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Spectroscopic investigation of gamma irradiated PAA-graphite membranes

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Electrical conductivity and structural properties of PAA-graphite membranes after gamma irradiation at D=1.7 KGy, have been studied. The electrical conductivity of pure PAA membranes is very low, but the introduction of small quantity of graphite increases this property significantly due to the connections established between the graphite trapped in the polymeric holes. The electrical conductivity of the doped membranes increases after irradiation. This behaviour is correlated with the modification of the local ordered structure of the polymeric matrix and the apparition of supplementary unpaired electrons from the graphite. These microscopic modifications have been investigated by XRD and ESR methods.

Keywords: Poly (acrylicl acide), Graphite, Gamma irradiation, Electrical conductivity

1 Introduction

The use of polymeric matrix as a support of the medical drugs is a new trend in the pharmaceutical industry due to some advantages offered by such systems, the application of the active substance only in the desired area of the body, (especially in dermatology), the delivery of the drug at controlled rate and the biocompatibility with the human body[1,2]. One of the major problems of such systems is the activation and the control of the delivery process of the drug. Usually, the activation is determined by chemical reaction between the organic liquids of the body and the polymeric matrix, having as a result the destruction of the polymeric support. The delivery rate is determined by the chemical composition and the concentration of organic liquids, the nature and the thickness of the polymeric support. Some disadvantages appear here. The composition and concentration of organic liquids cannot be controlled from the outside of the body; the nature. The physical characteristics of the polymeric support are set only during the process of fabrication and cannot be modified during the therapy. Once the delivery process being activated, (especially for the systems introduced in the body), the delivery process cannot be stopped. More convenient method for activation of the delivery process could be the stimulation of the polymeric matrix by electric fields, applied directly from outside by direct connection to an electric power source, or by electric field induced by irradiation with radio frequency waves. The mechanism of delivery is simple. The local currents induced by the electric field produce the heating of polymeric matrix, determining the dilatation of the pores of the matrix, the increase of the thermal agitation of the drug, and the stimulation of the diffusion process of the medical active substance. One of the polymers with high potential of use for this purpose is the poly (acrylic acid) PAA, known for its good chemical stability and good biocompatibility[3,4]. Like the majority of the polymers, its electric conductivity is low. However, the introduction of small quantity of carbon (graphite), increases significantly its electric conductivity[5,13]. During the therapy or during the sterilization, these systems are submitted frequently to high dose of gamma radiation. Such radiation could have dramatic effects on the structure and physical properties of the polymeric support. For the applications presented previously, the effect of such radiation on the electrical conductivity and the modification induced on the local structure of the polymer has been studied. The observations can be made on macroscopic scale by electrical conductivity measurements on microscopic scale by spectroscopic methods, X-ray diffraction (XRD) and Electronic Spin Resonance (ESR). In the present study, PAA membranes containing different concentration of graphite have been investigated.

2 Experimental Details

The pure membranes were prepared from the aqueous gel of PAA. The gel is obtained by mixing the PAA powder polymer, during 4 h at room temperature, in mass proportion of 10%, with distilled water until a homogeneous composition is obtained. This gel was displayed on glass plates and kept at room temperature until the water completely evaporates[6]. The doped membranes were obtained from the aqueous gel in which the graphite was added in the desired concentration, (5%, 15% and 30%). The mixture is stirred for 3-4 h to ensure homogeneous dispersion of graphite into the polymeric matrix, and then the composition was displayed on glass plates and kept in dark at room temperature until the water evaporates. The samples were analyzed in their original state after gamma exposure. The gamma irradiation was realized using ^{60}Co source with the radiation flux 5.6 Gy/h until the 1.7 KGy dose was accumulated. The XRD measurements were performed with Brucker X-ray diffractometer with Cu Kα (λ = 0,154 nm) at 45 KV and 40 mA. The 2θ range 10-100° was recorded with 0.1° resolution. ESR spectra were recorded at room temperature with Brucker-Biospin EMX spectrometer operating at X-band (9.4 GHz). The electric conductivity was measured with special head of Tesla109 Q-meter, well shielded from the external electric noisy, specially conceived for electric measurements. In this device, the samples were placed between two circular electrodes, copper gold plated, 5 cm in diameter, and adjustable distance between them. The distance is measured with 1 μm accuracy. The membranes were pressed between the two plates with the same force, until they became perfectly plane in order to ensure good electric contact. The same quantity of sample is used for each measurement and all the time the same experimental setup is utilized in order to minimize the experimental errors. The measurements were done at the same temperature, (room temperature, 21°C, with variations smaller than 1°C) in a chamber with good ventilation to eliminate the water vapours. A high tension between 100 and 3000 V was applied and the intensity of current was measured with very sensitive Orion micro ammeter. The tension and the intensity were measured with accuracy better than 0.5%. Measurements were made at least three times for each sample and the average data were collected. The electric measurements were done which showed important changes of the properties of these samples when the graphite is added and when the samples were gamma irradiated. Starting from these observations, the modifications induced on molecular scale by these actions have been investigated.

3 Results and Discussion

Pure state PAA, like many other polymers, is characterized by very low electric conductivity. Generally, the electric conductivity appears only in the case of particular polymers (for instance the poly aniline), being determined by the charge transfer along the polymeric chains and the charge transfer between two neighbouring chains. These mechanisms do not appear in pure PAA. Another possibility to obtain electric conduction in polymers is the introduction of inorganic elements in the polymeric matrix. Usually, a composite material is obtained, without chemical connection between the polymer and dopant. In these systems, the dopant is trapped in the spaces (holes) determined by the entanglements of the polymeric chains. The polymer itself is not conducting, the electrical conductivity being determined by the connections established between the spatial domains occupied by the dopant. Two factors contribute to these connections, the concentration of the dopant, and the particularities of the polymeric network, (the distance between the spaces (holes) occupied by the dopant, the persistence of these spaces, (determined by the thermal fluctuations of the entanglements between the chains), the size of these holes, the length of the polymeric chains. For a given sample, the concentration of the components remains constant, but the particularities of the polymeric network can be changed under the action of external factors, temperature, solvents, or irradiation. The interaction of the gamma radiation with the polymeric chains affect the scission of the polymeric chains or the breaking of chemical bonds of the monomer followed by the apparition of free ions and electrons. The scission of the chains leads to the modification of the segmental local dynamics, followed by the modification of the size and distance between the holes of polymeric network. In this situation, the probability of apparition of the connections between the domains occupied by the dopant increases, that leads to the increase of the electrical conductivity. These aspects have been investigated in our work. The resistivity of the samples was measured before and after gamma irradiation. Before irradiation, the pure polymer is characterized by a very high resistivity. Addition of small quantity of graphite, i.e. 1%, increases significantly the electric conductivity of the samples. The resistivity decreases monotonically when the concentration of graphite increases, (Table 1). The explanation is simple. When the quantity of graphite increases, the number of holes of the polymeric network occupied by the dopant increases. The density of conducting domains and the probability of apparition of the connections between them are higher than in the case of low doped samples. After irradiation, the resistivity of the pure PAA remains almost constant. The pure PAA membranes do not contain conducting domains occupied by the dopant. Under the effect of gamma radiations, some chains are broken and the dynamics of polymeric segments increase and the entanglements of the polymeric chains are affected. The concentration and the distribution of free spaces between the polymeric chains, (the holes), determined by the entanglements, susceptible to be occupied by the graphite, are modified. Supplementary holes or connections between them can appear in the polymeric network. But these spaces, being unoccupied by the dopant, (in the pure membranes), do not affect the electric conductivity of the polymer. The weak modification of the electric conductivity is determined only by the apparition of some ions after irradiation. Similar process appears for doped membranes but in this case, the holes being occupied by the dopant, the modification of theirs concentration or connectivity between them, leads to the increase of the electric conductivity. In this situation, the modification of electric properties appears as consequence of the modifications of the polymeric matrix. In order to verify the modification of polymeric network under the irradiation, the samples were investigated by XRD method.

The polymers are known as amorphous materials, but in some cases the interaction between the neighboring segments induces a local ordered arrangement of the chains, which behaves like a crystalline domain. In PAA,this local order is determined by the hydrogen bonds appearing between the OH part of bending COOH group belonging to a given polymeric segment and the H bending atom of another neighbouring segment[7]. Such structures can be investigated by XRD method because the lattice parameter of the ordered domains is of the same order of magnitude as the wavelength of X radiation. But not all the ordered domains are characterized by the same lattice constant, like in the case of solid crystalline substances. The polymeric chains have different lengths and spatial conformations and continuously change of the conformation under the thermal agitation. The sample is characterized by a distribution of the values of inter-planar distances around the most probable value. As a consequence, the maximum of diffraction is observed for many diffraction angles, not for a single value of 2θ like in the case of monocrystals. The diffraction signal is broad and maximum corresponding to the most probable distance between the planes of ordered domains. The area under the diffraction peak is proportional with the concentration of the ordered domains into the sample and the width of the signal is correlated with the size of the ordered domains[8].

Table 1 — Decrease in resistivity with concentration

Sample	Resistivity [Ωm] Before irradiation	Resistivity [Ωm] After irradiation
PAA pure	$50\times10^9 \pm 0.5\times10^9$	$49\times10^9 \pm 0.5\times10^9$
PAA 1% graphite	3600 ± 36	3450 ± 34
PAA 5% graphite	900 ± 9	750 ± 7.5
PAA 15% graphite	380 ± 3.6	270 ± 2.7
PAA 30% graphite	120 ± 1.2	80 ± 0.8
Graphite pure	1.8 ± 0.02	1 ± 0.01

The diffraction pattern of pure PAA membrane, before irradiation, shows a maximum at $2\theta=17.2°$ and a shoulder at $2\theta=35°$, (Fig. 1). Ours results are found to be in good agreement with the observations performed by other researchers on polyvinyl alcohol (PVA), which has a chemical composition [20]close to PAA. As shown by other researchers, the signal is the result of the superposition of two peaks centered on these angles[9]. These components appear clearly after

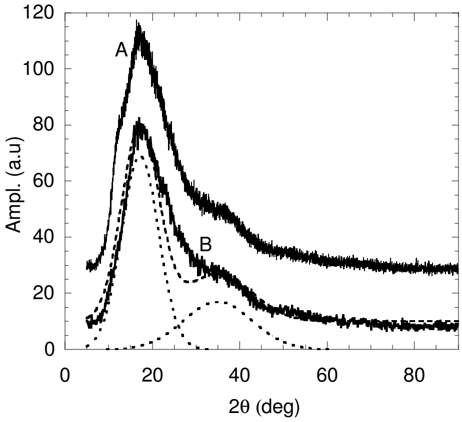

Fig. 1 — XRD pattern of pure PAA membrane before irradiation (curve A); after irradiation (curve B); simulation of each peak and of the whole the diffractogram of the irradiated sample, (dashed lines)

simulation with Gaussian functions. The center of the function was established at the diffraction angle 2θ. Then the amplitude and the width were adjusted until the best fit of the experiment was obtained. From the value of the diffraction angle 2θ, the inter-planar distances are calculated with the Bragg's equation, $d=\frac{k\cdot\lambda}{2\sin\theta}$, where k is the diffraction order[10]. We obtained the values d = 5.15 Å for 2θ = 17.2° and d = 2.5 Å for 2θ = 35°. The size of ordered domains was calculated with Debye-Scherrer's equation applied to the simulated spectrum, $D=\frac{K\cdot\lambda}{\beta\cdot\cos\theta}$, where D is the size of ordered domains, K = 0.9 is a proportionality factor and β the half line width of the peak expressed in radians. The value D = 8.9 Å is obtained. The parameters of the diffractogram of pure PAA before irradiation and the method of calculation, were presented[19] already. The amplitudes of the peaks are 85 and 20 au and the areas under these peaks are S = 900 and S =387 au.

After irradiation, no significant modifications appear. The peaks appear at the same diffraction angles as before irradiation, their width remains unchanged, but the amplitude decreases slowly (Fig. 1). Same method is used to analyze and simulation presented above for the unirradiated samples. The amplitudes of the peaks are A = 69 a u and A =17 au and the areas under these peaks are S = 731 au and S =331 au. That means no modification of the inter-planar distances or of the size of ordered domains, only a weak modification of the total concentration of ordered phase in the sample. This diminution of the ordered phase is determined by the breaking of the chains induced by irradiation followed by the increase of their dynamics. The increase of the mobility facilitates the disengagement of the chains from the entanglements and the perturbation of the ordered phase.

Then, the membranes with graphite have been investigated. The spectra of these membranes show both the lines of pure PAA and graphite. Initially, pure graphite analyzed. The graphite is one of the four allotropic states of carbon, containing hexagonal cells arranged on intercalated planes. The pure graphite exhibits characteristics diffraction peaks at 2θ= 25.2°, 2θ= 43° and 2θ=55°, (Fig. 2). These peaks correspond to the diffraction[11, 12] on the planes (002), (101) and (004). The (002) direction is perpendicular on the hexagonal planes and represents the c-axis of the graphite unit cell. The peaks appear with different intensities in function of the probabilities of the diffraction on the corresponding planes. The parameters of the pure graphite structure before irradiation were calculated from these diffractograms using the same algorithm as those presented above for pure PAA membranes, and the results were reported in previously ours work[19].

After irradiation, the position of the diffraction peaks does not change, only the amplitude decreases (Fig. 2). That means no modification of the inter-planar distances, but a modification of the concentration of the ordered phase. These distances are d = 3.5 Å for 2θ= 25.2° and d = 2.1Å for 2θ= 43°.

The samples with graphite contain a superposition of the characteristics peaks of PAA and graphite without modification of the diffraction angles, but with different amplitudes in function of the graphite concentration. For instances, at low graphite concentration, i.e. 5%, all the peaks are broad, the peaks of graphite have small amplitude and can be seen with difficulty due to the superposition with the peaks of PAA. When the concentration of graphite increases, the peaks of graphite become more evident and appear clearly in the diffractograms, (Fig. 3). At 15% graphite concentration, the peaks at 2θ= 25.2° and 2θ= 43° appear as shoulders of the spectrum, but at 30% concentration they appear almost separately. However, whatever the concentration of the graphite, the parameters of the peaks of the two components, amplitude, width and areas can be evaluated quantitatively only after the simulation of the diffractograms. Detailed characterization of the

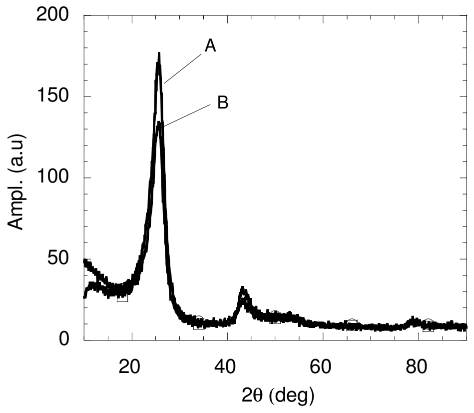

Fig. 2 — XRD pattern of pure graphite before irradiation (curve A); and after irradiation (curve B)

diffractograms of unirradiated samples was presented in previous work[19].

After irradiation, the diffractograms do not change substantially. The peaks of PAA and graphite can be seen again at the same angles as before irradiation, but their amplitudes are reduced. The characteristics parameters of diffractograms were calculated from simulation using the same algorithm as for the unirradiated samples. One of such example is shown in Fig. 4 for the concentration 30%. For this concentration, (the irradiated sample), the diffraction peaks of PAA appear at the angles $2\theta = 18.2°$ and $2\theta = 35°$ with the amplitudes $A = 68$ au and $A = 21$ au, respectively. The half line width of these peaks are $\beta = 10°$ and $\beta = 20°$ and their areas are $S = 720$ au and $S = 398$ au. The diffraction peaks of graphite appear at the angles $2\theta = 25.2°$ and $2\theta = 43°$ with amplitudes $A = 55$ au, $A = 8$ au, the half line widths are $\beta = 3.5°$ and $\beta = 1.8°$, and the area $S = 195$ au and $S = 14$ au. No shift of the diffraction peaks of the graphite appears, meaning no modification of the inter-planar distances. As general observation, after irradiation the amplitudes of all the peaks of the PAA and graphite decrease (Fig. 4). Similar behaviour is observed for the areas under the peaks. The area under the peak at $2\theta = 18.2°$ (PAA) after irradiation represents 62% from the area under the same peak before irradiation. For the graphite, at the angle $2\theta = 25.2°$, the area under the peak after irradiation represents 55% from the area under the same peak before irradiation. The areas under the peaks being proportional with the concentration of the ordered phase, these reports show the diminution of ordered phase after irradiation. This behaviour can be explained if we suppose an effect of breaking of polymeric chains followed by the increase of their dynamics and consequently a destruction of the local ordered arrangement.

The possibility of increasing the electric conductivity due to apparition of free electrons after irradiation was tested by Electronic Spin Resonance, (ESR). This technique is very sensitive to the existence of unpaired electrons and provides information about the electronic structure of atoms or molecules[14,15]. Polymers with simplest monomers like PAA, which contain only C, H, and O atoms, usually do not give any ESR signal, all the valence electrons being included in saturated bonds. This behaviour can be clearly shown for pure PAA membrane before irradiation, (Fig. 5, curve A). Practically the sample does not give any ESR signal. Unpaired electrons can appear when some chemical bonds of the monomer

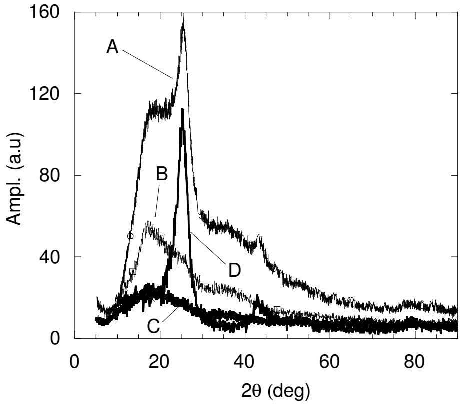

Fig. 3 — Diffractograms of PAA membranes with 30% graphite (curve A); 15% graphite (curve B); 5% graphite (curve C); and pure graphite (curve D), before irradiation

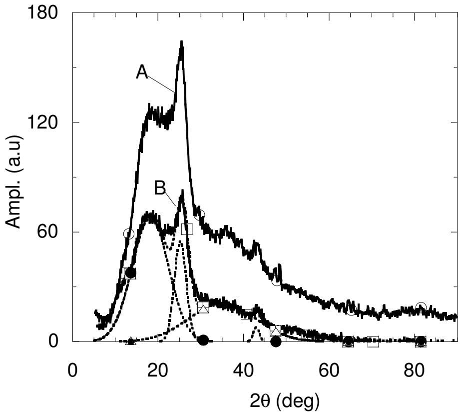

Fig. 4 — Diffractograms of PAA membrane with 30% graphite before irradiation (curve A); after irradiation (curve B); and simulation of the each peak and of the total diffractogram of the irradiated sample (dashed lines)

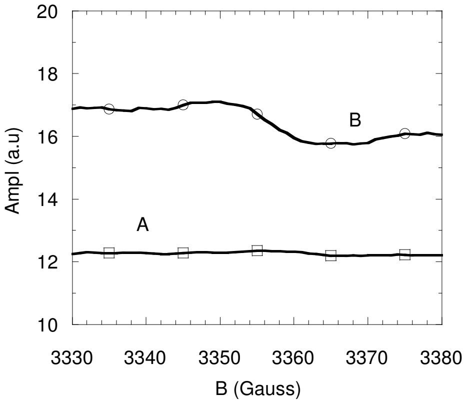

Fig. 5 — ESR spectra of pure PAA membrane before irradiation (curve A) and after irradiation, (curve B)

are broken by radiation. For instance, in the case of poly(vinyl alcohol) (PVA), which has a very close molecular structure to the PAA, (CH_2-CH-OH) versus (CH_2-CH-COOH), the gamma radiation affects mainly the bending (-OH) groups producing H^+ and OH^-ions[16,17]. The PAA contains also the (-OH) groups included into the bending group (–COOH) susceptible to be affected by the radiation. However, at 1.7 KGy dose only few bonds are broken and very few unpaired electrons are produced. As a consequence, the ESR signal is very weak, (Fig. 5, curve B). This behaviour is in accordance with XRD and electric measurements. XRD shows some modification of the ordered domains of the polymer after irradiation, confirming this effect of breaking of chemical bonds. Electric conductivity of the pure PAA membranes increases slowly after irradiation indicating small increase of the number of electrons participating to the conduction.

The introduction of small quantity of graphite in the polymeric matrix, before irradiation, determines the apparition of a strong ESR signal without hyperfine structure. For all the concentration, the signal is centered at 3357 Gs that corresponds to gyromagnetic factor $g = 2$. This value of gyromagnetic factor corresponds to free unpaired electrons[18]. The amplitude of the signal increases progressively with the concentration of the graphite (Fig. 6). From this behaviour and knowing that the polymer has not given any signal before irradiation, it is concluded that the ESR signal of doped samples is provided only by the graphite. This signal is determined by the unpaired electrons of the colour centers of the graphite. The colour centers can appear in the graphite during process, that involves the oxidation of the natural carbon (coal), followed by purification and elimination of water and other residues. A measure of the concentration of these spins is the area under the absorption signal[18]. The absorption signal at different concentrations is shown in Fig. 7 and the areas are reported in Table 2. The areas increase when the concentration of graphite increases giving its maximum value for pure graphite. On the other hand, the electrical conductivity increases progressively with the concentration of the dopant being maximum for pure graphite. This behaviour suggests a correlation between the electric conductivity and the concentration of unpaired electrons. As results from electric measurements, the electrical conductivity of pure PAA membrane before irradiation is very low. On the other hand, the ESR measurements performed on pure PAA membranes show very low concentration of unpaired electrons. The addition of graphite to the polymer increases significantly the electrical conductivity and leads to the apparition of strong ESR signal. From these observations, it is concluded that the contribution of the polymer to the total electric conductivity and the

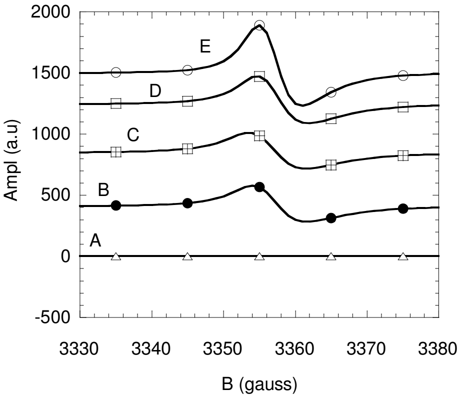

Fig. 6 — ESR spectra of pure PAA (curve A); PAA with 5% graphite (curve B); PAA with 15% graphite (curve C); PAA with 30% graphite (curve D); pure graphite (curve E); before irradiation

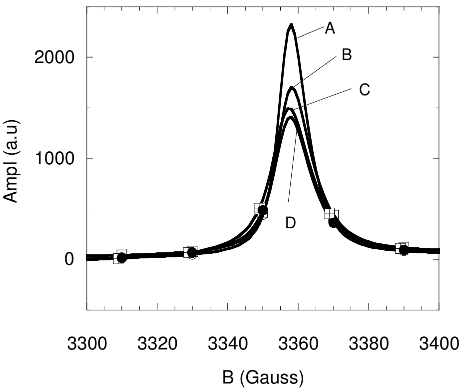

Fig. 7 — Absorption ESR signal before irradiation for pure graphite (curve A); PAA with 30% graphite (curve B); PAA with 15% graphite (curve C) and PAA with 5% graphite (curve D)

Table 2 — Variation of area of absorption signal with concentration

Sample	Area [a.u] Before irradiation	Area [a.u] After irradiation
PAA 5% C	26976	36100
PAA 15%C	29720	51230
PAA 30% C	31544	63934
Graphite pure	32891	282994

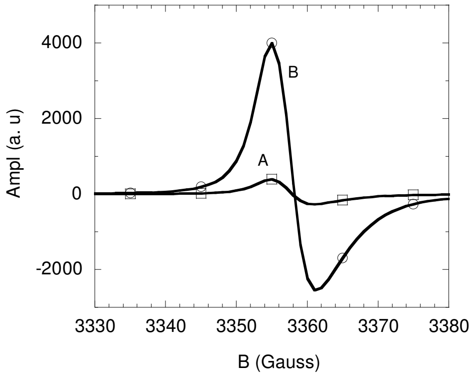

Fig. 8 — ESR spectra of pure graphite before irradiation (curve A) and after irradiation (curve B)

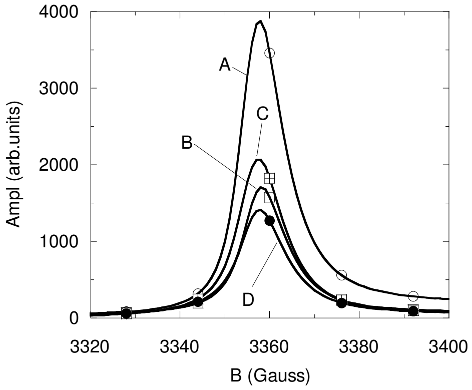

Fig. 9 — ESR absorption signal for PAA with 30% graphite after irradiation (curve A), before irradiation (curve B) and PAA with 5% graphite after irradiation (curve C) and before irradiation (curve D)

ESR signal of doped samples is very weak. The majority of unpaired electrons are the free electrons of graphite which are involved in the electric conduction and give the major contribution to the ESR signal. Very few unpaired electrons of the polymer, only those belonging to the broken chemical bonds, participate to the electrical conductivity.

After irradiation, the amplitude of the ESR signal of pure graphite increases significantly, indicating the apparition of important number of unpaired electrons (Fig. 8). Generally, the irradiation of solid substances leads to the apparition of colour centers, characterized by paramagnetic behaviour[14,15]. The natural graphite is susceptible to provide colour centers with paramagnetic behaviour under intense gamma irradiation. On the other hand, the XRD measurements show a degradation of the ordered organization of graphite after irradiation. Such perturbation of ordered phase is accompanied by apparition of unpaired electrons. Similar behaviour is observed for doped samples after irradiation. For a given concentration of graphite, the amplitude of the ESR signals as compared with the amplitude before irradiation increases. This behaviour is shown for concentrations 5% and 30% graphite in Fig. 9, but this effect is observed for all the samples. Taking into account the fact that the signal of pure PAA after irradiation is very small as compared to those of the graphite, we can affirm that the increase of the ESR signal of doped samples is determined mainly by the graphite. On the other hand, the electrical conductivity increases after irradiation. Correlating this behaviour with the increase of the amplitude of the ESR signal, it is considered that a part of unpaired electrons created by irradiation became free electrons and participate to the electric conduction. Very few conducting electrons are provided by the polymer, the majority belonging to the graphite.

4 Conclusions

Electrical conductivity, XRD and ESR investigations were done on PAA membranes with graphite, before and after gamma irradiation, in order to observe the effect of irradiation on the structure and electric properties of these systems. The electrical conductivity of pure PAA membranes, before irradiation, is very low, but the introduction of small quantity of graphite increases significantly this property. The electric conductivity of the doped samples is determined by the connections established between the graphite particles trapped in the polymeric holes. Modifications of the ordered domains of the polymer appear after gamma irradiation. These structural modifications were observed by XRD technique. The breaking of the polymeric chains induced by irradiation increases the polymeric dynamics, facilitating the realization of the connections between the domains occupied by the graphite. The result is the increase of the electrical conductivity of the samples after irradiation.

Another effect that contributes to the increase of the electrical conductivity is the apparition of supplementary unpaired electrons from the graphite after irradiation. This effect is probed by ESR method. Some of these electrons became free and participate to the electrical conductivity. Our experiments show that the electrical conductivity of doped membranes is determined mainly by the graphite particles trapped in the polymeric matrix, and low dose of gamma radiation affects especially these particles.

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References

1 Hoffman A S, *Adv Drug Del Rev,* 43 (2002) 3.
2 Sriamornsak P & Kennedy R A, *Int J Pharm,* 323 (2006) 78.
3 Todica M, Pop C V, Udrescu L & Pop M, *Chin Phys Lett*, 27 (2010) 018301.
4 Todica M, Pop C V, Udrescu L & Traian S, *Chin Phys Lett*, 28 (2010) 128201.
5 Ruixia H, Leigang W, Jin W & Nan H, *Appl Surf Sci,* 256 (2010) 5000.
6 Kim J-Y, Song J-Y, Lee E-J & Park S-K, *Colloid Polym Sci,* 281 (2003) 614.
7 Hoerter M, Oprea A, Barsan N & Weimar U, *Sensor and Actuators B*, 134 (2008) 743.
8 Stuart B, *Polymer analysis*, John Wiley & Sons, Chichester 2002.
9 Lin C-L, Lee C-F & Chiu W-Y, *J Colloid Interf Sci,* 291 (2005) 411.
10 Kittel C, *Introduction to Solid State Physics*, John Wiley & Sons, 8th Edn, New York 2004.
11 Ban F Y, Majid S R, Huang N M & Lim H N, *Int J Electrochem Sc,* 7 (2012) 4345.
12 Titelman G I, Gelman V & Bron S, *Carbon,* 43 (2005) 641.
13 Ui C, Kikurchi S & Mikami F, *J Power Sources,* 173 (2007) 518.
14 Damian G, *Talanta*, 60 (2003) 923.
15 Cozar O, Chis V & David L, *J Radioanal Nucl Ch,* 220 (1997) 241.
16 Bhat N V, Nate M M & Kurup M B, *Nucl Instrum Methods B,* 237 (2005) 585.
17 Todica M, Udrescu L & Simon S, *Cen. Eur J Phys,* 10 (2012) 329.
18 Pake G E, *Paramagnetic Resonance*, Benjamin Inc, New York 1962.
19 Todica M, Stefan T, Simon S, Balasz I & Daraban L, *Turk J Phy*, 38 (2014) 261.
20 Farjami Shayesteh S, Kolahi S & Azizian-Kalandarragh Y, *Indian J Pure & Appl. Phys.* 51 (2013) 780.