

RADIATION-INDUCED MACRORADICALS IN PLASTIC WASTE PYROLYSIS RESIDUES

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The nature of macroradicals in the solid residue formed from the pyrolysis of a plastic waste mixture, polyethylene terephthalate + polypropylene (PET-PP) and polypropylene + polystyrene (PP-PS), gamma-irradiated at doses of 32 and 476 kGy, were studied using the Electron Paramagnet Resonance (EPR) method and the results were compared with paramagnetic centers formed as a result of lignite coal irradiated at dose of 10 kGy. The obtained results shows that the nature of macroradicals formed as a result of pyrolysis of plastic materials are similar to the nature of macroradicals in lignite.

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INTRODUCTION

The production of plastic materials used in engineering, medicine, packaging, etc. is growing rapidly and is expected to reach one billion tons by 2050 [1]. Currently, only 10...12% of them can be recycled, the rest is buried in landfills, incinerated, or released into the environment [2]. The disposal of plastic waste is mainly based on their pyrolysis. It is known that the processes of pyrolysis and radiolysis occur with the participation of free radicals. The study of the nature and properties of active free radicals formed in solid residues of plastic waste is of particular interest. The main method for studying free radicals is the EPR.

The aim of the work is to study the nature and spectral parameters of macroradicals using of EPR method in the solid residue formed from the pyrolysis of gamma irradiated plastic waste mixture at different doses of gamma irradiation. The results obtained were compared with paramagnetic centers formed as a result of gamma-irradiation of lignite coal.

1. EXPERIMENTAL PART

The PET, PP, and PS polymers used to prepare both mixtures were selected from packaging waste and were taken in a 1:1 ratio in each mixture. The elemental composition and thermal properties of these polymer wastes are given in the Table below.

Elemental composition and thermal properties of polymer waste [3]

Polymers	C, %	H, %	O, %	T _{melting} , °C	T _{star} , °C	T _{dest} , °C
PP	85.7	14.3	—	168...175	328	434
PET	62.5	4.2	33.3	245	395	510
PS	92.26	7.74	—	240...270	355	467

The unirradiated and irradiated with doses of 32 and 476 kGy samples were filled into glass ampoules under

vacuum conditions and then pyrolysis at 450 °C at a rate of 5 °C/min.

Additionally, for the study of natural coal, lignite samples were sieved and separated into different fractions, and the 0.5...1 mm fraction was selected for the study. After mixing, the samples were dried in the open air for 24 h and filled into molybdenum glass ampoule containing 1 g of the substance. The ampoule were subjected to heat treatment at 105 °C and 0.1 mm Hg for 1 h and sealed under vacuum. The prepared sample were irradiated with gamma rays of ⁶⁰Co isotope in the range at different dose under static conditions.

EPR spectra of the samples were recorded at room temperature on a Bruker EMX PLUS radiospectrometer. The operating frequency of the radio wave was 9.8 GHz, the magnetic field interval 0...6000 G, and the modulation frequency was chosen 100 kHz.

2. EXPERIMENTAL RESULTS AND DISCUSSION

In the EPR spectra of the thermally decomposed PET-PP mixed plastic waste samples, a very strong singlet line and a sextet consisting of 6 lines symmetrically located around it were determined in the region of $g \approx 2.00$ (Fig. 1).

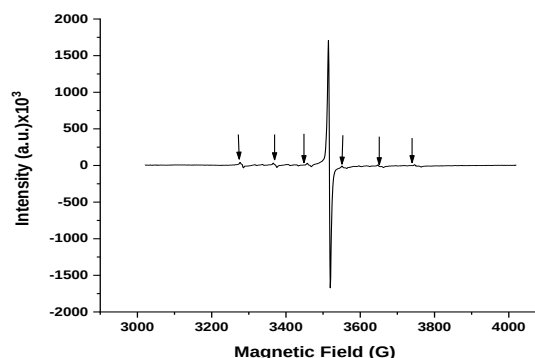


Fig. 1. Typical EPR spectrum of samples PET-PP system

The sextet located in the spectrum belongs to Mn^{2+} ions, which are widespread in nature and penetrate every mineral and organic material through water. These ions probably existed as small impurities in the chemical reagents used in the synthesis of polymers. This sextet is shown by arrows in Fig. 1.

The singlet line, which is formed during the pyrolysis process and is delocalized in the cyclic rings of carbon, belongs to free radicals. This singlet lines of three samples are shown in Fig. 2.

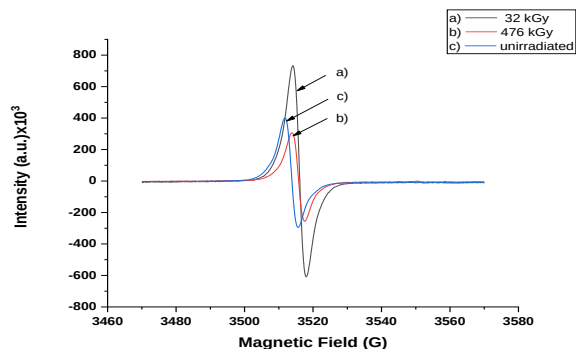


Fig. 2. Singlet lines in the EPR spectrum of the pyrolysis product of the PET-PP system

The spectroscopic parameters of these lines were: $g \approx 2.0042$ and the line width $\Delta B \approx 3.97$ G.

The EPR spectra of the products obtained from the pyrolysis of the samples of the PP-PS blend, unirradiated and irradiated with doses of 32 and 476 kGy, were similar, and a typical example is shown in Fig. 3.

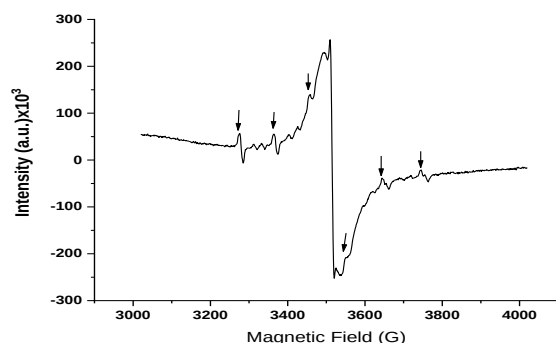


Fig. 3. Typical EPR spectrum obtained from samples of the PP-PS system

This spectrum shows that its structure is the same as in the PET-PP blend, the 6-line belonging to Mn^{2+} ions is symmetrically located around a very intense central singlet line. This sextet is shown by arrows in Fig. 3.

The central singlet lines in the EPR spectra of these samples are shown in Fig. 4. It can be seen from the figure that all three lines have identical structure and parameters. The spectroscopic parameters of these lines were: $g \approx 2.0045$ and the line width $\Delta B \approx 7.26$ G.

These two parameters differ somewhat from the parameters of the singlet line in the PET-PP blend. In both cases, the values of the g-factors are quite close. This means that the unpaired electron is significantly delocalized in the cyclic carbon rings. It is known that during the delocalization of the unpaired electron, the width of the singlet line decreases as the number of rings in the polycyclic system increases [4, 5]. Therefore, it can be said that in the PET-PP system, the unpaired electron

of the free radical is delocalized in the polycyclic group with a large number of carbon rings. This difference can be explained by the fact that the polycyclic groups in the PET-PP and PP-PS blends have different configurations during the pyrolysis process. It should be noted that the EPR signals observed in the pyrolysis of these blend products are different from the signals of irradiated individual polymer wastes [4–7].

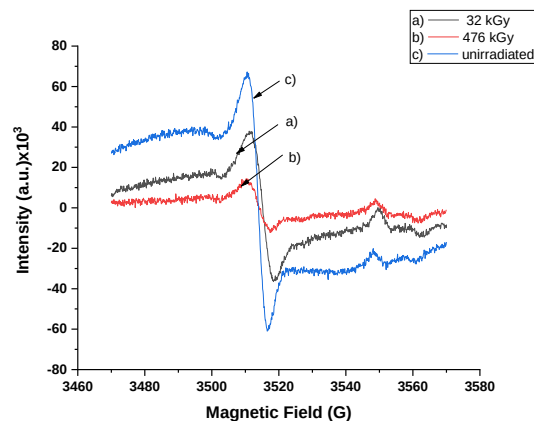


Fig. 4. Singlet lines in the EPR spectrum of the pyrolysis product of the PP-PS system

To compare the results obtained, paramagnetic centers formed by the action of gamma rays in lignite-type coal samples were studied. EPR spectra obtained from gamma-irradiated lignite-type coal samples are shown in Fig. 5.

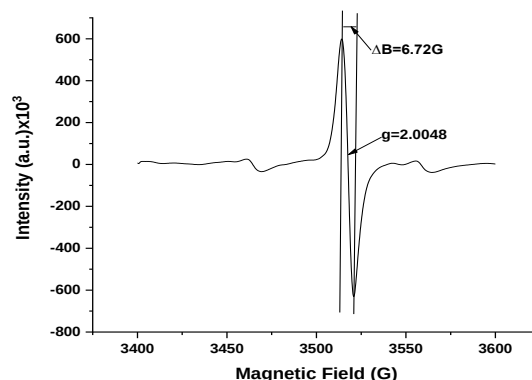


Fig. 5. EPR spectrum of a lignite-type coal sample irradiated at a dose of 10 kGy

This figure shows that the obtained EPR spectrum of a lignite-type coal sample is identical to the EPR spectrum of paramagnetic centers observed in polymer waste mixtures. Observed EPR signal is characterized by the parameters $g \approx 2.0048$ and $\Delta B \approx 7.00$ G and belongs to a free radical (see Fig. 5). The unpaired electron in this radical is associated with the carbon system. The shape of the spectrum, the g-factor, and the line width ΔB depend on the chemical composition of the nearest environment of the unpaired electron, its symmetry, and the level of delocalization of the electron in this environment. It is known that under the influence of gamma-rays, the components surrounding the electron can change. This causes certain changes in the parameters of the singlet line.

CONCLUSIONS

As a result of the conducted studies, it was determined that in the EPR spectra of the solid residues obtained as a result of pyrolysis of unirradiated and irradiated samples of PET-PP and PP-PS mixtures, a symmetric singlet with spectral parameters $g \approx 2.0042$ and the line width $\Delta B \approx 3.97$ G and $g \approx 2.0045$ and the line width $\Delta B \approx 7.26$ G is observed, respectively. The chemical source of which is free radicals with free electrons delocalized in the polycyclic carbon system. For comparison, in the EPR spectra of lignite-type coal samples irradiated at a dose of 10 kGy, an analogous singlet line with parameters $g \approx 2.0048$ and $\Delta B \approx 7.00$ G was also obtained. The very close values of the g-factor and the line width ΔB in all three spectra allowed to confirm that free radicals with the same chemical nature were formed in all three cases. The exposure of the samples to gamma-irradiation before pyrolysis did not affect the chemical nature of the free radicals formed as a result of pyrolysis.

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РАДІАЦІЙНО-ІНДУКОВАНІ МАКРОРАДИКАЛИ У ЗАЛИШКАХ ПІРОЛІЗУ ПЛАСТИКОВИХ ВІДХОДІВ

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Природу макрорадикалів у твердому залишку, що утворився в результаті піролізу суміші пластикових відходів, поліетилентерефталату + поліпропілену (ПЕТ-ПП) та поліпропілену + полістиролу (ПП-ПС), опромінених гамма-випромінюванням у дозах 32 та 476 кГр, досліджували за допомогою методу електронного парамагнітного резонансу (ЕПР). Результати порівнювали з парамагнітними центрами, що утворилися в результаті опромінення бурого вугілля дозою 10 кГр. Отримані результати показують, що природа макрорадикалів, які утворюються в результаті піролізу пластикових матеріалів, подібна до природи макрорадикалів у бурому вугіллі.