Investigation of adding fluoroapatite nanoparticles on compressive strength and corrosion behaviour of dental amalgams

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Abstract

In recent years, there have been many efforts to improve biological and biocompatibility features of amalgam. The aim of this research was investigating the effect of adding fluoroapatite (FA) nanoparticles on compressive strength and corrosion behaviour of dental amalgam. An amalgam alloy powder was mixed with 1, 3 and 5 wt.% of FA nanoparticles to form composite powders. Compressive strength of the corresponding dental amalgam samples was measured on the first and seventh day after preparation and the corrosion behaviour was investigated by potentiodynamic polarization electrochemical test in 0.9 wt.% salt solution (physiologic serum). The results showed that the amalgam containing 1 wt.% FA nanoparticles has higher compressive strength then the pure amalgam and with increasing the FA content in amalgam to 3 and 5 wt.%, the compressive strength decreases. The results also indicated that the corrosion behaviour of the amalgam sample with 1 wt.% FA is similar to the corrosion behaviour of the original amalgam, while with increasing the weight percentage of fluorapatite, the corrosion resistance decreases. The results of this research showed that adding FA nanoparticles in amounts of up to 1 wt.% to amalgam alloy improve compressive strength, has no destructive effect on corrosion behaviour of the material and can increase its biocompatibility and biological activity.

Keywords*: dental amalgam, fluoroapatite, compressive strength, corrosion resistance*

I. Introduction

Dental amalgam is an alloy made of silver, copper, tin and mercury, and can be prepared by mixing the alloy powder with liquid mercury at room temperature. It has dough-like texture for a short time and can be shaped. Therefore dentists can insert it with applying pressure in the hole dug in the tooth and make it condensed [1].

Though a proof of amalgam biocompatibility has never been presented, amalgam is still by far the most extensively used material for dental restorations [1,2]. Amalgam has been one of the most useful and the most common materials for tooth treatment for decades and today it is used more than any other treatment materials for treating decayed teeth [2]. In the recent decade, great attention has been paid to amalgam corrosion and its biocompatibility due to its possible biological effects on human body [3–5].

In biocompatibility view, measuring corrosion means measuring the elements that are released due to the corrosion and after being released affect the tissue surrounding the dental amalgam. The biochemical reactions of the tissues with the released element depend on their type and reactivity, as well as the contact time between the element and the tissue [6]. Amalgam corrosion has usually been measured by electrochemical polarization tests and the electrochemical behaviour of an alloy is considered as an index for its biocompatibility characteristic [7,8].

Up to now, several materials such as Au, In, Pa and organic materials were added to dental amalgam in order to improve its properties [9–11]. Thus, Johnson *et al.* [9] investigated the effect of indium on properties

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of a dispersed-phase high-copper dental amalgam. Colon *et al*. [11] evaluated the influence of palladium addition on corrosion behaviour of dental amalgams. Chung *et al*. [12] investigated morphology and electrochemical behaviour of Ag–Cu nanoparticle doped amalgams.

Fluoroapatite (FA) is a bioceramic containing fluoride ion which is very resistant against attacks and acidic environment. It has been proven that fluoride ion strengthens dental enamel and through inserting primary enamel decays can prevent tooth decays in the first stage. Finally, the enamel on which the decay is stopped turns out to be stronger than natural enamel [2,13]. Therefore fluoroapatite can have such a significant role in prevention of tooth decay.

In recent years, there have been many efforts made to improve the biological function of dental amalgams. Improving biocompatibility of dental amalgam with adding bioactive materials is an example of these efforts [3]. The aim of this research was adding fluoroapatite nanoparticles to dental amalgam to improve its biocompatibility and biological activity. We were tried to prove that fluoroapatite nanoparticles have no harmful and negative effects on the corrosion resistance of amalgam, and on this way created a big step towards improving amalgam alloys. In the present research, fluoroapatite nanoparticles with varying amounts were added to dental amalgam and corrosion of the amalgam/FA nanocomposites was compared to the conventional pure amalgam.

II. Materials and methods

2.1. Synthesis of fluoroapatite nanoparticles

Fluoroapatite (FA) nanoparticles were synthesized by an ethanol-based sol-gel method. In the experimental procedure initially 6.6 g of $(NH_4)_2HPO_4$ was dissolved in 50 ml of ethanol, then 19.70 g of $Ca(NO_3)_2{\times}4H_2O$ was dissolved in 50 ml of ethanol in order to make a 0.5 M solution. Subsequently, 140 µl of HPF_6 was added to the above solution as the source of fluoride ion. The reaction was carried out at a constant temperature of 85 °C for 4 h. The produced nanopowders were dried at 120 °C for 24 h and then heated at 600 °C for 1 h. Upon cooling, the powders were gently ground for 10 min using a mortar and pestle. All chemicals were of analytical grade and purchased from Merck.

2.2. Preparation of amalgam based nanocomposites

To prepare amalgam nanocomposite samples, a commercially available dental amalgam alloy powder (World-Cap®, Ivoclar Vivadent AG, Liechtenstein) was selected. Then 1 wt.% (24 mg), 3 wt.% (72 mg) and 5 wt.% (120 mg) of FA nanoparticles were added to this alloy powder (2400 mg, 45 wt.% Ag, 25 wt.% Cu, 30 wt.% Sn) to fabricate the nanocomposite powders. The original amalgam alloy powder was used for preparation of the control sample. The experimental mixtures were first triturated in a screw-on bakelite capsule with amalgamator (VARI-MIX III, Dentsply International, York, PA, USA) for 9 s at high speed in order to obtain a homogeneous dispersion. The final amalgamation of the control pure alloy and composite powders was accomplished with Hg (2000 mg) using VARI-MIX III for 12 s at high speed. The amalgam mixtures were condensed into an acrylic mold in order to prepare 6 mm × 2 mm disk specimens using a hand condenser. Specimens were allowed to bench set initially for 15 min prior to removal from the molds. The disk specimen was then placed in a dry heat incubator for 24 h at 37 °C for final setting. Finally, the condensed surface of each specimen was finished and polished. The following sample notation was used: A-FA0 for the original amalgam (control sample), A-FA1 for the amalgam with 1 wt.% FA, A-FA3 for the amalgam with 3 wt.% FA and A-FA5 for the amalgam with 5 wt.% FA.

2.3. Structural characterization

The particle size, shape and morphology of the synthesized FA nanoparticles were evaluated with an analytical transmission electron microscope (TEM, CM200-FEG-Philips). X-ray diffraction (XRD) technique (Philips X'Pert-MPD system with a Cu Kα wavelength of 1.5418 Å) was then used to characterize and determine the phases in the FA nanoparticles and the amalgam containing 5 wt.% FA. The diffractometer was operated at 40 kV and 30 mA and XRD data were recorded over the 2θ range from 20 to 80° and with a step size of 0.02°/s.

Microstructure of the investigated specimens was observed with scanning electron microscope (SEM) and the elemental composition of the amalgam samples was confirmed by energy dispersive X-ray analysis (EDXA) technique (Phillips XL 30). The investigated samples were mounted on aluminium pins and coated with Au and then observed with the SEM operated at an acceleration voltage of 20 kV.

2.4. Compressive strength measurement

For testing the compressive strength, specimens with 8.0 mm length and 6.0 mm diameter were prepared, according to standard ISO:1559 specification. Compressive strength of the samples was measured on the 1st and 7th day after the dental amalgams were prepared. Five specimens were used for each measurement, so 10 specimens were prepared for each dental amalgam and 40 specimens in total. The specimens were stored at 37±1 °C in an incubator prior to compressive strength testing. Test was carried out on a universal testing machine (Zwick/Roell, Z020, Germany) at a crosshead speed of 0.25 mm/min. Ultimate compressive strength (*UCS*) was calculated from the formula $UCS=4F/\pi d^2$, where F is maximum applied load (N) and d the cylindrical specimen diameter (mm) [3,4,14]. The data were analysed by the analysis of variance (ANOVA) and Scheffe tests for multiple comparison among the means, $p<0.05$.

2.5. Potentiodynamic polarization tests

The effect of FA nanoparticles addition on corrosion behaviour of dental amalgam was determined by electrochemical polarization test. The evaluation of corrosion resistance of all samples was performed under identical conditions in the physiological solution. To apply potentiodynamic polarization experiments, three specimens were prepared for each dental amalgam and all the samples were kept at 37±1 °C for 24 h. Prior to each test, the surface of specimens in contact with the electrolyte were measured and the samples were subjected to the physiological solution at the temperature of 37±1 °C in order to obtain desired equilibrium. A three-electrode glass cell was used for in vitro potentiodynamic corrosion tests. Graphite electrode was used as the counter electrode and saturated calomel electrode (SCE) as a reference electrode. Physiological normal saline solution (0.9 wt.% NaCl) was used as electrolyte. In order to evaluate and compare the corrosion behaviour of specimens, they were dynamically polarized in the physiological solution. Potentiodynamic polarization curves were determined at 37±1 °C, using an EG&G model 263A potentiostat/galvanostat interfaced with a computer and a recorder [8,12,15]. The tests were started after a steady open-circuit potential was attained (not more than ±5 mV drift in 5 min). For this reason, the immersion time of the each specimen in the physiological solution was at least 2 h. The anodic and cathodic polarization curves were obtained for each specimen. The corrosion current densities and corrosion potentials of all specimens were determined from the potentiodynamic polarization curves by Tafel extrapolation method. The mean value and standard deviations of the results were calculated. The mean values were statistically compared by the analysis of variance (ANOVA) [12].

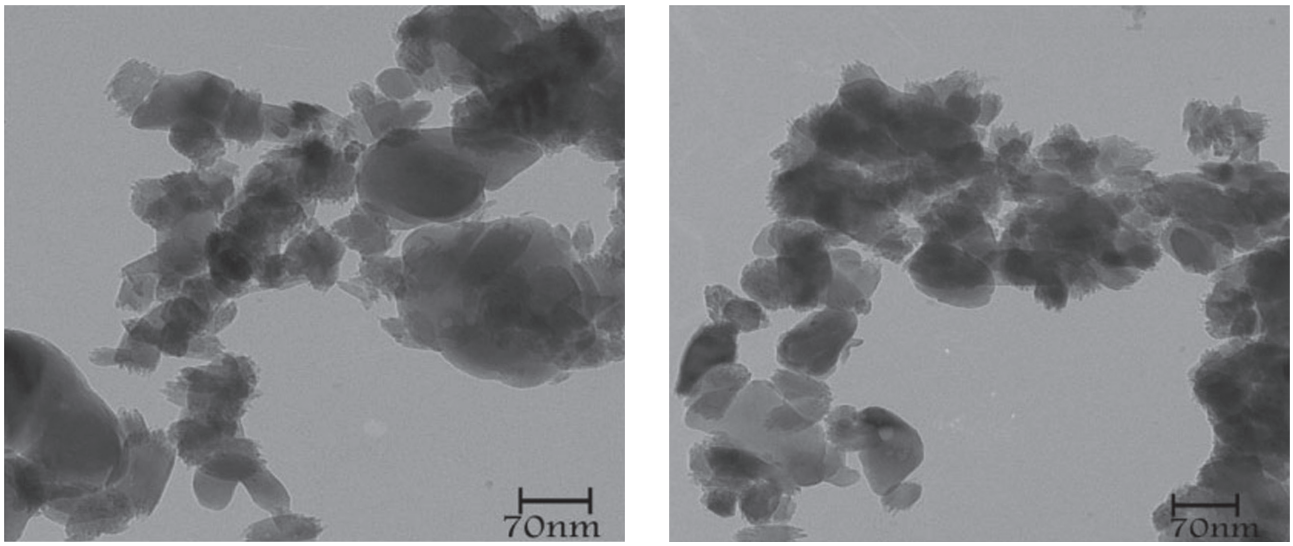

Figure 1. TEM micrographs of prepared FA nanoparticles

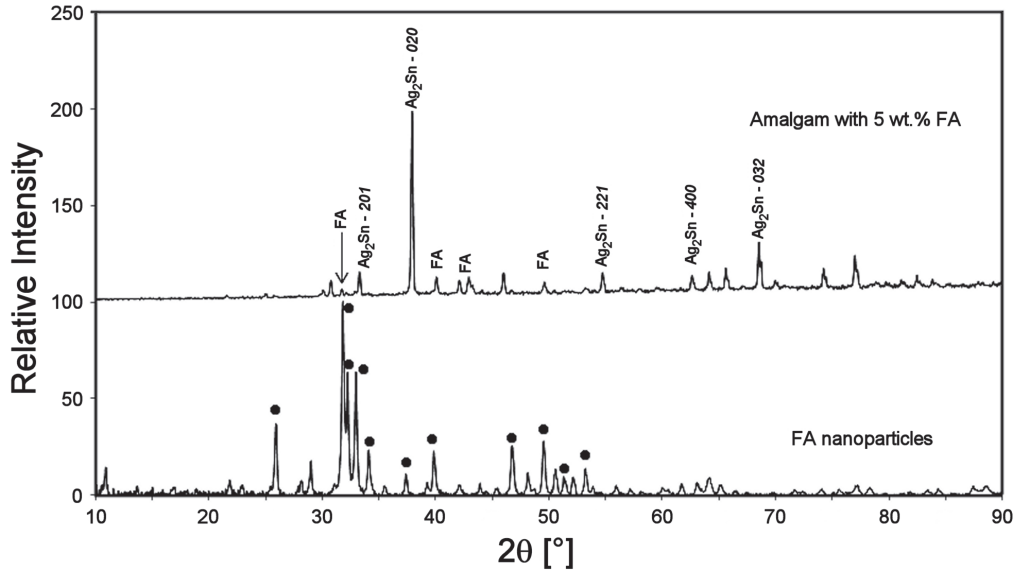

Figure 2. XRD patterns of FA nanopowder and amalgam nanocomposite with 5 wt.% FA

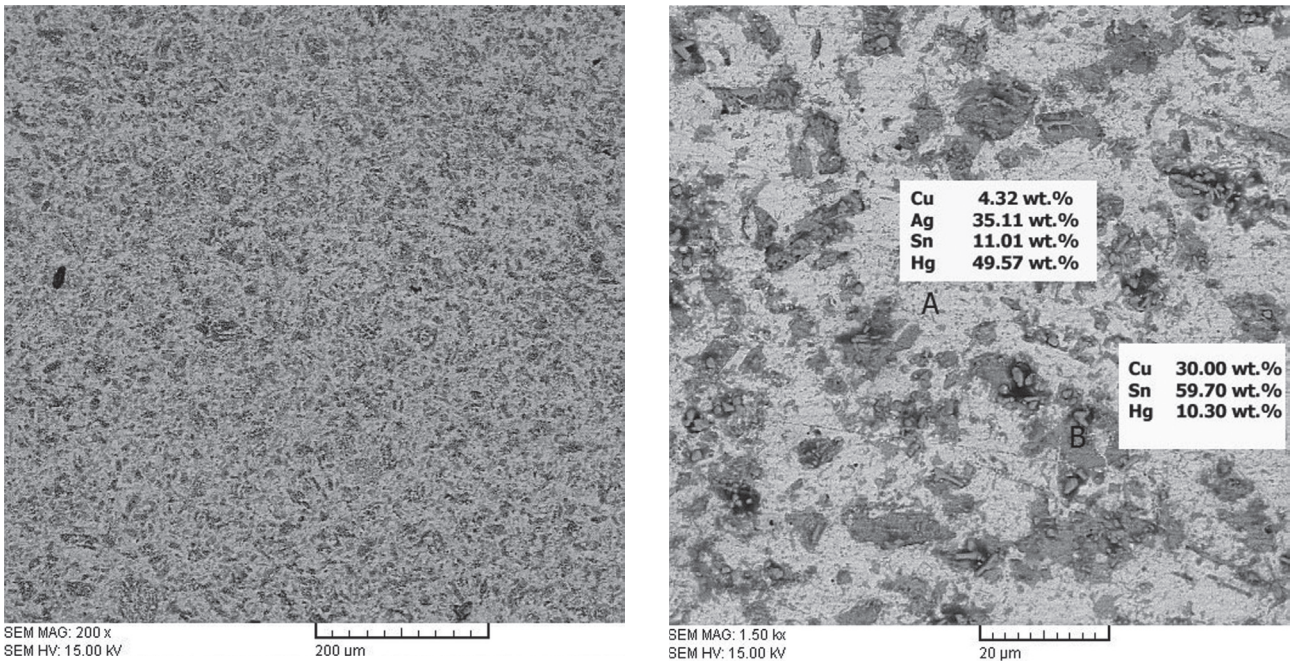

Figure 3. SEM micrographs of original amalgam, showing distribution of the present phases

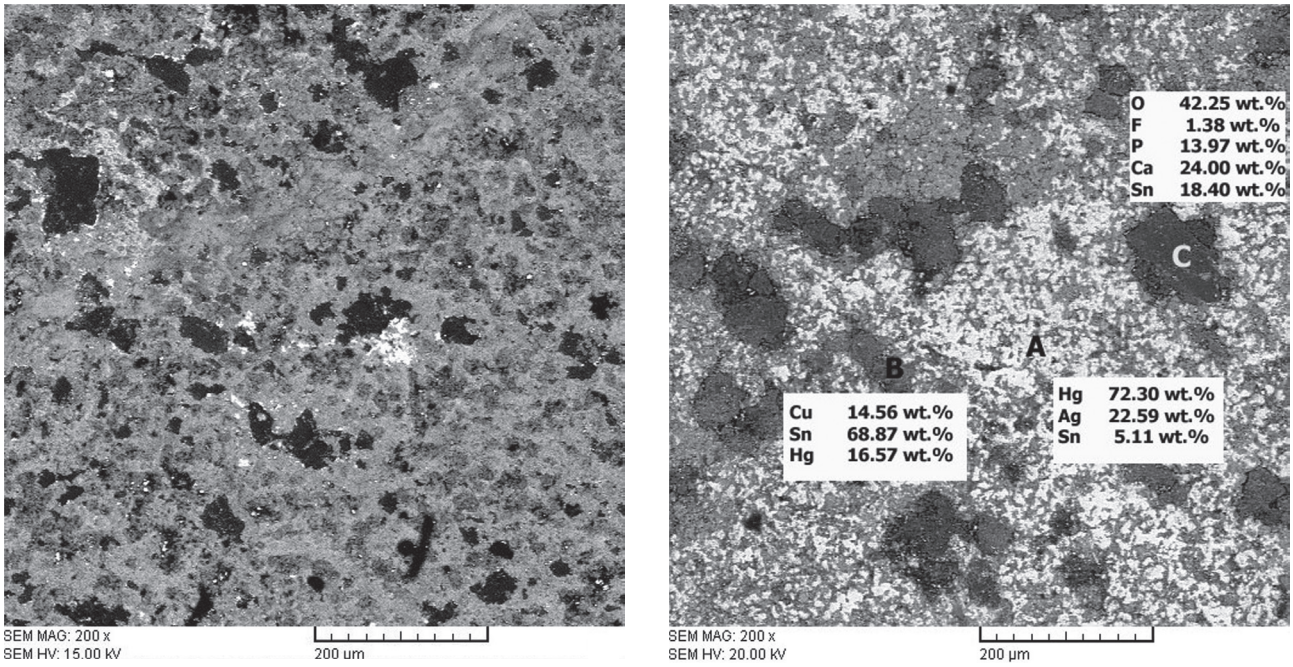

Figure 4. SEM micrographs of amalgam containing 5 wt.% FA nanoparticles showing distribution of the present phases

III. Results

3.1. Structural characterization

TEM micrographs of the FA nanoparticles are shown in Fig. 1. As can be seen the average particle diameters are estimated to be less than 50 nm.

The XRD results shown in Fig. 2a confirmed the presence of the fluoroapatite phase [13]. The diffraction pattern of the composite powder containing amalgam alloy and 5 wt.% FA nanoparticle shows major peaks for Ag-Sn phases from the amalgam alloy particles beside the main FA peaks (Fig. 2b).

The back-scattered electron scanning images show the phases present in the original amalgam, A-FA0 (Fig. 3), and the amalgam nanocomposite containing 5 wt.% FA (Fig. 4). The shades of grey reflect the average atomic number of the phases (for example, the lightest phase has the highest average atomic number). Elemental composition analysis by EDXA is also shown for the marked points. A reaction phase consisting primarily of Cu and Sn was disclosed around each particle. The unreacted particles were heterogeneous and showed segregation of the Ag-Sn and Cu-Sn phases, the darker spots

being the Cu-Sn phases and the lighter areas the Ag-Sn and Ag-Hg phases [12]. Also, FA nanoparticles agglomerations are shown in Fig. 4 (point C).

3.2 Compressive strength testing

The mean compressive strengths of all dental amalgams after 1 and 7 days are shown in Table 1. The analysis of variance (ANOVA) showed that the mean compressive strength of the amalgam nanocomposite A-FA1 after 1 and 7 days was higher than for the A-FA0 (the control sample) (p<0.05). The mean compressive strength of the amalgam composite A-FA3 was lower than that of A-FA1 (p<0.05), but the mean compressive strength of A-FA3 was not significantly different from A-FA0 (p>0.05). Thus, ANOVA showed that A-FA1 (the amalgam with 1 wt.% FA) had the highest compressive strength among all the tested dental amalgams (p<0.05) and A-FA5 had the lowest.

These results confirmed that adding 1 wt.% FA nanoparticles improved the compressive strength of the amalgam alloy. The results also indicated that with increasing the FA content to 3 wt.%, the compressive strength decreased but it was absolutely comparable to the original amalgam (the control sample). The dental amalgam nanocomposite with more than 3 wt.% FA nanoparticles showed a high decrease in the compressive strength (p<0.05).

3.3 Corrosion tests

Figure 5 shows potentiodynamic polarization curves of the prepared dental amalgams. The corrosion current densities of various specimens (the amalgam with and without FA nanoparticles) were determined from the potentiodynamic polarization curves by Tafel extrapolation method. These results align with corrosion potentials of the investigated dental amalgams kept in normal saline solution, are summarized in Table 2. The standard deviations of the corrosion current densities are also given in parentheses in Table 2. The results showed that there was no statistically significant difference between the mean value of corrosion current density of the original dental amalgam and the amalgam nanocomposite with 1 wt.% FA (p>0.05). However, the mean of corrosion current density in the dental amalgam with 3 wt.% and 5 wt.% FA showed an increase compared to the other two samples (p<0.05). The results of this ex-

Table1. Mean compressive strength with corresponding standard deviation (given in parentheses) of different dental amalgams, after 1 and 7 days

Dental amalgam	Compressive strength after 1 day [MPa]	Compressive strength after 7 days [MPa]
A-FA0	400.5 (5.5)	430.3 (5.2)
A-FA1	488.8 (4.3)	520.6 (6.1)
A-FA3	402.6 (5.0)	428.1 (4.4)
A-FA5	280.5 (6.8)	288.8 (6.1)

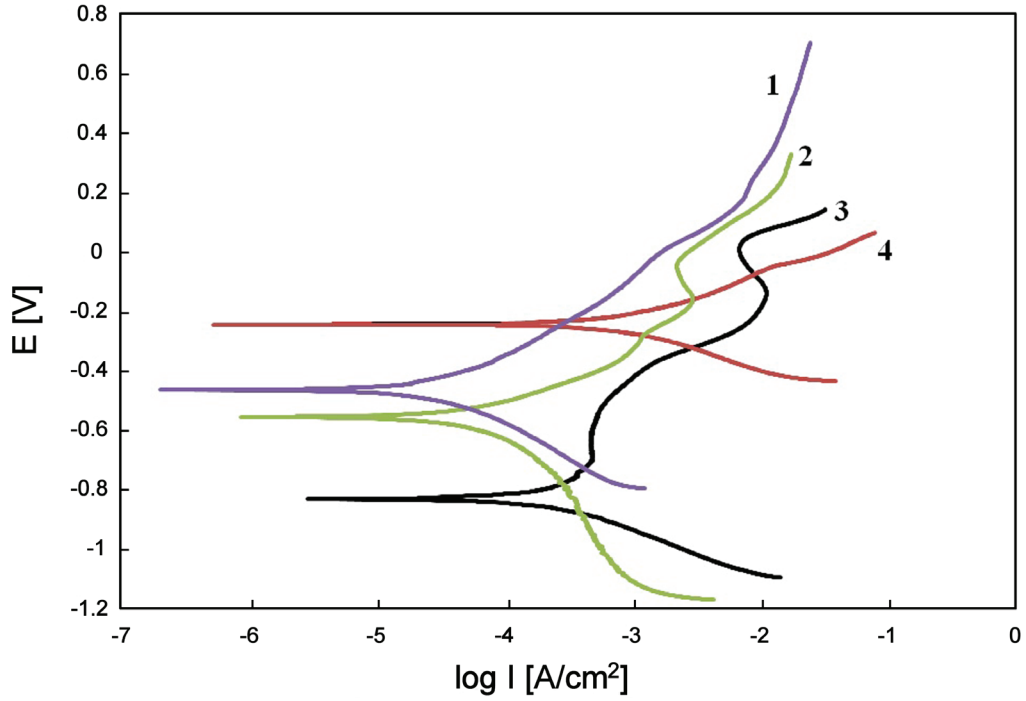

Figure 5. Potentiodynamic polarization curves of: (1) original dental amalgam, (2) amalgam with 1 wt.% FA, (3) amalgam with 3 wt.% FA, (4) amalgam with 5 wt.% FA in the normal saline solution (0.9 wt.% NaCl) at 37 ˚C

Table 2. Mean values of corrosion current densities, E_{corr}, and corrosion potentials, I_{corr}, with corresponding standard deviation (given in parentheses) for different dental amalgams kept in normal saline solution at 37 °C

Dental amalgam	E_{corr} [mV]	I_{corr} [μA/cm^2]
A-FA0	-490 (30)	86 (8)
A-FA1	-630 (24)	89 (5)
A-FA3	-860 (35)	730 (34)
A-FA5	-250 (15)	6850 (18)

periment confirmed that addition of up to 1 wt.% FA nanoparticles had no improper effect on the corrosion resistance of dental amalgam alloy.

IV. Discussion

The XRD results showed that the synthesized FA has low degrees of impurity, high crystallinity and structures correlated with hydroxyl and FA chemical compositions [13]. This observation was in agreement with the fact that fluorine addition tends to decrease the lattice parameter *a*, but not obviously affect the lattice parameter *c* [16,17].

The results of compressive strength tests showed that with increasing the FA content in amalgam, the compressive strength firstly increases (for the sample with 1 wt.% FA) and then decreases (for the samples with 3 and 5 wt.% FA). The improvement of compressive strength of dental amalgams has been considered in previous studies. Johnson *et al.* [9] showed that dental amalgams containing admixed indium have higher compressive strength. Mante *et al.* [10] concluded that existence of noble metals in dental amalgams can lead to improvement of compressive strength. Beside these results, some recent studies have indicated on positive effect of bioceramic nanoparticles on the compressive strength of dental materials. Thus, Arita *et al.* [17] reported that glass ionomer with 4 wt.% hydroxyapatite (HA) had higher compressive strength than non-reinforced commercial glass. Also, Moshaverinia *et al.* [16] showed that nanoparticles of both hydroxyapatite and fluoroapatite in glass ionomer powder (5 wt.%) can improve the compressive strength. In this study we confirmed that the FA nanoparticles (up to 1 wt.%) improve the compressive strength of dental amalgam. It is due to the small sizes of the nanoceramic (FA) incorporated into the amalgam structure. The deleterious effect of particles on mechanical properties and compressive strength of amalgam occurs in the amalgam with higher FA content. Thus, if concentration of FA particles is higher (more than 3 wt.%) the amalgamation process faces disturbance and thus the compressive strength decreases.

Corrosion behaviour of amalgam / FA nanocomposite was evaluated by the electrochemical corrosion test in the normal saline solution. It can be concluded that there is not a significant difference between the original dental amalgam and amalgam nanocomposites containing 1 wt.% FA nanoparticles. However, by increasing of bioceramic nanoparticles content, the corrosion current density increases and therefore, corrosion rate is higher. This occurrence can be related to the microstructural changes of nanocomposite due to higher level of additives which caused porosity formation. The pores in surrounding to alloy particles have deleterious effect on properties of dental amalgam, i.e. decrease corrosion resistance and compressive strength [12].

The obtained results are important because they confirm that addition of FA nanoparticles can improve corrosion resistance of amalgam, and also indicate on positive effects of fluoride ion on treatment and strength of dental enamel and decrease dental decay. This is particularly effective in improving and enhancing the functionality and biological activity of amalgam. In addition, it is proved that the nanoparticle additives in amalgam structure can decrease the level of released mercury from dental amalgam [18–20].

Development of the bioactive nanocomposite with amalgam / fluoroapatite structure is an important step toward improving and expanding the applicability and biological function of amalgam alloys.

V. Conclusions

This report presents a new investigation about the synthesis of amalgam / fluoroapatite nanocomposite. The results showed that adding 1 wt.% fluoroapatite (FA) nanoparticles can improve the compressive strength of the amalgam alloy. In addition, the results indicated that corrosion current density and corrosion potentials of the nanocomposites containing 1 wt.% FA do not change significantly, while changes are bigger for amalgams with higher FA content. Hence, it can be concluded that small amount of FA nanoparticles is suitable and seems to be a promising to improve the properties of this dental material. The results of present study suggest that amalgam / FA nanocomposite with 1 wt.% FA nanoparticles could be considered as a bioactive amalgam composite and provide a better characters for dental applications.

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