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STUDY OF GRAPHITE – POLYMER – TURBOSTRATIC CARBON COMPOSITES BY ACOUSTIC EMISSION METHOD AT PERPENDICULAR GEOMETRY

The purpose of this paper was to search the relations between the structure of the compressed expanded graphite – polymer – turbostratic carbon composites on successive stages of technological treatment and parameters describing the acoustic emission phenomena in these materials. The acoustic emission method can be used for measurements of changes in the structure and many different properties of materials. These investigations are a continuation of our earlier studies concerning physical, mechanical and chemical properties of porous composites created on the basis of a compressed expanded graphite matrix, obtained after successive technological procedures of impregnation, polymerization and carbonization of polyfurfuryl alcohol. 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.

In compressed expanded graphite composites structures one can differentiate two basic directions: perpendicular to the bedding plane of graphite flakes and parallel to this one. The all presented results were obtained for the uniaxial strain applied in the direction perpendicular to the bedding plane of the composite structure. Analysis of acoustic emission parameters provides information on physical and chemical processes in these materials.

Keywords: Compressed expanded graphite, Polyfurfuryl alcohol, Turbostratic carbon, Acoustic emission, Composite membrane

1. Introduction

The described technological procedures and the resulting composite materials are perfect examples of practical application of achievements of materials engineering.

Determination of many properties of the compressed expanded graphite – polymer – turbostratic carbon composites prepared from poly-furfuryl alcohol is important to resolve whether the materials can be used as good quality catalysts [1-3] or composite membranes for gas separation [4-7] or proton exchange membranes in fuel cells [8-12] and also as biotechnological materials [13-14].

The main aim of the study was to search the relations between the structure of the compressed expanded graphite (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 concerning physical and chemical properties of porous composites created on the basis of a CEG matrix, obtained after successive technological procedures of impregnation, polymerization and carbonization of poly-furfuryl alcohol [15,16]. Exact description of the technological process can be found in our earlier paper [15]. The purpose 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.

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

2. Technological procedures

Exact description of the all technological processes can be found in our earlier paper [15].

Compressed expanded graphite 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.

The scheme of all steps technological procedures is presented in Fig. 1. They lead from the precursor, which is the crystalline graphite, goes through all the successive chemical

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and physical actions up to the final material, which is a heterogeneous composite structure. This composite material is built of graphite matrix and carbonized polymer material created on the basis of polyfurfuryl alcohol – it is turbostratic carbon, which fills up the open pores.

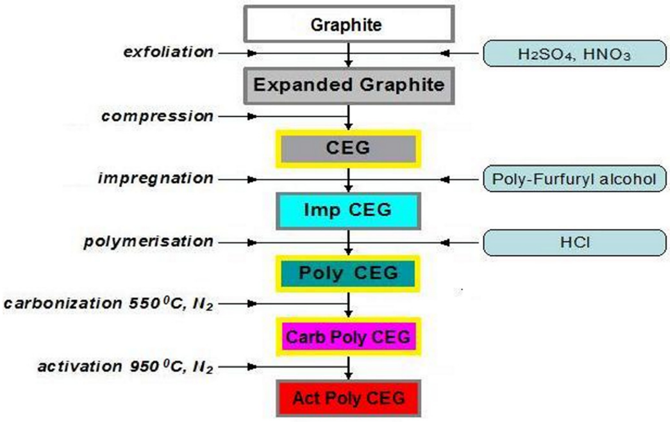

Fig. 1. Scheme of the technological procedures of the compressed expanded graphite – polymer – turbostratic carbon composites

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

3. Researches of the AE phenomena in composites on different steps of their technological treatment

In structures of composites prepared on the basis of compressed expanded graphite 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.

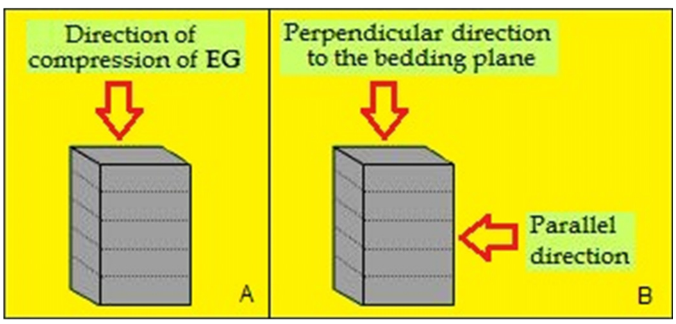

Fig. 2. Basic directions used for describing bedding structure of composites. A) Direction of compression during CEG production, B) Directions of pressure applied during AE measurements

Some results of AE measurements in CEG composites for strain applied in the direction parallel to the bedding plane are described in our previously published paper [16]. The all presented in this paper results were obtained for the uniaxial strain applied in the direction perpendicular to the bedding plane of the composite structure. It should be emphasized that because of very low elasticity of CEG the measurements in perpendicular geometry were much more difficult to perform than in parallel geometry.

Investigations of many AE parameters provides information on physical and chemical processes in these materials. The acoustic emission resulting from the applied pressure [17-18] can be also used for measurements of changes in the structure and many different properties of materials.

Researches of the acoustic emission phenomena in the group of the three chosen 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*. Exact description of the procedure of the AE signals measurements can be found in our paper [9].

Since recording and analysis AE pulses are done with the use of computer, it is possible to find out a larger number of AE parameters in a single experiment [19-20], thus increase the amount of information provided by the investigated materials. 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 root mean square (RMS) and also changes in spectrum distribution of AE waves – chosen and they are presented in this paper. The results of measurements of the AE parameters for the three groups of studied composites are shown below.

3.1. Comparison of sum of events and sum of counts of the AE pulses for the three groups of composites

The 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 these three materials 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 composites.

Results of the mean value for the sum of events and sum of counts of the AE signals for three groups of composites obtained during a single-axis-compression applied in the direction perpendicular to the bedding plane of the structure 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. These AE parameters are more greater than one order for the CARB

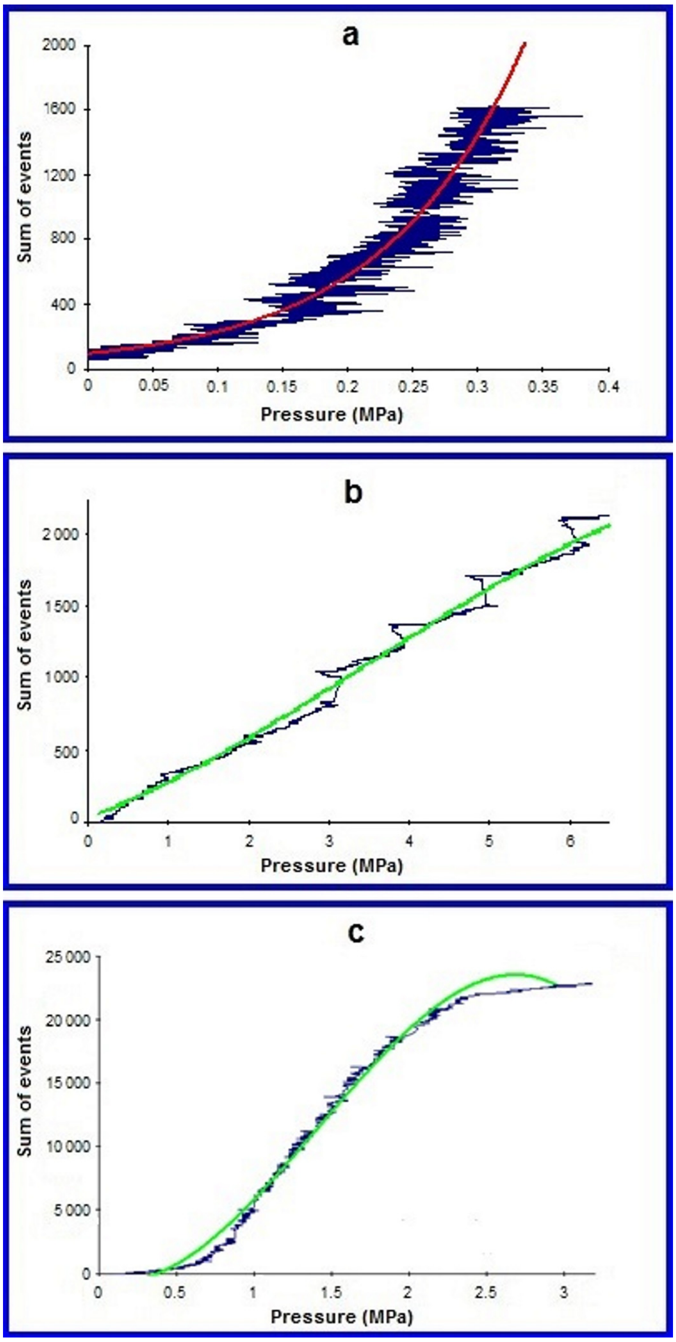

Fig. 3. Dependence of sum of events of the AE pulses for the three groups of materials vs. pressure applied in the direction perpendicular to the bedding plane. a) CEG, ρ = 107 mg/cm^3; b) POL, ρ = 660 mg/cm^3; c) CARB, ρ = 498 mg/cm^3. Navy-blue curve – results of measurements, red line – exponential fitting, green line – polynomial fitting

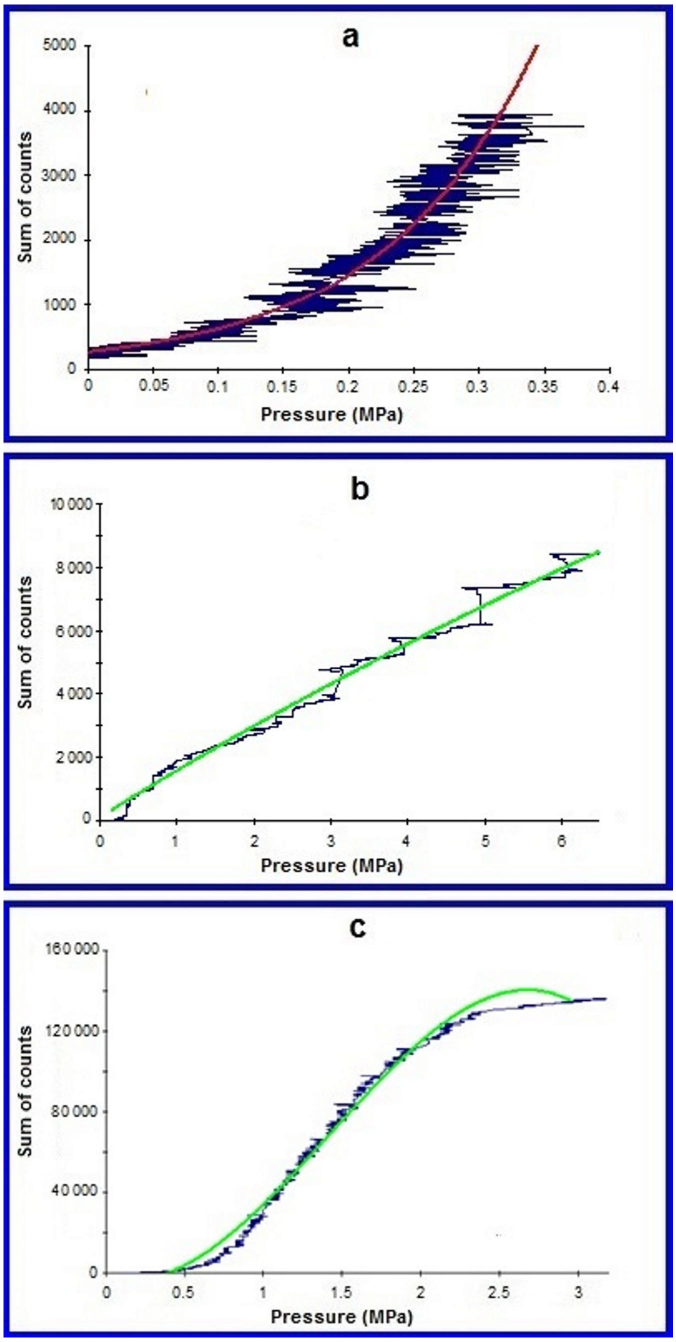

Fig. 4. Comparison of sum of counts of the AE signals on pressure applied in the direction perpendicular to the bedding plane. a) CEG, ρ = 107 mg/cm^3; b) POL, ρ = 660 mg/cm^3; c) CARB, ρ = 498 mg/cm^3. Navy-blue curve – results of measurements, red line – exponential fitting, green line – polynomial fitting

than in another investigated composites. Mean values were recorded for the POLY material and the lowest were recorded for the CEG composite. The results are evidence of the highest activity of acoustic emission in the CARB composite.

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 open pores and polymerization which turns it into a quasi-isotropic structure, is a hard and elastic composite. Following

TABLE 1

Sum of events and sum of counts of the AE pulses for the three groups of composites, pressure applied in the direction perpendicular to the bedding plane

Composite	**Density, [mg/cm^3]**	ΣN_{ev}	ΣN_{cnt}	$\frac{\Sigma N_{cnt}}{\Sigma N_{ev}}$
CEG	107	1 284	2 915	2.3
POL	660	1 835	7 651	4.2
CARB	498	22 120	135 084	6.1

carbonization material CARB, regains partialy its anisotropic properties and becomes hard, but brittle.

In Table 1 also are presented the calculated ratios of the mean value of the sum of counts to the sum of events. The value of this ratio is connected to a mean frequency of the AE waves [21]. 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 process.

3.2. Comparison of sum of amplitudes and sum of the root-mean-square of the acoustic waves for the three groups of composites

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 for the uniaxial strain applied in the direction perpendicular to the bedding plane of the structure in the three groups of the studied composites are presented in Fig. 5 and in Fig. 6. The RMS value of the signals is directly proportional to the generated energy of the acoustical waves.

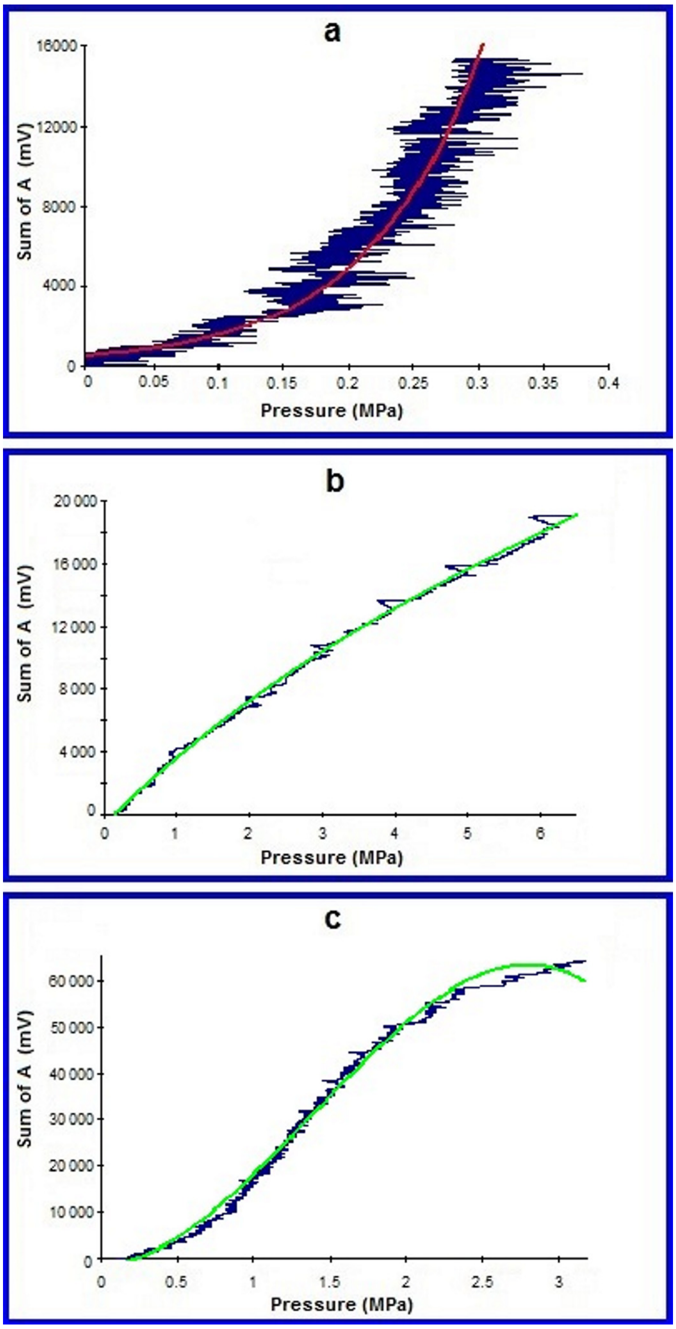

Fig. 5. Dependence of sum of amplitudes of the AE waves for the three groups of materials vs. pressure applied in the direction perpendicular to the bedding plane. a) CEG, $\rho = 107$ mg/cm^3; b) POL, $\rho = 660$ mg/cm^3; c) CARB, $\rho = 498$ mg/cm^3. Navy-blue curve – results of measurements, red line – exponential fitting, green line – polynomial fitting

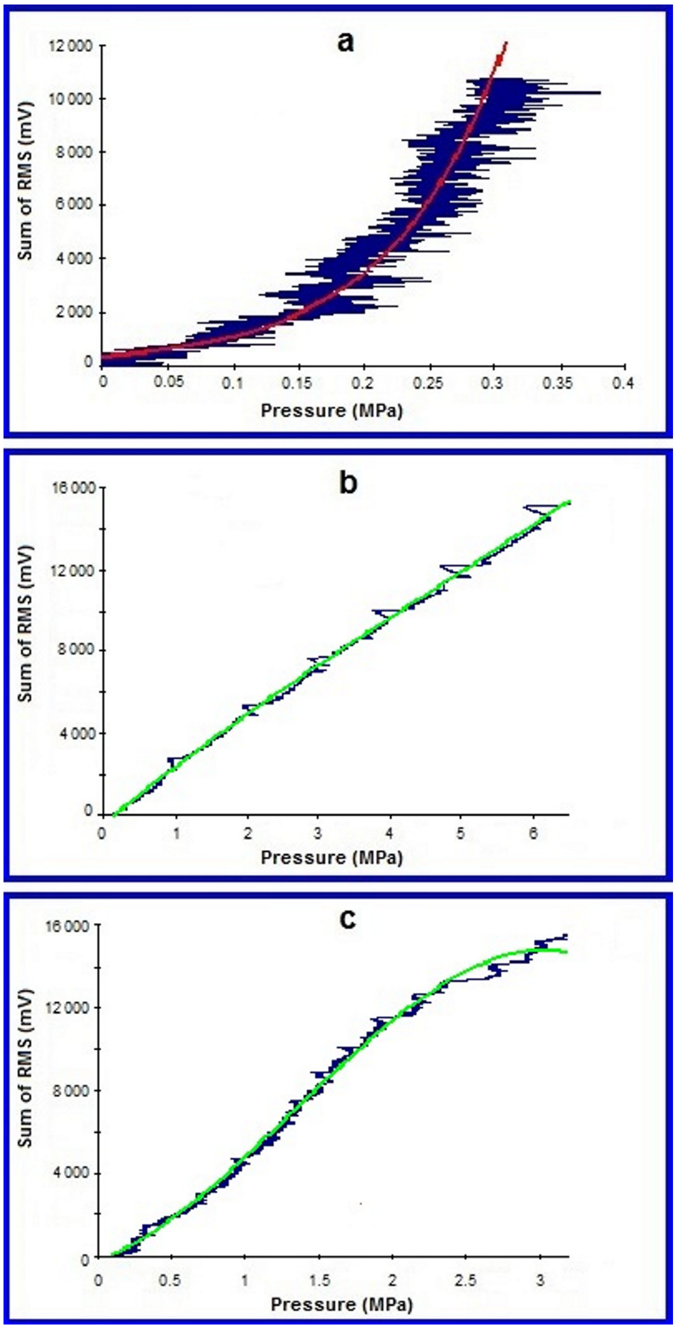

Fig. 6. Comparison of sum of RMS of the AE signals on pressure applied in the direction perpendicular to the bedding plane. a) CEG, $\rho = 107$ mg/cm^3; b) POL, $\rho = 660$ mg/cm^3; c) CARB, $\rho = 498$ mg/cm^3. Navy-blue curve – results of measurements, red line – exponential fitting, green line – polynomial fitting

Results of researches 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 POLY, and the lowest in CEG. 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 sum of RMS of the AE pulses for the three groups of composites

Composite	Density [mg/cm^3]	ΣA	ΣU_{RMS}	$\frac{\Sigma U_{RMS}}{\Sigma U_{RMS}^{CEG}}$
CEG	107	14 020	7 907	1.00
POL	660	17 145	13 728	1.74
CARB	498	63 477	13 994	1.77

Analyzing dependences of the sum of each of the four above mentioned AE parameters on the applied compression pressure, Figs. 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 dependences on pressure are the same kind but they are essentially different then for CEG. It is described by the x^3 type polynomial function.

3.3. Investigations of dependences of AE parameters on densities of composites

Dependences of the sum of each of the four measured AE parameters on the density of material in the three analyzed groups of composites are compared in Fig. 7. The all results were obtained for the strain applied in the direction perpendicular to the bedding plane of composite structure.

Investigations of the obtained dependences showed that within the studied range none of the four AE parameters depends on density in CEG material. In the POL composite, the sum of events 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 RMS value of the signals increase with the composite density. Also the sum of counts increase with the density. In CARB composite, values of the sum of events and the sum of the RMS of the signal do not depend on the density of the composite. Whereas, the sum of counts and the sum of amplitudes increase vs. density of material.

3.4. Analysis of spectrum distributions of AE waves for three groups of composites

The investigation of spectrum distribution was received as a result of frequency analysis of AE signals with use Fourrier transformation procedure [17,22,23]. Results of measuring and computation of spectrum distribution of AE signals for the three groups of investigated materials are shown in Fig. 8. The results were obtained at stress applied in the perpendicular direction to the bedding plane of the structure.

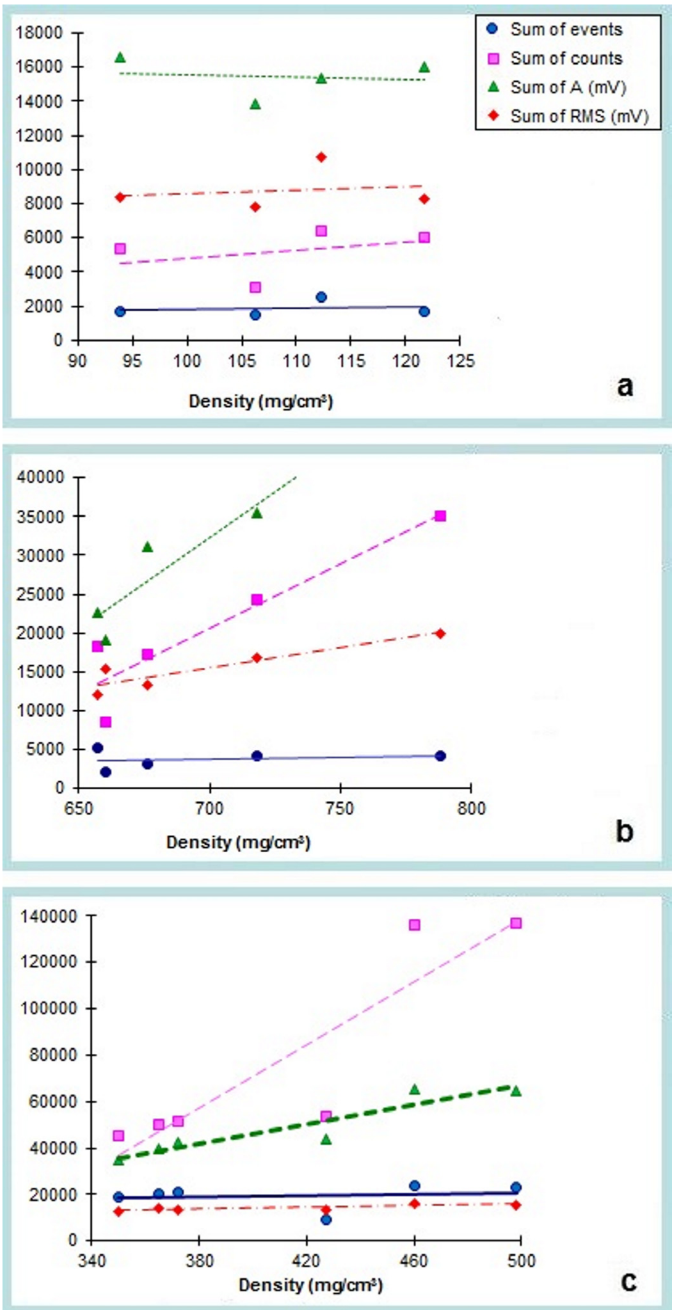

Fig. 7. Evolution of AE parameters depending on densities of three groups of composites: a) CEG, b) POL, c) CARB

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 three 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 fre-

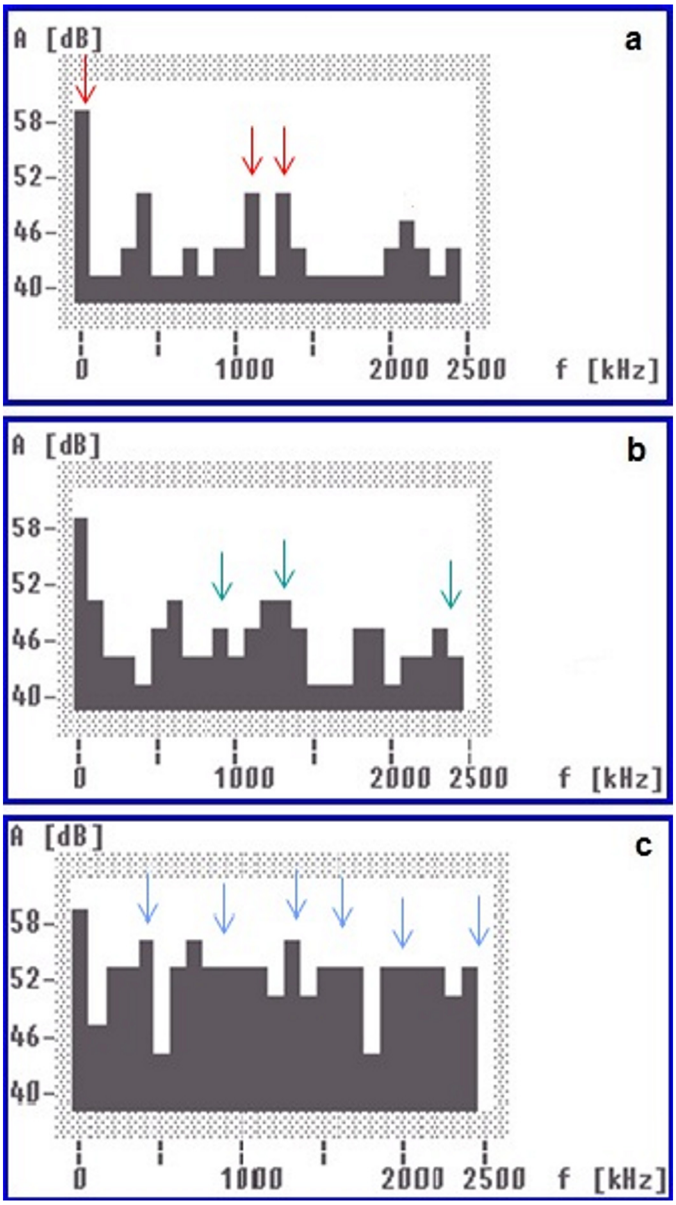

Fig. 8. Fourier transformation of frequency distribution of AE pulses for the three groups of composites, pressure applied in the direction perpendicular to the bedding plane. a) CEG, $\rho = 107$ mg/cm^3; b) POL, $\rho = 660$ mg/cm^3; c) CARB, $\rho = 498$ mg/cm^3

quency, 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 six 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.

Characteristic bands of the frequencies generated waves in the three examined groups of materials are compared in Table 3.

TABLE 3

Frequencies of bands of AE pulses for the three groups of materials

Composite	Density [mg/cm^3]	Frequency bands of AE activity, [MHz]
CEG	107	0.1 1.1 1.3
POL	660	0.9 1.1-1.4 2.3
CARB	498	**0.2-0.4** **0.6-1.2** **1.4** **1.5-1.8** **1.9-2.3** **2.5**

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 high frequency range of the spectrum (1.3 and 2.3 MHz) in the POLY composite.

Whereas carbonization of the POLY composite is reflected in the Fourier image transformation of the AE waves by occurrence in spectrum of intensive very wide bands in all investigated frequency range. There appear two intensive bands of frequencies at 2.1 and 2.5 MHz.

The results are in good agreement with the results shown above in Table 1, which yielded conclusions concerning increased frequency of the generated acoustic waves when passing to a successive group of compressed expanded graphite – polymer – turbostratic carbon composites. The shift of spectrum maxima to higher frequencies indicates a decrease of the size of AE sources [21]. 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 paper [15]. It should be emphasized, however, that in CARB composite, at perpendicular geometry, occur intensive generation of the acoustic waves in all range of the analyzed frequencies. In contrast, for the case of parallel geometry in this material, a completely different spectrum distributions of frequency were obtained with the dominance of peaks in the upper bands of the range.

4. Conclusions

The above described studies of the AE phenomena taking place in porous compressed expanded graphite – polymer – turbostratic carbon composites created on the basis of a graphite matrix obtained after successive technological treatments of impregnation, polymerization, and carbonization leads to the following conclusions:

– The maximum 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 also for pressure applied in the direction perpendicular to the bedding plane of the composite structure. Such a high level of activity is characteristic for hard, brittle and porous materials. These properties mean that the compressed expanded graphite – polymer – turbostratic carbon composites prepared from poly-furfuryl alcohol are good materials and can be used as good quality catalyst support and also as composite membranes for gas separation.

– The greatest value maximum sum of amplitudes and the sum of RMS of the signals measured in CARB composite correspond to the highest energy and power of AE signals which were generated in this group of materials at perpendicular geometry.
– Dependences of four 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 functions for pressure applied in the direction perpendicular to the bedding plane.
– It is shown in this study that each of the four studied AE parameters, for the stress applied in direction perpendicular 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 is almost independent on density of samples but the sum of counts, the sum of amplitudes and the sum of RMS signals increase vs. density. For CARB composites sum of events and the sum of the RMS do not depend on the density, whereas the sum of counts and the sum of amplitudes increase vs. density of composite. This allows to assume that the measurement of some parameters of AE gives possibility to determine the porosite of the samples.
– 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 conclusions resulting from the Fourrier analysis of the registered spectrum are very interesting and provide much information about composite structure as well as bonds occur between the graphite matrix and the polymer or turbostratic carbon that fills up open pores.
– It was confirmed that shift of the bands to higher frequencies in spectrum distribution which appear in POLY and CARB composites indicates a decrease in the dimensions of the sources generating AE signals.
– Knowledge of physical and chemical properties of the compressed expanded graphite – polymer – turbostratic carbon composites is important to resolve whether the materials can be used as good quality catalysts or composite membranes for gas separation and also as proton exchange membranes in fuel cells

REFERENCES

[1] W. Li, Ch. Han, W. Liu, M. Zhang, K. Tao, Catal. Today **125**, 3-4, 278 (2007).
[2] A. Celzard, M. Krzesinska, D. Begin, J. Mareche, S. Puricelli, G. Furdin, Carbon **40**, 557 (2002).
[3] A. Celzard, J. Mareche, G. Furdin, Prog. Mater. Sci. **50**, 93 (2005).
[4] M.B. Shiflett, H.C. Foley, Science **285**, 1902 (1999).
[5] M.B. Shiflett, H.C. Foley, J. Membr. Sci. **179**, 275 (2000).
[6] C. Song, T. Wang, X. Wang, J. Qiu, Y. Cao, Sep. Purif. Technol. **58**, 412 (2008).
[7] C. Song, T. Wang, J. Qiu, T. Cai, J. Porous Mater. **10**, 9044 (2007).
[8] X. Yan, M. Hou, H. Zhang, F. Jing, P. Ming, B. Yi, J. Power Sourc. **160**, 252 (2006).
[9] C. Du, P. Ming, M. Hou, J. Fu, Y. Fu, X. Luo, Q. Shen, Z. Shao, B. Yi, J. Power Sourc. **195**, 5312 (2010).
[10] J. Fu, H. Xu, Y. Wu, Y. Shen, Ch. Du, J. Reinf. Plast. Compos. **31**, 3 (2012).
[11] C. Du, P. Ming, M. Hou, J. Fu, Q. Shen, D. Liang, et al., J. Power Sourc. **195**, 794 (2010).
[12] Wlodarczyk, Arch. Metal. and Materials **60**, 1, 117 (2015).
[13] L. Zhang, M. Zhang, Y. Zhou, L. Hu, Polym. Degrad. Stab. **98**, 12, 2784 (2013),
[14] L. Shi, Z. Li, W. Yang, M. Yang, Q. Zhou, R. Huang, Powder Technol. **170**, 3, 178 (2006).
[15] J. Berdowski, S. Berdowska, F. Aubry, Arch. Metall. Mater. **58**, 4, 1331 (2013).
[16] A. Berdowska, J. Berdowski, F. Aubry, Arch. Metall. Mater. **60**, 4, 2479 (2015).
[17] Z. Ranachowski, Pomiary i analiza sygnału emisji akustycznej, Prace IPPT PAN **6**, Warszawa (1996).
[18] A. Zakupin et al., Acoustic Emission, ed. by W. Sikorski, InTech. 173, (2012).
[19] J. Li, F. Beall, T. Breiner, Advances in Acoustic Emission, ed. by K. Ono, Acoustic Emission Working Group, Nevada, USA, 202, (2007).
[20] I. Malecki, J. Ranachowski, Emisja akustyczna, PASCAL, Warszawa (1994).
[21] A. Jaroszewska, J. Ranachowski, F. Rejmund, Procesy niszczenia i wytrzymałość, ed. by J. Ranachowski, IPPT PAN, Warszawa, 183, (1996).
[22] A. Dode, M. Rao, NDT.net, **7**, 09 (2002).
[23] K. Ito, M. Enoki, Advances in Acoustic Emission, ed. by K. Ono, Acoustic Emission Working Group, Nevada, USA, 94 (2007).