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A. BERDOWSKA*, J. BERDOWSKI**,#, F. AUBRY***

CORRELATIONS BETWEEN STRUCTURES OF EXPANDED GRAPHITE – POLYMER COMPOSITES AND ACOUSTIC EMISSION PHENOMENA

KORELACJE POMIĘDZY STRUKTURĄ KOMPOZYTÓW GRAFIT EKSPANDOWANY-POLIMER A ZJAWISKAMI EMISJI AKUSTYCZNEJ

Compressed expanded graphite was applied as a base matrix to the preparation of microporous composites as products of impregnation, polymerization and carbonization of poly-furfuryl alcohol. During carbonization, the original polymeric structure is transformed into an amorphous turbostratic carbon structure with ultramicropores. The structure, porosity and many chemical and physical properties change after each stage of their technological treatment.

The acoustic emission method was used for accurate determination of these changes. It is possible to determine a large number of acoustic emission parameters and therefore to increase the amount of information provided by the studied materials. Acoustic emission pulses, counts rate, events rate, signal peak value and their sums were measured. Also frequency spectrum was received as a result of acoustic emission signal analysis with use of Fourier transformation procedure. The conclusions resulting from the Fourier analysis of the registered spectrum are very interesting and provide information about composite structures as well as bonds between the graphite matrix and the polymer that fills it. Analysis of acoustic emission parameters provides data on physical and chemical processes that would be very difficult to study by means of other techniques. Wide applications of these porous composites make them very interesting subject of the study.

Keywords: Compressed expanded graphite, Polymer, Composite, Acoustic emission parameters.

Sprasowany grafit ekspandowany użyto jako bazową matrycę do wytworzenia mikroporowatych kompozytów będących produktami impregnacji, polimeryzacji i karbonizacji alkoholu polifurfurylowego. Podczas procesu karbonizacji oryginalna struktura polimerowa jest przekształcana w strukturę turbostratyczną węgla amorficznego z ultramikroporami. Struktura, porowatość oraz wiele chemicznych i fizycznych własności ulega zmianie na poszczególnych etapach technologicznego procesu.

Metodę emisji akustycznej użyto w celu dokładnego przebadania tych zmian. Możliwym jest wyznaczenie w eksperymentach dużej liczby parametrów emisji akustycznej co pozwala uzyskać dużą ilość informacji o badanych materiałach. Zmierzono następujące parametry emisji akustycznej: szybkość zliczeń, szybkość zdarzeń, amplituda impulsu, średnia wartość skuteczna sygnałów oraz sumy tych parametrów. Także analizowano widmo częstotliwościowe sygnałów przy pomocy transformaty Fouriera. Wnioski wynikające z analizy fourierowskiej widm są niezwykle interesujące i dostarczają informacje o strukturze kompozytów oraz o wiązaniach między grafitową matrycą a polimerem wypełniającym ją. Analiza parametrów emisji akustycznej dostarcza wielu danych o fizycznych i chemicznych własnościach, które byłyby bardzo trudne do zbadania przy użyciu innych metod. Szerokie zastosowania omawianej grupy porowatych kompozytów czyni je bardzo interesującym przedmiotem badań.

1. Introduction

Determination of physical, mechanical and chemical properties of the compressed expanded graphite (CEG) composites prepared from poly-furfuryl alcohol is important to resolve whether the materials can be used as good quality catalysts [1-2] or composite membranes for gas separation [3-4] and also as proton exchange membranes in fuel cells [5-8].

The purpose of this paper was to search the relations between the structure of the CEG composites on successive stages of technological treatment and parameters describing the acoustic emission (AE) phenomena in these materials.

These investigations are a continuation of our earlier studies [9] concerning physical and chemical properties of porous composites created on the basis of a CEG matrix, obtained after successive technological procedures of

* J. DLUGOSZ UNIVERSITY, INSTITUTE OF CHEMISTRY, ENVIRONMENTAL PROTECTION AND BIOTECHNOLOGY, 13/15 ARMII KRAJOWEJ AV., 42-200 CZĘSTOCHOWA, POLAND
** J. DLUGOSZ UNIVERSITY, INSTITUTE OF PHYSICS, 13/15. ARMII KRAJOWEJ AV., 42-200 CZĘSTOCHOWA, POLAND
*** LABORATOIRE DE CHIMIE DU SOLIDE MINERAL, UNIVERSITE H. POINCARE, NANCY, FRANCE
#Corresponding author: j.berdowski@ajd.czest.pl

impregnation, polymerization and carbonization of poly-furfuryl alcohol. Exact description of the technological process can be found in our earlier paper [9]. The aim of this work was to investigate materials obtained at different levels of technological processing, thus with different densities, porosity, physical and chemical properties, by using the acoustic emission method. CEG and porous composites that have been created so far have not been studied yet by means of the AE method.

2. Technological procedures

The scheme of successive steps of technological procedures is presented in Fig. 1. It begins from the crystalline graphite, which is the precursor, goes through all the chemical and physical actions up to the final material, which is a heterogeneous composite structure. This material is composed of graphite matrix and carbonized polymer created on the basis of poly-furfuryl alcohol, which fills up the open pores.

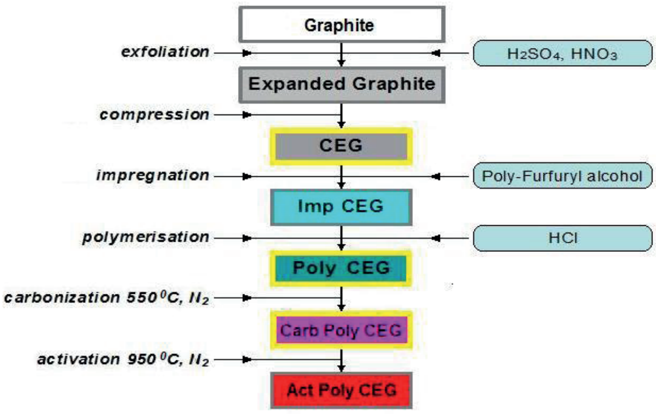

Fig. 1. Scheme of the technological procedures

It can be considered that each of the product shown in this diagram has a wide, diverse use in practice. This is the reason why we have included three different composites from this diagram in our study: 1) compressed expanded graphite (CEG) – a homogeneous, anisotropic, very porous material; 2) (POLY) - compressed expanded graphite impregnated with the polymerized poly-furfuryl alcohol; 3) (CARB) - material created as a result of carbonization of the composite No 2. Three composites at different stages of technological treatment, which we took for investigating, are marked with yellow frames on the diagram Fig. 1.

3. Acoustic emission phenomena in composites on different steps of their technological treatment

In compressed expanded graphite structure one can differentiate two basic directions: perpendicular to the bedding plane of graphite flakes and parallel to this one as it is shown in Fig. 2. The compression pressure was applied in these basic directions during the measurements.

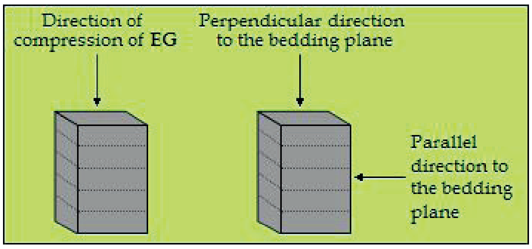

Fig. 2. Main directions used for describing bedding structure of composites

The acoustic emission method can be used for measurements of changes in the structure and many different properties of materials, resulting from the applied stress [10-11].

Investigations of the acoustic emission phenomena in the group of the three composites described above were carried out with the use of Acoustic Emission Analyzer type EA-100 NEUR, Institute of Fundamental Technological Research PAS and Materials Testing Machine type LRX, Lloyd Instruments, Great Britain. The measurements of all AE parameters were carried out in a wide range of elastic waves frequencies (0.1-2.5 MHz), by the use of piezoelectric transducer model SE2MEG-P, Dunegan Engineering Consultants Inc. (DECI), USA. Since recording and analysis are done with the use of computer, it is possible to find out a larger number of AE parameters in a single experiment [12-13], thus increase the amount of information provided by the investigated materials. Some results of AE measurements in various graphite materials are described in our previously published papers [9,14-15]. From amongst many registered parameters describing the AE pulses, there are changes in four of them: – sum of events, sum of counts, sum of amplitudes, sum of RMS and also spectrum distribution of AE waves – presented in this paper.

Acoustic emission signals events and counts were measured in the following approach. In the sample, the first five hundred data recorded only noise, subsequently uniaxial compression stress was applied to the sample by the use of Lloyd Machine. The pressure started from zero and increased linearly up to the maximum value. The events and counts rate was defined as the quantity of registered AE pulses within the 0,1 s time interval.

The results of measurements of the AE parameters for the three groups of studied composites are shown below. The all presented results were obtained for the uniaxial strain applied in the direction parallel to the bedding plane of the composite structure. Analysis of AE parameters provides information on physical and chemical processes in materials that would be very difficult to study by means of other techniques.

3.1. Comparison of sum of events and sum of counts of the AE signals for the three groups of materials

Results of measurements of the sum of AE events for CEG, POLY and CARB composites are compared in Fig. 3. Whereas results of measurements of the sum of counts of the AE impulses for the three composites are shown in Fig. 4. Measurements of stress for CEG, in respect for its softness, were carried out with sensitivity 10 times higher than for the other materials.

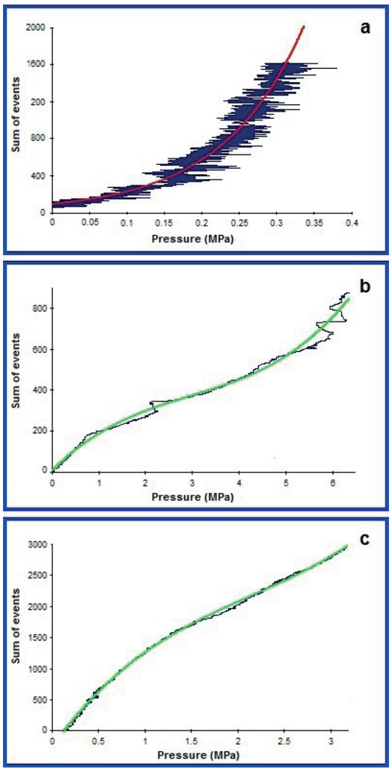

Fig. 3. Comparison of sum of events of the AE signals for the three groups of materials vs. pressure applied in the direction parallel to the bedding plane. a) CEG, ρ = 112 mg/cm^3; b) POL, ρ = 660 mg/cm^3; c) CARB, ρ = 498 mg/cm^3

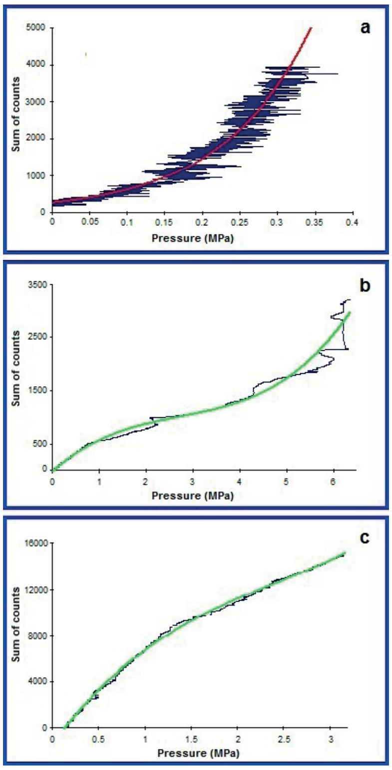

Fig. 4. Dependence of sum of counts of the AE pulses on pressure applied in the direction parallel to the bedding plane. a) CEG, ρ = 112 mg/cm^3; b) POL, ρ = 660 mg/cm^3; c) CARB, ρ = 498 mg/cm^3

Results of the mean value for the sum of events and sum of counts of the AE signals for three groups of composites recorded during a single-axis-compression are presented in TABLE 1. The highest values of the sum of events and of the sum of counts were recorded for the CARB composite, mean values were recorded for the CEG material and the lowest were recorded for POLY composite. The results are evidence of the highest activity of acoustic emission in the CARB composite.

TABLE 1

Values of the sum of events and the sum of counts of the AE pulses for the three groups of materials, pressure applied in the direction parallel to the bedding plane

Composite	Density [mg/cm^3]	ΣN_{ev}	ΣN_{cnt}	$\frac{\Sigma N_{cnt}}{\Sigma N_{ev}}$
CEG	112	1 423	3 511	2.5
POL	660	712	2 490	3.5
CARB	498	2 750	14 505	5.3

Differences between these three groups of materials are understandable. The results clearly reflect elastic properties of the studied composites. CEG material is soft and brittle. Following impregnation material POLY with the poly-furfuryl alcohol in pores and polymerization which turns it into a quasi-isotropic structure, is a hard and elastic composite. Following carbonization material CARB, regains partly its anisotropic properties and becomes hard, but brittle.

The Table 1 also shows the calculated ratios of the mean value of the sum of counts to the sum of events. The value of the ratio is connected to a mean frequency of the AE waves [16]. The lowest quantity of the ratio was observed in CEG, the mean one in POLY and the highest in CARB composite. This is indicated by an abrupt increase of frequency of the generated acoustic waves in each group of the composites after technological treatment.

3.2. Comparison of sum of amplitudes and sum of the root-mean-square of the AE pulses for the three groups of materials

The results of measurements of the sum of maximum amplitudes and of the sum of the root-mean-square (RMS) value of the AE impulses recorded during the single-axis-compression in the plane parallel to the bedding plane of the structure in the three groups of the studied composites are presented in Fig. 5 and in Fig. 6.

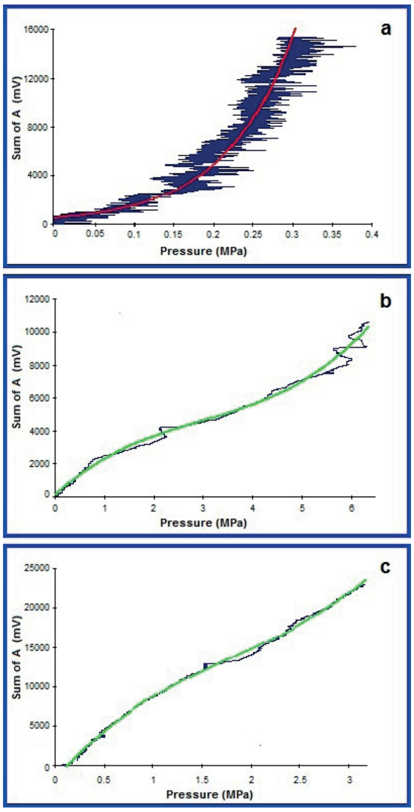

Fig. 5. Comparison of sum of amplitudes of the AE waves for the three groups of materials vs. pressure applied in the direction parallel to the bedding plane. a) CEG, ρ = 112 mg/cm^3; b) POL, ρ = 660 mg/cm^3; c) CARB, ρ = 498 mg/cm^3

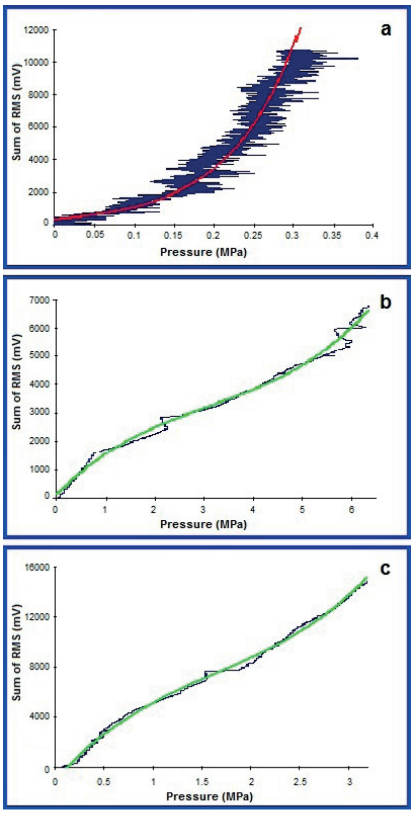

Fig. 6. Dependence of sum of RMS of the AE signals on pressure applied in the direction parallel to the bedding plane. a) CEG, ρ = 112 mg/cm^3; b) POL, ρ = 660 mg/cm^3; c) CARB, ρ = 498 mg/cm^3

Results of measurements of these acoustic parameters in the three groups of the studied composites are shown in TABLE 2. The highest values of both parameters were recorded in the CARB composite, the mean ones in CEG, and the lowest in POLY. The results confirm that the maximum summary energy of the AE impulses is generated in the structure of the CARB composite. The highest speed of its emission was observed in the same material.

TABLE 2

Sum of amplitudes and the sum of RMS of the AE signals for the three groups of materials

Composite	Density [mg/cm^3]	Σ A	ΣU_{RMS}	$\frac{\Sigma U_{RMS}}{\Sigma U_{RMS}^{CEG}}$
CEG	112	16 021	9 807	1.00
POL	660	9 493	5 889	0.59
CARB	498	22 100	13 842	1.41

Analyzing dependences of the sum of each of the four above mentioned AE parameters on the applied compression pressure, Fig. 3-6, it was found that for CEG – i.e. the material forming the graphite matrix – it is an exponential kind of dependence. Whereas for the POL and CARB composite materials, the dependence on pressure is described by the x^3 type polynomial.

3.3. Evolution of AE parameters depending on densities of composites

Dependences of the sum of each of the four measured AE parameters on the density of material in each of the three analyzed groups of composites are compared in Fig. 7.

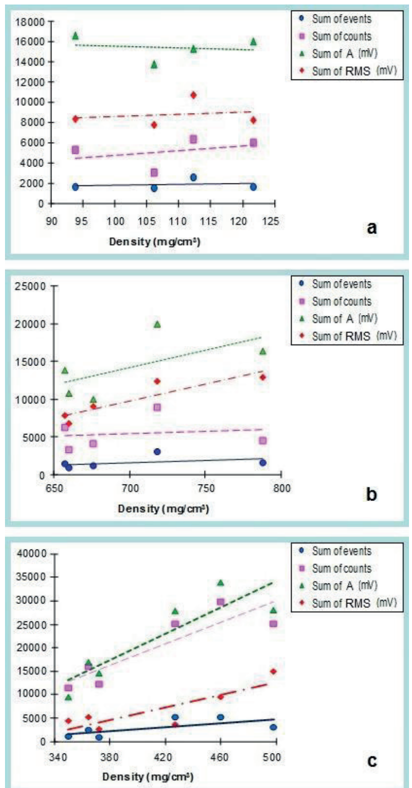

Fig. 7. Evolution of four AE parameters depending on densities of composites. a) CEG, b) POL, c) CARB

Analysis of the obtained dependences showed that within the studied range none of the four AE parameters depends on material density in CEG material. In the POL composite, the sum of events and the sum of counts do not depend on the density of the composite. Whereas, the parameters describing energy of AE impulses, i.e. the sum of amplitudes and the sum of the root-mean-square value increase with the composite density. In CARB composite, values of all four studied AE parameters increase vs. density of this group of composites.

3.4. Spectral distributions of AE signals recorded in described forms of composite

Spectrum distribution was recorded as a result of frequency analysis of acoustic emission by using the Fourier transformation procedure [10,17]. Results of measuring spectrum distribution of AE frequencies of signals for the three groups of investigated materials are shown in Fig. 8. The results were obtained at uniaxial compression pressure applied in the direction parallel to the bedding plane of a composite structure.

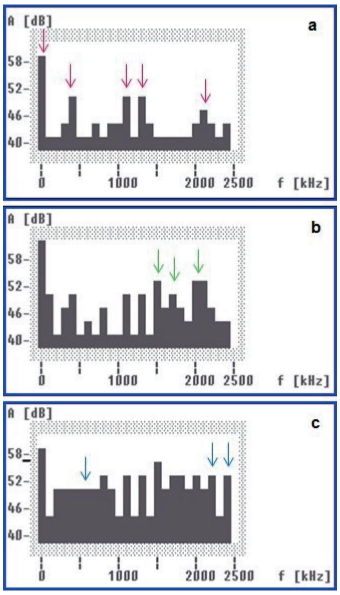

Fig. 8. Fourier transformation of spectrum distribution of AE waves for the three groups of composites, pressure applied in the direction parallel to the bedding plane. a) CEG, ρ = 112 mg/cm^3; b) POL, ρ = 660 mg/cm^3; c) CARB, ρ = 498 mg/cm^3

The spectrum of frequency of AE waves recorded in the CEG graphite matrix is shown in Fig. 8a. Red arrows have been used to mark five bands of frequencies of AE impulses, which also appear in the spectra of the POLY and CARB composites. From these observations we can conclude that in the graphite matrix acoustic waves of the same frequency and similar intensity as in the heterogeneous structures of the POLY composite and in the CARB composite are generated.

Fig. 8b shows the frequencies spectrum of AE impulses registered in the POLY composite. The three bands of wave frequency, which also occur in the CARB composite spectrum, but do not appear in the CEG graphite matrix are marked with green arrows. The results lead to a conclusion that acoustic waves of these frequencies are generated in polymerized furfuryl alcohol material filling up the open pores of the composite both, before and after the carbonization.

Fig. 8c displays spectrum distribution of the AE signals recorded in the CARB composite. Blue arrows point to the three dominating bands of wave frequency which occur only in the spectrum of the composite after carbonization of the polymerized material. They were not generated in the earlier technological phases of this material.

The obtained results are very interesting. Characteristic bands of the frequencies generated in the three examined groups of materials are compared in TABLE 3.

TABLE 3

Frequencies of bands of AE waves for the three groups of composites

Composite	Density [mg/cm^3]	Frequency bands of AE activity [MHz]
CEG	112	0.1 0.4 1.1 1.3 2.0 - 2.2
POL	660	1.5 - 1.8 2.0 - 2.2
CARB	498	0.2 - 0.9 2.2 2.4

Analysis of these results shows that introducing a polymer of the poly-furfuryl alcohol into a CEG graphite matrix results in a shift of spectrum maxima towards higher frequencies. There appear quite wide bands in the POLY composite. Carbonization of the POLY composite results in further shift of the spectrum maxima towards higher frequencies. There appear two intensive bands of frequencies at 2.2 and 2.4 MHz

The results are in perfect agreement with the results shown in TABLE 1, which yielded conclusions concerning increased frequency of the generated acoustic waves when passing to a successive group of composites. The shift of spectrum maxima to higher frequencies indicates a decrease of the size of AE sources [16]. The conclusions are also in compatibility with the results of our earlier studies pertaining to structure, strength and elastic properties of the three groups of studied composites presented in [9].

4. Conclusions

The conducted studies of the AE phenomena taking place in porous composites created on the basis of a CEG matrix obtained after successive technological treatments of impregnation, polymerization, and carbonization of the poly-furfuryl alcohol allowed to draw the following conclusions:

- Dependences of all investigated AE parameters in function of the applied pressure are exponential in CEGs materials. These dependences in POLY and CARB composites are type x^3 polynomials for pressure applied in the direction parallel to the bedding plane.
- The greatest value of the sum of events and the sum of counts of the AE signals was measured in the CARB composite. This demonstrates that CARB materials are the most active in generating the AE waves. Such a high level of activity is characteristic for hard, brittle and porous materials.
- The maximum sum of amplitudes and the sum of RMS signals measured in CARB composite correspond to the highest energy and power of AE signals which were generated in this group of materials.
- It was confirmed that sums of the AE parameters, for the stress applied in direction parallel to the bedding plane, do not change with density (or porosity) of CEGs. As for the POLY composites, it was determined that the sum of events and the sum of counts are almost independent on density of samples but the sum of amplitudes and the sum of RMS signals increase vs. density. For CARB composites all four AE parameters increase vs. density of composites.
- Comparison of spectrum distributions of the AE waves in each group of composites (CEGs, POLYs and CARBs) turned out to be very different from one another but certain frequency bands are the same.
- The shift of the bands to higher frequencies in spectrum distribution in POLY and CARB composites indicates a decrease in the dimensions of the sources generating AE signals.

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