Vol. **108** (2005) *ACTA PHYSICA POLONICA A* No. 1

Proceedings of the XXI International Meeting on Radio and Microwave Spectroscopy
RAMIS 2005, Poznań-Będlewo, Poland, April 24–28, 2005

EPR Studies of Carbonized Cellulose — Oxygen Interactions

B. Pilawa[a,*], R. Pietrzak[b], H. Wachowska[b] and K. Babeł[c]

[a]Institute of Coal Chemistry, Polish Academy of Sciences
Sowińskiego 5, 44-121 Gliwice, Poland
[b]Laboratory of Coal Chemistry and Technology, Faculty of Chemistry
Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland
[c]Institute of Chemical Wood Technology, Agricultural Academy of Poznań
Wojska Polskiego 38/42, 60-637 Poznań, Poland

EPR examination of cellulose carbonized at 400°C and 600°C has been performed. The aim of this work was to search a sample useful as the oximetric probe in biology and medicine. The higher paramagnetic centers concentration characterizes cellulose carbonized at 600°C, which was found as the sensitive oximetric probe. Quasi-chemical bonds between cellulose molecules and paramagnetic O_2 molecules decrease paramagnetic centers concentration. A linear increase in paramagnetic centers concentration and a linear decrease in EPR linewidth with increasing time of sample evacuation were observed for cellulose carbonized at 600°C. Oxygen affects spin–lattice interactions in carbonized cellulose.

PACS numbers: 61.66.Hq, 76.30.Rn

1. Introduction

EPR spectra of organic systems strongly depend on existence of paramagnetic oxygen molecules in the environment of the samples [1]. Oxygen O_2 affects shape, linewidths, and amplitudes of resonance curves. Spin–lattice relaxation processes change in samples in air. Both broadening and narrowing of broad ($\Delta B_{\rm pp}$: 0.50-0.90 mT) EPR lines of macerals carbonized at 300−650°C were observed in air [2]. Narrowing of the narrow EPR lines ($\Delta B_{\rm pp}$: 0.06–0.34 mT) of thermally

*corresponding author; e-mail: pilawa@karboch.gliwice.pl

decomposed macerals dominates in air [2]. A decrease in concentration of paramagnetic centers with narrow ($\Delta B_{\rm pp}$: 0.29–0.34 mT) EPR lines caused by maceral interactions with oxygen is known [1, 2]. A decrease in spin–lattice relaxation time for macerals in air is also measured [2].

In this work interactions of carbonized cellulose with paramagnetic oxygen are examined. The aim of this study was to find oxygen sensitive probe for biological systems. It is expected that thermally treated cellulose is inert for cell cultures, whereas its EPR lines is susceptible for oxygen effect.

2. Experimental

EPR spectra of the original cellulose, and cellulose carbonized at 400°C and 600°C for samples evacuated 24 hours were measured. Cellulose carbonized at 600°C and evacuated 1–5 hours were studied by EPR method.

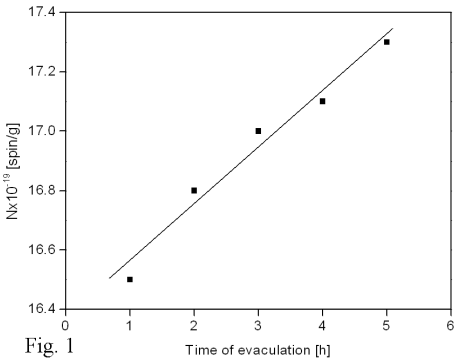
EPR measurements were performed using an X-band (9.3 GHz) spectrometer with modulation of magnetic field 100 kHz. The microwave frequency was measured. The g-factors, linewidths $\Delta B_{\rm pp}$, amplitudes, concentrations of paramagnetic centers were obtained.

Ultramarine was used as the reference of paramagnetic centers concentration. Area under absorption curve was obtained as double integration of the first derivative EPR line. The influence of microwave power on EPR lines was analyzed.

3. Results and discussion

To find a cellulose sample useful as the oximetric probe, the paramagnetic centers in the original cellulose and cellulose carbonized at 400°C and 600°C were tested. The original cellulose sample in vacuum reveals EPR lines with a linewidth of 0.30 mT and low paramagnetic centers concentration (1.0×10^{16} spin/g). Concentrations of paramagnetic centers in cellulose carbonized at 400°C and 600°C for the evacuated samples were determined as 4.7×10^{19} spin/g and 17.7×10^{19} spin/g, respectively. EPR linewidth $\Delta B_{\rm pp}$ of cellulose decreases from 0.56 mT to 0.43 mT with increasing heating temperature from 400°C to 600°C. The g-factors in the range of 2.0031–2.0035 were calculated from the resonance condition. EPR lines of cellulose carbonized at 600°C saturate at higher microwave power than those of cellulose carbonized at 400°C. Faster spin–lattice relaxation processes exist in the sample carbonized at 600°C.

Cellulose carbonized at 600°C was chosen as oximetric probe. Because of higher paramagnetic centers concentration and formation of multi-ring aromatic structures during thermal decomposition, probability of interactions with O_2 molecules is higher for cellulose carbonized at 600°C. The linear decrease in paramagnetic centers concentration with increasing oxygen concentration in environment of cellulose carbonized at 600°C was observed (Fig. 1). Quasi-chemical



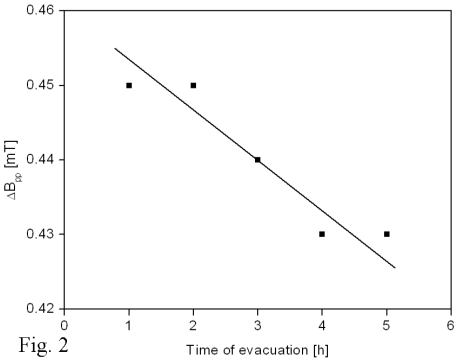


Fig. 1. Changes of paramagnetic centers concentration in cellulose carbonized at 600°C with increasing time of sample evacuation.

Fig. 2. Changes of linewidth ΔB_{pp} of EPR line of cellulose carbonized at 600°C with increasing time of sample evacuation.

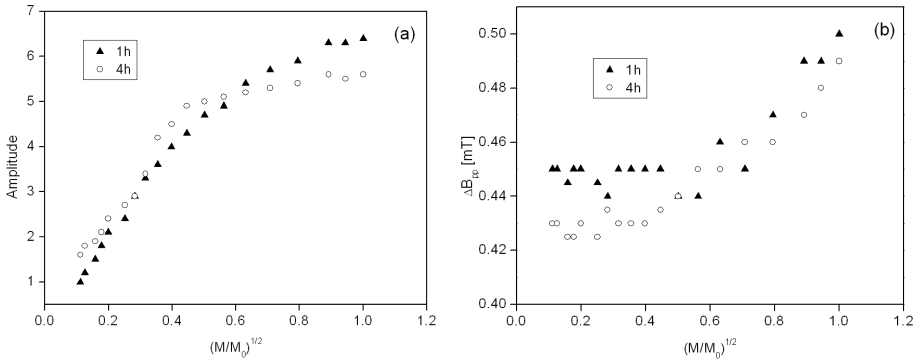


Fig. 3. Influence of microwave power on amplitudes (a) and linewidths ΔB_{pp} (b) of EPR lines of cellulose carbonized at 600°C for sample evacuated 1 and 4 hours.

bonds between the sample and O_2 are formed. The broadening of EPR lines of cellulose sample for higher oxygen concentrations was observed (Fig. 2).

Changes of amplitudes and linewidths of EPR lines in carbonized cellulose with microwave power for samples evacuated 1 and 4 hours are presented in Fig. 3a, b, respectively. EPR lines of cellulose carbonized at 600°C are homogeneously broadened (Fig. 3). EPR lines of cellulose sample with lower oxygen content in the environment (longer evacuated) saturate earlier than EPR lines of the sample with a higher oxygen content in the environment (Fig. 3a).

4. Conclusions

Spin–lattice and spin–spin interactions, and paramagnetic centers concentration in cellulose carbonized at 600°C depend on the oxygen concentration in

the environment of the sample. Paramagnetic oxygen molecules cause fastening of spin–lattice relaxation processes in the carbonized cellulose. The linear increase in linewidth and decrease in paramagnetic centers concentration with increasing time of sample evacuation were observed. The electron paramagnetic resonance results pointed out that carbonized cellulose is useful as probe in oximetry.

References

[1] B. Pilawa, A.B. Więckowski, *Fuel* **76**, 1173 (1997).

[2] B. Pilawa, *Evolution of Paramagnetic Centers during Thermal Decomposition of Macerals*, WSP, Zielona Góra 2000 (in Polish).