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# Effect of microwave power on EPR spectra of natural and synthetic dental biocompatible materials

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**Abstract.** Paramagnetic centers in the two exemplary synthetic and natural dental biocompatible materials applied in implantology were examined by the use of an X-band (9.3 GHz) electron paramagnetic resonance (EPR) spectroscopy. The EPR spectra were measured in the range of microwave power 2.2–70 mW. The aims of this work were to compare paramagnetic centers concentrations in different dental biocompatible materials and to determine the effect of microwave power on parameters of their EPR spectra. It is the very first and innovatory examination of paramagnetic centers in these materials. It was pointed out that paramagnetic centers existed in both natural ($\sim 10^{18}$ spin/g) and synthetic ($\sim 10^{19}$ spin/g) dental biocompatible materials, but the lower free radical concentration characterized the natural sample. Continuous microwave saturation of EPR spectra indicated that faster spin-lattice relaxation processes existed in synthetic dental biocompatible materials than in natural material. Linewidths ($\Delta B_{pp}$) of the EPR spectra of the natural dental material slightly increased for the higher microwave powers. Such effect was not observed for the synthetic material. The broad EPR lines ($\Delta B_{pp}$): 2.4 mT, 3.9 mT, were measured for the natural and synthetic dental materials, respectively. Probably strong dipolar interactions between paramagnetic centers in the studied samples may be responsible for their line broadening. EPR spectroscopy is the useful experimental method in the examination of paramagnetic centers in dental biocompatible materials.

**Key words:** EPR • microwave saturation • paramagnetic centers • dental biocompatible materials

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## Introduction

There are a lot of modern dental biocompatible materials applied in implantology with unknown properties of their paramagnetic centers. Dental biocompatible materials and their modifications were tested by the use of nuclear magnetic resonance (NMR) spectroscopy [1, 2], Fourier-transform infrared (FTIR) [3, 4], and electron microscopy [5, 6]. Gamma irradiated dental materials were tested by electron paramagnetic resonance (EPR) method [7, 8]. The nonirradiated exemplary synthetic and natural dental biocompatible materials applied in implanthology were examined by the use of EPR spectroscopy in this work. The aims of this work were to compare paramagnetic centers concentrations in different dental biocompatible materials and to determine the effect of microwave power on parameters of their EPR spectra. It is our very preliminary investigation of the dental biocompatible materials applied in stomatology.

Paramagnetic centers with unpaired electrons reveal high chemical activity in tissues [7–13]. Paramagnetic centers may change the properties of dental materials during storage, which is the

negative effect because the chemical structure of materials for stomatology should be stable. Paramagnetic centers of materials during storage in air may interact with paramagnetic oxygen molecules $O_2$ ($S = 1$). Materials susceptible to oxygen should thus be stored in an inert atmosphere, e.g., in argon. In this work, we tested dental materials, which paramagnetic properties were not studied so far by EPR spectroscopy.

## Experimental

Two dental biocompatible materials were examined by EPR spectroscopy. The exemplary natural and synthetic samples were chosen for analysis. These samples differed in composition. The main constituent in the natural dental biocompatible materials was ceramic hydroxyapatite (pentacalcium hydroxide trisphosphate). The 60% synthetic hydroxyapatite and 40% β-tri-calcium phosphate mainly existed in the synthetic dental sample. The dental samples were obtained from Denon Dental (Poland).

The natural and synthetic dental biocompatible materials were grain samples. For the EPR measurements, the solid samples were located in thin walled glass tubes with the external diameter of 1 mm. The EPR signals were not observed for the empty tubes at the experimental conditions. The mass of the samples were determined by WPS 210/C/2 (Radwag, Poland).

## EPR measurements

The X-band (9.3. GHz) electron paramagnetic resonance measurements for the natural and synthetic dental biocompatible materials were done by the EPR spectrometer with magnetic modulation of 100 kHz produced by Radiopan (Poznań, Poland). The EPR spectra were numerically collected by the Rapid Scan Unit of Jagmar (Kraków, Poland). The total microwave power produced by the klystron of the EPR spectrometer was 70 mW. Continuous microwave saturation of the EPR spectra of the dental materials in the range of microwave power 2.2–70 mW was performed. Different microwave powers were obtained by changing attenuations in the range from 15 dB to 0 dB during the measurements of the EPR spectra. The influence of microwave power in the range of 2.2–70 mW on amplitudes and linewidths of the EPR spectra was evaluated. Apparent $g$ factors, amplitudes ($A$), integral intensities ($I$), and linewidths ($\Delta B_{pp}$) were analyzed. The signals for which the amplitude and linewidths were determined are marked in Figs. 1 and 2. Integral intensity was obtained by double integration of the first-derivative EPR spectra. Integral intensity was calculated for the whole EPR spectrum to obtain the total concentration of paramagnetic centers in the samples. The apparent $g$ values were calculated from the resonance condition according to the formula [14]:

$$g = h\nu/\mu_B B_r$$

where: $h$ – Planck constant; $\nu$ – microwave frequency; $\mu_B$ – Bohr magneton; $B_r$ – induction of resonance magnetic field.

Microwave frequency was measured by MCM101 recorder of EPRAD (Poznań, Poland). The magnetic induction of the center of the total EPR spectra was used in this formula. The total EPR spectra were superposition of signals of all the unpaired electrons in the samples.

Paramagnetic center concentrations ($N$) in the natural and synthetic dental biomaterials were compared. Ultramarine and a ruby crystal were used as the references. The spectroscopic programs of Jagmar (Kraków, Poland) and LabView (U.S.A.) were used. Paramagnetic center concentrations ($N$) in the tested samples were determined according to the formula [14]:

$$N = N_u[(W_u A_u)/I_u]\cdot[I/(WAm)]$$

where: $N_u$ – the number of paramagnetic centers in the ultramarine – the reference; $W$, $W_u$ – the receiver gains for sample and the ultramarine; $A$, $A_u$ – the amplitudes of ruby signal for the sample and the ultramarine; $I$, $I_u$ – the integral intensities for the sample and ultramarine; $m$ – the mass of the sample.

The integral intensities ($I$) of the EPR lines of the analyzed dental biocompatible materials were compared to integral intensity of ultramarine – the reference. A ruby crystal ($Al_2O_3$:$Cr^{3+}$) permanently placed in the resonance cavity was the second reference. EPR lines of the ruby crystal were measured for both the tested dental samples and for reference – ultramarine. The EPR lines of the ruby crystal were observed in the others magnetic fields than EPR lines of the tested samples and ultramarine. Amplitudes of the EPR lines of the ruby crystal were determined. The integral intensities ($I$) of both the samples and ultramarine were divided by amplitudes of the EPR lines of the ruby crystal. The measurements of concentration of paramagnetic centers in the dental materials were done at low microwave power of 2.2 mW to avoid microwave saturation of the signals. The used references (ultramarine and a ruby crystal) were stable, taking into account their EPR signals, during storage period of the dental materials.

The correlations between amplitudes ($A$), linewidths ($\Delta B_{pp}$), and microwave power were determined. The correlations between amplitudes and microwave power were used to characterize spin-lattice relaxation processes. Amplitudes of EPR lines of the samples with the faster spin-lattice relaxation processes decreases at the higher microwave powers [14].

## Results and discussion

For the tested dental biocompatible materials, EPR spectra were recorded at all the used microwave powers from 2.2 mW to 70 mW. The EPR spectra of natural dental biocompatible materials are presented in Fig. 1. These spectra were measured with microwave attenuation of 15 dB and 5 dB. The EPR spectra of synthetic

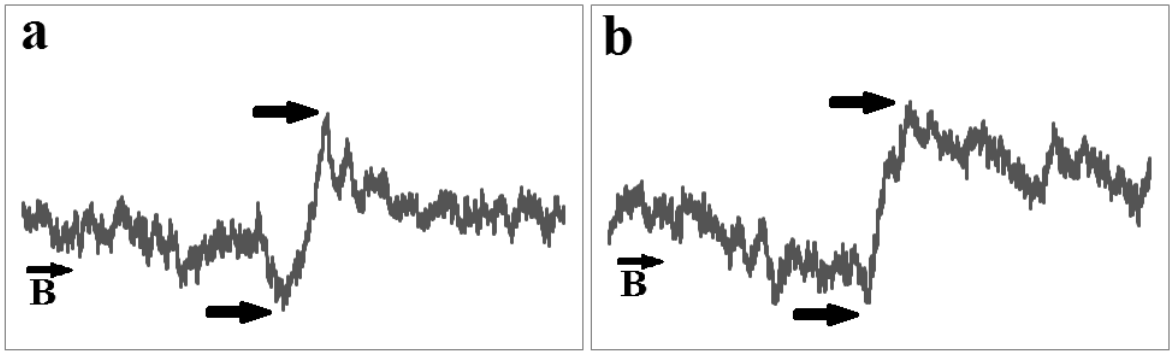


**Fig. 1.** EPR spectra of the tested natural dental biocompatible materials recorded with attenuations: (a) 15 dB, and (b) 5 dB. *B* – magnetic induction. The signals for which the amplitude and linewidths were determined are marked as (→).

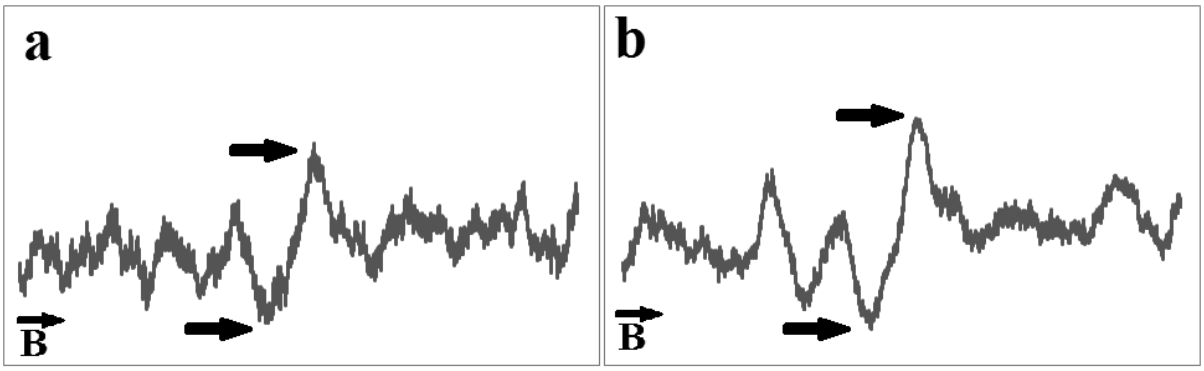


**Fig. 2.** EPR spectra of the tested synthetic dental biocompatible materials recorded with attenuations: (a) 15 dB and (b) 5 dB. *B* – magnetic induction. The signals for which the amplitude and linewidths were determined are marked as (→).

dental biocompatible materials measured with microwave attenuation of 15 dB and 5 dB are shown in Fig. 2. The shape of the EPR spectra of the tested dental materials was complex and the parameters for both natural and synthetic dental biocompatible materials depended on microwave power (Figs. 1 and 2). The noise visible in the EPR spectra may probably result from the magnetic properties of the samples, and their effect on the conditions in the resonance cavity. This work is a very preliminary study of paramagnetic centers in the two exemplary dental materials. The complex structure of the EPR spectra will be tested in the future. The apparent *g* values for both the dental materials were near 2. The complex shape of EPR spectra may be the result of existence of several types of paramagnetic centers in the samples. The shape of the EPR spectra changed with microwave power used during the measurement (Figs. 1 and 2), so we think that the spectra contained several component lines. The components changed with microwave power differently, what give the effect in the shape.

The analyzed dental biocompatible materials differ in paramagnetic center concentrations (*N*). Paramagnetic center concentrations (*N*) in the examined natural and synthetic dental biocompatible materials are presented in Table 1. In Table 1 are also shown linewidths ($\Delta B_{pp}$) and integral intensities (*I*) of their EPR spectra for attenuation of 15 dB and microwave power of 2.2 mW. Lower paramagnetic centers concentration characterized natural dental biocompatible materials (Table 1). Probably this natural dental material is more resistant regarding the interactions with paramagnetic oxygen molecules ($O_2$). In the future, the comparison of the EPR spectra of the samples in air and in argon may confirm our hypothesis.

The EPR lines of the tested natural and synthetic dental materials were very broad ($\Delta B_{pp}$ = 0.77 mT and 0.78 mT, respectively) (Table 1), so we think that probably dipolar interactions may be responsible for this broadening. The EPR spectra of natural and synthetic samples revealed similar high values of linewidths (Table 1). Strong dipolar interactions between paramagnetic centers are possible for low distances between the unpaired electrons [14]. If dipolar interactions broaden the measured EPR spectra, paramagnetic centers in the two tested biocompatible materials will be located at low distances. It is only our proposition of explaining the high values of linewidths ($\Delta B_{pp}$) of the EPR spectra.

**Table 1.** Free radical concentrations (*N*) in the examined natural and synthetic dental biocompatible materials, and linewidths ($\Delta B_{pp}$) and integral intensities (*I*) of their EPR spectra. Data for EPR spectra recorded with attenuation of 15 dB and microwave power of 2.2 mW

| Dental biomaterial | $N \times 10^{18}$ (±0.4 spin/g) | $\Delta B_{pp}$ (±0.02 mT) | *I* (±0.2 a.u.) |
|---|---|---|---|
| Natural | 6.8 | 0.77 | 2.4 |
| Synthetic | 11.0 | 0.78 | 3.9 |

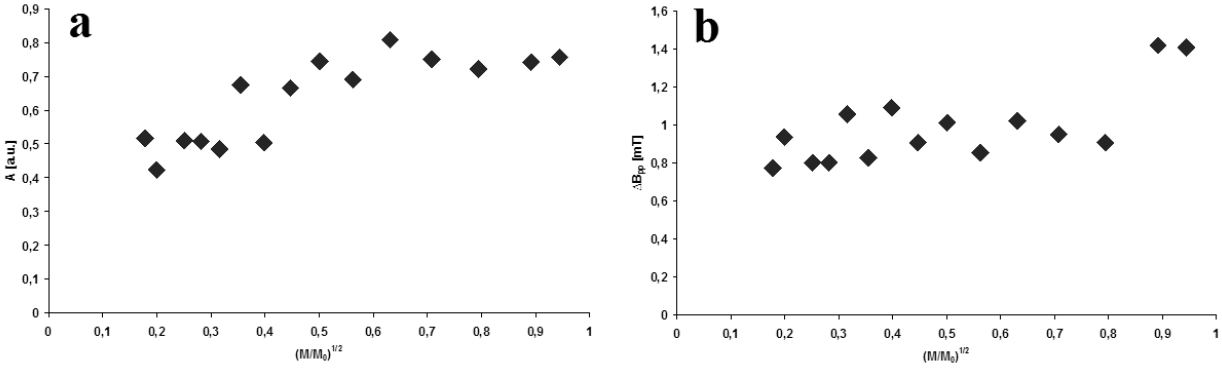


**Fig. 3.** The effect of microwave power on (a) amplitude ($A$), and (b) linewidth ($\Delta B_{pp}$), for the EPR spectra of the natural dental biocompatible materials. $M$ – microwave power used during the measurement of the EPR spectra, $M_o$ – total microwave power produced by klystron (70 mW).

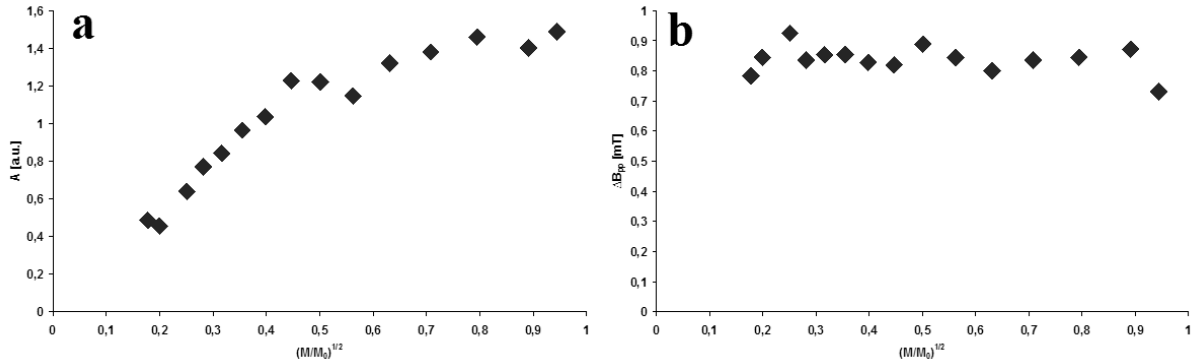


**Fig. 4.** The effect of microwave power on (a) amplitude ($A$), and (b) linewidth ($\Delta B_{pp}$), for the EPR spectra of the synthetic dental biocompatible materials. $M$ – microwave power used during the measurement of the EPR spectra, $M_o$ – total microwave power produced by klystron (70 mW).

In Fig. 3(a,b) the effect of microwave power on amplitude ($A$), and linewidth ($\Delta B_{pp}$), for the EPR spectra of the natural dental biocompatible materials is shown. In Fig. 4(a,b) the effect of microwave power on amplitude ($A$), and linewidth ($\Delta B_{pp}$), for the EPR spectra of the synthetic dental biocompatible materials is presented.

Continuous microwave saturation of EPR spectra indicated that faster spin-lattice relaxation processes existed in synthetic dental biocompatible materials than in natural material. Amplitude ($A$) of the EPR line of the natural sample increased with increasing of microwave power and it reached the maximum value (Fig. 3a), whereas amplitude ($A$) of the EPR line of the synthetic material did not reached the maximum (Fig. 4a). For the faster spin-lattice relaxation processes, EPR lines reach the maximal value for the higher microwave powers [14].

Linewidths ($\Delta B_{pp}$) of the EPR spectra of the natural dental material slightly increased at the higher microwave power (Fig. 3b). Such effect was not observed for the synthetic material. It is seen that linewidths ($\Delta B_{pp}$) of EPR spectra of synthetic sample did not depend on microwave power (Fig. 4b).

The obtained results confirmed that EPR spectroscopy is the useful method of examination of paramagnetic centers in dental biocompatible materials. EPR studies bring to light information about paramagnetic centers concentration in the dental biocompatible materials and about their properties.

## Conclusions

EPR examination of natural and synthetic dental biocompatible materials pointed out:

1) Paramagnetic centers existed in both natural and synthetic dental biocompatible materials, but lower free radical concentration characterized natural sample.
2) Continuous microwave saturation of EPR spectra indicated that faster spin-lattice relaxation processes exist in synthetic than natural dental biocompatible material.
3) Probably strong dipolar interactions exist in the tested dental biocompatible materials and they are responsible for line broadening.
4) EPR spectroscopy is the useful method of examination of paramagnetic centers in dental biocompatible materials.

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