The loaded diamond was allowed to rest on the surface for 10 s. Five indentations were performed on each specimen.

For the Diametral Tensile Strength (DTS), 10 cylindrical specimens were fabricated from each material (4.0 mm in diameter  $\times$  6.0 mm in height) according to specification n. 27 of ANSI/ADA. The composite was inserted and packed in a cylindrical silicon mold, blocked with two glass slabs on each side. Then the material was light-cured for 60 s on both ends of the tube. Next, the specimens were tested under compressive load in a universal testing machine (Zwick/Roell Z005, Germany). The load was applied vertically on the lateral part of the cylinder, at a crosshead speed of 2.0 mm/min, producing tensile stresses perpendicular to the vertical plane passing through the center of the specimen.

#### Statistical analysis

The Kolmogorov–Smirnov test was carried out to check the normality of the distribution of DTS, microhardness, and light transmission. Subsequently, two nonparametric procedures – the Kruskal–Wallis test and Mann–Whitney U test – were used to compare the groups, as the analyzed data significantly deviated from the normal distribution. A 95% confidence interval was assumed in all cases to indicate significant differences.

### 3. Results

Light transmission, ion release evaluation, microhardness and diametral tensile strength results are presented in Figs. 1–3.

In group 2 (20  $\mu$ L nano Ag 2000 ppm + 2 g SDR), 4 (15  $\mu$ L nano Ag 5000 ppm + 5  $\mu$ L nano Au 50 ppm + 2 g SDR) mean light transition values were significantly ( $p < 0.001$ ) lower in comparison to the control group. Also in group 2 mean light transition values were significantly ( $p < 0.001$ ) lower than in group 1 (24  $\mu$ g Arsil + 14  $\mu$ g Areosil + 2 g SDR).

There were no statistically significant differences between DTS values in experimental (1–4) and control group.

In the control group (SDR) mean microhardness value was significantly ( $p < 0.001$ ) lower in comparison to groups 1, 2, 3 and 4. Also in group 1, 2 and 3 mean microhardness values were significantly ( $p < 0.001$ ) higher than in group 4.

The ion release study revealed that silver ions were not released in significant quantity from the samples examined. The equally high silver ion amounts were released from group 3 (20  $\mu$ L nano Ag

Table 2. Mean value ( $\bar{x}$ ) and standard deviation (SD) of light transmission [ $\text{mW}/\text{cm}^2$ ] for experimental and control groups

Group	Composition	$\bar{x}$	SD
1	24 $\mu$ g Arsil + 14 $\mu$ g Areosil + 2 g SDR	209.7	2.25
2	20 $\mu$ L nano Ag 2000 ppm + 2 g SDR	41.7	1.03
3	20 $\mu$ L nano Ag 5000 ppm + 2 g SDR	57.0	1.00
4	15 $\mu$ L nano Ag 5000 ppm + 5 $\mu$ L nano Au 50 ppm + 2 g SDR	46.3	0.52
Control	SDR	593.0	9.34

Table 3. Mean value ( $\bar{x}$ ) and standard deviation (SD) of DTS [MPa] for experimental and control groups

Group	Composition	$\bar{x}$	SD
1	24 $\mu$ g Arsil + 14 $\mu$ g Areosil + 2 g SDR	37.11	6.25
2	20 $\mu$ L nano Ag 2000 ppm + 2 g SDR	27.42	4.86
3	20 $\mu$ L nano Ag 5000 ppm + 2 g SDR	24.17	2.16
4	15 $\mu$ L nano Ag 5000 ppm + 5 $\mu$ L nano Au 50 ppm + 2 g SDR	25.74	2.98
Control	SDR	34.01	3.81

Table 4. Mean value ( $\bar{x}$ ) and standard deviation (SD) of microhardness HV1 for experimental and control groups

Group	Compositon	$\bar{x}$	SD
1	24 $\mu$ g Arsil + 14 $\mu$ g Areosil + 2 g SDR	44.0	2.0
2	20 $\mu$ L nano Ag 2000 ppm + 2 g SDR	42.7	1.5
3	20 $\mu$ L nano Ag 5000 ppm + 2 g SDR	43.0	2.6
4	15 $\mu$ L nano Ag 5000 ppm + 5 $\mu$ L nano Au 50 ppm + 2 g SDR	38.0	2.08
Control	SDR	32.6	1.90

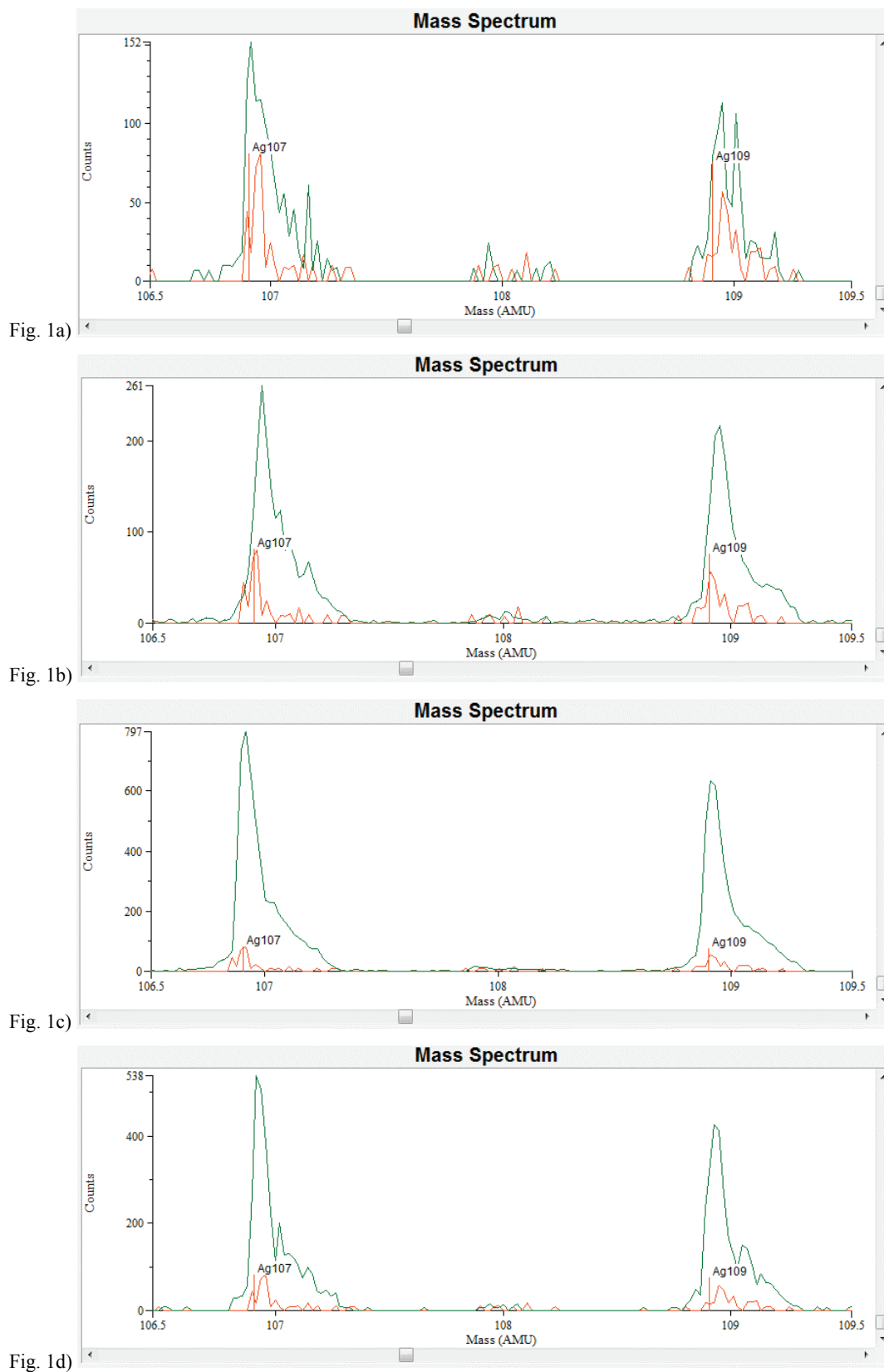


Fig. 1. ICP-ToF-MS spectra for the chosen region of the mass spectra corresponding to the Ag isotopes, showing the Ag ion release after 7 days of sample incubation. In red – signal for the SDR control sample vs. – in green:  
 (a) 24  $\mu\text{g}$  Arsil + 14  $\mu\text{g}$  Areosil + 2 g SDR; (b) 20  $\mu\text{L}$  nano Ag 2000 ppm + 2 g SDR;  
 (c) 20  $\mu\text{L}$  nano Ag 5000 ppm + 2 g SDR; (d) 15  $\mu\text{L}$  nano Ag 5000 ppm + 5  $\mu\text{L}$  nanoAu 50 ppm + 2 g SDR

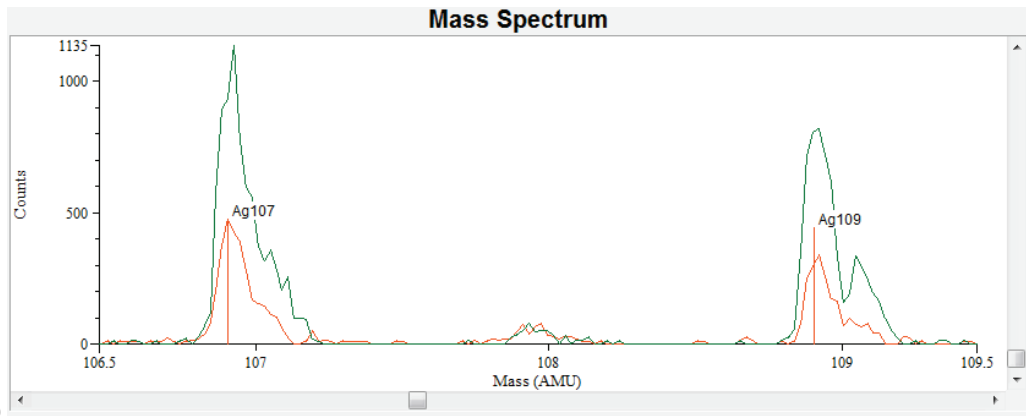


Fig. 2.1a)

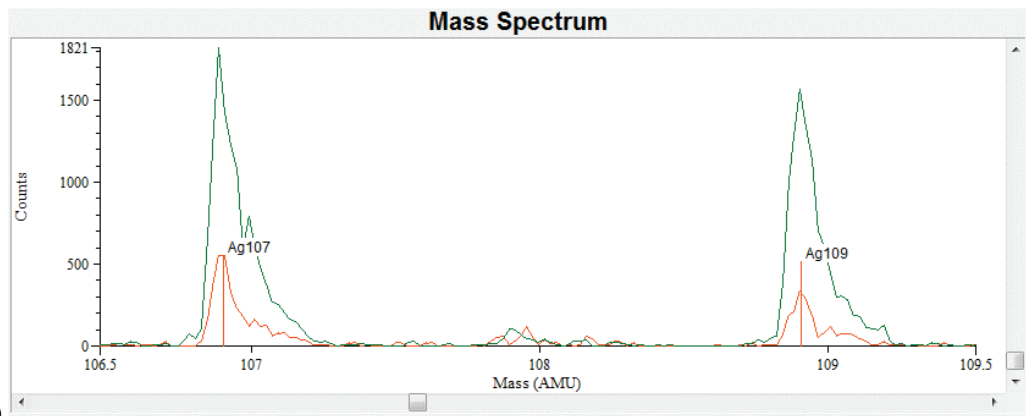


Fig. 2.1b)

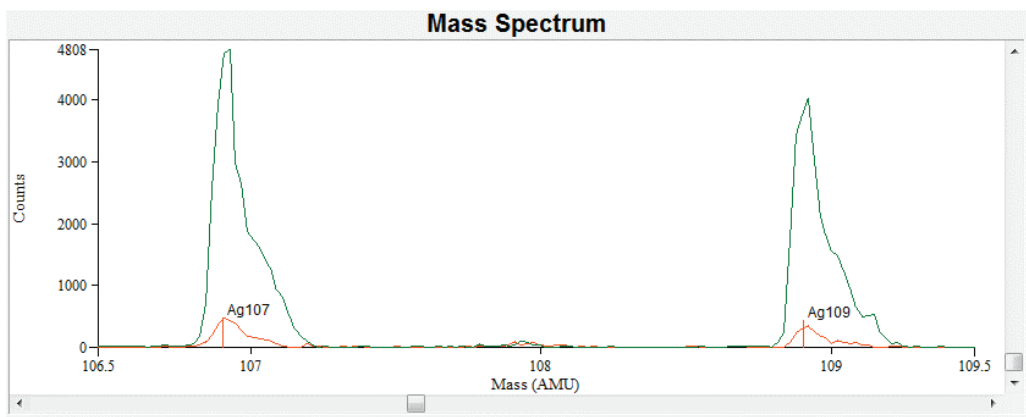


Fig. 2.1c)

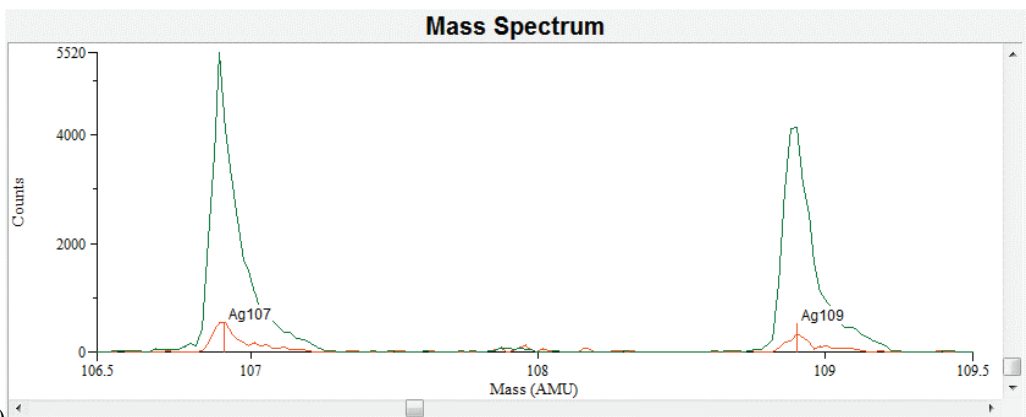


Fig. 2.1d)

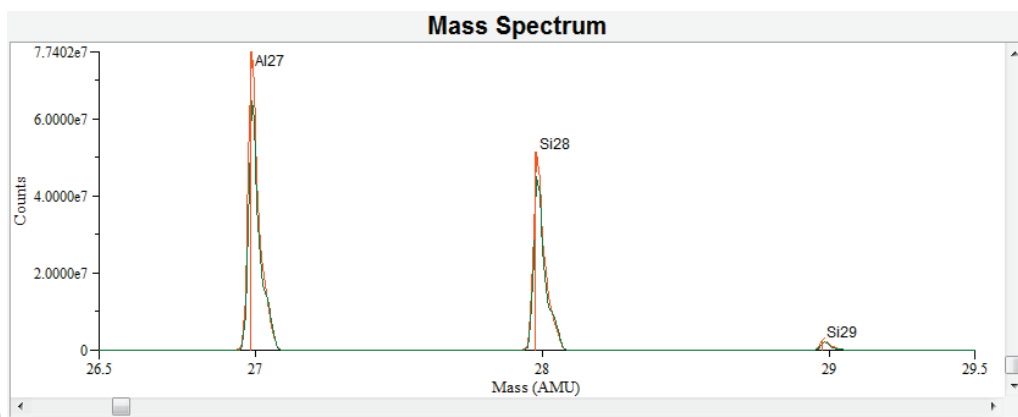


Fig. 2.2a)

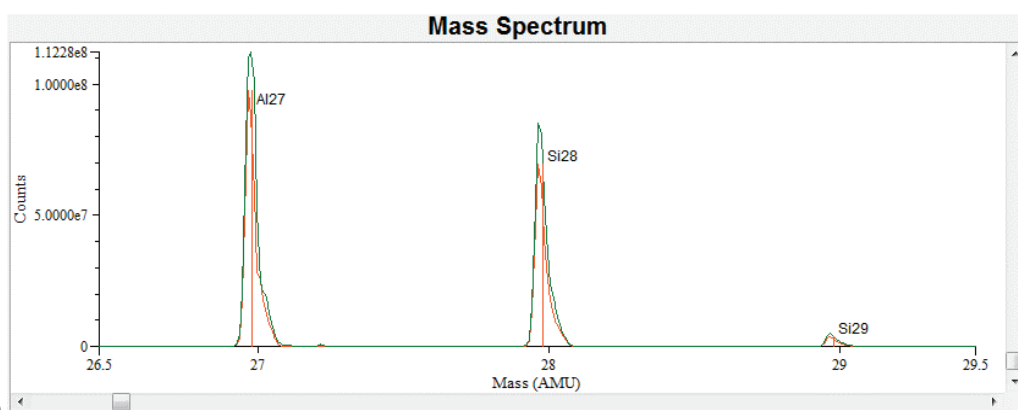


Fig. 2.2b)

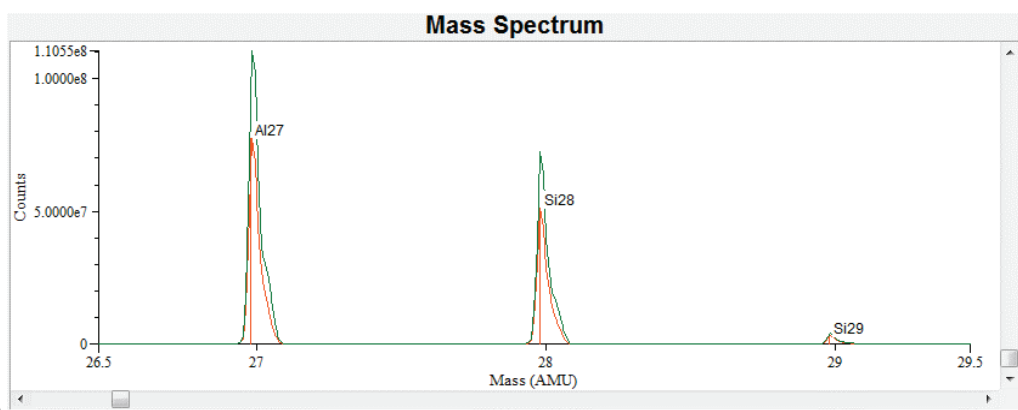


Fig. 2.2c)

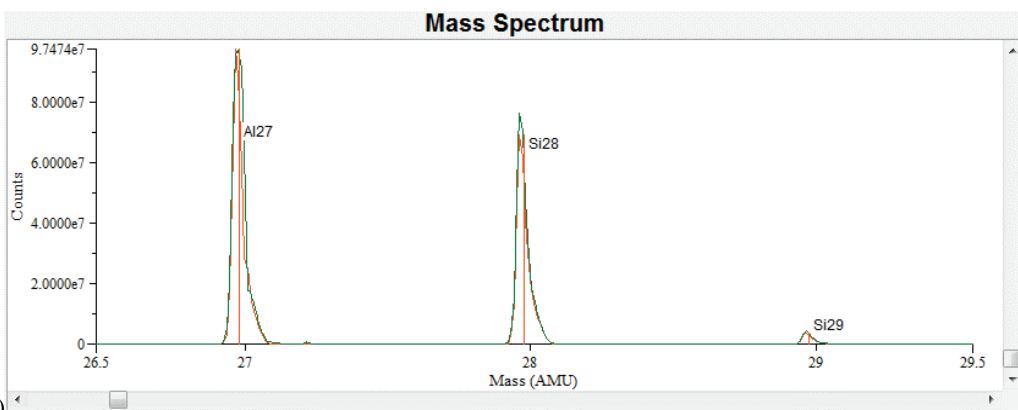


Fig. 2.2d)

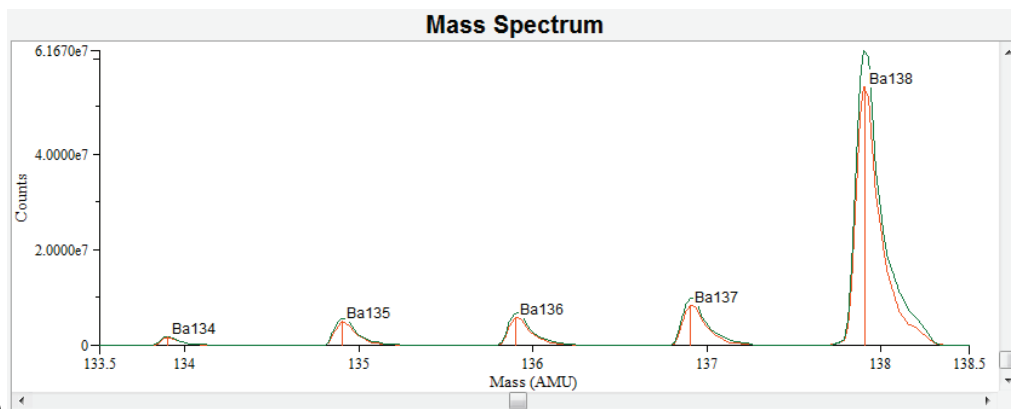


Fig. 2.3a)

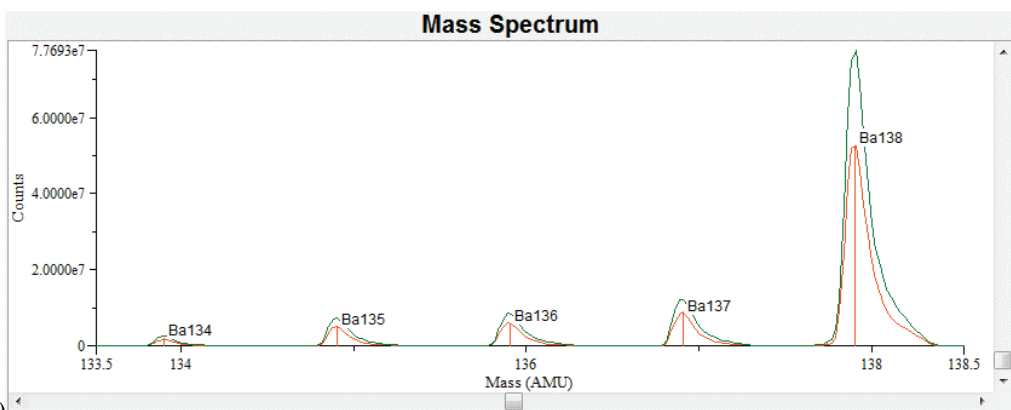


Fig. 2.3b)

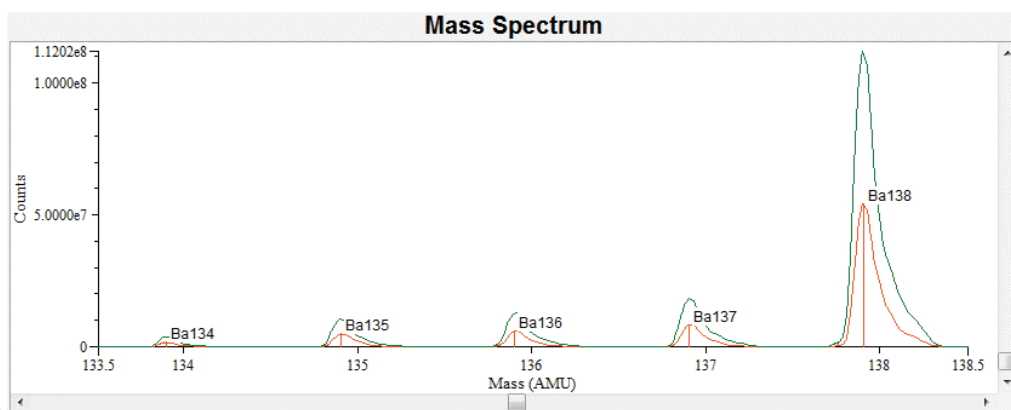


Fig. 2.3c)

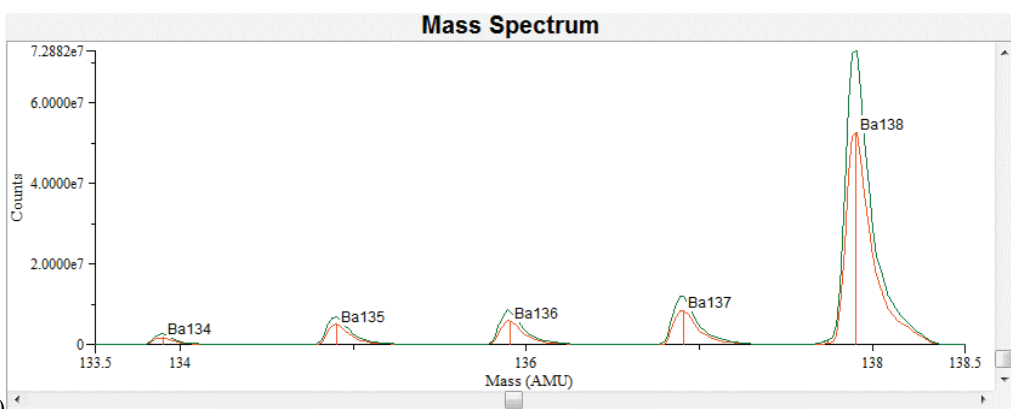


Fig. 2.3d)

Fig. 2. ICP-ToF-MS spectra for the chosen region of the mass spectra corresponding to the Ag (Fig. 2.1), Al and Si (Fig. 2.2) and Ba (Fig. 2.3) ion release after 30 days of sample incubation. In red – signal for the SDR control sample vs. – in green: (a) 24 µg Arsil + 14 µg Areosil + 2 g SDR; (b) 20 µL nano Ag 2000 ppm + 2 g SDR; (c) 20 µL nano Ag 5000 ppm + 2 g SDR; (d) 15 µL nano Ag 5000 ppm + 5 µL nanoAu 50 ppm + 2 g SDR

5000 ppm + 2 g SDR) and 4 (15  $\mu$ L nano Ag 5000 ppm + 5  $\mu$ L nano Au 50 ppm + 2 g SDR) after 7 and 30 days of incubation. Moreover, released amount of Ag ion slightly increased with the Ag quantity (15  $\mu$ L nano Ag 5000 ppm + 5  $\mu$ L nano Au 50 ppm + 2 g SDR  $\approx$  20  $\mu$ L nano Ag 5000 ppm + 2 g SDR > 20  $\mu$ L nano Ag 2000 ppm + 2 g SDR > 24  $\mu$ g Arsil + 14  $\mu$ g Areosil + 2 g SDR > SDR) (Figs. 1 and 2.1). Furthermore, the amount of silver ions slightly increased during the incubation period. No silver ions were released from the control sample. In the case of Al and Si ions the highest amount was released after 7 days of incubation of group 3, and after 30 days – groups 2 and 3. These results suggest that sample modification with nanosilver may have caused an increase in Al and Si ion release (Fig. 2.2). Significant amounts of strontium and barium ions were released after 7 days. The highest count number of Sr ions after 7 days of incubation was measured in groups 2 and 3. After 30 days of incubation comparable Sr ion amount was released from the samples modified with nanosilver or nanosilver and nanogold. After 7 days of incubation the highest intensity of Ba peaks was observed in group 3, followed by group 2. These results suggest that the high silver content in nanosilver-modified composites caused the increase in Ba ion release. Similar results were obtained after 30 days of incubation: the highest amount of Ba ions was counted for group 3 and then for group 2 (Fig. 2.3). The Au ion release was not detected after 7 and 30 days (Fig. 3) of incubation for group 4.

nanosilver modification. Slightly more yellow and opaque colour was observed in the samples modified with silica fillers (Arsil and Aerosil).

## 4. Discussion

There is a long history of medical use of silver as an antimicrobial agent. Many attempts have been made to develop antibacterial resin composites to prevent from recurrent caries [29].

In the present study all experimental resin composites (groups 1–4) in comparison to the control group were found to exhibit similar DTS. Diametral Tensile Strength value in group 1 was higher, however not statistically significant, than in control group, which can be explained by high silica filler content. Moreover, an increase was observed in all experimental composites concerning their microhardness evaluation in comparison to the control group. Arsil and Areosil addition resulted in the highest microhardness and relatively low DTS value, remaining on acceptable clinical level. Thus, the mechanical properties of nanogold- and nanosilver-modified composites examined in this study were similar to currently used flowable composite materials. These results indicate that experimental composites meet requirements for restorative dental materials and may be applied in clinical conditions in the future. Good mechanical

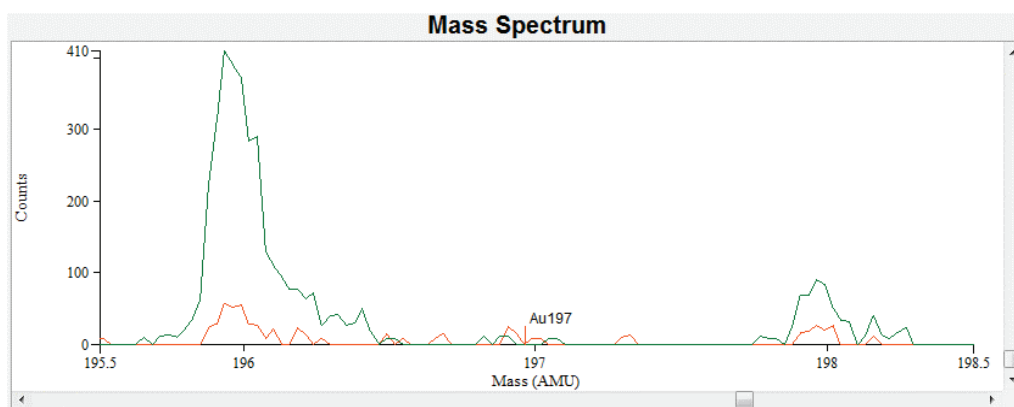


Fig. 3. ICP-ToF-MS spectra for the chosen region of the mass spectra corresponding to the Au isotope, showing the Au ion release after 30 days of the sample incubation.  
In red – signal for the SDR control sample vs. – in green: SDR + 15  $\mu$ l nAg 5000 ppm + 5  $\mu$ l nAu

The colour of nanosilver-modified composites turned from light yellow to dark brown. No difference in colour between addition of 2000 ppm and 5000 ppm nanosilver dispersion was observed. However, the addition of nanogold resulted in slightly lighter appearance than

properties also suggest that the curing process was not hampered by modification.

Ahn et al. [3] found no significant difference in shear bond strength and bond failure interface between composite adhesives containing silica nanofill-



ers and silver nanoparticles and conventional adhesives. This implies that incorporation of silver nanoparticles may not have an adverse effect on mechanical properties of composite adhesives containing silica nanofillers and silver nanoparticles if proper amounts of silver nanoparticles are used. However, the modulus and ultimate transverse strength (UTS) of silver nanoparticles-loaded resins (used as an implant material for cranioplasty) were significantly lower than the control [17]. The compressive and flexural strengths of the composites incorporating silver-supported antibacterial material (Novaron) were not significantly different from those of the controls when immersed in water for 6 months [29]. Thus, it was confirmed that the incorporation of Novaron had no effect on the mechanical properties of TEGDMA-UDMA-based resin composites [29]. However, another silver-supported antibacterial material (Amenitop) incorporated into dental composite caused a long-term deterioration of material mechanical properties [29]. On the other hand, the presence of silver nanoparticles in acrylic resin (Selecta Plus) improved flexural strength [30].

Fan et al. [31] demonstrated that according to the Rockwell hardness measurements, the higher the concentration of silver benzoate in light-cure composite resins, the lower the degree of cure. The authors suggested that  $\text{Ag}^+$  ion reduction and the generation of atom clusters and nanoparticles during curing causes the competition with the free radical polymerization process. The hardness of chemical-cure composite resins was unaffected by the nanoparticles addition [31].

Moreover, our light transmission study revealed significant differences between the control group and experimental groups. The light transmission value for nanogold- and nanosilver-modified composites was comparable to opaque flowable materials such as TetricEvoCeram 230op/A3.5 and Xflow O-A3 [32]. A decrease in light transmission was observed after adding nanosilver and nanogold. Colour change to dark brown was also observed. The amount of 20  $\mu\text{L}$  nanosilver seems to be the maximum, since larger quantities resulted in unacceptable colour and light transmission inhibition [32]. However, the material containing smaller amounts of nanosilver was indicated for aesthetic restorations. Moreover, nanogold addition gave slightly lighter appearance. Because of brownish and opaque colour our experimental composites can be applied as liner, composite core build-up material and fissure sealant. Materials used for these indications should exhibit antibacterial properties to prevent caries formation and have dentin-like

appearance (liner, composite core build-up material). They should also be visible on the surrounding enamel (fissure sealant). Colour is a possible disadvantage of composite adhesives containing silica nanofillers and silver nanoparticles [3]. This colour change may occur to be a potential limitation, especially when an aesthetic effect is important. However, finding appropriate proportion of nano-silver and composites or addition of small amounts of gold might partially solve the colour problem.

Balan et al. [33] found in TEM studies of the UV-cured nanocomposite that the  $\text{Ag}(0)$  nanoparticles (0.5%, w/w) remained well-dispersed in the polymer matrix. Their average diameter increased to 20 nm, which was explained by the authors as a tendency to agglomeration throughout the polymerization process [33]. Moreover, the addition of 0.2% (w/w) silver nanoparticles to the formulation had little influence (lower values) on the viscoelastic properties of an UV-cured sample [33]. Silver nanoparticles reduce the gloss of UV-cured coatings even at very small silver percentage: 0.2% (w/w) content – reduces the gloss value by 60%; 0.5% (w/w) content – 20% of the control value [33]. This behaviour was attributed to an increase of the surface roughness upon addition of silver nanoparticles [33].

Ahn et al. [3] found that the orthodontic composite adhesives containing silica nanofillers and silver nanoparticles had rougher surfaces than conventional adhesives due to the addition of silver nanoparticles, bacterial adhesion, however, was lower than in conventional adhesives. Moreover, the surface free energy of modified adhesives was similar to composite [3]. Silver nanoparticles-loaded chemical-cure resins showed bacterial inhibitory effect against *S. mutans* [31]. Composites incorporating 5 wt % or more of silver-supported antibacterial materials inhibited the growth of *S. mutans* for 6 months [29].

The ICP-ToF-MS technique seems to be a useful method to assess the process of metal ions release from dental materials. These data are very important since short-term (7 and 30 days) biological risk of novel nanometal-modified dental materials should be meticulously investigated before clinical application. Surprisingly, there was no Au ion release from nanogold-containing samples into 0.9% NaCl both after 7 and 30 days. Moreover, the amount of silver ion release was negligible at the small rate. However, the highest amount of Ag ions was released from the nanosilver-modified samples, that increased with time of incubation and the nanosilver amount in the composite resin. Moreover, it occurred that silver, incorporated in samples, may increase the ion release, such as

Al, Si, Sr and Ba. The highest ion release after 7 and 30 days was evident in group 3 (20  $\mu$ L nano Ag 5000 ppm + 2 g SDR), which suggests that this modification method causes an increase in not only Ag ion release, but also in Al, Si, Sr, Ba ion release. Supposedly, the addition of nanoparticles may cause deterioration of resin-filler interactions, composites may become less compact and thus, more susceptible to the component leaching. The modification of samples with Arsil and Aeosil did not influence significantly ion release. However, the amount of ion release from this sample (group 1) was slightly higher or comparable with the control group (SDR).

In literature only a few studies concerning metal ion release are available. A silver nanoparticles-loaded resins (polymethyl methacrylate) (used as an implant material for cranioplasty) released Ag<sup>+</sup> ions in vitro for over 28 days and caused significant bacteria growth inhibition [17]. A four-week ion release study showed that chemical-cure resins released the majority Ag<sup>+</sup> ions in all concentrations tested [31]. However, light-cure composite resins released only Ag<sup>+</sup> ions when silver benzoate concentration was greater than 0.1% (w/w) [31]. There was no or extremely slight release of silver ions from composites incorporating 5 wt. % or more of silver-supported antibacterial materials after 1 day or after 6 months [29].

In the present study, curing time was extended and polymerization from both sides of the specimen was applied to ensure complete hardening. The light-polymerization prolongation of resin composites loaded with silver particles up to 2 min (from both sides) was also described in the literature [6].

To conclude, experimental nanosilver-containing composites released significant amounts of Al, Si, Sr and Ba ions up to 30 days, and negligible silver ion amounts. Significant Ag ion release occurred in nanosilver- and nanogold-modified composites. Resin composites modified with nanogold and nanosilver deposited on silica carrier exhibit lower light transmission and have opaque appearance. All experimental composites exhibited higher microhardness in comparison to non-modified resin composites. Diametral Tensile Strength of the experimental composites was comparable to the control group.

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