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DIELECTRIC PROPERTIES OF ANNEALED ONION-LIKE CARBON COMPOSITES IN MICROWAVE REGION

J. Macutkevič [a], J. Banys [a], K. Glemža [a], V. Kuznetsov [b], V. Borjanovic [c], and O. Shenderova [c]

[a] *Vilnius University, Saulėtekio 9, LT-00122 Vilnius, Lithuania*
[b] *Boreskov Institute of Catalysis SB RAS, Lavrentiev 5, 630090 Novosibirsk, Russia*
[c] *International Technology Center, Raleigh, NC 27715, USA*
E-mail: jan.macutkevic@gmail.com

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The onion-like carbon composites prepared according to different technologies were studied by means of broadband dielectric/electric spectroscopy in a wide temperature range from 300 to 450 K. The value of complex dielectric permittivity of composites strongly increases after annealing. From complex dielectric spectra, complex impedance spectra and distribution of relaxation times were calculated. After annealing of composites on cooling the asymmetricity of distribution of relaxation times strongly increases. Annealed composites exhibit only a weak temperature dependence of microwave properties and are promising candidates for electromagnetic shielding materials.

Keywords: dielectric permittivity, composites, onion-like carbon

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1. Introduction

The dielectric properties of nanocarbon-based composites were investigated previously mainly in order to find an electrical percolation threshold [1]. At the percolation threshold, a continuous conducting network of conducting particles is formed inside the insulating matrix. Also, close to and above the percolation threshold the low-frequency dielectric permittivity is reported very high [2]. The main applications of such composites are related with microwave shielding; the value of complex dielectric permittivity at microwave frequencies is also reported high enough for the composites above and close to the percolation threshold [3, 4]. Among other carbon allotropes carbon black, single- or multi-wall carbon nanotubes or onion-like carbon were investigated.

However, the temperature dependence of dielectric properties of carbon-based composites was mainly investigated only at low frequencies and it was related with the temperature dependence of electrical conductivity [5]. At low temperatures (below room temperature) this dependence was mainly related with hopping or tunnelling models [6, 7]. In contrast, at higher temperatures the temperature dependence of conductivity is mainly related with different thermal expansion of polymer matrix and carbon fillers [8]. Two opposite effects can be observed here: a positive temperature coefficient effect where resistivity increases with temperature and a negative temperature coefficient effect where resistivity decreases with temperature [9, 10]. However, investigations of the temperature dependence of complex dielectric permittivity at higher frequencies (particularly, at microwaves) are rather rare. These investigations are very important in order to check thermal stability of microwave shielding coatings. On the other hand, at lower frequencies heating and

cooling procedures can drastically increase the value of complex dielectric permittivity close to the percolation threshold [11]. Therefore, it is reasonable to ask whether annealing has some impact on dielectric properties of carbon-based composites at microwave frequencies. In this paper we have investigated microwave dielectric properties of onion-like carbon/polyurethane (OLC/PU) composites in a wide temperature range.

2. Experiment

The OLC material was produced by annealing detonation nanodiamond (DND) powder in vacuum at 1800 K according to Ref. [12]. Nanodiamonds were purchased from *New Technologies*, Chelyabinsk. The average primary particle size of a DND was 4 nm and the average volumetric aggregate size was 120 nm. To achieve fully transformed DNDs into OLC, DNDs were heated in vacuum at 0.013 Pa and 1800 K for 2 hours. The size of primary OLC particles was around 6–7 nm, while average aggregate size was 130 nm for OLC dispersed in *N*-methylpyrrolidone solvent as measured by the dynamic light scattering technique [11].

The samples of OLC were mixed with commercial formulation of oil-based polyurethane Minwax Clear Satin containing 60% of volatile compounds. All samples contained 10 vol.% of OLC. Two different samples were prepared under different thermal treatment conditions. First, after manual mixing with the OLC powder, the polymer suspension was magnetically stirred at 400 rpm during 24 hours at 50 °C. Then, before casting a suspension, the samples were additionally heated at 90 °C on a hot plate with a purpose to improve uniformity in distribution of OLC in a polymer solution with a lower viscosity. Then suspensions were casted on a Teflon substrate and dried at ambient conditions at 45 °C overnight. Half of the dried samples were additionally annealed at 150 °C during 1 hour under pressure in an oven (these samples are hereinafter referred to as "annealed"). A motivation for this treatment originated from our observation that after testing the dielectric properties of the samples at high temperatures (for example, 450 K), dielectric permittivities and conductivities of the samples, when cooled to room temperature, were increased [11]. Thus, we introduced an annealing stage during sample preparation. The thickness of OLC/PU films varied between 250 and 700 μm.

The complex dielectric permittivity at low frequencies (20 Hz – 1 MHz) was measured by a LCR meter HP4284A. The obtained low frequency data is in good agreement with results presented in [11]. In the frequency range from 1 MHz to 3 GHz the dielectric investigations were performed by a coaxial dielectric spectrometer with a vector network analyser Agilent 8714ET. The measurements were performed by heating, starting from room temperature and up to 450 K, then at this temperature measurements were stopped for 0.5 hour, and thereafter measurements were performed on cooling down to room temperature. The measurements in the frequency range of 26–36 GHz were obtained using a scalar network analyser R2-408R (*ELMIKA*, Vilnius, Lithuania), including a sweep generator, a waveguide reflectometre, and an indicator unit (personal computer) at room temperature. The electromagnetic response of samples as ratios of transmitted/input (S_{21}) and reflected/input (S_{11}) signals was measured over the 26–37 GHz frequency range (K_a-band). In this frequency range the measurements were performed only at room temperature, because very weak temperature dependence was observed already at lower frequencies (at 3 GHz and lower). The samples used for the measurements in different frequency ranges were cut from the same big piece.

3. Results and discussion

The temperature dependence of complex dielectric permittivity of not annealed samples at various microwave frequencies is presented in Fig. 1. It is clearly evident that the value of complex dielectric permittivity increases on heating at all frequencies; however, with increasing frequency the increasing of permittivity saturates. A small dielectric anomaly close to T = 360 K is related with the alpha relaxation in the pure PU matrix, while another step-like dielectric anomaly close to T = 440 K is related with the onset of electrical conductivity in the pure PU matrix and together with the appearance carrier's tunnelling from the OLC clusters to the PU matrix [11]. At the frequencies above 1 GHz the change of dielectric permittivity is negligible in comparison with dielectric permittivity changes observed at lower frequencies [11]. However, dielectric permittivity is still temperature dependent. The value of complex dielectric permittivity increases after annealing in both annealed and not annealed samples (Fig. 2).

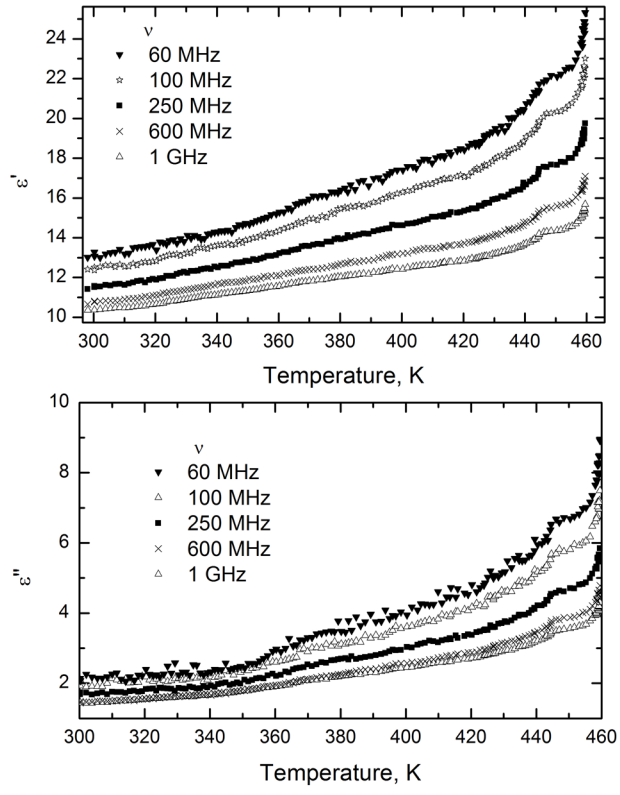

Fig. 1. Temperature dependence of not annealed OLC/PU composites at different microwave frequencies on heating.

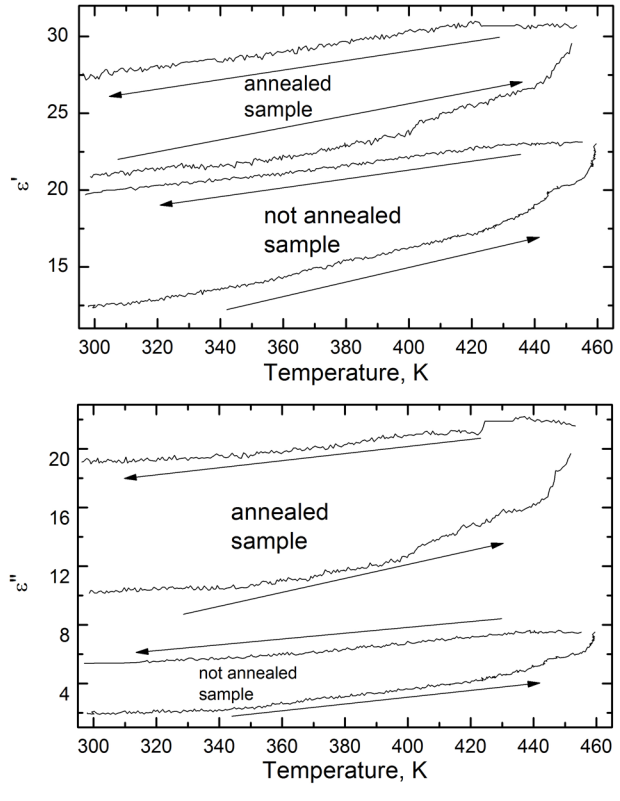

Fig. 2. Temperature dependence of not annealed and annealed OLC/PU composites at 100 MHz on heating and on cooling.

The complex dielectric permittivity at the frequency of 100 MHz is higher in annealed samples in comparison with not annealed. In order to understand the impact of heating/cooling at different frequencies we have employed impedance formalism. The complex impedance Z^* is related with the complex dielectric permittivity ε^* via

$$Z^* = 1/(\varepsilon^*\varepsilon_0\omega) = (\varepsilon'+i\varepsilon'') / (\varepsilon_0\omega(\varepsilon'^2 + \varepsilon''^2), \quad (1)$$

where ε_0 is the dielectric permittivity of vacuum, ω is the angular frequency. Complex impedance formalism is very often employed for investigations of various disordered conductors, including ionic conductors [13]. The obtained frequency spectra of complex impedance Z^* are presented in Fig. 3. The frequency dependence of Z^* is very broad and cannot be described by a single RC circuit

$$Z^* = R / (1 + i\,\omega CR) = R / (1 + i\omega\tau), \quad (2)$$

where R and C are resistance and capacitance, respectively, and $\tau = RC$. The maximum of the imaginary part of complex impedance Z'' is observed at the frequencies of several MHz (Fig. 3). It is important to note that the frequency spectrum of Z'' is almost symmetric at room temperature. On heating and on cooling the values of complex impedance Z^* decrease unevenly at different frequencies and the frequency spectra of Z^* becomes more asymmetric. To describe such behaviour the complex impedance spectra of composites were modelled as infinite chain of RC circuits connected in series, and corresponding distribution of relaxation times was calculated by solving an integral equation

$$Z^*(\nu) = Z_\infty + \Delta Z \int_{-\infty}^{\infty} \frac{f(\tau)\mathrm{d}\lg\tau}{1+i\omega\tau} \quad (3)$$

and the method described elsewhere [14]. The discrepancies between the experimental points and the fit lines appear due to finite measurements accuracy (Fig. 3). The calculated distributions of relaxation times are presented in Fig. 4. In the not annealed sample on heating the distributions of relaxation times exhibit the pronounced temperature dependence, the maximum of distributions shifts from milliseconds to 10^{-5} seconds and distributions become narrower. However, the most pronounced effect occurs after a one half-hour isothermal annealing at T = 450 K. After annealing, the position of the maximum of distributions of relaxation times

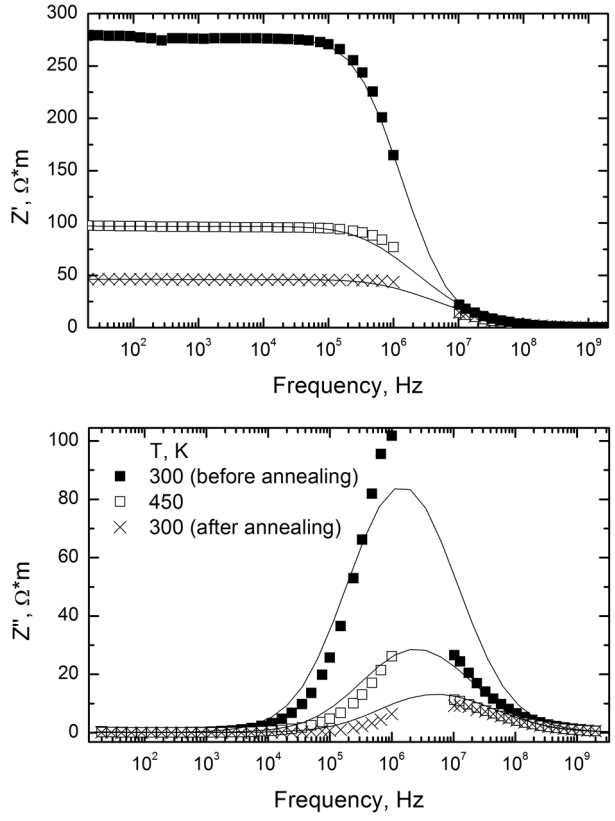

Fig. 3. Complex impedance spectra of annealed OLC/PU composites at different temperatures.

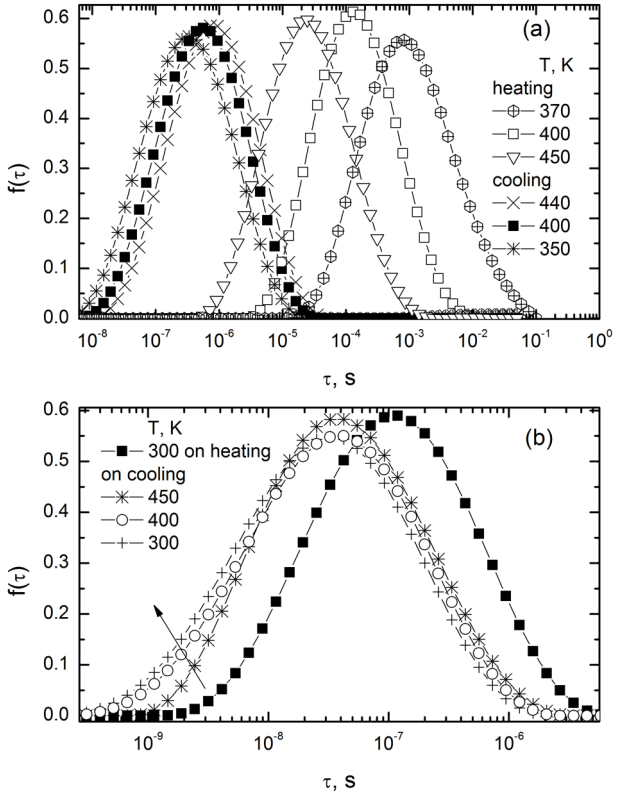

Fig. 4. Distribution of relaxation times of (a) not annealed and (b) annealed OLC/PUcomposites.

shifts by two orders of magnitude. In contrast, on cooling the distributions of relaxation times are only very weakly temperature independent. On cooling the distributions become more asymmetric. Considering the physical interpretation of distribution of relaxation times in composites, the relaxation time $\tau = RC = C/\sigma$, where C is the capacitance of one OLC cluster, R is the resistivity and σ is the conductivity inside one OLC cluster or between neighbouring OLC clusters. It was demonstrated that the distribution of OLC clusters inside a composite changes after annealing [11]. The capacitance of OLC clusters is dependent only on geometrical parameters of OLC clusters, for example if we assume spherical OLC clusters, their capacitance is

$$C = 4\pi\varepsilon_0 r, \tag{4}$$

where r is the effective radius of OLC clusters. The tunnelling conductivity between OLC clusters is also dependent on OLC distribution inside the polymer matrix and together also on OLC shape distributions. Thus, short relaxation times in distributions (Fig. 4) correspond to the relaxation in small OLC clusters where they are distributed more homogeneously, and long relaxation times correspond to large OLC clusters. From the distribution of relaxation times it is difficult to speak about the real OLC clusters geometrical shape distribution because the conductivity σ is also dependent on the OLC concentration and on the potential barrier for curriers tunnelling between OLC clusters. However, we can conclude that on heating and particularly after annealing all OLC clusters split into smaller. In contrast, on cooling the decrease only of big OLC clusters is observed, while concentration of small OLC clusters (short relaxation times) increases. This is related with the smallest cluster OLC size, it should coincide with OLC aggregate size (130 nm according to dynamic light scattering measurements [11]). Thus, the complex impedance spectra Z^* is a good mirror to monitor distribution of conductive particles inside an insulating polymer matrix. Let us consider Eqs. (1) and (2): for very high frequencies ($\omega\tau >> 1$) the value of complex impedance Z^* and therefore dielectric permittivity ε^* is very small. Therefore, the main contribution of an equivalent RC circuit to the complex impedance Z^* (and together the complex dielectric permittivity ε^*) occurs at frequencies $\omega > 1/\tau$. At these frequencies is also the main temperature dependence of complex dielectric permittivity, which is caused by

OLC clusters redistribution [11]. By this the decrease of annealing impact on OLC/PU dielectric properties with frequency can be explained (Figs. 1, 2).

From the distributions of relaxation times the most probable relaxation was obtained (Fig. 5). In the not annealed sample the relaxation time decreases on heating and on cooling. In contrast, in the annealed sample the relaxation time decreases only on heating. The temperature dependence was described by the Arrhenius law

$$\tau = \tau_0 e^{E/kT}, \quad (5)$$

where τ_0 is the pre-exponential factor, E is the activation energy, k is the Boltzmann constant. The obtained values are τ_0 = 15.5 ps, E/k = 3586 K for the annealed sample on heating and τ_0 = 8 ps, E/k = 6773 K for the not annealed sample on heating and τ_0 = 24.9 μs, E/k = –1502 K for the not annealed sample on cooling. The different sign of the activation energy on heating and on cooling is related with the opposite behaviour of τ on heating and on cooling.

Finally, the dielectric properties of both annealed and not annealed OLC/PU composites were checked in the frequency range of 26–37 GHz at room temperature. It was obtained that the value of complex dielectric permittivity was ε^* = 11–9*i for an annealed sample and ε^* = 3.5–1.5*i for a not annealed sample at the frequency of 30 GHz. No significant dielectric dispersion was observed in this frequency range. The value of the complex dielectric permittivity is higher than the one obtained for epoxy resin/CNT or CB composites above the percolation threshold [15, 16]. However, it is lower than the dielectric permittivity of functionalized CNT composites [17].

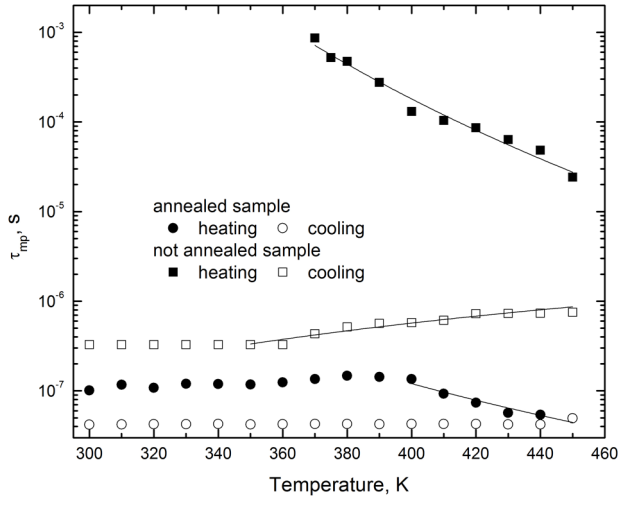

Fig. 5. Temperature dependence of relaxation time of not annealed and annealed OLC/PU composites on heating and on cooling.

Thus, the electromagnetic absorption of OLC-based composites at microwaves can be further improved in two ways: first, by selecting the initial OLC powder with the highest electrical conductivity and, second, by selecting OLC powder with the lowest OLC aggregate size. However, previously presented results demonstrate that OLC/PU composites are promising candidates for electromagnetic shielding materials.

4. Conclusions

OLC/PU composites are suitable candidates for temperature stable electromagnetic shielding materials. At microwaves the complex dielectric permittivity of the annealed samples is only weakly temperature dependent due to the asymmetric distributions of relaxation times. The asymmetricity of distribution of relaxation times increases on cooling. The complex impedance is a good mirror to monitor distribution of particles inside the insulating matrix.

Acknowledgements

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References

[1] M.B. Isichenko, Percolation, statistical topography, and transport in random media, Rev. Mod. Phys. **64**, 961–1043 (1982), http://dx.doi.org/10.1103/RevModPhys.64.961

[2] W. Bauhofer and J.Z. Kovacs, A review and analysis of electrical percolation in carbon nanotube polymer composite, Composites Sci. Technol. **69**, 1486–1498 (2009), http://dx.doi.org/10.1016/j.compscitech.2008.06.018

[3] Ju Wu and L. Kong, High microwave permittivity of multiwalled carbon nanotubes composites, Appl. Phys. Lett. **84**, 4956 (2004), http://dx.doi.org/10.1063/1.1762693

[4] N. Li, Y. Huang, F. Du, X. He, X. Lin, H. Gao, Y. Ma, F. Li, Y. Chen, and P.C. Eklund, Electromagnetic interference (EMI) shielding of single-walled carbon nanotube epoxy composites, Nano Lett. **6**, 1141–1145 (2006), http://dx.doi.org/10.1021/nl0602589

[5] M.T. Connor, S. Roy, T.A. Ezguerra, and F.Z. Balta Calleja, Broadband ac conductivity of conductor-polymer composites, Phys. Rev. B **57**,

2286–2294 (1998), http://dx.doi.org/10.1103/PhysRevB.57.2286
[6] P. Mandal, A. Neumann, A.G.M. Jansen, and P. Wyder, Temperature and magnetic-field dependence of the resistivity of carbon-black polymer composites, Phys. Rev. B **55**, 452–456 (1997), http://dx.doi.org/10.1103/PhysRevB.55.452
[7] A. Mdarhi, C. Brosseau, M. Zaghiroui, and I. El Aboudi, Electronic conduction and microstructure in polymer composites filled with carbonaceous particles, J. Appl. Phys. **112**, 034118 (2012), http://dx.doi.org/10.1063/1.4740239
[8] C.P.L. Rubinger, M.Y. Leyva, B.G. Soares, G.M. Ribeiro, and R.M. Rubinger, Hopping conduction on carbon black/styrene-butadienestyrene composites, J. Mater. Sci. **47**, 860–865 (2012), http://dx.doi.org/10.1007/s10853-011-5864-2
[9] K.M. Jager, D.H. McQueen, and J. Vilcakova, Ac conductance and capacitance of carbon black polymer composites during thermal cycling and isothermal annealing, J. Phys. D: Appl. Phys. **35**, 1068–1075 (2002), http://dx.doi:10.1088/0022-3727/35/10/316
[10] M. Hindermann-Bischoff and Fr. Erburger-Dolle, Electrical conductivity of carbon black–polyethylene composites: Experimental evidence of the change of cluster connectivity in the PTC effect, Carbon **39**, 375–382 (2001), http://dx.doi.org/10.1016/S0008-6223(00)00130-5
[11] J. Macutkevic, D. Seliuta, G. Valusis, J. Banys, S. Hens, V. Borjanovic, V. Kuznetsov, and O. Shenderova, Effect of thermal conditions on the properties of onion-like-carbon based polymer composite, Composites Sci. Technol. **70**, 2298–2303 (2010), http://dx.doi.org/10.1016/j.compscitech.2010.09.008
[12] V.L. Kuznetsov, Yu.V. Butenko, A.L. Chuvilin, A.I. Romanenko, and A.V. Okotrub, Electrical resistivity of graphitized ultra-disperse diamond and onion-like carbon, Chem. Phys. Lett. **336**, 397–404 (2001), http://dx.doi.org/10.1016/S0009-2614(01)00135-X
[13] J. Jamnik, Impedance spectroscopy of mixed conductors with semi-blocking boundaries, Solid State Ionics **157**, 19–28 (2003), http://dx.doi.org/10.1016/S0167-2738(02)00183-2
[14] J. Macutkevic, J. Banys, and A. Matulis, Determination of distribution of the relaxation times from dielectric spectra, Nonlin. Analysis Model. Control **9**, 75–84 (2004).
[15] B.J.P. Adohi, A. Mdarhri, C. Prunier, B. Haidar, and C. Brosseau, A comparison between physical properties of carbon black-polymer and carbon nanotubes-polymer composites, J. Appl. Phys. **108**, 074108 (2010), http://dx.doi.org/10.1063/1.3486491
[16] D. Bychanok, P. Kuzhir, S. Maksimenko, S. Bellucci, and C. Brosseau, Characterizing epoxy composites filled with carbonaceous nanoparticles from dc to microwave, J. Appl. Phys. **113**, 124103 (2013), http://dx.doi.org/10.1063/1.4798296
[17] S.H. Park, P. Thielemann, P. Asbeck, and P.R. Bandaru, Enhanced dielectric constants and shielding effectiveness of uniformly dispersed, functionalized carbon nanotube composites, Appl. Phys. Lett. **94**, 243111 (2009), http://dx.doi.org/10.1063/1.3156032

ATKAITINIMO ĮTAKA SVOGŪNINĖS SANDAROS ANGLIES KOMPOZITŲ DIELEKTRINĖMS SAVYBĖMS MIKROBANGŲ RUOŽE

J. Macutkevič [a], J. Banys [a], K. Glemža [a], V. Kuznetsov [b], V. Borjanovic [c], O. Shenderova [c]

[a] *Vilniaus universitetas, Vilnius, Lietuva*
[b] *Boreskov katalizės institutas, Novosibirskas, Rusija*
[c] *Tarptautinis technologijų centras, Raleigh, JAV*

Santrauka

Straipsnyje nagrinėjamos svogūninės anglies kompozitų dielektrinės mikrobangės savybės plačiame temperatūrų intervale – nuo 300 K iki 450 K. Parodyta, kad didėjant temperatūrai šių kompozitų kompleksinės dielektrinės skvarbos vertė didėja plačiame dažnių diapazone, tačiau ši priklausomybė įsisotina esant aukštiems dažniams (per 1 GHz). Toks kompleksinės dielektrinės skvarbos kitimas buvo paaiškintas pasinaudojus elektrinio impedanso sąvoka. Iš kompleksinio impedanso spektrų buvo apskaičiuoti relaksacijos trukmių pasiskirstymai. Kompozitus kaitinat relaksacijos trukmių pasiskirstymai tampa siauresni ir slenka į trumpesnių trukmių pusę. Šaldant kompozitus relaksacijos trukmių pasiskirstymai praktiškai nesislenka, tačiau didėja jų asimetriškumas. Kompozitus šaldant neatsiranda svogūninės anglies klasteriai su dar mažesniu tūriu, didėja tik mažų klasterių skaičius. Kompleksinei dielektrinei skvarbai svarbūs tik tie klasteriai, kurių atvirkštinė relaksacijos trukmė yra daug didesnė negu elektromagnetinės bangos dažnis. Parodyta, kad svogūninės anglies kompozitai yra tinkami kandidatai į elektromagnetinio suderinamumo medžiagas. Tolesnis šių medžiagų tobulinimas galimai yra dvejopas: pasirenkant svogūninės anglies miltelius su didesniu elektriniu laidžiu bei su mažesniu svogūninės anglies agregato dydžiu.