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INVESTIGATION OF PROPERTIES OF ELECTROCONDUCTING NANOZONES IN MATERIALS OF VARIOUS NATURE BY THE ELECTRON PARAMAGNETIC RESONANCE METHOD

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Методом електронного парамагнітного резонансу вивчені електропровідні області в біомінералах (емаль зубів, кістки), і в поліамідних полотнах, що містять наночастинки поліаніліну. Встановлено, що характеристики електронного парамагнітного резонансу електропровідних нанообластей в біомінералах і текстильних матеріалах, що містять наночастинки поліаніліну, є подібними. Це обумовлено схожістю парамагнітних носіїв заряду, локалізованих в нанорозмірних електропровідних областях біомінералів і органічних полімерів

Ключові слова: наночастинки, поліанілін, біомінерал, емаль зубів, кістки, текстильний матеріал, електронний парамагнітний резонанс, електропровідні нанообласті

Методом электронного парамагнитного резонанса изучены электропроводящие области в биоминералах (эмаль зубов, кости), и в полиамидных полотнах, содержащих наночастицы полианилина. Установлено, что характеристики электронного парамагнитного резонанса электропроводящих нанообластей в биоминералах и текстильных материалах, содержащих наночастицы полианилина, являются подобными. Это обусловлено сходством парамагнитных носителей заряда, которые локализованы в наноразмерных электропроводящих областях биоминералов и органических полимеров

Ключевые слова: наночастицы, полианилин, биоминерал, эмаль зубов, кости, текстильный материал, электронный парамагнитный резонанс, электропроводящие нанообласти

1. Introduction

Availability of local, including nano-sized, zones of high electrical conductance is likely in biominerals [1, 2] and organic polymers [3, 4]. Besides, mechanisms of electrical conductance and many other properties of conductive zones in these objects turn out to be similar. Study of conductive nano-sized zones localized in objects of various types is of interest in solving variety of both basic and applied problems. Such studies are of importance in solution of basic problems, for example, elucidation of mechanisms of charge transfer and description of features of internal structure in both minerals of biogenic origin [1, 2] and conductive organic polymers [3, 4]. Among applied problems, retrospective human dosimetry [5–7] and the problems associated with creation of conductive textile materials with the use of conductive polymers [8, 9] should be mentioned. Availability of conductive zones in biominerals exerts an essential influence on veracity of the results associated with reconstruction of radiation-absorbed doses a person got in the past. It is due to the fact that conductive zones in biominerals generate signals of electron paramagnetic resonance (EPR) which overlap with the signals used in reconstruction of the human radiation dose [5, 6]. Elucidation of connection of the EPR characteristics with the mechanisms of electrical conductance in organic polymers is an urgent problem. Solution of similar problems is of high importance for development of nanotechnologies for creation of conductive materials containing nanoparticles of polyaniline on the basis of textile materials [8, 9].

2. Literature review and problem statement

Numerous works [3–7, 10–14] are dedicated to the study of properties of biominerals (enamel, bones) and organic polymers. Interaction of magnesium ions with a surface enamel mineral was shown in [10], however variation of EPR signals under effect of metal ions of various concentrations on properties of human teeth and bones was not taken in account. Work [6] investigated properties of enamel by the method of optically stimulated luminescence (OSL). Intensity of OSL signal decreased with the growth of annealing temperature from 260 to 450 °C. Study of features of EPR characteristics at the mentioned and higher annealing temperatures was not presented. In work [5], properties of native and radiation stimulated radicals in enamel were studied by EPR method but the properties associated with availability of conductive regions in biominerals have not been considered. It is known that there was an investigation of nanocomposites based on nanoparticles of silicon carbide incapsulated in conductive polyaniline. Features of EPR spectra were analyzed with an account of paramagnetic particles such as polarons with spin of $S=1/2$ taking part in the composite formation [11]. Dependence of characteristics of the EPR spectra on the quantity of initial materials in nanocomposite synthesis was not studied. Information on the study of the EPR spin centers associated with charge transfer in a metallic polyaniline was presented in work [12]. With the help of the EPR method, variation of properties of nanoparticles of zirconium dioxide under various external actions was studied in [13]. Specimen anneal in hydrogen atmosphere results in appearance of a singlet EPR signal associated with conductive regions formed at the surface on zirconium dioxide particles during anneal in a hydrogen atmosphere. The anneal process was not considered for other conditions. Aniline-to-polyaniline microwave polymerization was conducted in work [14]. It was shown that the EPR signals in polyaniline originate from polarons formed during protonation and alloying of aniline. Microwave radiation induces growth of spin concentration however the issue of influence of various levels of microwave power was not broached. To study properties of conductivezones, electron paramagnetic resonance (EPR) was used which can be treated as a noncontact method enabling one to obtain comprehensive information on the electrical conductance mechanisms. It should be noted application of noncontact study procedures for the objects under consideration is of high importance. It is connected with the fact that the resultant conductance of the studied specimens is determined not only by the properties of conductive nano-sized zones but also by the contacts between the conductive regions localized in various sections of the studied objects. Despite the large number of performed works, the considered investigation field is just at the starting stage of its development. The issues connected with the properties of local conductive regions in textile materials containing nanoparticles of polyaniline are not studied so far.

3. The aim and objectives of the study

This work purpose was to study properties of conductive nano-sized zones depending on the material nature by the method of electron paramagnetic resonance and elucidation of the mechanisms of electrical conductance and the possibility of interpretation of interconnected EPR studies for various materials.

To achieve this objective, the following tasks were solved:

– study of intensity, width and form of the EPR signals in conductive nanozones depending on the annealing temperature and power of the microwave field in annealed biominerals;

– determination of conductive properties of textile materials containing various quantities of synthesized nano-sized polyaniline depending on the EPR signal parameters;

– substantiation of possibility of interpretation of interconnected EPR studies for annealed biominerals and organic polymers synthesized in textile materials;

– establishment of features of interconnection of the EPR characteristics with the mechanisms of electrical conductance of organic polymers for further development of nanotechnologies for creation of textile materials possessing electrical conductance.

4. Materials and methods of studying characteristics of electron paramagnetic resonance for various materials

4. 1. Materials used in the study

As the objects of studies, samples of biominerals (enamel, bone) annealed at 200 to 900 °C [5] and polyamide cloth containing nanoparticles of polyaniline were used. Polyamide stockinet of satin-stitch texture was used as the textile material. Conductive textile material is prepared as follows. Aniline is subjected to oxidation in a processing solution at a certain bath module in the presence of surfactant and textile material. Ammonium peroxysulphate was used as an oxidizer. Equivalent oxidizer/aniline ratio was 1.3. The treatment process lasted for 15–30 min at the temperature of 18–22 ºC. Thus, nanodispersed aniline was formed on the polyamide textile by heterocoagulation mechanism [8]. Next, the conductive textile material was washed with distilled water and dried.

4. 2. Methods used in the study

EPR characteristics were studied with the help of two spectrometers (PS.100-X and RE-1306, Russian Federation) working in a 3 cm wave length range. The tested sample weight was 10 to 20 mg. To determine radiospectroscopic characteristics of the samples, a reference specimen ($MgO:Mn^{2+}$) was used. Accuracy in determining relative intensity and width of EPR signals was about 5 %.

5. Results obtained in the study of the test specimen EPR characteristics

5. 1. Electron paramagnetic resonance study of biogenic mineral

EPR signals from so-called native radicals (R_n) in unannealed biogenic minerals (enamel, bone) can be successfully recorded. In this case, the factor of spectroscopic splitting (g-factor) is 2.0045 ± 0.0002 and the signal width is $0.8\pm\pm0.2$ mT. EPR signals from R_n radicals exist in all biominerals, however their intensity is low. Anneal of biominerals leads to the changes in EPR signal characteristics. At the same time, when anneal is done within the temperature range of 200 to 300 °C, only intensity of the EPR signals is changed while the g-factor and signal width remain unchanged within the test accuracy. When the specimens are annealed at higher temperatures ($T>300$ °C), intensity (I), g-factor and signal width alter (ΔB). Alteration of the EPR signal form in the annealed enamel is illustrated in Fig. 1.

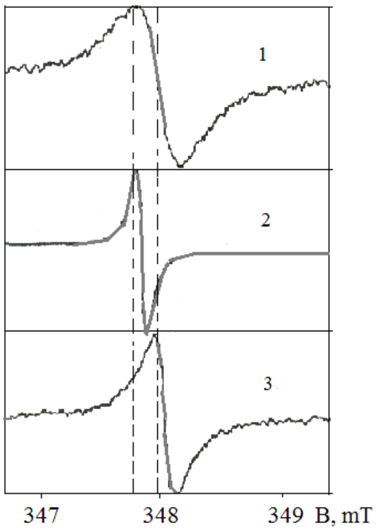


Fig. 1. The EPR signal form in annealed enamel:
1 — spectrum of enamel annealed at 500 °C;
2 — spectrum of enamel annealed at 600 °C;
spectrum of enamel annealed at 850 °C

Since the signal g-factor changes at T>300 °C, this is an indication of variation of the EPR signal nature at these anneal temperatures. Following anneal at T≈400 °C, magnitude of g-factor becomes equal to 2.0036±0.0005 and does not change with further rise of anneal temperature. When anneal is proceeded within temperature range from 400 to 900 °C, g-factor magnitude remains constant, however the EPR signal intensity (Fig. 2) and width (Fig. 3) change materially.

The EPR signal intensity gets lower at anneal temperatures T>650 °C. Width of EPR signals tends to increase. Dependences of g-factor, width and intensity of EPR signals on the specimen anneal temperature for bone were similar to those obtained for enamel. The data presented in Fig. 1–3 correspond to specimen anneal in ceramic boats, i. e. at an unlimited access for oxygen. When anneal was carried out in a quartz sleeve, i. e. at a limited access for oxygen, the following was observed. Extremum of dependence of the signal intensity on the anneal temperature (Fig. 2) shifted to the region of higher temperatures both for bone and enamel.

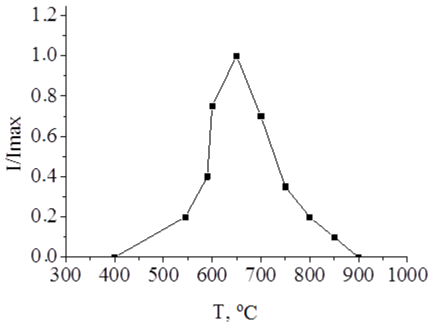


Fig. 2. Dependence of the EPR signal intensity I on enamel anneal temperature T. I_{max} is maximum signal intensity

Dependences of the EPR signal intensity and form on the microwave field power at which annealed biomineral spectra were recorded have been studied as well. It was established that small signal form variations took place in the specimens annealed at relatively low (400–450 °C) temperatures for which exchange narrowing was less significant. In addition, signs of the EPR signal saturation with microwave field were observed. For the specimens annealed at T≈650 °C, signs of signal saturation with the microwave field were absent and no noticeable effects on the EPR signal form were found.

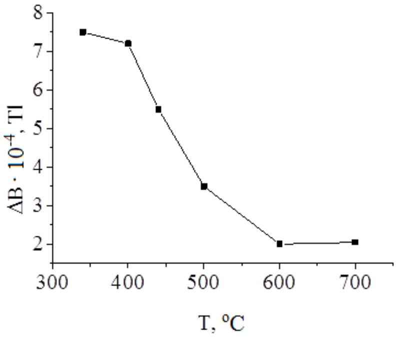


Fig. 3. Dependence of EPR signal width ΔB in enamel on anneal temperature T

It can be assumed that the signals in annealed biominerals consist of wide and narrow components. Wide-to-narrow component ratio differs among different specimens. Conclusions can be drawn from the experiments conducted at various levels of microwave field that the narrow component is not saturated with the microwave field while the wide component shows signs of saturation. The abovementioned influence of the microwave field on the EPR signal form can be associated with nonlinear effects or with manifestation of effects of fast resonance-line passage [7]. As known, effects of fast passage [7] manifest themselves when there is saturation of the EPR signals with microwave power, if $\omega \times T_1$ parameter is commensurable by magnitude or larger than one. Here ω is frequency of magnetic field modulation and T_1 is time of spin-lattice relaxation of paramagnetic centers. Based on the experimental data, it can be supposed that the specimens annealed at 450 °C have a longer relaxation time T_1 than those annealed at 650 °C.

5. 2. Electron paramagnetic resonance of textile materials containing nanoparticles of polyaniline

At the present-day stage of the technology developed for synthesis of polyaniline particles in the presence of textile material, it appears difficult to investigate quantitatively dependences of the signal intensity on optical density (D) and other technological parameters. Optical density (D) characterizes quantity of the synthesized nano-sized polyaniline in a textile material [8, 9]. It is connected with a large scatter of the EPR signal values for different parts of the textile material characterized by the same total value of optical density. Inhomogeneity of properties of the textile materials containing polyaniline particles resulting in the scatter of the EPR signal intensities can be due to the specified conditions of polyaniline particle synthesis in the presence of the textile material. Hence the EPR signal intensity defined for different zones of the textile material can be used as a parameter. The mentioned parameter can characterize homogeneity of distribution of the polyaniline particles in a polyamide cloth.

Emergence of the first percolation threshold in synthesis of polyaniline particles in the textile material [8, 9] could be associated with the quantitative side of the process i. e. appearance of the first “endless” conductive cluster or with the qualitative side of the process. When synthesis of nano-sized particles of polyaniline at the used experimental conditions did not result in synthesis of polyaniline with a sufficiently high level of polymerization, consequently it did not ensure obtaining of polyaniline with conductive properties. To reveal conductive areas in the polyamide cloth obtained at various conditions of polyaniline particle synthesis, the EPR method was used.

There were no EPR signals with a significant signal/noise ratio in the initial polyamide cloth samples, which did not contain nano-sized polyaniline. However, following synthesis of nano-sized polyaniline particles in the polyamide cloth, the EPR signal with a g-factor equal to 2.0036±0.0005 (Fig. 4) was detected. Width, form and intensity of this signal depended on polyaniline content. The EPR signal intensity in the specimens characterized by low (0.025) and high (0.5) optical density of cloth solutions in sulphuric acid changed by more than two orders increasing with increase in polyaniline content. Regardless concentration of polyaniline in the specimens of fibrous material (optical density of solutions of dyed fibers was 0.025 to 0.5), an EPR signal was detected which indicated presence of conductive zones (domains).

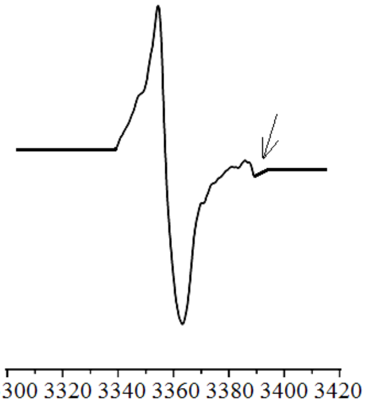


Fig. 4. Form of the EPR signal in textile materials containing nanoparticles of polyaniline. Arrow shows signal from a reference specimen (the fourth line in hyperfine structure of Mn^{2+} ions in MgO for g=1.9810±0.0002)

Hence, nature of conductive domains is analogous both for polyaniline nanoparticle content lower than percolation threshold and for polyaniline nanoparticle concentrations higher than the first percolation threshold. Presence of polyaniline nanoparticles in a form of emeraldine salt with polymerization level sufficient for electrical conductance was confirmed. However, domains are discrete before the first percolation threshold and a penetrating cluster consisting of conductive domains appears during phase transition (first percolation threshold).

This conclusion conforms with the spectral data: the absorption spectrum for solutions of dyed cloths in the visible region is practically the same at polyaniline contents lower and higher than the concentration corresponding to the first percolation threshold (Fig. 5).

It has been established that the EPR signal width in textile materials containing polyaniline nanoparticles decreases with the growth of the signal intensity. Correspondingly, signals are wider in the specimens characterized by low optical density than in the specimens characterized by higher optical density. Decrease in the EPR signal width with increase in the quantity (concentration) of paramagnetic centers is typical for the centers with a strong exchange interaction. Based on this fact, it can be said that the EPR signals in the developed conductive textile materials are exchange-narrowed. It was known in [7] that the exchange interaction is due to the overlap of wave functions in the paramagnetic centers (PC) and indicates a high local concentration of centers.

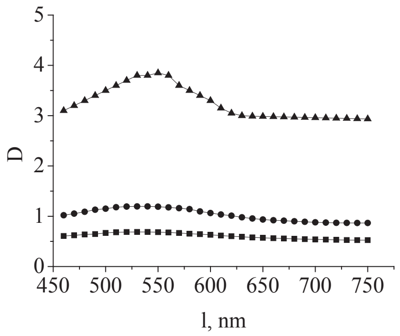


Fig. 5. Absorption spectra: 1 — polyaniline nanoparticles of; 2 and 3 — polyamide textile material containing polyaniline nanoparticles ahead and behind the first percolation threshold

The EPR signal width in the tested specimens depends also on the microwave field power at which spectra are recorded. Fig. 6 demonstrates dependence of the EPR signal line width on the microwave field power for specimens 1, 2, 3 characterized by low (D=0.025), medium (D=0.15) and high (D=0.5) optical density. It should be pointed out that the EPR signals, as a rule, [7] get wider and not narrower with the growth of the electromagnetic field power. Correspondingly, dependences shown in Fig. 6 should be considered rare or unique.

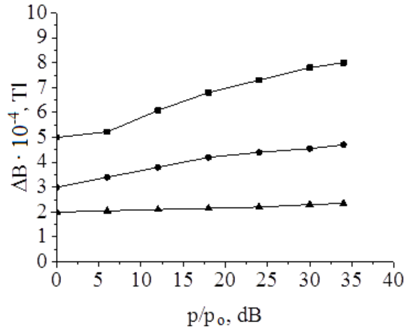


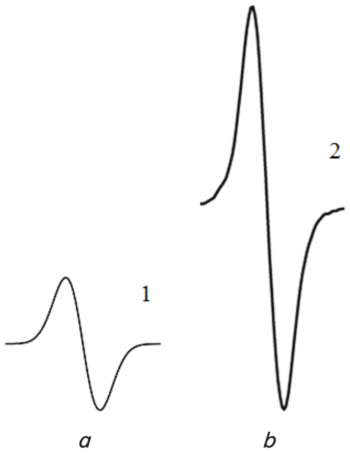
Fig. 6. Variations of the EPR signal width ΔB (peak-to-peak) determined by the changes in the level of microwave field power, p/p_0: 1 —specimen with D=0.025; 2 — specimen with D=0.15; 3 — specimen with D=0.5. Abscissa axis: decay of microwave field power, dB

Narrowing of the EPR signal width with the growth of the microwave field power is possible if the dipole-dipole reservoir of electron spins plays an important role in the processes of the EPR signal saturation [7]. However, connection of the dependences shown in Fig. 6 with the dipole-dipole reservoir is seemingly unlikely since the revealed effect is greatest in specimens with a low PC concentration. Besides, as it will be shown hereinafter, saturation of the EPR signals with microwave fields is weak for the tested specimens.

The EPR signal form presented in Fig. 4 can be characterized by A/B ratio where A and B are intensities of low-field and high-field EPR signal peaks. It has been established that the A/B ratio depends on the level of microwave field power at which spectra are recorded. This effect is illustrated in Fig 7 for a specimen characterized by optical density of (0.5). Dependences of the A/B ratio on the microwave field power are presented in Fig. 8 for specimens 1, 2 characterized by low (0.025) and middle (0.15) optical density.

To elucidate nature of the effects presented in Fig. 6–8, dependences of the EPR signal intensities in the developed conductive textile materials on the microwave field power (Fig. 9) were studied. .

Curves 1 and 2 shown in Fig. 9 correspond to specimens 1 and 2 for which optical density was equal to 0.025 and 0.15, correspondingly. For specimens with higher optical density, dependences of the EPR signal intensities on the microwave field power coincide with curve 2. As it is seen in Fig. 9, there are no signs of saturation of the EPR signals with the microwave field for specimen 2. For specimen 1, an insignificant saturation of the EPR signals takes place at high levels of the field power, but this saturation is weak.



a *b*

Fig. 7. The EPR signal form variations recorded at various levels of microwave field power decay: *a* —30 dB; *b* —0 dB

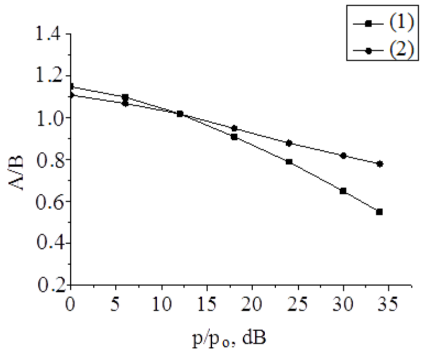


Fig. 8. Dependence of the A/B ratio characterizing the EPR signal form on the microwave field power: 1 — specimen with D=0.025; 2 — specimen with D=0.15. Abscissa axis: the microwave field power decay p/p_0, dB

Based on the data presented in Fig. 6–9, conclusions can be drawn on that the EPR signals from polyaniline nanoparticles consist of two components differing in the line width. The wide line component manifests itself mostly in the specimens with low PC concentrations. Besides, the wide component is most pronounced when spectra are recorded at low levels of the microwave field power. Dependence of the wide component on the microwave field power can be explained within the frames of two models.

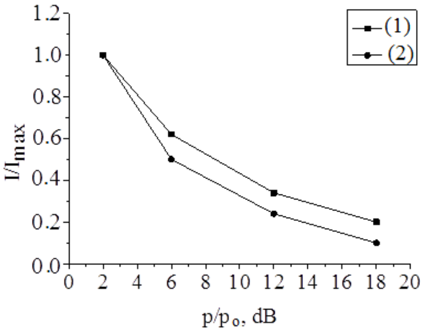


Fig. 9. Graphs of saturation of the EPR signals with the microwave field: 1 — specimen with D=0.025; 2 — specimen with D=0.15. Abscissa axis: the microwave field power decay p/p_0, dB. I_{max} is maximum EPR signal intensity

The first model is associated with availability of passage effects. A conclusion can be drawn from the experiments that the time of spin-lattice relaxation is longer for the wide component than for the narrow one. Wide component dominates in the specimens with a high PC concentration. At the same time, since the passage effects influence [7] the EPR signal form in the presence of saturation, the second model should be mentioned: it can explain experiments presented in Fig. 6–8. Within the frames of the second model, it can be conjectured that the nature of the dependences under consideration is associated with the fact that response of conductive zones to the action with a resonance microwave field is essentially nonlinear. It is connected with special properties of paramagnetic centers localized in conductive nano-sized zones.

6. Discussion of the results concerning interconnection of the EPR characteristics and the mechanisms of electrical conductance

Based on the above data on g-factor, width and form of the EPR signals and the data on signal narrowing with the growth of intensity, conclusions can be drawn that properties of the EPR signals in annealed biominerals and conductive textile materials are similar. Additionally, above conclusions are confirmed by the demonstrated data on the regularity of variation of the signal width and form with variation of the microwave field power. It is worth to note also that the EPR signals can be recorded in nanoparticles of zirconium dioxide [13] even after its treatment in hydrogen atmosphere. Properties of the recorded signals are similar to the properties of the abovementioned signals in biominerals and nanosructured polyaniline. Thus, such conditions are realized in different materials that lead to formation of the EPR signals with related characteristics. It can be supposed that the nature of particles, which determine the EPR signals under consideration in the abovementioned objects is similar in many respects. Correspondingly, information on the mechanisms of appearance of the EPR signals in one group of specimens can be used in interpretation of the signal nature in other specimen group.

It can also be used in elucidation of properties of local conductive zones in the materials under consideration.

As work [3] shows, dependences on the oxidation level for electrical conductance of polyaniline with direct current and for paramagnetic susceptibility in a 3 cm range of wave lengths are similar. This experimental fact shows that electrical conductivity of polyaniline is determined to a considerable degree by the number and dynamics of paramagnetic centers. Dependences of the EPR signal parameters on polyaniline characteristics such as the oxidation level and electrical conductance were described in works [3, 4]. Hence, defining experimentally characteristics of the EPR signals one can judge on electrical characteristics of polyaniline. The EPR method can also be used for optimization of nanotechnologies for creation of conductive textile materials on the basis of nanoparticles of polyaniline in a form of emeraldine salt.

Using data from articles [3, 4] on the dependence of width of the EPR signal in conductive textile materials, one can judge on the oxidation level of polyamine in the tested specimens. Preliminary estimates by the width of the EPR signals show that the oxidation level for specimens with low (0.025), middle (0.15) and high (0.5) optical density is approximately equal to 0.01, 0.03 and 0.3, respectively. Using data on the connection between the oxidation level and electrical conductivity of polyaniline [3, 4], it can be considered that electrical conductance for abovementioned specimens is approximately equal to 1×10^{-3}; 1×10^{-2}; and 1×10^{2} S/m. The above numerical values should be considered as preliminary. Besides, it is important to point out that these figures belong to the characteristics of polyaniline nanoparticles. Electrical conductance of textile materials depends also on uniformity of distribution of polyamine nanoparticles in the textile material, which is formed in the course of synthesis.

7. Conclusions

1. Depending on the used anneal temperature, nature of the EPR signal varies in conductive nano-sized zones of biominerals. It was established that the magnitude of g-factor after anneal at T≈400 °C becomes equal to 2.0036±0.0005 and does not change with the further anneal temperature growth. During anneal in the temperature range of 400 to 900 °C, the value of g-factor remains constant, the EPR signal intensity decreases and the EPR signal width tends to grow. Dependences of the EPR signal intensity and form on the microwave field power at which spectra in biominerals are recorded at various anneal temperatures were studied. It was established that small changes in the signal form connected with appearance of the EPR signal saturation by the microwave field are observed at relatively low (400–450 °C) temperatures. There were no signs of signal saturation with the microwave field and visible effects on the EPR signal form in the specimens annealed at T≈650 °C. Taking into account the assumption on the presence of wide and narrow components in the signals of annealed biominerals obtained at various levels of the microwave field, a conclusion can be drawn. The narrow component is not saturated with the microwave field. The wide component shows signs of saturation. Influence of the microwave field on the form of the EPR signals can be connected with nonlinear effects or demonstration of effects of fast passage of resonance lines.

2. It was established that the width, form and intensity of the EPR signals depend on the quantity of polyamine particles in the textile material. With the growth of content of polyamine particles, the EPR signal intensity increases by more than two orders. Regardless of higher or lower concentration of polyamine particles in the textile material, the EPR signal is recorded which points to the fact that conductive nano-sized zones, domains, are available. The EPR signal width in conductive materials decreases with the growth of the EPR signal intensity. Decrease in the EPR signal width with increase in concentration of paramagnetic centers points to the presence of exchange-narrowed EPR signals. Exchange interaction suggests that there is high local concentration of these centers in the developed conductive materials. Based on the obtained data on the EPR signal width in conductive textile materials, the oxidation level of the polyaniline synthesized in the presence of textile material has been determined. Oxidation level depends on the quantity of polyamine nanoparticles in the textile material. The oxidation level and therefore, the textile material electrical conductance grow with increase in content of polyamine particles. It was found that electrical conductance of textile materials depends also on uniformity of distribution of polyamine particles in the textile material which is realized in the process of synthesis.

3. It was shown that characteristics of conductive nano-sized zones in annealed biominerals and in oxidized polyamine are similar in many respects. The EPR has appeared to be an effective noncontact method, which enables study of electrical properties of biominerals and conductive polymers. It is connected with the fact that the EPR signals in the materials under consideration are conditioned by the electrical charge carriers and variation of electrical properties results in variation of the EPR signal characteristics. At the same time, it should be noted that the processes associated with charge transfer in the studied materials are quite complex. Many issues in this field remain unclear so far and require further theoretical and experimental studied to be carried out with the use of various methods and approaches. Since theoretical and experimental studies connected with polyamine were performed in a relatively large volume, information obtained for nanostructured polyamine can be used in interpretation of the data obtained for biominerals. In annealed biominerals, like in polyamine in a form of emeraldine salt, charge carrier delocalization along with strong exchange interactions between paramagnetic centers take place. Disappearance of the EPR signals in biominerals after their anneal at high temperatures is connected with the fact that delocalized charge carriers both in biominerals and polyamine form pairs analogous to bipolarons. Bipolarons possess zero magnetic moment. Hence, formation of diamagnetic bipolarons in biominerals proceeds more efficiently than in polyamine. Bipolaron mobility appears to be smaller than that of individual polarons, which leads to a smaller electrical conductance.

4. Since biominerals, unlike polyaniline, can be subjected to a high-temperature anneal, this broadens abilities of the EPR method in solving issues associated with the properties of the conductive zones in nano-sized polyaniline. The data obtained with the help of the EPR method for biominerals can be useful in interpretation of the results obtained for nanoparticles of polyaniline with a high oxidation level. Hence, the interconnected EPR studies of conductive zones in various materials can promote a more successive application of the EPR method for optimizing nanotechnologies for creation of conductive textile materials containing nanoparticles of polyaniline.

References

1. Betekhtin, A. G. Kurs mineralogii [Text] / A. G. Betekhtin. – Moscow: KDU, 2007. – 720 p.
2. Handbook of Biomineralization: Biological Aspects and Structure Formation [Text] / E. Bauerlein (Ed.). – WILEY-VCH Verlag GmbH & Co. KGaA, 2007. – 440 p. doi: 10.1002/9783527619443
3. Stejskal, J. Reprotonation of polyaniline: A route to various conducting polymer materials [Text] / J. Stejskal, J. Prokes, M. Trchova // Reactive and Functional Polymers. – 2008. – Vol. 68, Issue 9. – P. 1355–1361. doi: 10.1016/j.reactfunctpolym.2008.06.012
4. Blinova, N. V. The oxidation of aniline with silver nitrate to polyaniline–silver composites [Text] / N. V. Blinova, J. Stejskal, M. Trchova, I. Sapurina, G. Ciric-Marjanovic // Polymer. – 2009. – Vol. 50, Issue 1. – P. 50–56. doi: 10.1016/j.polymer.2008.10.040
5. Brik, A. B. Structure and properties of biominerals localized in human organism [Text] / A. B. Brik, V. V. Radchuk // Heokhimiya ta rudoutvorennya. – 2009. – Issue 27. – P. 63–66.
6. Soni, A. OSL and thermally assisted OSL response in dental enamel for its possible application in retrospective dosimetry [Text] / A. Soni, D. R. Mishra, G. S. Polymeris, B. C. Bhatt, M. S. Kulkarni // Radiation and Environmental Biophysics. – 2014. – Vol. 53, Issue 4. – P. 763–774. doi: 10.1007/s00411-014-0554-5
7. Weil, J. A. Electron paramagnetic resonance: elementary theory and practical applications [Text] / J. A. Weil, J. R. Bolton. – 2nd ed. – John Wiley & Sons, Inc., Hoboken, New Jersey, 2006. – 688 p.
8. Red'ko, Ya. V. Vzaimosvyaz' usloviy sinteza nanodispersnogo polianilina s ehlektroprovodnost'yu voloknistogo materiala [Text] / Ya. V. Red'ko, O. V. Romankevich, S. B. Shekhunova // Problemy legkoy i tekstil'noy promyshlennosti Ukrainy. – 2011. – Issue 1. – P. 69–73.
9. Red'ko, Ya. V. Elektroprovodyashchie voloknistye materialy so sloevoy strukturoy [Text] / Ya. V. Red'ko, A. N. Yushchishina, O. V. Romankevich // Elektronnaya obrabotka materialov. – 2016. – Vol. 52, Issue 6. – P. 103–108.
10. Abdallah, M.-N. Diagenesis-inspired reaction of magnesium ions with surface enamel mineral modifies properties of human teeth [Text] / M.-N. Abdallah, H. Eimar, D. C. Bassett, M. Schnabel, O. Ciobanu, V. Nelea et. al. // Acta Biomaterialia. – 2016. – Vol. 37. – P. 174–183. doi: 10.1016/j.actbio.2016.04.005
11. Karray, F. EPR investigations of silicon carbide nanoparticles functionalized by acid doped polyaniline [Text] / F. Karray, A. Kassiba // Physica B: Condensed Matter. – 2012. – Vol. 407, Issue 12. – P. 2119–2125. doi: 10.1016/j.physb.2012.02.018
12. Krinichnyi, V. I. Electron paramagnetic resonance study of spin centers related to charge transport in metallic polyaniline [Text] / V. I. Krinichnyi, A. L. Konkin, A. P. Monkman // Synthetic Metals. – 2012. – Vol. 162, Issue 13-14. – P. 1147–1155. doi: 10.1016/j.synthmet.2012.04.030
13. Bykov, I. P. Izmeneniya EPR-harakteristik nanorazmernyh chastic dioksida cirkoniya pri rentgenovskom obluchenii i otzhige v atmosfere vodoroda [Text] / I. P. Bykov, A. B. Brik, M. D. Glinchuk, V. V. Bevz, E. A. Kalinichenko, T. E. Konstantinova, I. A. Danilenko // Fizika tverdogo tela. – 2008. – Vol. 50, Issue 12. – P. 91–99.
14. Gizdavic-Nikolaidis, M. R. Self-assembly of nanostructures obtained in a microwave-assisted oxidative polymerization of aniline [Text] / M. R. Gizdavic-Nikolaidis, M. M. Jevremovic, M. C. Allison, D. R. Stanisavljev, G. A. Bowmaker, Z. D. Zujovic // Express Polymer Letters. – 2014. – Vol. 8, Issue 10. – P. 745–755. doi: 10.3144/expresspolymlett.2014.77
15. Poklonskiy, N. A. Opticheskie i paramagnitnye svoystva obluchennyh ehlektronami i otozhzhennyh kristallov sinteticheskogo almaza [Text] / N. A. Poklonskiy, G. A. Gusakov, V. G. Baev, N. M. Lapchuk // Fizika i tekhnika poluprovodnikov. – 2009. – Vol. 43, Issue 5. – P. 595–603.