



Study of the characteristic features of the strongest broadening of the EPR signal in polystyrene-based polymer compositions

Umarov A.V.¹, Kamalova D.²

¹Tashkent Institute of Railway Engineers, Uzbekistan

²State Unitary Enterprise “Fan va Taraqqiyot”, Uzbekistan

Abstract

A composite material based on polystyrene with the addition of microparticles of soot has been developed. The electron paramagnetic resonance (EPR) spectra were studied.

Keywords: composite material, polystyrene, microparticles of soot, electron paramagnetic resonance, X-ray fluorescence analysis, paramagnetic centers

EPR spectra of PS (polystyrene) with a carbon black content of $V_1 = 0.01; 0.04; 0.09$ and 0.20 are shown in Fig. 1, 2, 3, and 4, respectively. The reproducibility of the measurement results is quite high (periodic verification over several years) and, therefore, the radicals responsible for these signals can be considered stable. However, it is easy to notice that in all these cases we are talking about a striking scientific phenomenon - the strongest broadening of the EPR signal line (ΔH_{pp} , Oe), because the reality is that the DG-100 soot itself in air gives a singlet signal with $\Delta H_{pp} = 22$ Oe, and polystyrene does not signal at all, i.e. it is diamagnetic [1, 2].

In this case, it is reasonable to find the answer to the question whether the broadening is associated with the superposition of signals from different centers of localization of spins or does it come from hyperfine interactions (HFI) of electrons localized at paramagnetic centers (PMC) of organic origin.

According to factory data, DG-100 carbon black has the following composition: 94.8% carbon (C), 0.9% hydrogen (H), 4.3% oxygen (O), less than 0.1% sulfur, less than 0, 1% of the mineral residue. Despite the fact that the main part of the carbon black composition consists of elements of organic origin, it is nevertheless alarming that it contains even the smallest amount (0.1%) of the mineral residue, because according to fairly firmly established facts [1–3, 5] even the presence of the smallest amounts of some transition metal ions can lead to a strong broadening of the EPR line width. In order to get a reasonable conviction that the broadening of the EPR line width observed by us in experiments is not related to any elements of inorganic origin, we performed the following works.

First of all, we used X-ray fluorescence analysis (XRF analysis) for a more detailed analysis of the structure of soot (Fig. 5). As seen in fig. 5, such elements as Kr, Nb, Ru, In and In, Cs and Cs are distinguished; moreover, in quantitative terms, all these elements taken together do not exceed 0.1% of the total carbon black composition and are apparently consistent with the factory data of the filler. Secondly, we used IR spectroscopy (“Specord 75 IR”) to determine elements such as Fe, Ni, Co, Mn, Mg in the studied objects [14]. We were not able to obtain good IR spectra for pure soot, which is apparently due to the strong absorption of infrared rays by soot particles. However, in the IR spectra of the PS+soot (0.01), as shown by the results of studies in the wavelength range from 400 cm^{-1} to 4000 cm^{-1} , there are no characteristic absorption bands of Fe, Ni, Co, Mn, Mg or compounds on their basis. The facts established by IR and X-ray fluorescence analysis stubbornly deny the possibility of the origin of such a wide EPR signal (Fig. 1-4) from elements of Fe, Ni, Co, Mn, Mg.

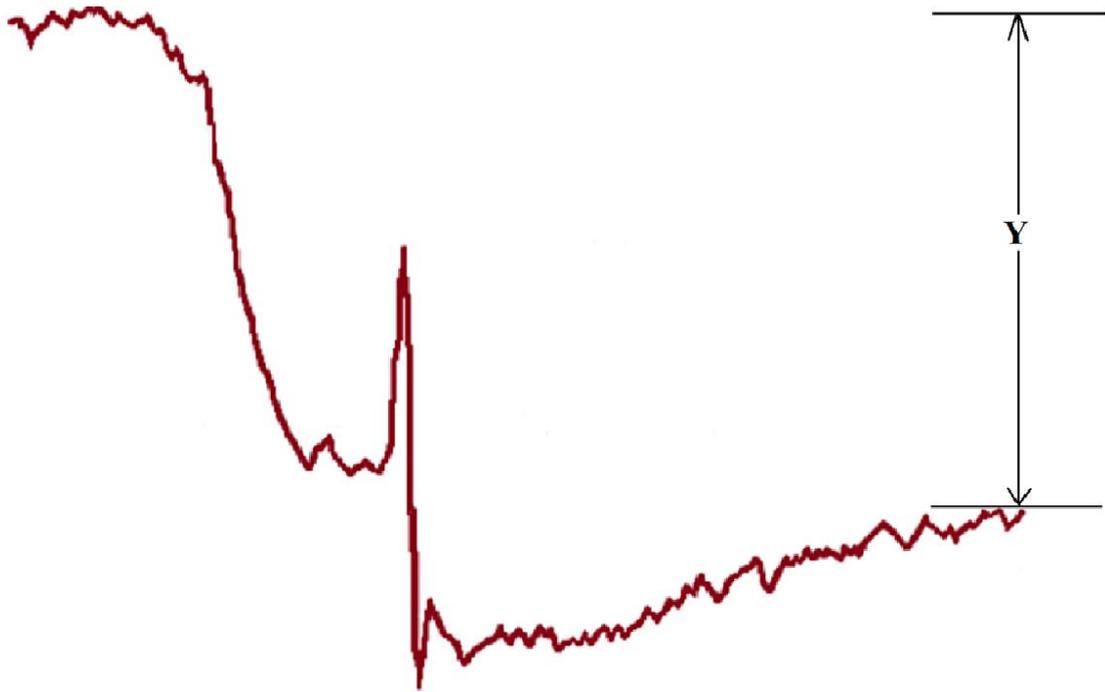


Fig.1 EPR spectrum of the PS + soot (0,01)

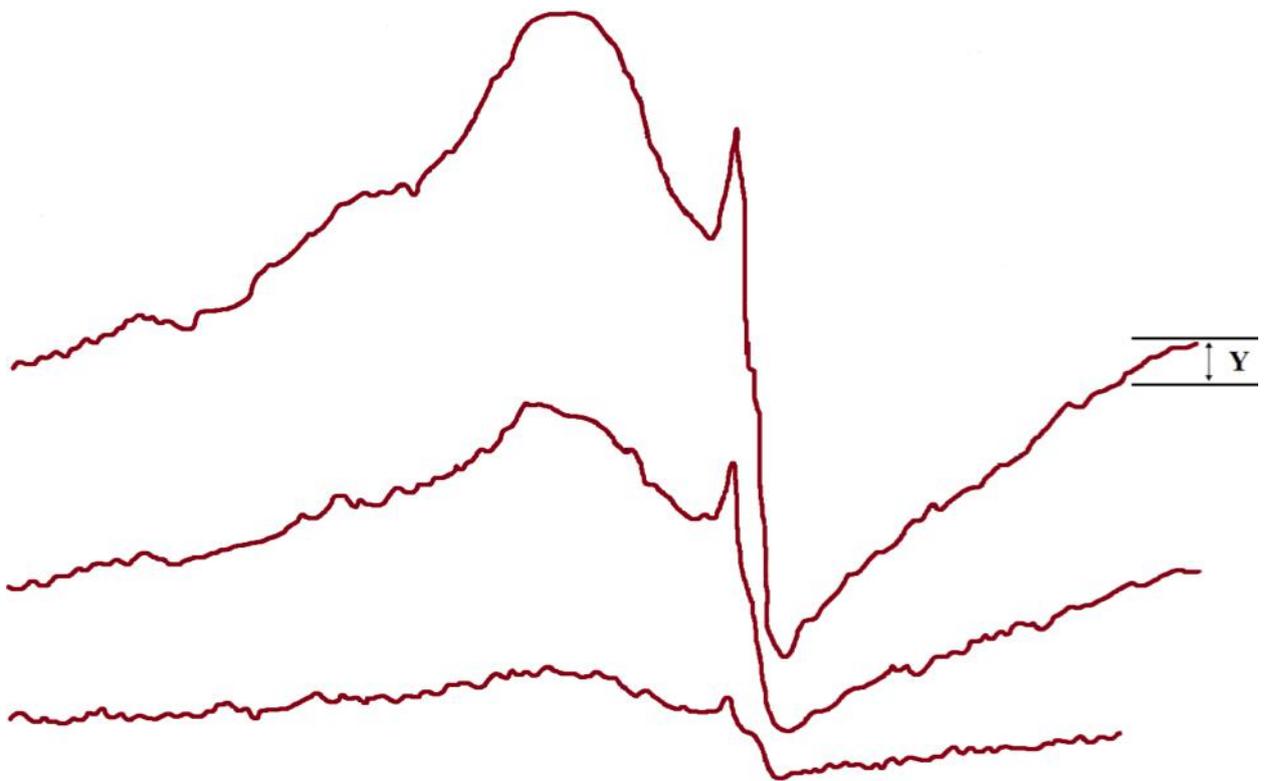


Fig.2. Dependence of intensity on the microwave power of a large PS + soot (0.04)

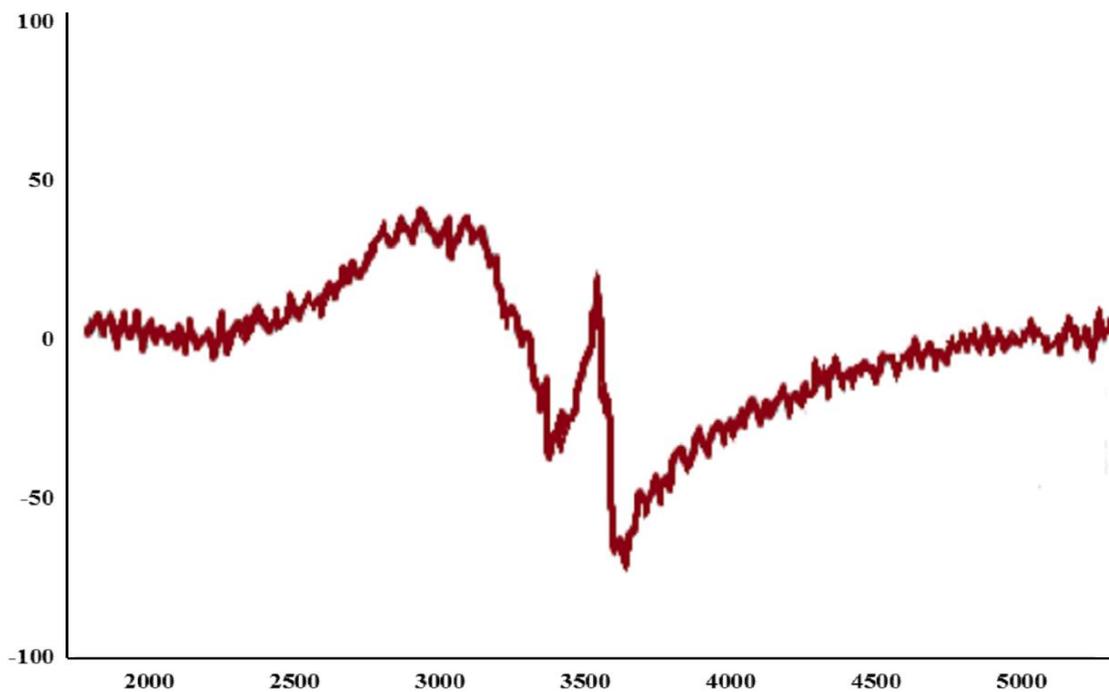


Fig.3. EPR spectrum PS + soot (0.09)

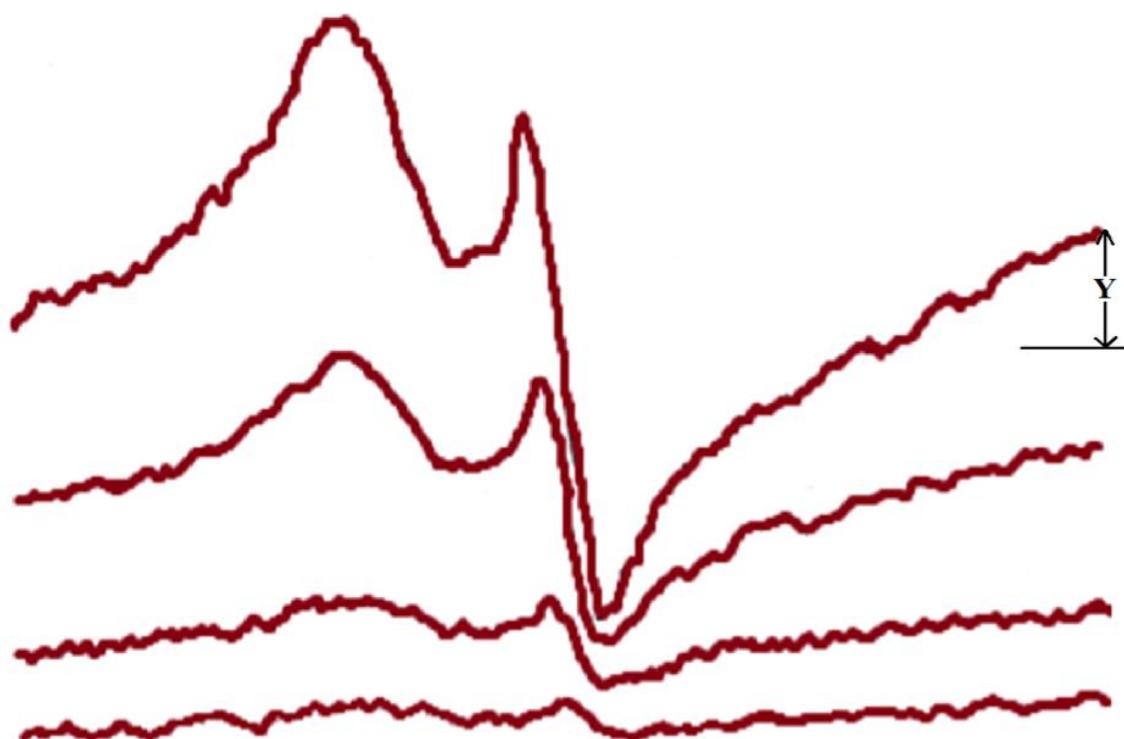


Fig. 4. The spectrum of a large EPR signal PS + soot (0.20) depending on the microwave power

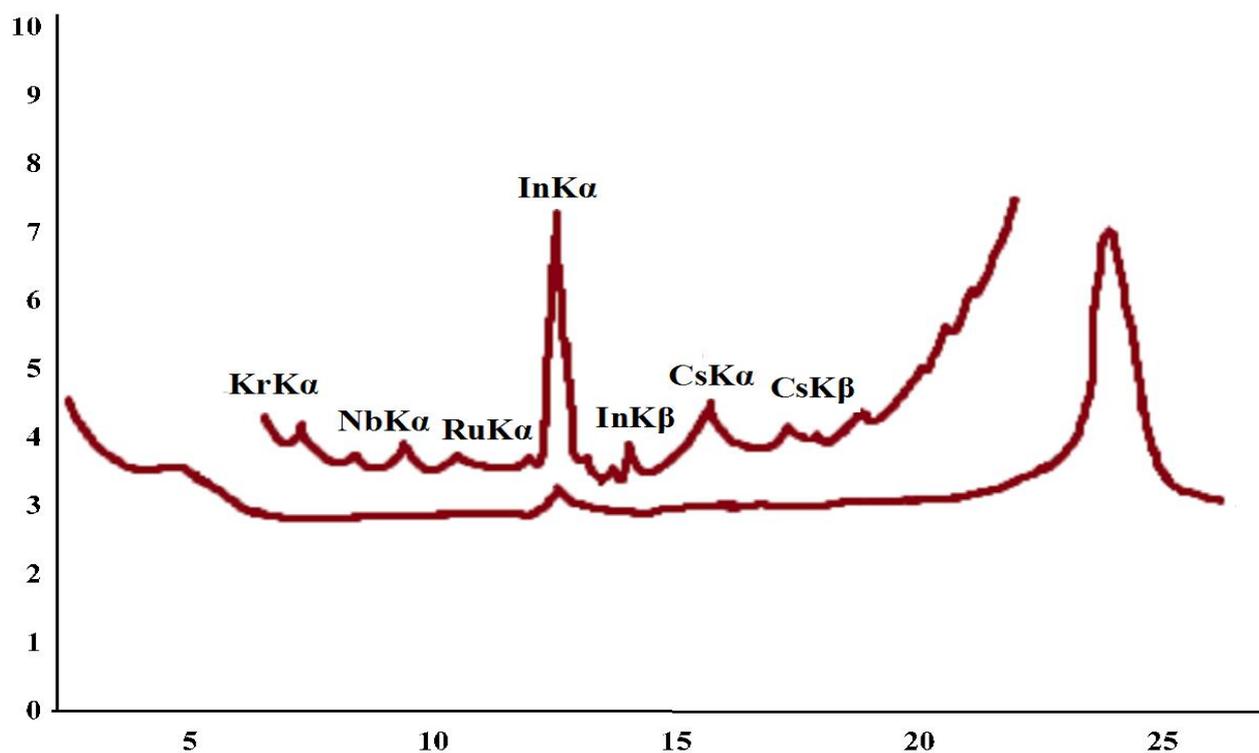


Fig.5. X-ray fluorescence analysis of the structure of soot

Our further efforts to identify the cause of broadening were associated with the use of the capabilities of EPR spectroscopy itself. One way to establish the nature of the broadening of the EPR signal is to study the growth rate of the intensity of the EPR signal components (I , m rel. Units) depending on the power of the supplied microwave field. In the case when the broadening occurs due to the superposition of signals from different PMCs, then usually their rates of change of intensities do not correspond to each other [1-3, 6]. On the contrary, when the broadened EPR signal is the result of hyperfine interaction (HFI), then their rate of change in intensity is consistent. As seen in fig. 1-4, in our case it is precisely the latter case that is realized. In this connection, it seems to us impossible that the origin of the components of the general EPR signal come from local free radicals with different centres of nature.

Thus, the EPR study of the created composition shows the presence of ultrafine signal splitting associated with the interaction of electrons [6].

In order to solve the question of whether the object under study is effectively an isotropic system or whether it is a highly oriented system, it is necessary, as noted [6, 13-15], to conduct experiments on the angular dependence of the EPR signals. Usually, in the strongly oriented system, both the anisotropy of the g factor and the anisotropy of the HFI are manifested [13-15]. But, at the same time, as was noted in [1, 13], isotropic and anisotropic

components can simultaneously appear in EPR signals broadened by HFI. The results of our experiments on the angular dependence of the EPR signals are presented in Figures 6 and 7. As can be seen from Figures 6 and 7, when turning at three different angles, relative to the initial state, they appear:

1. The apparent variability of the signal intensity of a narrow doublet;
2. The practical dependence of the intensity of the overall large signal on cornering;

This experiment suggests the manifestation of the anisotropy of the hyperfine structure for a narrow small doublet and the relative isotropy of the overall signal. Without making an attempt now to solve the question of whether the objects under study are strongly oriented, non-oriented, or effectively isotropic systems and not touching upon the solution of the manifestation of anisotropy of the g factor [6-9], let us first try to clarify the question of the possibility of the contribution from hyperfine fission (HFF) to nuclei : In, Kr, Nb, Ru, Cg, H, and S

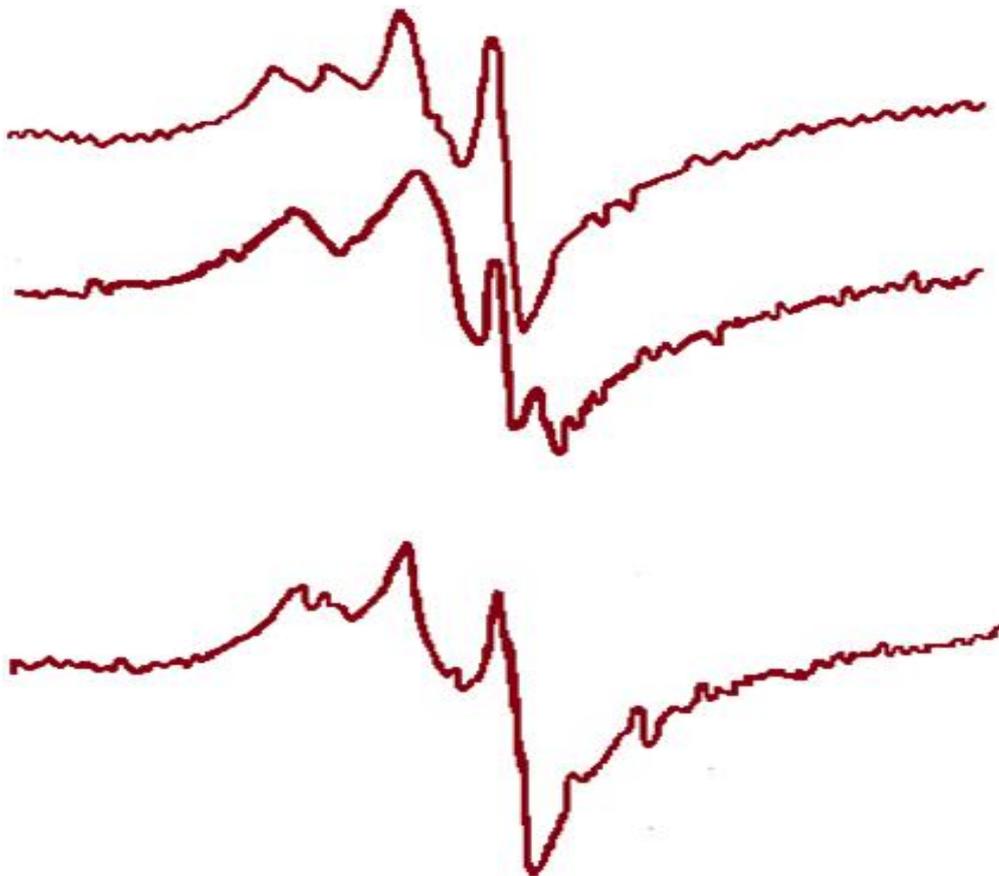


Fig.6. The angular dependence (a - 8 °; b - 17 °; c - 29 °) of the large total ESR signal of the PS + soot (0.09)

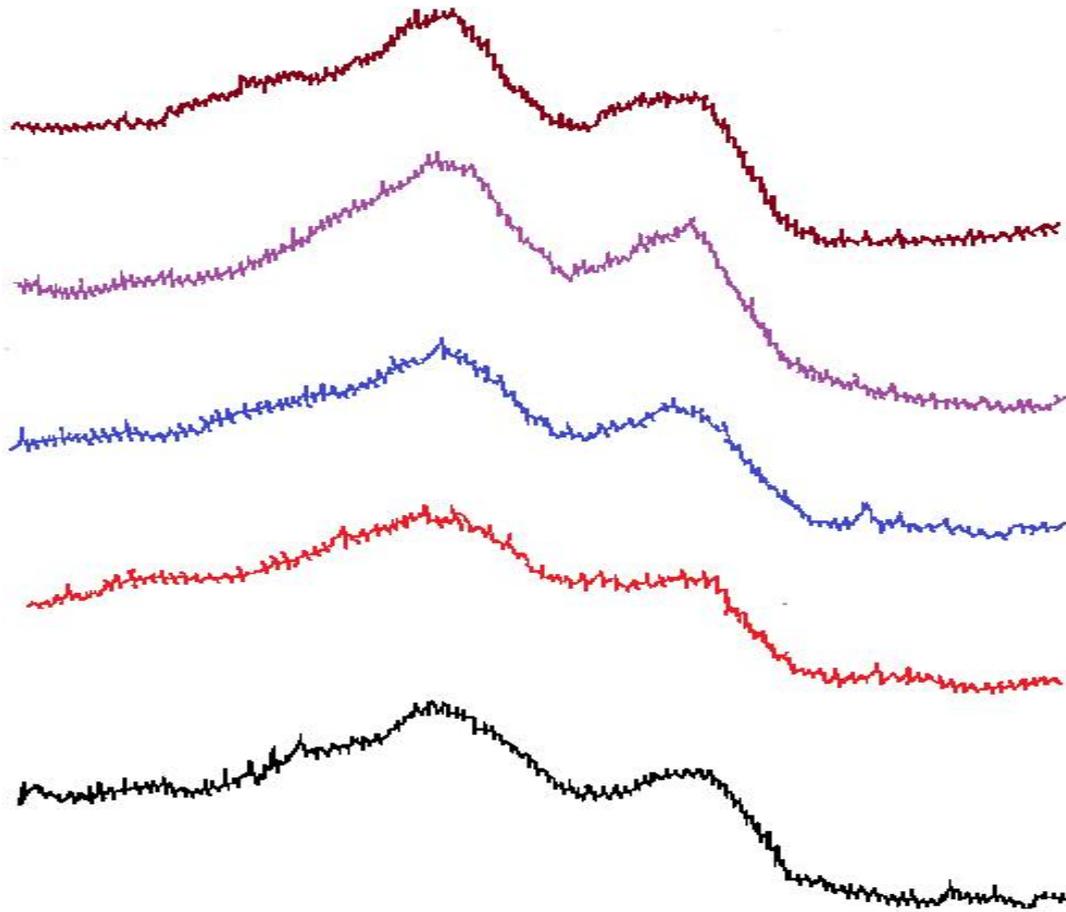


Fig.7. Angular dependence of the narrow-doublet component of the EPR signal of the PS + soot (0.09)

According to [13], no SR should be observed for ^{83}Kr at all. Both in [13] and in [1, 14] there is no information regarding the possibility of HFF in nuclei: In, Nb, Ru. So among the listed elements, you should initially focus on the possible HFF on the ^{133}Cs and ^{33}S nuclei. In the simplest case, there is a proportional relationship between the spin density p_i and the distance between the split lines a_i (Oersted):

$$a_i = Q \cdot p_i \quad (1)$$

Where Q is the HFF parameter on protons, which for each individual case can have its own specific values, but for most cases according to [13] it can be used as $Q = -27$ Hz. The index “ i ” in the equation corresponds to a specific orbit. Due to the fact that both negative and positive spin densities of the quantities a_i and Q can exist, they can also take negative and positive values depending on the condition. A characteristic feature of negative spin densities of π electrons is the presence of a large spectral extent.

On the other hand, as noted in [14], if a_i is positive, then this fact means the presence of a negative chemical shift (towards low magnetic fields) and vice versa. It should be added that for a compound such as: benzene, biphenyl, naphthalene, anthracene, tetracene and tropylium, the values of Q (in Hz) have values: 22.5; 22.9; 27.3; 27.7; 27.7 and 27.4 respectively. For pyrene, $Q = 29.2$ Hz, and a perinaphthalene-type compound has $Q = 43.1$ Hz. All of these compounds are a number of conjugated radicals and are of course interesting in that it is in them that there exists an π electron cloud, which, as indicated, is of particular interest in the study of exchange interaction processes [10-12].

In regards to the question of possible splitting at the ^{33}S proton, one should take into account the fact established in [13], according to which, for a HFF on ^{33}S , one can also use an equation of type (1), in which Q_3 (C) ^{33}S . The isotropic splitting constant A_0 noted earlier (in MHz) has the following dependence with the distance between lines a :

$$a = \frac{h \cdot A_0}{g} \quad (2)$$

Where h is the Planck constant, g is the factor, β is the Bohr magneton. To determine the spin density on S - orbitals, use the following relation:

$$P_S = \frac{A_{0\text{exp}}}{A_{0\text{teor}}} \quad (3)$$

Where $A_{0\text{exp}}$ is the value of A_0 determined from the experiment, $A_{0\text{teor}}$ is the value of A_0 taken from the data [15], which is compiled for the free atoms of these elements.

The isotropic constant HFI for ^{33}S A_0 is 2715 MHz, the anisotropic constant is $B = 78$ MHz. If we follow our experiments on EPR spectroscopy, then for PS with a soot content of $V_1 = 0.01$ $A_{0\text{exp}} = 420$ MHz. When calculating the formula for ^{33}S according to (3), we get $P_s = 0.154$, and determining the distance between the lines “ a ” according to formula (1) taking $Q \sim 33$ Hz into account, we get $a = 5.1$ Hz, while the experimentally observed quantity, $a = 47$ Hz. Consequently, the probability of HFF on ^{33}S disappears.

Conclusion

1. A soot polystyrene has been developed, which is a multilayer disordered amorphous-crystalline material resembling an integrated circuit, and consisting of active and passive nanoscale electronic components.

2. Technological methods used during the preparation of the composite showed the possibility of forcibly transforming some parts of ordinary black amorphous soot into such allotropic forms of carbon, such as the similarity to fullerene C₆₀, carbon nanotubes, and intermediate forms of fullerene are graphite-like structures. In this case, the similarity of fullerene C₆₀ and carbon nanotubes are active electronic nanocomponents.
3. The developed composite does not have layers that would allow characterizing the layer as ferromagnetic. And, nevertheless, the presence of: a) areas with highly developed π -electron clouds; b) the predominant role of the indirect exchange interaction between the spins with decreasing temperature may favor the development of one of the magnetically ordered states.
4. The ultrafine interaction (HFI) and a strong broadening of the electron-paramagnetic spectra were experimentally found in the PS + soot composition.
5. It was experimentally proven that the spin densities of π electrons for the PS + soot composition (0.20) coincide with theoretical calculations. Also, it was shown that the possibility of HFI at ¹³C in the composite PS + soot (0.20). The above facts indicate significant structural changes that occur during the transition from the composite PS + soot (0.01) to the composite PS + soot (0.20).
6. Scientifically and experimentally substantiated the possibility of the origin of the HFI at ¹³C for PS + soot (0.01) is reduced to nothing. And for PS samples with a soot content of $V_1 = 0.04$ and especially with $V_1 = 0.09$ and $V_1 = 0.20$, there is the possibility of a HFI at ¹³C.
7. It is shown that with an increase in the degree of filling from $V_1 = 0.01$ to $V_1 = 0.04$ and especially to $V_1 = 0.09$ and $V_1 = 0.20$ in PS, PMC localization moves from ¹⁷O to ¹³C. Also, the experimental results indicate that usually a normal EPR signal, regardless of the nature of the PMC, its quantity and line width, makes it possible to draw a straight line between its beginning and end. This consequence of strong absorption of the microwave field is experimentally proven.
8. It has been experimentally proven for the presence of spin polarization in the developed composites. For the first time, the configuration of paramagnetic centers in the PS + soot composition was shown. It is shown that it is precisely the polarization of S electrons with the local spin density of π electrons in this case that plays a very tangible role.

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