Resistivity Characteristics and Noise Spectroscopy of Composites with Carbon Fiber Felts

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***Abstract*— Resistivity and low frequency (from 10 Hz to 20 kHz) noise characteristics of composites materials with carbon fiber felts of two types: PAN (polyacrylonitrile) and Rayon (regenerated cellulose), have been carried out. Measurements were performed in the temperature range from 73 K to 380 K. Resistivity of the investigated materials is a constant at lower voltage and starts to decrease above (0.1-1) V due to increased charge carriers tunneling. The spectrum of low-frequency noise consists of $1/f^{\alpha}$ type components over the entire range of measured frequencies and the noise spectral density is proportional to the voltage square. The observed fluctuations in the investigated materials are resistance ones. The resistivity and low frequency noise intensity of the investigated composites is almost constant in temperature range from 75 K to 250 K, their increase above 250 K is caused by the matrix expansion and decrease above 360 K is due to an onset of the electrical conductivity in the matrix. In the (307-332) K temperature range a kink in resistivity and noise characteristics was observed. And it is determined by reduction of carbon fiber dimensions. This shrinkage of carbon fibers does not introduce additional noise origins in the investigated materials.**

Keywords—bisphenol A, carbon felt, composite, noise, resistivity

I. INTRODUCTION

Carbon-epoxy composites are widely used in various modern sophisticated technologies: as functional layers of electronic devices, in the aviation industry as a solid protective material, in robotic structures and automotive components, etc. [1-3]. Composites with carbon fibers are more wanted than other high-performance fiber composites because of their general stability of characteristics in the most difficult operating conditions: mechanical load, humidity and corrosive environment, radiation, elevated temperature, thermal cycles [4-6]. Materials with carbon fibers are widespread in fabrication of structures with special mechanical characteristics [3, 7]. Carbon fiber reinforced composites exhibit a very high specific strength and elastic modulus, and their weakness lies in their sensitivity to mechanical damage. To achieve the high strength, the composite material is heated and its structure and properties are obtained in the field of mechanical stress. When composites are subjected to mechanical stress, an interlayer stratification is observed [5]. Therefore, when carbon fibers or polymer composite materials based on them are heated, a decrease in linear dimensions of the fibers is observed in the direction of reinforcement [7].

An important issue of the carbon composites employment in electronic devices is charge carrier transport mechanisms in such materials, their dependencies on type of the carbon filler, filler density, dimensions, distribution, orientation etc. In most composites, where the matrix is a dielectric substance and the filler is conductive, two types of conductivity can be expected: charge carriers movement inside the conductor filler and charge carrier tunneling through the dielectric matrix between the filler particles [8, 9]. One of the most sensitive methods to study charge carrier transport and related physical processes in various materials is low frequency noise spectroscopy [10-13]. Nevertheless, there are not many papers on the low frequency noise investigation in carbon composite materials. The spectral analysis of low frequency noise is important as fixing noise spectrum type and intensity can determine the prospect of using such materials in electronic and sensory applications, since noise is a limiting factor for signal detection.

To study a composite with new proportions of fillers and their manufacturing techniques, it is necessary to make many different measurements. This paper looks at the analysis of the low-frequency noise and resistivity characteristics of composite materials with carbon fiber felts, which help to clarify the charge carrier transport mechanisms and their variation during structural changes (due to temperature changes) of the composite.

II. MATERIALS

The investigated materials are composites with carbon fiber felts. The binding matrix is bisphenol A epoxy resin. The used graphitized soft carbon felts are anisotropic materials and comprise of randomly laid/dispersed fiber layers, consolidated by needle-punching. The SEM micrographs of the materials are presented in Fig. 1 (a) and (b). The sample's *x*- and *y*-directions are fully equivalent and define the "in-plane" direction, i.e., the bedding plane of the fibers within which no

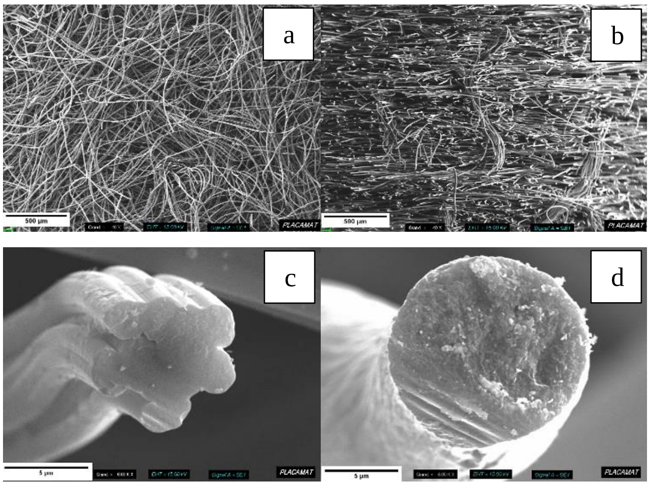

Fig. 1. SEM micrographs of the investigated materials: (a) in-plane direction, (b) out-of-plane direction, and cross-section of Rayon (c) and PAN (d) fibers.

preferential orientation exists. The orthogonal direction, *z*, is the “out-of-plane” direction of the material.

The results presented in the paper were carried out for materials with two different types of carbon fibers: Ryon (regenerated cellulose) and PAN (polyacrylonitrile). The cross sections of the both types of fibers can be seen in the SEM micrographs in Fig. 1 (c) and (d). Deviations from circular cross-section were much more obvious in the case of Rayon-derived carbon fibers than for PAN-derived ones.

Samples which have the same filler were cut out from one piece of the fabricated material. The difference between samples “PAN II” and “PAN X” and between “Rayon II” and “Rayon X” is in the contact plane: the “II” samples have contacts at the *xy* plane while the “X” ones - at the *xz* plane. The fiber cross-section diameter, bulk density, skeletal density and overall porosity are presented in Table 1.

III. MEASUREMENT TECHIC

The low frequency (from 10 Hz to 20 kHz) noise and resistivity characteristics were measured at room temperature and in temperature range from 78 K to 380 K. The noise measurements were carried out in a specially shielded laboratory room (Faraday cage) to avoid the interference from electrical network and communication systems.

The measured noise signal was processed by low-noise amplifier, filter system, and analogue digital converter (the measuring scheme is shown in Fig. 2). Noise signal spectrum was obtained by the fast Fourier transform, and voltage noise spectral density, S_U, was evaluated by comparing with the thermal noise of the standard resistor, which was at least 100 times larger comparing to the resistance of the sample under test. The equation for S_U is:

$$S_U = \frac{\overline{U^2}-\overline{U_{\mathrm{s}}^2}}{\overline{U_{\mathrm{st}}^2}-\overline{U_{\mathrm{s}}^2}} 4kT_0 R_{\mathrm{load}}; \qquad (1)$$

where $\overline{U^2}$, $\overline{U_{\mathrm{s}}^2}$ and $\overline{U_{\mathrm{st}}^2}$ are the sample (and the measuring system), the measuring system, and the standard (load) resistor (and the measuring system), respectively, noise variances in the narrow frequency band Δf; T_0 is the absolute temperature of the standard resistor, and k is the Boltzmann constant.

The sample resistance was measured by the semiconductor device parameter analyzer “Keysight Technologies B1500A”.

TABLE I. PARAMETERS OF THE INVESTIGATED FIBERS

Fiber type:	**Fiber diameter (μm)**	**Bulk density (g cm^{-3})**	**Skeletal density (g cm^{-3})**	**Overall porosity (%)**
Rayon (regenerated cellulose)	10.70 (±2.36)	0.073	1.700	95.7
PAN (polyacrylonitrile)	19.71 (±1.49)	0.110	1.776	93.8

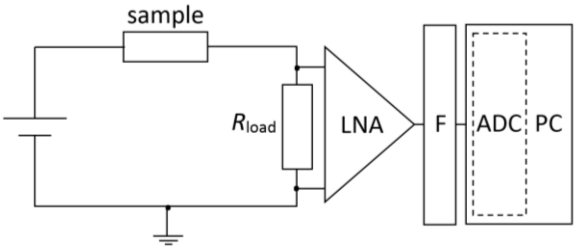

Fig. 2. Scheme of the noise measuring system: LNA is low noise amplifier, F is filter system, ADC is analogue digital converter, and PC is personal computer.

IV. RESULTS AND DISCUSSION

The resistivity characteristics were measured not exceeding 100 mA current in order to avoid a breakdown of the sample. The resistivity dependencies on voltage at room temperature are presented in Fig. 3. The resistivity of the investigated materials does not vary with voltage at low its values. Above the certain voltage (approximately (0.1-1) V), a deviation from the Ohmic resistance is observed (Fig. 3). Depending on the sample resistivity, the variation in the voltage of the start of the nonlinear characteristic is not large: the slope for the investigated materials is 0.985. Two factors can be indicated as origin of this non-linear current-voltage characteristic: in one case, the conductive particles may be non-linear in nature [14], in the other case, the macroscopic conductivity becomes not Ohmic due to the possible appearance of additional conductive channels (e.g., charge carriers tunneling through the dielectric matrix) that arise at higher electrical field [15, 16].

The resistivity of the samples depends on the measurement direction (in relation to the carbon fibers direction) as well as on the diameter of the carbon fiber. Carbon fibers roughly can be treated as having metallic conductivity. PAN fibers are

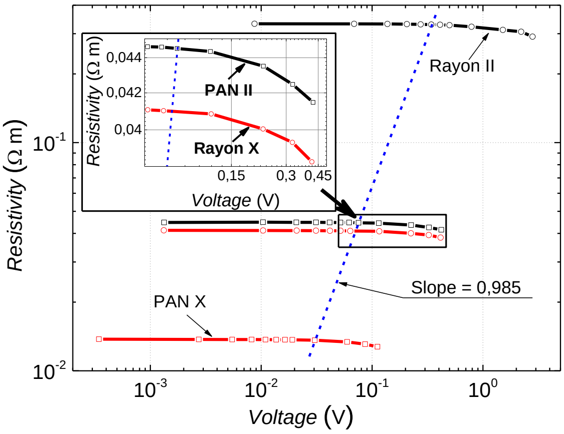

Fig. 3. Dependences of resistivity of PAN and Rayon composites on voltage at room temperature.

larger in diameter than Rajon ones. Hence, composites with PAN fibers filling are better conductors and the obtained results confirm this (Figs. 3 and 4). It was also observed that resistance of the samples with contacts applied along the carbon fibers is larger than for samples with contacts in the perpendicular direction to the fibers. This is caused by the fact that in the composite sample resistance for current flowing along the conductive fiber is smaller comparing to the case of charge carrier tunneling from fiber to fiber through a non-conducting matrix (what takes place when current flows in the perpendicular direction to the fibers).

Temperature characteristics of resistivity from 75 K to 380 K are presented in Fig. 4. The resistance from 75 K to 225 K varies very slightly with temperature. The resistivity decreases with temperature for Rayon samples below 250 K due to the electron tunneling, while for PAN ones the resistivity is much smaller and electron tunneling is less important. Starting from 275 K the resistance grows with temperature more steeply. Above 360 K a decrease of resistance with temperature increase is observed. Such resistance dependence on temperature is explained by the expansion of the matrix (resistance growth in ((275-360) K)) and by the appearance of electrical conductivity in the matrix (resistance decrease above 360 K) [17].

Temperature characteristics of the investigated materials have a kink in the temperature range from 307 K to 332 K (Figs. 4 and 5). The appearance of this kink can be caused by two origins: decrease in the linear dimensions of the carbon fiber in the reinforcement direction of the composite and the glass transition of the epoxy matrix of the sample. In the first case, reduced size of the conductive particles in a non-conductive matrix creates an increase of resistance. When repeating measuring cycles the carbon fibers lose their ability to shrink [7]. As it is shown for sample PAN X in Figs. 4 and 5, the kink maximum decreases after the repeating measurements. The glass transition can have a small impact to the composites resistivity only as a softening of the matrix, what creates a better environment for the carbon fiber shrinkage, but this should not have a significant effect on the resistance in temperature range from 307 K to 332 K.

Measurements of the low-frequency noise spectra have showed that investigated materials have a $1/f^{\alpha}$ type spectrum in all investigated temperature range (Figs. 6 and 7). As well known, there are several theories explaining the nature of $1/f^{\alpha}$ noise, however, for composite materials the most suitable one is based on the superposition of many processes with widely distributed characteristic times that randomly change number of free charge carriers in the sample - superposition of many charge carrier capture and release processes. It was observed that at room temperature noise spectra are mostly $1/f$ type in all investigated frequency range – the slope is almost constant and does not depend on

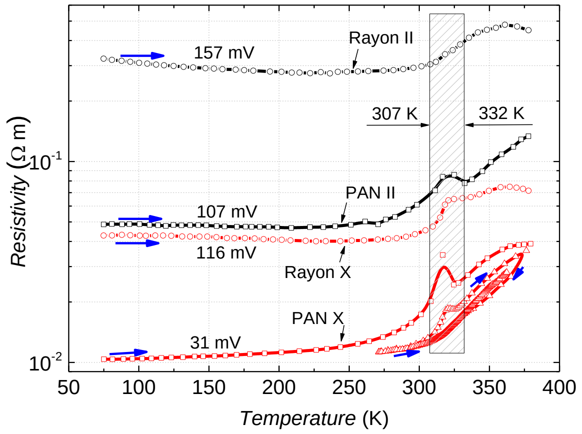

Fig. 4. Dependences of resistivity of PAN and Rayon composites on temperature at fixed voltage (the blue arrows indicate the measuring direction).

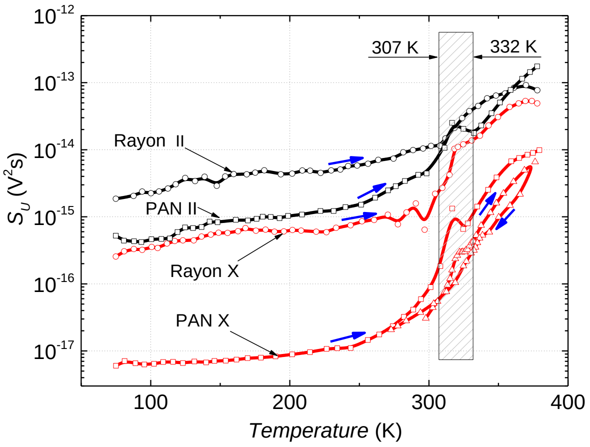

Fig. 5. Voltage noise spectral density dependencies on temperature of PAN and Rayon composites at fixed voltage at 968 Hz frequency (the blue arrows indicate the measuring direction).

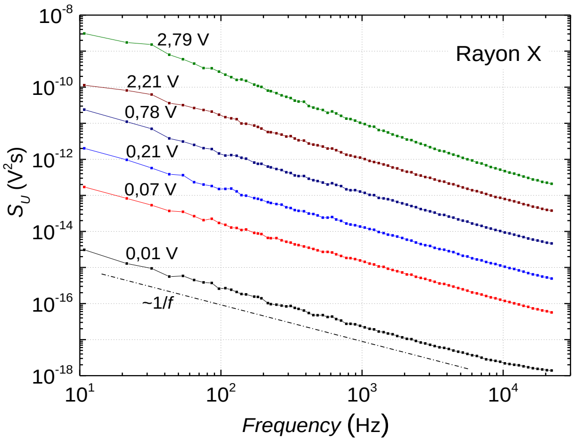

Fig. 6. Spectra of voltage noise for Rayon X composite at different voltages at room temperature.

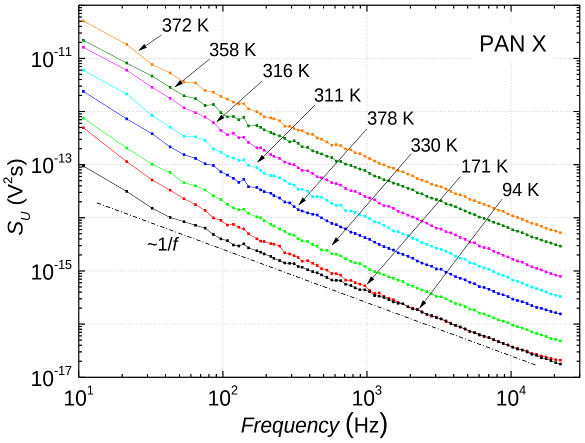

Fig. 7. Spectra of voltage noise of PAN X composite at different temperature at fixed voltage (U=31 mV).

voltage (Fig. 6). While at lower temperature approaching the lower frequencies $1/f$ type spectrum slightly changes to $1/f^{\alpha}$ form, where $\alpha>1$ (Fig. 7). This indicates that at lower temperature the deeper charge carrier capture centers are detected at lower frequency.

The noise spectral density is proportional to the square of voltage (Fig. 8). And the voltage noise spectral density dependency on temperature roughly repeats the resistivity characteristic (Fig. 5). Such noise spectral density features are characteristic for resistance fluctuation. Noise spectral density proportionality to voltage square in all investigated voltage range shows that tunneling that's probability increases with voltage increase is not significant, nevertheless, small decrease of resistivity was observed above (0.1-1) V (Fig. 3). Therefore, the dominant charge carrier transport mechanism is charge carriers generation and recombination processes in the carbon fibers.

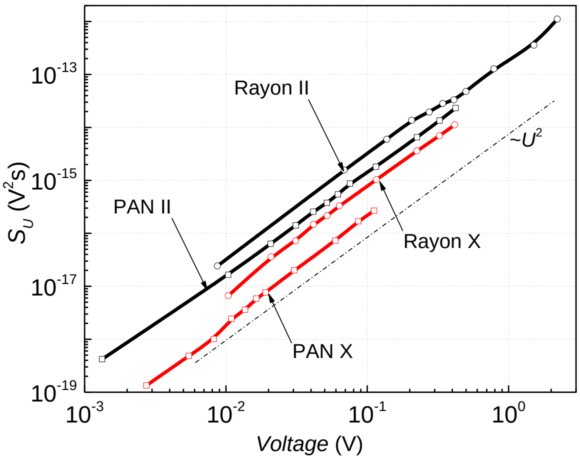

Fig. 8. Voltage noise spectral density dependencies on voltage of PAN and Rayon composites at room temperature at 968 Hz frequency.

In temperature range (307-332) K, where the kink in resistivity and noise intensity was observed (Figs. 4 and 5), noise spectra stay $1/f$ type, what shows that physical processes that cause this kink in temperature characteristics do not introduce new noise origins. Noise characteristics compliance with resistivity dependencies indicate that in the investigated samples resistance fluctuation due to the fluctuation of number of free charge carriers is the main noise origin.

V. CONCLUSIONS

Low frequency noise and resistivity characteristics of composite materials: bisphenol A epoxy resin reinforced by the carbon fiber felts (PAN and Rayon), have been investigated in a wide temperature range. Low frequency voltage fluctuations in the investigated materials are $1/f^{\alpha}$ type and are caused by the resistance fluctuations due to random charge carrier capture and release processes in centers inside the carbon fibers. Tunneling through the dielectric matrix is small and have no effect on noise characteristics.

The samples with contacts deposited in perpendicular direction to the fibers are more conductive and demonstrate lower $1/f^{\alpha}$ type noise comparing with samples with contacts applied along the carbon fibers.

An observed kink in the resistivity and noise characteristics in (307-332) K temperature range is caused by the reduction of carbon fiber dimensions. This shrinkage of carbon fibers does not introduce additional noise origins in the investigated materials.

REFERENCES

[1] N. Yoon, Y. Lee, D. Kang, J. Min, J. Won, M. Kim, Y. S. Kan, S.-H. Kim, and J.-J. Kim, "Modification of hidrogenated bisphenol A epoxy adhesives using nanomaterials," Int. J. Adhesion and Adhesives, vol. 31, pp. 119–125, March 2011.

[2] J. M. Faulstich de Paiva, S. Mayer, and M. C. Rezende, "Evaluation of mechanical properties of four different carbon/epoxy composites used in aeronautical field," Mat. Res., vol. 8, pp. 91-97 Jan./March, 2005.

[3] A. Baker, S. Dutton, and D. Kelly, Composite Materials for Aircraft Structures, 2nd ed., American Inst. of Aeronautics and Astronautic, 2004, p. 599.

[4] V. O. Starcev, A. E. Raskutin, O. V. Starcev, G. M. Guniaev, "Thermal expansion of carbon fibers and carbon plastics based on them," Technique and technology for the production of thermal insulation materials from mineral raw materials, pp. 153–159, June 2009. В. О. Старцев, А. Е. Раскутин, О. В. Старцев, Г. М. Гуняев. «Термическое расширение углеродных волокон и углепластиков на их основе,» Техника и технология производства теплоизоляционных материалов из минерального сырья, ст. 153–159, июнь 2009.

[5] I. Choi, D. G. Lee, "Surface modification of carbon fiber/epoxy composites with randomly oriented aramid fiber felt for adhesion strength enhancement," Composites Part A: Applied Science and Manufacturing, vol. 48, pp. 1-8, May 2013.

[6] R. Luo, T. Liu, J. Li, H. Zhang, Z. Chen, G. Tian, "Thermophysical properties of carbon/carbon composites and physical mechanism of thermal expansion and thermal conductivity," Carbon, vol. 42, pp. 2887-2895, Aug. 2004.

[7] O. V. Starcev, D. A. Hristoforov, A. B. Kliusnicenko, A. F. Rumiancev, G. M. Guniaev, and A. E. Raskutin, "Relaxation of temperature deformations of carbon fibers," Academy of Sciences reports, vol. 390, p. 9, Oct. 2002. / О. В. Старцев, Д. А. Христофоров, А. Б. Клюшниченко, А. Ф. Румянцев, Г. М. Гуняев, А. Е. Раскутин, «Релаксация температурных деформаций углеродных волокон,» Доклады академии наук, т. 390, № 4, ст. 9, Октябрь 2002.

[8] F. L. Jin, and S. J. Park, "Recent Advances in Carbon-Nanotube-Based Epoxy Composites," Carbon Lett., vol. 14, pp. 1-13, Jan. 2013.

[9] L. Guadagno, M. Raimondo, V. Vittoria, L. Vertuccio, K. Lafdi, B. De Vivo, P. Lamberti, G. Spinelli, and V. Tucci, "The role of carbon nanofiber defects on the electrical and mechanical properties of CNF-based resins," Nanotechnology, vol. 24, pp. 1-12, July 2013.

[10] V. Palenskis, J. Matukas, J. Vyšniauskas, S. Pralgauskaitė, H. Shtrikman, D. Seliuta, I. Kašalynas, and G. Valušis, "Analysis of noise characteristics of GaAs tunnel diodes," Fluctuation and Noise Lett., vol. 12, pp. 1350014 – 1350027, Aug. 2013.

[11] V. Palenskis, J. Matukas, S. Pralgauskaitė, D. Seliuta, I. Kašalynas, L. Subačius, G. Valušis, S. P. Khanna, and E. H. Linfield, "Low-frequency noise properties of beryllium δ-doped GaAs/AlAs quantum wells near the Mott transition," J. Appl. Phys., vol. 113, p. 083707, Feb. 2013.

[12] S. Pralgauskaitė, V. Palenskis, J. Matukas, B. Šaulys, V. Kornijčuk, and V. Verdingovas, "Analysis of mode-hopping effect in Fabry-Pérot multiple-quantum well laser diodes via low frequency noise investigation," Solide-State Electron., vol. 79, pp. 104-110, Jan. 2013.

[13] B. K. Jones, "Low-frequency noise spectroscopy," IEEE Trans. Electron Dev., vol. 41, pp. 2188-2197, November 1994.

[14] X. C. Zeng, D. J. Bergman, P. M. Hui, and D. Stroud, "Effective-medium theory for weakly nonlinear composites," Phys. Rev. vol. 37, p. 10970 Nov. 1988.

[15] Y. Gefen, W.-H. Shih, R. B. Laibowitz and J. M. Viggiano "Nonlinear Behavior near the Percolation Metal-Insulator Transition," Phys. Rev. Lett., vol. 57, p. 3097, Dec. 1986.

[16] D. van der Putten, S. T. Moonen, H. B. Brom, 1. C. M. Brookken-Zijp, and M. A. 1. Michels, "Evidence for superlocalization on a fractal network in conductive carbon-black-polymer composites," Phys. Rev. Lett., vol. 69, pp. 494-497, July 1992.

[17] W. F. A. Su, K. F. Schoch, and J. D. B. Smith, "Comparison of Cure Conditions for Rigid Rod Epoxy and Bisphenol A Epoxy Using Thermomechanical Analysis," J. Applied Polymer Science, vol. 70, pp. 2163–2167, Dec. 1998