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STUDY OF PROPERTIES OF EXPANDED GRAPHITE – POLYMER POROUS COMPOSITES BY ACOUSTIC EMISSION METHOD

BADANIE WŁAŚCIWOŚCI POROWATYCH KOMPOZYTÓW GRAFIT EKSPANDOWANY – POLIMER METODĄ EMISJI AKUSTYCZNEJ

The purpose of this paper was to investigate the physical and mechanical properties of compressed expanded graphite (CEG) and their porous derivatives after impregnation, polymerization; and carbonization by the use of acoustic emission method (AE). The mechanical and structural characteristics of compressed expanded graphite and their three groups of porous composites after each technological process are presented and discussed. The measurements of acoustic emission parameters in these materials were carried out at wide range of frequency of the waves (0.1÷2.5 MHz). The changes of two of parameters: – AE pulses counts rate and spectrum distribution of AE waves – are presented in this paper. The analysis of the respective parameters AE also gives possibility to determine the micro- and macro structural changes of materials at different levels of technological processes.

Applications of these materials as catalysts with high specific surface make them very interesting subject of study. Also compressed expanded graphite composite membranes prepared from furfuryl alcohol polymers are promising for gas separation.

Keywords: compressed expanded graphite, polymerization, carbonization, composite membrane, acoustic emission

Cel pracy stanowiło zbadanie przy użyciu metody emisji akustycznej (EA) fizycznych i mechanicznych właściwości spraso-wanego grafitu ekspandowanego (SGE) i jego porowatych pochodnych kompozytowych, otrzymanych po procesach impregnacji, polimeryzacji i karbonizacji. Przedstawiono i przedyskutowano mechaniczne i strukturalne charakterystyki sprasowanego gra-fitu ekspandowanego i trzech porowatych kompozytów otrzymanych na jego bazie, po kolejnych procesach technologicznych. Pomiary parametrów zarejestrowanych sygnałów EA w tych materiałach wykonano w szerokim przedziale częstotliwości emi-towanych w materiale fal (0,1-2,5 MHz). W pracy przedstawiono zmiany dwu z tych parametrów: szybkości zliczeń impulsów i rozkładu widmowego emitowanych fal. Analiza poszczególnych parametrów emisji akustycznej stwarza możliwości określenia mikro- i makrostrukturalnych zmian w materiałach, wytworzonych na różnych etapach procesu technologicznego.

Przewidywane szerokie zastosowanie tych materiałów jako katalizatorów, posiadających bardzo duże powierzchnie właści-we, czyni je niezwykle interesującym przedmiotem badań. Również bardzo perspektywiczne jest wykorzystanie kompozytowych membran z matrycą ze sprasowanego grafitu ekspandowanego, wypełnionego polimerem alkoholu furfurylowego, do separacji gazów.

1. Introduction

Mechanical properties of compressed expanded graphite (CEG) samples and the porous products of their impregnation and carbonization have not been explored yet by the use of acoustic emission (AE) methods. However, studies of electrode or reactor graphite samples have already been carried out, and the use of acoustic emission methods in such studies have been found to be very useful [1-3]. Actually, when submitted to any kind of stress (temperature, compression, etc.), vari-ous parts of graphite samples were revealed to be sources of acoustic waves [4]. Although many studies of graphite samples were carried out with the use of acoustic emission methods, none of them dealt with CEG samples and their properties,

therefore it seems to be a really interesting new field of re-search to explore. One of the possible applications of those materials as a catalyst support with an extensive specific sur-face makes it, therefore, a really interesting subject of study [5-6]. Compressed expanded graphite composite membranes prepared from furfuryl alcohol polymers are promising for gas separation [7-8] as well and also as a proton exchange membrane in fuel cell. [9-11].

The authors attempt to do this investigation using the acoustic emission methods on samples, obtained at different levels of technological processing, with different densities, shapes, physical and chemical properties.

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2. Technological procedures

Compressed expanded graphite (CEG) blocks produced from expanded graphite (EG) of apparent density of 2.6 kg m^{-3} and specific surface area of 20-40 m^2/g, provided by Carbone-Lorraine Group (France), were applied to the preparation of microporous composites. Expanded graphite is obtained from the exfoliation of graphite intercalation compounds by application of thermal shock. The composite used by EG manufactory is most often the result of the intercalation of sulphuric or nitric acid. The properties of expanded graphites and compressed expanded graphites are presented in TABLE 1.

TABLE 1

Values of apparent density and porosity of initial materials – expanded graphite's (EG) and compressed expanded graphite's (CEG) samples

	EG	CEG	
Manufacture	**Apparent density [mg/cm^3]**	**Apparent density [mg/cm^3]**	**Porosity [%]**
Carbone Lorraine France	2.6	49 - 260	97.8 - 88.2
Carbone Lorraine France	7.5	18 - 279	99.2 - 87.3

The scheme of all technological procedures is presented in Fig. 1. They lead from the precursor, which is the crystalline graphite, through all the successive chemical and physical actions to the final material, which is a heterogeneous composite structure. The composite is built of graphite matrix and carbonized polymer material created on the basis of polyfurfuryl alcohol, which fills up the open macropores.
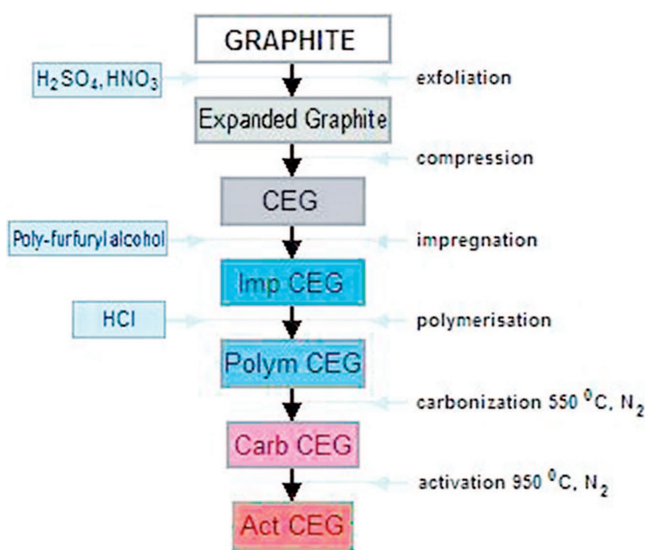

Fig. 1. Scheme of the technological procedures of derivatives of graphite

It should also be noted that each of the seven products shown in this diagram has a wide, diverse use in practice. This is why we have included three of the materials in our study: 1) compressed expanded graphite (CEG) – a homogeneous, anisotropic, very porous material; 2) a composite material, compressed expanded graphite, impregnated with the polymerized polyfurfuryl alcohol (POLY); 3) a composite material created as a result of carbonization (also called pyrolysis) of the material No 2 (CARB). The described technological procedures and the resulting composite materials are perfect examples of practical application of achievements of materials engineering.

3. Structures of composites at different steps of their technological treatment

Compression of expanded graphite allows to differentiate two main directions: perpendicular and parallel to the bedding plane of graphite as it is shown in Fig. 2.
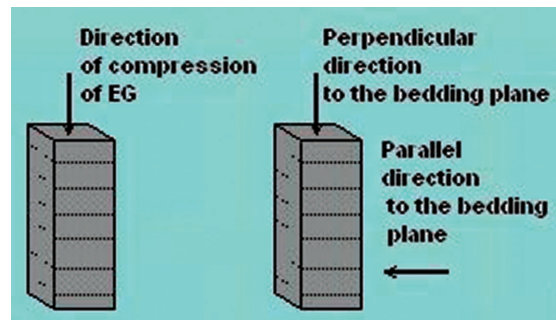

Fig. 2. Principle directions used for describing physical and mechanical properties of composites

Figures 3 and 4 show photos of the surfaces of the samples without any polishing. One photo was taken in the parallel and one in the perpendicular direction in relation to the bedding plane, for each type of material. The apparatus used to take pictures of the samples at each stage of their treatment was the *Axioskop MPM 200, Carl Zeiss* type optical microscope. All pictures were taken using reflected light.

The three photos in Fig. 3 show the evolution of the texture of the materials, after technological treatments, in the parallel direction to the bedding plane. It is clearly seen on these photos that the structure and porosity change. These photos make visible the differences between the CEG state, polymerized state, and carbonized state of the materials. The, so called, 'accordion' structure of the samples is still observable in POLY and CARB materials even after the process of pyrolysis.

The next three photos in Fig. 4 show the evolution of the texture of the materials in the perpendicular direction to the bedding plane after each stage of their technological treatment. They also show the differences in the samples visible from the two main directions.
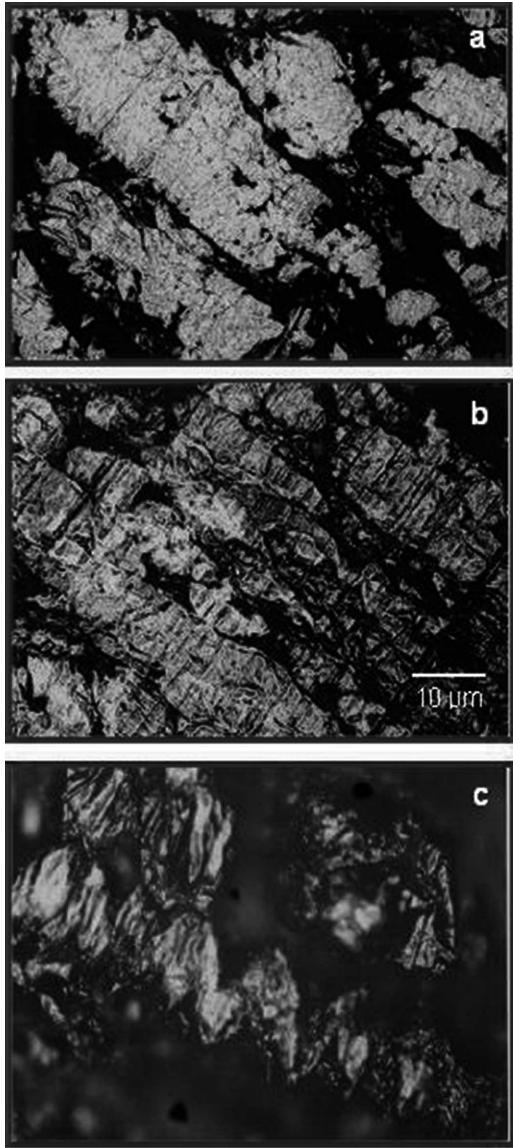
Fig. 3. Microscopic images of the three groups of materials. Cross-section to the bedding plane. a) CEG, $\rho = 260$ mg/cm^3; b) POLY, $\rho = 669$ mg/cm^3; c) CARB, $\rho = 428$ mg/cm^3

Fig. 4. Microscopic images of the three groups of materials. Direction parallel to the bedding plane. a) CEG, $\rho = 171$ mg/cm^3; b) POLY, $\rho = 555$ mg/cm^3; c) CARB, $\rho = 365$ mg/cm^3

3.1. Evolution of densities of the composites during technological treatment

Evolution of densities of the three groups of composites, at different stages of their technological procedures, is predictable – Fig. 5.

Moreover, the forecast of densities of POLYs and CARBs starting from CEGs seems to be more accurate for the smallest size samples. It can be interpreted as a reflection of the increasing heterogeneity of CEGs with their size and their production process. Moreover, it seems that the evolution between POLYs and CARBs states is more regular than between CEG and IMP states. It can be explained as the result of the fact that the process of impregnation for each sample was not exactly the same.
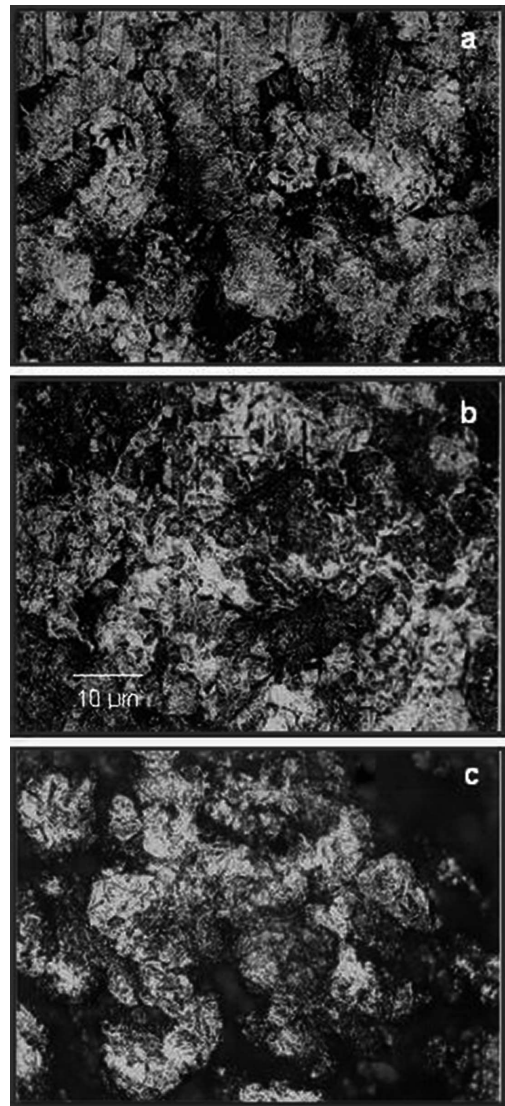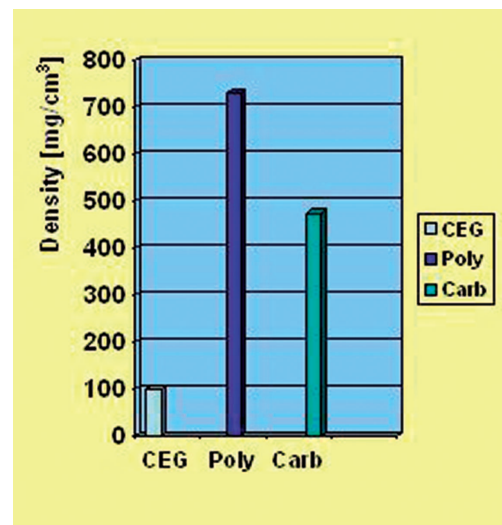

Fig. 5. Apparent density changes of compressed expanded graphite (CEG) after impregnation with furfuryl alcohol, polymerization (POLY) and subsequent carbonization to 550°C (CARB). The initial density of CEG was 100 mg/cm^3

4. Investigation of mechanical properties of the CEG, POLY, CARB composites

4.1. Evolution of the compressive strength of composites depending on their densities

The acoustic emission method can be used for accurate determination of changes in the structure of materials, resulting from e.g. the applied stress [12]. In this way, it is possible to measure the compression strength of the materials, the exceeding of which results in occurrence of macro-fractures in the structure. This phenomenon is recorded as a very intensive generation of AE signals. This method was used to determine the strength of the three groups of the investigated composite materials. Compression strength of each sample was tested in two basic directions – parallel and perpendicular to its bedding plane. The results are listed in Figs. 6 and 7.
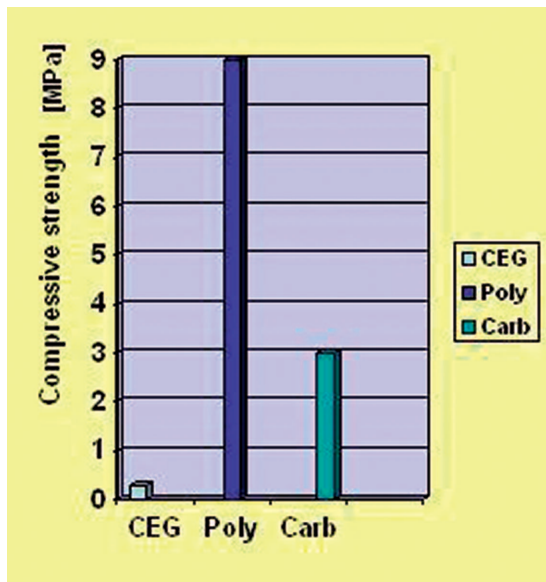

Fig. 6. Evolution of compressive strength in the parallel direction for CEG, after impregnation with furfuryl alcohol, polymerization (POLY) and subsequent carbonization to 550°C (CARB). Densities of the samples are the same as in Fig. 5

It was expected that the maximum pressure applied (compressive strength) in both directions would increase inside each of the three groups of composites (CEG, POLY, CARB) as the density of samples increases. However, the evolution of that compressive strength seems independent of densities in the investigated range in the parallel direction for CARB composite (Fig. 7c). It was also found that for POLY both directions are equivalent (Fig. 7b). It can be explained by the fact that after impregnation and polymerization the anisotropy of CEG is almost masked and gives quasi-isotropic structure of IMP. It can be explained by the fact that assuming that all opened porosity of the samples is filled up with the polymer, only closed porosity is left to differentiate the two directions.

The comparison of the three groups of samples confirms that the stiffness of POLYs is greater than that of CARBs, which in turn is much greater than that of CEGs, TABLE 2.
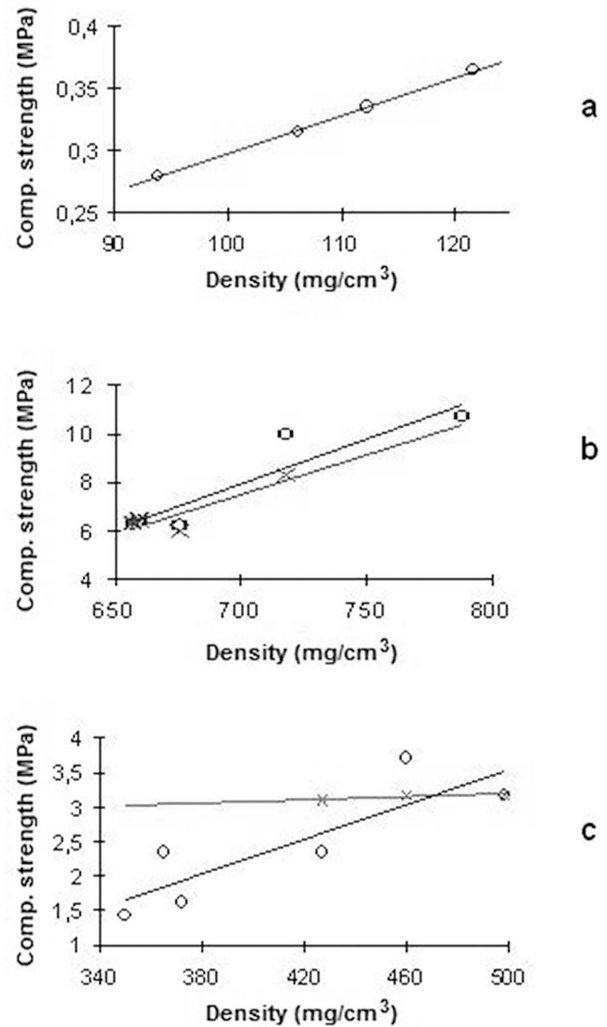

Fig. 7. Compressive strength of the composites vs. their densities: a) CEG; b) POLY; c) CARB. The black lines are for the parallel direction to the bedding plane. The red lines are for the perpendicular direction to the bedding plane

TABLE 2

Evolution of the compressive strength of three groups of composites for pressure applied in the parallel direction to the bedding plane

Material	CEG	POLY	CARB
Range of compressive strength [MPa]	<1	5 - 12	1 - 4

5. Comparison of AE parameters for the three groups of composites

Investigation of the AE phenomenon in the group of the three composites was carried out with the use of *Acoustic Emission Analyzer type EA-100 NEUR, Institute of Fundamental Technological Research PAS* and computer controlled *Materials Testing Machine type LRX, Lloyd Instruments*. The measurements of acoustic emission parameters were carried out in a wide range of wave frequencies (0.1÷2.5 MHz), by the use of transducer model *SE2MEG-P, Dunegan Engineering Consultants Inc. (DECI), USA*. Since analysis and recording

are done with use of the computer, it is possible to determine a larger number of AE parameters [17], and therefore to increase the amount of information provided by the studied materials. Some results of AE measurements in CEG materials are described in our previously published papers [13-14]. Out of more than a dozen registered parameters describing the AE signals, there are changes two of them: – AE pulses counts rate and spectrum distribution of AE waves – presented in this paper.

Analysis of AE parameters provides data on physical and chemical processes that would be very difficult to study by means of other techniques.

5.1. Comparison of AE counts rate for the three groups of materials

AE pulses counts rate were measured in the following way. In each sample, the first five hundred data recorded only noise, then compression pressure was applied to the sample by the Lloyd Machine. It started from zero and increased linearly up to the maximum value. The counts rate was defined as the number of registered AE signals within the 0,1 s time interval.

The results of measurements of the parameter for the three groups of studied composites are shown in Fig. 8. In Fig. 8 a, b, c the results were obtained for the stress applied in the direction parallel to the bedding plane of the structure, whereas Fig. 8d shows results obtained when the applied stress was perpendicular to the bedding plane of CARB composite.

Visible in Fig. 8a noise was measured between 0 and 50 s. After 50 s, stress was applied (the first red line). The second red line denotes the moment when macro-fractures appeared in the sample.

Differences between these three groups of composites are clear. The largest number of AE pulses were recorded for CARB composite whereas the fewest AE pulses were generated for POLY composite, the intermediate being the number recorded for CEGs. The results clearly reflect elastic properties of the studied materials. CEG is a soft and brittle. Following impregnation with the polyfurfuryl alcohol and polymerization its turns into a quasi-isotropic, hard and elastic composite. Following carbonization, the anisotropic properties are partly recovered and the composite becomes hard, but brittle.

5.2. Spectrum distributions of AE waves for each group of composites

Spectrum distribution was received as a result of frequency analysis of AE signals with use Fourier transformation procedure [18]. Results of measuring spectrum distribution of AE frequency for the three groups of studied materials are shown in Fig. 9. The results were obtained at stress applied in the parallel direction to the bedding plane of the structure. The obtained results are very interesting.
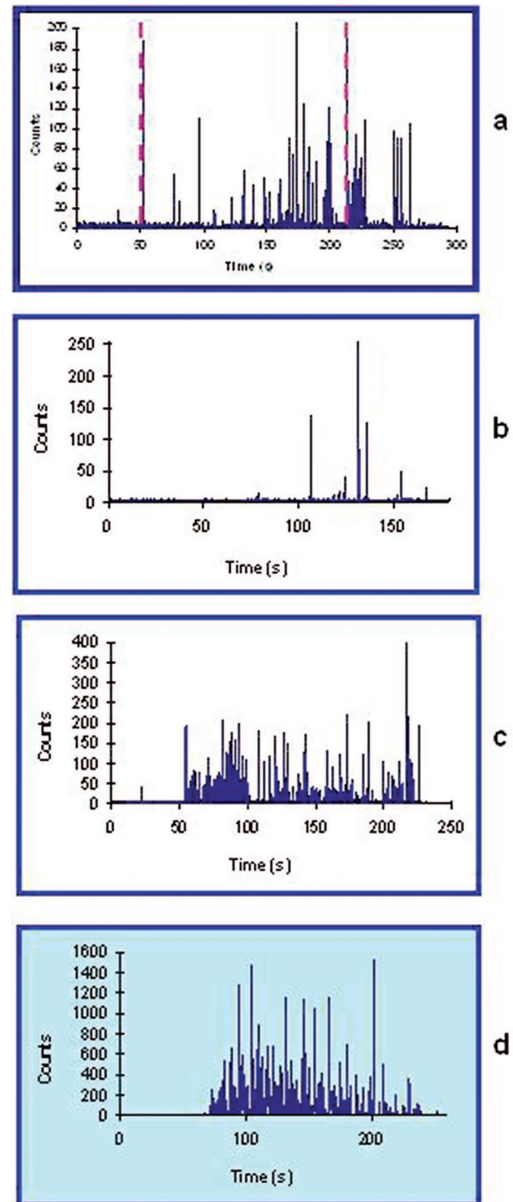

Fig. 8. Comparison of AE counts rate for the three groups of materials, pressure applied in the parallel direction. a) CEG, $\rho = 112$ mg/cm^3; b) POLY, $\rho = 660$ mg/cm^3; c) CARB, $\rho = 498$ mg/cm^3; d) pressure applied in the perpendicular direction to the bedding plane, CARB $\rho = 498$ mg/cm^3. Detailed description in the text

In Fig. 9a, which shows the spectrum distribution registered in the CEG graphite matrix, there are four red arrows marking four frequency bands of the generated waves which recur in the spectrum of the POLY composite and in the spectrum of the CARB composite. This gives rise to the conclusion that the graphite matrix generates waves of the same frequency and amplitude also when it is a heterogeneous composite structure of both the POLY and CARB type.

Whereas, Fig. 9b shows the AE spectrum distribution in the POLY composite structure in which green arrows mark three frequencies of the generated bands, which recur in the CARB composite spectrum, but do not occur in the CEG matrix. These observations give rise to the conclusion that generation of elastic waves in these frequency ranges occurs in the polymer material filling up the open macropores both before and after carbonization. Analysis of the obtained results clearly

shows that introducing polymer of the polyfurfuryl alcohol to a CEG graphite matrix results in considerable generation of AE in the high frequency wave band (1.5-2.5 MHz). Whereas carbonization of the POLY composite is reflected in the Fourier image transform of the AE spectrum by occurrence of intensive generation of waves of (0.2-0.9 MHz) mean frequency range. The results are in perfect compatibility with the results pertaining to elasticity and strength of the three groups of studied composites presented in Section 4 of the paper.
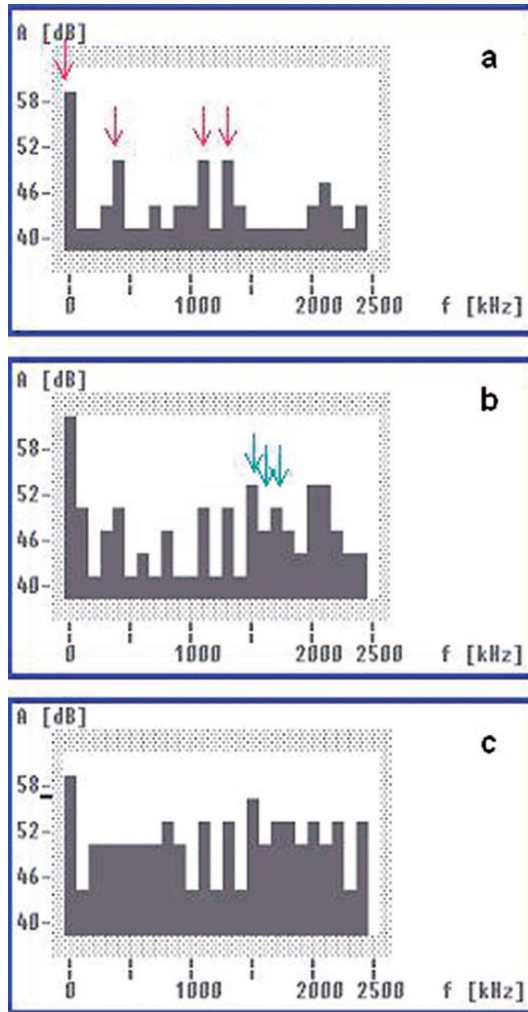

Fig. 9. Fourier transformation of frequency distribution of AE signals, pressure applied in the parallel direction to the bedding plane. a) CEG, ρ = 112 mg/cm^3; b) POLY, ρ = 660 mg/cm^3; c) CARB, ρ = 498 mg/cm^3. Detailed description in the text

6. Conclusions

This study of the properties of compressed expanded graphite's and the porous composites as products of their impregnation, polymerization and carbonization leads to the following conclusions:

– Production of Compressed Expanded Graphites and their porous derivatives after impregnation, polymerization

and carbonization with assumed densities (porosities) is achievable.

– In relation to mechanical properties of the three kinds of composites, regarding evolution of compressive strength it was confirmed that the stiffest materials are POLYs composites. The ranges of strength of each of the three studied groups of materials are presented in Table 2. The strength within each group depends on density and porosity of a given composite.

– Comparison of spectrum distributions of AE waves for each group of composites (CEGs, POLYs and CARBs) turned out to be very different from each other but certain frequency bands are the same. 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.

– Determination of density of the studied composites, their mechanical properties, strength, porosity, specific surface is really important to decide whether the materials can be used as good catalysts or composite membranes for gas separation, even as a proton exchange membranes in fuel cells.

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