

The impact of nanosilver addition on element ions release from light-cured dental composite and compomer into 0.9% NaCl

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The aim of this paper was to identify and to assess in semi-quantified way the release of different ions from composite and compomer restorative materials subjected to 0.9% NaCl solution, which simulates the environment of the human body. In the present study, the number of ions (Al, Ag, Ba, Sr, Ti) released from dental fillings over time (one week, one month and 3 months), in different temperatures (23°C, 37°C) and depending on the materials applied (unmodified/modified with nanosilver) was investigated. The results suggest that nanosilver addition influences directly on the process of metal ion releasing into 0.9% NaCl solution. The increase in the number of counts of metal ions was observed in the solutions in which samples modified with nanosilver were kept. Higher amount of metal ion release was observed for composite samples rather than for compomer materials. The study revealed that in general the number of released metal ions increases with the time of storage (for metal ions: Ti, Ba, Sr) and at higher temperature (Ag, Ti, Ba). Reverse tendency observed for silver ion release versus incubation time may be caused by the process of silver adsorption, which takes place on the surface of analyzed material and test-tube walls, where samples were incubated.

Key words: dental composites, dental compomer, nanosilver, ion release, ICP-ToF-MS

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INTRODUCTION

Caries is a disease of tooth hard tissues with nearly 100% frequency in human population, leading to the damage and as a result the premature loss of teeth. The complex etiology of this disease includes the vulnerability of hard tissues, the cariogenic diet rich in carbohydrates and cariogenic bacteria, which are believed to be the main factor for developing caries and prevalence of inflammatory complications in its progress. Bacteria of the following genera: *Streptococcus*, *Lactobacillus* and *Actinomyces* are considered to be cariogenic, especially *Streptococcus mutans* (Hahn *et al.*, 2000). Bacteria produce lactic acid, which affects and dematerializes enamel and dentine that leads to creation of carious lesion. The presence of bacteria in the cavity, the colonization of dentine tubules and the bacterial microleakage between restoration and dental tissues connected mainly with loss of restoration seal, may result in pulpitis and in extreme

cases even in pulp necrosis, as well as in secondary caries, periodontitis and general infections leading to various complications, including: vascular, renal, cardiac diseases, etc. (Ohara *et al.*, 1993; Hahn *et al.*, 2000). Complications mentioned above may be avoided by application of the clinical procedures, such as cavity preparation and restoration. During cavity preparation, carious dentine is removed, that eliminates only a part of present microbes. Bacteria are the part of smear layer created during preparation with rotary tools, present on the dentine surface and inside dentine tubules. Microorganisms can remain in the cavity over one year due to excellent conditions for reproduction. Disinfectants, e.g. chlorhexidine gluconate (CHG), sodium hypochlorite (NaOCl) and hydrogen peroxide (H₂O₂), should be employed during dental treatment to eliminate bacterial complications. Therefore, the cavity disinfection before application of filling material becomes a principal preventive procedure. In fact, this procedure does not appear to be fully effective, because bacteria *in vivo* are much more resistant to bactericides than *in vitro* because of the phenomenon of protective biofilm formation and insufficient penetration into infected dentine, for instance by chlorhexidine (Schmalz *et al.*, 2004; Imazato *et al.*, 2006). It should be also taken into account, that bonding systems show strong antibacterial properties only directly after application and lose this ability with time, depending on the type of bonding system, from 1 to 14 days. Also, polymerization of dental composites additionally decreases their bactericidal potential (Kozai *et al.*, 2000; Slutzky *et al.*, 2004; Feuerstein *et al.*, 2007). Moreover, restorative materials without antibacterial properties is a large problem on the grounds of the phenomenon of marginal seal loss on the composite- or bonding-tooth interface, when rapidly reproducing bacteria colonize the forming gap. Nowadays, dental composites have to face high expectations, mainly in terms of aesthetic, durability, wear resistance and bonding strength to tooth hard tissues. The proper bonding between composite and tissues is significant since material has no biological influence on cariogenic bacteria. That is why the sound restoration is the only way to stop bacterial invasion along the cavity margin and to avoid complications including secondary caries

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Abbreviations: AAS, atomic absorption spectrometry; AgNO₃, silver nitrate; CHG, chlorhexidine gluconate; CH₃OH, methanol; Cts, counts; H₂O₂, hydrogen peroxide; ICP-ToF-MS, inductively coupled plasma time-of-flight mass spectrometry; NaBH₄, sodium borohydride; nAg particles, silver nanoparticles; NaOCl, sodium hypochlorite; PEI, polyethylenimine; PVP, polyvinylpyrrolidone; UV-VIS range, ultraviolet-visible range; XRD, X-ray diffractometry

and, as a result, treatment failure. Hence, the need for modifications of dental composites, aiming at material with antibacterial properties, seems to be clinically justifiable.

Many efforts have been made to modify bonding systems and restorative materials in order to improve antibacterial properties by adding strong bactericides (Imazato *et al.*, 1997; Imazato *et al.*, 2002; Wicht *et al.*, 2005; Imazato *et al.*, 2007; Hiraishi *et al.*, 2008; Imazato, 2009; Jandt & Sigusch, 2009; Fong *et al.*, 2010). Results of researches showed higher antibacterial properties of modified materials, but it is rather unlikely to expect their long-term action.

Bactericidal agents based on nanoparticles and nanometal are widely applied (Beyth *et al.*, 2006). Many researches recommend, for instance nanosilver solutions, for disinfection of burn wounds, creating antibacterial coatings on implants (Slenters *et al.*, 2008). First efforts to use nanosilver to improve temporary filling material (Hotta *et al.*, 2008) such as acrylic resins used for prosthetic appliances (She *et al.*, 2004), elastic-tissue conditioners (Matsuura *et al.*, 1997) as well as composite resins (Yoshida *et al.*, 1999; Fang *et al.*, 2006; Bürgers *et al.*, 2009), and orthodontic cements (Sug-Joon *et al.*, 2009) have been already made. Materials incorporating nanosilver and nanogold particles (e.g. Nano Care Silver Plus) are in use for disinfection of the root canal during treatment.

Considering this, the absence of secondary caries over many years in cavities restored with amalgam fillings, takes on a new importance. This can be explained by antibacterial properties of the amalgam, particularly by silver release into saline which is a result of Ag-Sn amalgam material corrosion (Morrier *et al.*, 1998).

The addition of nanosilver to restorative materials, including composites and glassionomer cements, should increase their antibacterial properties. This should be a result of silver ion diffusion to surrounding environment after material polymerization, especially directly after filling the cavity when dental pulp presents the decrease in defensive abilities due to preparation and filling procedures. The diffusion of nanosilver particles into dentine tubules and antibacterial activity on superficial layer of dentine seem to be particularly important, because dental bactericidal products e.g. chlorhexidine exert no specific action. Researches proved the presence of metals and products of corrosion in enamel and dentine in the direct proximity of amalgam fillings, as well as an increase of metals concentration in connective or osseous tissue in the neighborhood of implants. Higher concentrations of cobalt ions, even up to several hundred times, were observed around CoCr implants (Howie *et al.*, 1996).

Currently, most dental practitioners use a technique of flow composite application in a thin layer on a previously applied bonding system before final restoration of the cavity. The flow composite modified with nanosilver particles could be used as a liner, from which silver ions would diffuse through bonding system directly to the hard tissues of the tooth and provide antibacterial properties. However, this kind of action requires silver ion release from restorative material into biological environment.

The main objective of this study was to assess the influence of nanosilver addition on metal ion release from dental fillings (compomer, composite) into 0.9% NaCl solution. Different time intervals and various temperatures were taken into consideration.

The application of the inductively coupled plasma time-of-flight mass spectrometry (ICP-ToF-MS) allows

the preliminary estimation of investigated material stability in the environment of oral cavity (0.9% NaCl). It seems to be a solution which enables the explanation of many not yet fully known phenomena occurring in dental composites, especially these modified with nanosilver.

MATERIALS AND METHODS

Materials preparation. The investigated material comprises samples of composites X Flow/Dentsply and compomer Dyract Flow/Dentsply DeTrey, both being a light-cured restorative material with flow characteristics, which makes it ideal for small cavities in anterior and posterior teeth. The main elemental components for both compomer and composite samples are Sr, Al, Na, F, Si, Fe, Ti. In this work, nanoparticles of silver were employed to modify the properties of studied samples of composites and compomers. Silver nanoparticles can be synthesized through various methods including spark discharging, electrochemical reduction, solution irradiating and cryochemical synthesis (Slistan-Grijalva *et al.*, 2005; Yan *et al.*, 2006; Zhang *et al.*, 2007; Chen & Schluesener, 2008; Li *et al.*, 2008; Tien *et al.*, 2009; Rai *et al.*, 2009; Revathi Janardhanan *et al.*, 2009; Satyanarayana Reddy *et al.*, 2009; Chladek *et al.*, 2012; Mavani & Shah, 2013). The most commonly applied method of metal nanoparticles preparation in solution is chemical reduction of metal ions. Recently, the attention is focused on the laser ablation of bulk metal in water, a methodology that appeared for generating metal nanoparticles. The use of surfactants promotes improved size uniformity as well as reduces the coalescence during the fabrication of nanoparticles (Yan *et al.*, 2006; Zhang *et al.*, 2007; Chen & Schluesener, 2008; Li *et al.*, 2008; Tien *et al.*, 2009; Rai *et al.*, 2009). In this study, silver nanoparticles were obtained by chemical reduction method as reported by Mavani & Shah, 2013 (Mavani & Shah, 2013). This method includes the reduction of a silver salt such as silver nitrate (AgNO_3) with a reducing agent like sodium borohydride (NaBH_4) in the presence of colloidal stabilizer. In our case, nAg particles were prepared by the chemical reduction of AgNO_3 using NaBH_4 . The borohydride anions were adsorbed onto silver nanoparticles. The addition of PVP (polyvinylpyrrolidone) prevented the aggregation of particles. The synthesized silver colloid contained 5000 ppm of silver in methanol (CH_3OH). All reagents used in this study were analytically pure. PVP average M.W. 8000 was purchased from Acros Organics, UK while AgNO_3 , NaBH_4 and CH_3OH were purchased from POCh, Poland. The dispersion of silver was prepared as follows: AgNO_3 was dissolved in methanol solution containing 5% of PVP in order to obtain the final concentration of silver of about 5000 ppm. The mixture was stirred using magnetic stir bar until the ingredients were dissolved. Then, the NaBH_4 dissolved in 5% PVP was added to the mixture (the molar ratio of NaBH_4 to Ag was equal 0.1; a large excess of sodium borohydride is needed both to reduce the ionic silver and to stabilize the formed nanoparticles), and the mixture was stirred again with magnetic stir bar for 15 minutes. By mixing both solutions (i.e. NaBH_4 and AgNO_3), Ag ions were reduced and clustered to form monodispersed nanoparticles as a transparent sol in the methanol medium. After this time, the whole system was cooled. Cooling is used to slow down the reaction as well as to give better control over final particle size/shape. There are also known other methods of nanosilver incorporation into composites in order to reduce the microbial colonization

of lining materials, e.g. Chladek *et al.*, incorporated nAg into a soft lining material and in modified materials such parameters as sorption, solubility, hardness and tensile bond strength were tested. It was proved that the best properties (including antifungal efficacy) were achieved for silver nanoparticle concentrations ranging from 20 ppm to 40 ppm (Chladek *et al.*, 2012).

The exact concentration of silver in methanol dispersion was determined using AAS (atomic absorption spectrometry) technique (AAnalyst 300 by Perkin Elmer). The analysis was performed using air-acetylene flame and flame atomizer. The silver dispersion was also studied in UV-VIS range (300–700 nm) using Marcel spectrophotometer by Marcel Media in order to assess the size of particles. Moreover, the phase composition was analyzed using Philips X'Pert X-Ray Diffractometer (XRD), equipped with graphite monochromator PW 1752/00, Cu K α 1,54, Ni filter (40 kV, 30 mA). The test sample was prepared by complete evaporation of solvent at room temperature.

Subsequently, the corresponding group of samples of composite and compomer modified with nanosilver solution was prepared. Modified material was fabricated by mixing composite/compomer material with 5000 ppm nanosilver alcohol solution, proportions were set on 0.025 ml of nanosilver per 2 g of material. Disc-shaped samples, 5 mm in diameter and 3 mm in height, were polymerized in two layers in silicone forms with use of light-curing diode lamp Demi/Kerr Sybron with light intensity amounting to 1400 mW/cm². Before semi-quantitative investigations each sample was washed with ethanol and then placed in a test-tube in 10 mL 0.9% NaCl solution.

Composite restorations seem to represent excellent aesthetics properties, but due to the polymerization shrinkage during setting, they are associated with marginal leakage, which causes bacterial penetration and, as a consequence, the potential damage to the tooth. Notwithstanding, fluoride-releasing materials in combination with silver ions can influence the surrounding micro-environment, involving bacteria. However, Dyract flow material is believed to be more restoration-protecting fluoride than conventional flowable composite (Gjorgievska *et al.*, 2009).

Methods. A number of counts of metal ions released into NaCl solution from the dental materials were determined using Optimass 8000 ICP-ToF-MS spectrometer (inductively coupled plasma mass spectrometer with time-of-flight analyzer; GBC Scientific Equipment, Australia) after a week, a month and three months of storage at a room (23°C) and at human body (37°C) temperature. The time-of-flight-ICP mass spectrometry allows the carrying out rapid multielement analysis at ultra-trace level and the collection of almost a full mass spectrum at exactly the same moment in time. This kind of investigation enables the semi-quantitative assessment of corrosion ability of studied dental materials based on the amount of ions released into the adjacent environment of artificial saliva solution. The operating parameters were optimized using multielemental solution delivered by Merck. The acquisition time was 3 seconds. The mass spectra were compared using multi-element spectral fingerprinting OptiMass 9500 software application.

RESULTS AND DISCUSSION

The rapid development in modern nanotechnology has spurred significant interest in the environmental

applications of nanomaterials, which are thought to be excellent adsorbents, catalysts, and sensors due to their large specific surface area per mass (Li *et al.*, 2008) (a large proportion of atoms are in immediate contact with ambient and readily available for reaction), high reactivity (Li *et al.*, 2008; Rai *et al.*, 2009), and their ultrasize, which offers greater particle mobility both in the environment and in the body. It has been demonstrated that nanoparticles can be successfully applied in diagnostics, biomarkers, cell labeling, contrast agents for biological imaging, drug delivery systems and nano-drugs for treatment of various diseases (Rai *et al.*, 2009). Nowadays, strong antimicrobial properties of some natural and engineered nanomaterials including silver nanoparticles (nAg) have been reported. So far, the antimicrobial properties of silver compounds and silver ions have been used in many applications such as disinfecting medical devices (there are wound dressings, contraceptive devices, surgical instruments and bone prostheses - all of them are coated or embedded with nanosilver) or in daily life (home appliances to water treatment, room sprays, laundry detergents, wall paint) (Li *et al.*, 2008; Rai *et al.*, 2009). Silver nanoparticles are also incorporated into textiles for manufacture of clothing, underwear and socks (Rai *et al.*, 2009).

Up to now, few mechanisms of antimicrobial silver nanoparticles have been proposed: (1) adhesion of nanoparticles to the surface altering the membrane properties (nAg particles degrade lipopolysaccharide molecules), (2) DNA damage by nAg particle penetration inside bacterial cell, (3) release of silver Ag⁺ ions after the dissolution of nAg (it was shown that silver ions interact with thiol groups in proteins, causing the inactivation of respiratory enzymes and the production of reactive oxygen species; moreover, Ag ions prevent DNA replication and affect the structure and permeability of the cell membrane). In this study, silver nanoparticles were obtained by chemical reduction method. The obtained silver dispersion in alcohol solution was also analyzed. The concentration of silver in methanol dispersion was determined using AAS technique. The determined concentration of silver (4542 ppm) was slightly lower than assumed value (5000 ppm). It is a well-known fact that nAg particles can take various shapes such as: spheres, rods, cubes, wires and multifacets, normally within a size range of <100 nm (Rai *et al.*, 2009). The size of nAg plays a crucial role in their antimicrobial activity, those less than 10 nm have shown to be more toxic to bacteria such as *Escherichia coli* and *Pseudomonas aeruginosa*, while particles with size from 1 to 10 nm can inhibit certain viruses from binding to host cells (Li *et al.*, 2008). In our work, the size and phase composition were additionally evaluated for prepared silver in methanol dispersion. The silver dispersion was studied in UV-VIS range (300–700 nm) using spectrophotometer. For analyzed sample wide absorption band was noticed in the VIS range. The absorbance maximum was located at 428 nm. Owing to the fact that silver nanoparticles are able to absorb VIS radiation caused by the presence of surface plasmon, the shifting of the maximum of Ag⁰ peak in the range from 390 nm to 500 nm is observed, depending on the shape and size of silver nanoparticles. Based on the obtained results the silver nanoparticles were estimated to be 15 to 20 nm in diameter. Moreover, the phase composition was analyzed using X-Ray Diffractometer (XRD). In X-ray diffractograms reflexes of metallic silver were only observed. X-ray diffraction peak broadening suggests nanometric structure of studied sample. What is more, the antimicrobial activity of silver dispersion in alcohol,

that was tested in this study, was also investigated in the past. In our previous work, the antibacterial properties against *Streptococcus mutans*, *Lactobacillus acidophilus* and *Enterococcus faecalis* were assessed for nanosilver dispersion in alcohol. We observed a linear relationship between a concentration of silver in the dispersion (from 125 up to 5000 ppm) and the bacteria growth inhibition zone (mm) (the increase of silver concentration caused statistically significant increase of inhibition zone growth). There was also a significantly greater zone of growth inhibition for three studied bacteria in 0.2% chlorhexidine digluconate when compared with methanol and 2-propanol and a nanosilver dispersion in alcohol at a range of silver concentration from 125 to 500 ppm. The same tendency was stated for 1000 ppm and 5000 ppm (*E. faecalis* and *S. mutans*) and 2000 ppm (*S. mutans* and *L. acidophilus*). The obtained results showed that in comparison with chlorhexidine the antibacterial activity of nanosilver dispersion in alcohol at a concentration below 500 ppm is weaker. The results proved that nanosilver in a concentration of 5000 ppm, for which the linear concentration dependence of nanosilver in the dispersion in relation to its antibacterial activity was noticed, are the most promising (Łukomska-Szymańska *et al.*, 2013). Similar studies were performed by other authors as well. In the work of Beyth and coworkers (2006) antimicrobial tests using *S. mutans* showed that PEI (polyethylenimine) nanoparticles while being incorporated into dental composite resin at low concentration (1%) and exhibit a strong antibacterial effect against the tested bacteria quaternary ammonium polyethylenimine (Beyth *et al.*, 2006).

In the second part of this study, the degree of releasing of chosen metal ions depending both on the temperature of samples incubation and on the type of tested material (modified/not modified) was evaluated. The influence of temperature on the process of metal ion release into 0.9% NaCl solution was not unequivocal for all tested samples. The amount of silver ions released at different temperatures for unmodified materials was similar to the results obtained for blank sample (0.9% NaCl solution), and in general no significant differences were stated among studied unmodified samples. In case of compomer and composite nanosilver modified materials the significant amount of silver ions released into 0.9% NaCl solution was observed. The exemplary comparison of the amount of silver ions released (^{107}Ag , ^{109}Ag) from modified and unmodified composite X Flow Demi at room temperature after a week of storage into 0.9% NaCl solution is presented in Fig. 1.

It was observed, that in case of compomer and composite materials modified with nanosilver, the number of counts of silver ion release clearly amplifies with the in-

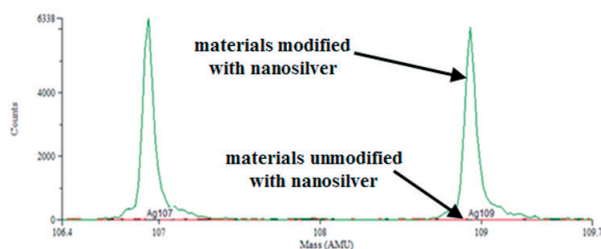


Figure 1. Mass spectrum showing the intensity of Ag (^{107}Ag , ^{109}Ag) ions released from unmodified and modified materials with nanosilver composites X Flow Demi at room temperature after a week of storage in 0.9% NaCl solution.

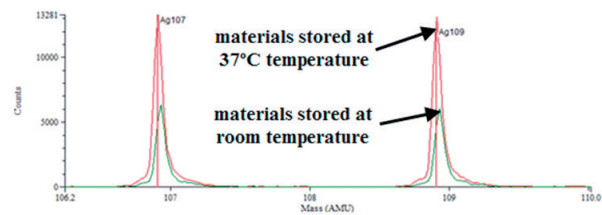


Figure 2. Mass spectrum showing the comparison of the intensity of Ag (^{107}Ag , ^{109}Ag) ions released from X Flow Demi modified with nanosilver stored at room temperature and 37°C after one week of incubation.

crease of storage temperature (Figs. 2, 3), and the biggest number of counts was noticed at temperature of 37°C.

From all investigated samples, X Flow Demi composite modified material showed the highest level of silver ion release into saliva solution at 37°C. Also, about twice-fold higher amount of silver ion release after one week of storage at 37°C (13281 cts) comparing to room temperature (6338 cts) was measured (Fig. 2).

In most cases for Ba and Ti, higher amount of ions was released at human body temperature (37°C) comparing to room temperature. The number of counts of Sr ions released in various temperatures was correlated with the presence of Ag in composite and compomer samples. The X-Flow composite (Fig. 4) and Dyract Flow compomer (Fig. 5) modified with nanosilver and incubated at higher temperature released more Sr ions in comparison to the samples stored at room temperature. The reverse tendency was observed for unmodified materials (composite and compomer). The strong relation between the number of Ti ions and temperature was also noted for all samples. The increase in temperature caused the corresponding increase in number of counts for Ti ions. However, it should be mentioned that basing on the natural abundance of Ti isotopes the number of counts related to Ti ion release was also affected by possible interferences connected with the creation of biatomic molecules Si-O. The results show also the increase in the amount of Sr and Ti ion release with the storage time both for X-Flow composite and for Dyract Flow compomer materials. The number of counts for Sr and Ti ions were higher for X-Flow and Dyract Flow materials modified with nanosilver than for unmodified samples (Fig. 6). The number of counts for Sr and Ti ions obtained for modified composite and compomer samples especially at 37°C were similar and it seems that there is no direct dependence on the type of studied material. Moreover, the results suggest that compomers and composites modified with nanosilver seem to be in gen-

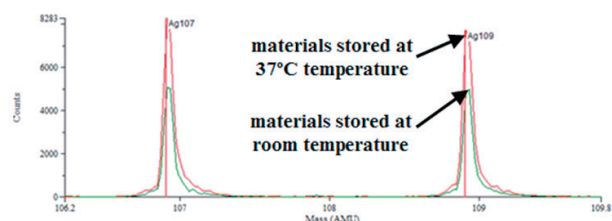


Figure 3. Mass spectrum showing the comparison of the intensity of Ag (^{107}Ag , ^{109}Ag) ions released from Dyract Flow Demi modified with nanosilver stored at room temperature and 37°C after one week of incubation.

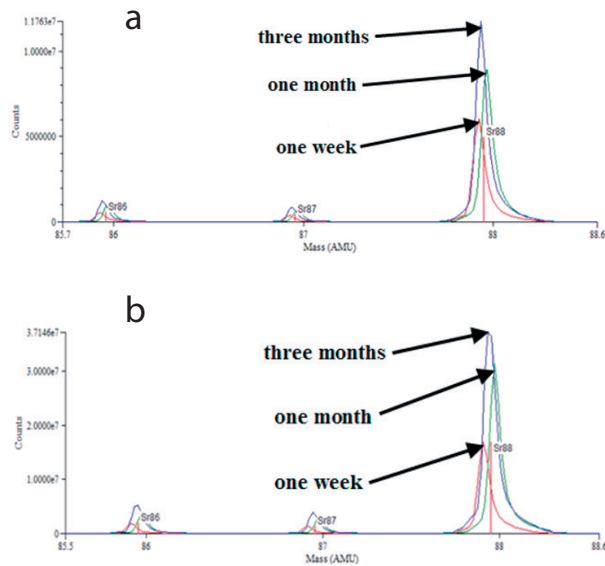


Figure 4. Mass spectrum showing the comparison of the intensity of Sr (^{86}Sr , ^{87}Sr , ^{88}Sr) ions released from X Flow Demi modified with nanosilver stored at (a) room temperature and (b) 37°C after a week, a month and three months of incubation.

eral more susceptible for these metal ion release process than the materials without nanosilver addition.

The addition of nanosilver influenced also the increase of Al releasing process, however, no relation with time and storage temperature for this metal was stated. Generally, the process of Al ion release was stronger for composite-based materials. The lowest amount of Al ion release was noticed for unmodified Dyract Flow material among all investigated samples.

The amount of metal ions such as Ti, Ba, Sr increased with the time of study, with the exception of Ag. The lower amount of Ag ions released during 1 month and 3 months of incubation in comparison with the first week

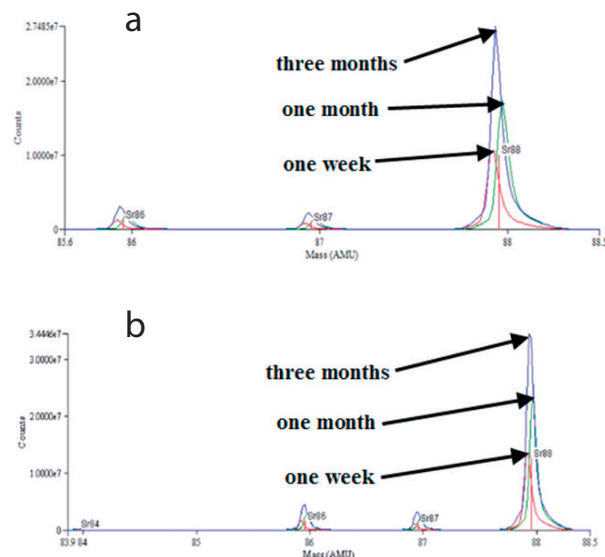


Figure 5. Mass spectrum showing the comparison of the intensity of Sr (^{86}Sr , ^{87}Sr , ^{88}Sr) ions released from Dyract Fow Demi compomer modified with nanosilver stored at (a) room temperature and (b) 37°C after a week, a month and three months of incubation.

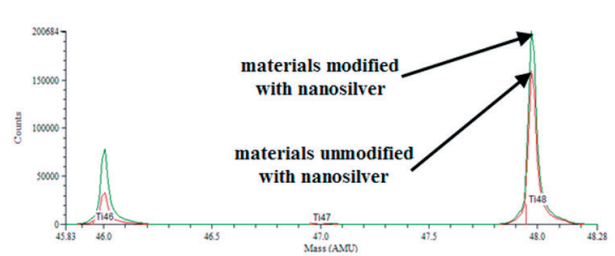


Figure 6. Mass spectrum showing the comparison of the intensity of Ti (^{46}Ti , ^{47}Ti , ^{48}Ti) ions released from X Flow Demi composite unmodified and modified with nanosilver stored at 37°C after three months of incubation.

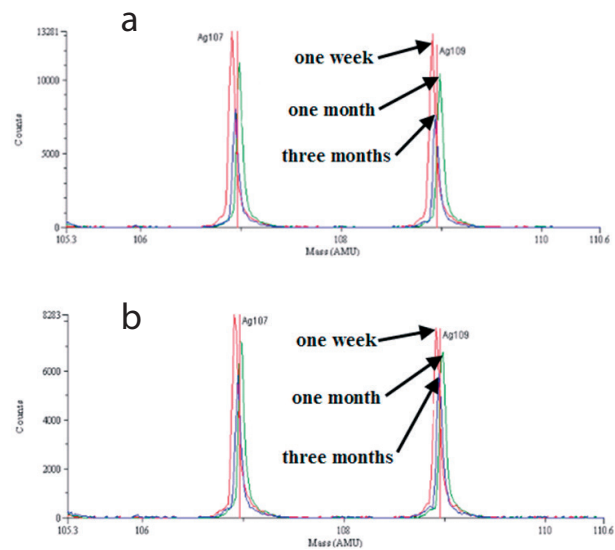


Figure 7. Mass spectrum showing the intensity Ag peaks for (a) X Flow Demi and (b) Dyract Flow modified with nanosilver vs. incubation time at human body temperature.

of storage was noticed (Fig. 7). It is probably connected with the process of Ag ion adsorption on the sample surface and test-tube walls, where samples were incubated. This phenomena is confirmed by the studies on the metal ion release from CoCr alloys in case of the same metals: at the beginning, the increase in Cr ion release and later the decrease in the amount of Cr ions in the NaCl solution was observed. It can be interpreted as a result of Cr ion incorporation in created passive layers.

In many fields of life, including medicine and dentistry, scientists concentrate on products with antibacterial properties (Yoshida *et al.*, 1999; Furno *et al.*, 2004; Kangwansupamonkon *et al.*, 2009; Rai *et al.*, 2009). In the present study, the silver ion release from X Flow and Dyract Flow materials modified with nanosilver is of prior importance and indicates potentially better antibacterial properties of nanosilver-modified materials. Many studies suggest, that different materials exhibit antibacterial, antifungal and antiviral action thanks to the addition of nanosilver (Yoshida *et al.*, 1999; Kawashita *et al.*, 2000; Yan *et al.*, 2001; Kumar & Munstedt, 2005; Bürgers *et al.*, 2009; Sug-Joon *et al.*, 2009).

The antibacterial properties of the examined materials do not depend solely on the nanosilver addition. The tested resin composite materials contain, as inorganic filler, reactive silicate glass (strontium-aluminium-fluoro-silicate glass) and aerosil — highly dispersed glass fill-

er embedded in matrix creating composite matrix. The reactive silicate glass (strontium-aluminium-fluorosilicate glass) is an important component, because the fluoride release is determined mainly by the glass filler. Fluoride released from silicate glass possesses anticariogenic action, due to the conversion of hydroxyapatite, the mineral constituent of enamel and dentine, to fluoroapatite, that is more difficult to dissolve in acids. Fluoride exhibits strong antibacterial action because of the cell cycle block of bacterial cells (Wiegand *et al.*, 2007). The released Ba and Sr ions, observed in the present study, come from silicate glass. The difference in the amount of the element release can result from the amount and from the degree of bonding of the elements in glass. As far as the amount of the elements released from tested materials is concerned, the highest amount of Sr should be underlined. This effect is also very beneficial, especially if we take into account antibacterial properties of materials applied in caries cavity. It was found that Sr released from resin composite possesses strong antibacterial properties (Dabsie *et al.*, 2009). The higher amount of Sr release from nanosilver-modified materials indicates significant improvement in antibacterial properties, that are the result of both Sr and Ag release. Syafiuddin and coworkers (1997) added powdered filler Apacider-AW, containing Ag and Zn, to resin composite and obtained better antibacterial and anticariogenic properties, however, at the cost of mechanical properties (decrease) of the tested material.

The lowest quantity of Al ion release is certainly connected with slight percentage of this element in glass and filler, that is added during production process to increase the chemical durability of filler. Titanium released from resin composite comes not from glass, but from titan dioxide, that is added to resin materials as dye to give tooth-like color to the material. It should be noted that nanosilver, added to the tested materials, changed its color to yellowish brown. The color of modified material was similar to the color of dentine material, that is used during tooth reconstruction of inner (dentine) filling part. The color modification is beneficial, particularly while applying flow resin composite as a liner, that is liquid, first material layer used in reconstruction of the tooth cavity.

The present study is the part of the mainstream aiming at the improvement in antibacterial properties of bonding systems and reconstruction materials, that should result in materials with good antibacterial properties, elimination or limitation of cariogenic bacterial flora and the decrease in secondary caries risk and inflammatory complication of the pulp and periapical tissues and systemic complications (Jandt & Sigusch, 2009).

CONCLUSIONS

Materials modified with nanosilver due to their antibacterial properties are increasingly applied in many areas of medicine. However, the results obtained may suggest that the nanosilver addition can have a direct influence on the process of metal ion release into 0.9% NaCl solution. The increase in the number of counts of metal ions was found in the solutions in which modified samples were kept. The contribution of blank (0.9% NaCl) was negligible.

For majority of the studied samples higher extent of metal ion release was observed for composite samples: X-Flow Demi and X-Flow Demi modified with nanosilver in comparison with compomer materials: Dyr-

act Flow Demi and Dyract Flow Demi modified with nanosilver. As a result, the application of Dyract Flow-type material is assumed to offer better protection comparing to X Flow Demi materials, as well as the samples based on compomer material reduce the release of metal ions into physiological solution of NaCl. The modification with nanosilver, simultaneously provides silver ions into biological environment and enables to obtain material with antibacterial properties. The study revealed also that in general the number of metal ions released increases with the time of storage (Ti, Ba, Sr) and at higher temperature (Ag, Ti, Ba). Reverse tendency observed for silver ion release versus incubation time is caused probably by the process of silver adsorption, which takes place on the surface of analyzed material and test-tube walls, where samples were incubated.

Semi-qualitative studies based on the analysis of mass spectra may become the key factor in the estimation of the dental filling stability in the surrounding environment and corrosion resistance.

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