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Citation: J. Appl. Phys. **114**, 033707 (2013); doi: 10.1063/1.4815870
View online: http://dx.doi.org/10.1063/1.4815870
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Electrical transport in carbon black-epoxy resin composites at different temperatures

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(Received 3 May 2013; accepted 27 June 2013; published online 17 July 2013)

Results of broadband electric/dielectric properties of different surface area—carbon black/epoxy resin composites above the percolation threshold are reported in a wide temperature range (25–500 K). At higher temperatures (above 400 K), the electrical conductivity of composites is governed by electrical transport in polymer matrix and current carriers tunneling from carbon black clusters to polymer matrix. The activation energy of such processes decreases when the carrier concentration increases, i.e., with the increase of carbon black concentration. At lower temperatures, the electrical conductivity is governed by electron tunneling and hopping. The electrical conductivity and dielectric permittivity of composites strongly decrease after annealing composites at high temperatures (500 K); at the same time potential barrier for carriers tunneling strongly increases. All the observed peculiarities can be used for producing effective low-cost materials on the basis of epoxy resin working at different temperatures for electrical applications. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4815870]

I. INTRODUCTION

Conducting polymeric composites, constituted by conducting filler dispersed into an insulating polymer matrix, have important applications in antistatic materials, electrostatic discharge, dissipation, electromagnetic interference shielding,[1–5] temperature, pressure, and gas sensors.[6] These composites are usually characterized by a sharp insulator–conductor transition at a specific volume fraction of filler. At this point, known as percolation threshold, a continuous conducting network of conducting particles is formed inside the insulating matrix.[7] Among the available fillers, carbon black (CB) has been extensively employed because of its ability to give high electrical conductivity to an insulating polymer at relatively low filler content.[7] Adriaanse *et al.*[8] demonstrated that percolation threshold in CB/polymer composites in some cases could be extremely low (lower than 0.03 vol. %). The percolation threshold in CB/polymer composites is strictly dependent on CB aggregate structure, and an aggregate structure model was proposed to describe percolation threshold in CB-based composites.[9]

At low temperatures (below room temperature), temperature dependence of dc conductivity of CB-based composites does not obey Arrhenius law. There are some models of electrical transport in composites containing CB in the literature, among them Mott's variable range hopping (M-VRH) theory[10,11] and Efros-Shklovskii model (ES-VRH) associated with Coulomb effects.[12] Transport phenomena can also be interpreted in terms of superlocalization of electronic states in the presumably fractal CB/polymer percolation network.[12] Another model proposed for electrical conductivity is ascribed to tunneling through a potential barrier of variable height.[13–17] Finally, for describing electrical conductivity of CB-based composites, a Differential Activation Energy (DAE) method was applied.[18]

At higher temperatures (above room temperature), the dielectric and electric investigations of CB-based composites above percolation threshold are rather rare.[19–21] The investigations of CB/Poly(methyl methacrylate) (PMMA) and Ethylene Butylacrilate (EBA) composites demonstrate a minimum in dc conductivity temperature dependence close to polymer softening temperature (i.e., close to the glass transition temperature for PMMA and to the melting point for EBA).[19] The dc conductivity significantly decreases after the first thermal cycling, then in next heating-cooling experiments, its dependence saturates. This effect was explained by rearrangement of gaps between the carbon black aggregates.[20]

The major field of applications for electrically conductive composites, such as electrostatic dissipation, antistatic, organic solar cells, printing electronic circuits, organic light-emitting diodes, actuators, supercapacitors, chemical sensors and biosensors, flexible transparent displays, electromagnetic shielding, depends on the magnitude of their dc and ac conductivities and how they are influenced by the environment, especially temperature. What is also important, the conductivity levels required for various electrical applications should be reached without compromising the other host polymers preferred physical properties and processability. That is why our idea is to use: (i) epoxy resin EPIKOTE Resin 828, well known for its wide engineering applications and (ii) highly conductive carbon black ENSACO of different surface areas in relatively low nanocarbon concentrations in order to

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estimate the influence of carbon surface area on electrical and dielectric properties of epoxy composites at different temperature regimes. The final aim is to provide some input of using CB/epoxy spectral peculiarities for manufacturing effective low-cost material for different electrical applications.

The present study focuses on the relationship between the morphology of carbon black polymer composites and their electrical and dielectric properties. We have investigated the electrical/dielectric properties of epoxy resin filled with carbon black of high and low surface areas in a wide temperature range, 25–500 K, in order to determine the basic conduction mechanisms. This work is complementary to our previous investigation of CB/epoxy composites below the percolation threshold that could fit for antistatic applications.[22–24]

II. EXPERIMENTAL DETAILS

Commercially available ENSACO conductive carbon blacks were kindly supplied by Timcal Ltd. (Bodio, Switzerland). Such materials are widely used as black pigment, UV stabilizer, rubber reinforcement, and were utilized for epoxy resin composites fabrication. ENSACO CBs with a high to very high void volume allow the retention of a carbon network at low to very low filler content. The void volume can originate from the interstices between the carbon black particles due to their complex arrangement and from their own porosity. The two following carbon blacks were used: Carbon Black of High surface area - CBH (ENSACO 350 G: BET surface area = 770 m^2/g; oil absorption = 320 ml/100g,) and Carbon Black of Low surface area—CBL (ENSACO 250 G: BET surface area = 65 m^2/g; oil absorption = 190 ml/100 g).

Although values were not provided by the supplier, it is known that the electrical conductivity of CBH is much higher than that of CBL, and the differences in terms of surface area and oil absorption are related to the structure of the carbon blacks. The higher is the structure (meaning that the CB comprises chain-like agglomerates, whereas less structured materials have more individual particles, not so much associated), the higher is the conductivity but the lower is the dispersibility.

EPIKOTE^{TM}Resin 828 was used for composites fabrication. EPIKOTE Resin 828 is a medium viscosity liquid epoxy resin (viscosity 12–14 Pa s at 298 K) produced from bisphenol A resin and epichlorhydrin. It contains no diluent. EPIKOTE 828 provides good pigment wetting and good resistance to filler settling and a high level of mechanical and chemical resistance properties in cured state. However, as an unmodified pure bisphenol A resin, EPIKOTE 828 is prone to crystallize on storage, particularly in cold conditions. EPIKOTE 828 matrix had a glass transition temperature of $T_g = 393$ K and a density of 1.16 g cm^{-3} at 298 K.[25] A series of composite samples, realized in different thicknesses, using an epoxy resin, i.e., Epikote 828, a curing agent called A1 (i.e., a modified TEPA) and 0.25, 0.5, 1, 1.5 and 2.0 wt. % of carbon black fillers were fabricated as follows:[15–18] the resin was degassed under vacuum (1–3 mbar) for 12/14 h, then it was put into an oven at 338 K. In the meantime, the carbon black was dispersed in propanol through ultrasonic bath for 1.5 h. Afterwards, the solution of alcohol and carbon black was mixed with the resin. The obtained mixture was placed in the oven at 403–423 K for the evaporation of alcohol. The curing agent (A1) was added to the mixture of resin and nanofiller through slow manual mixing for about 7 min. The mix was then poured into 1 cm × 1 cm × 7 cm molds, and left as such for 20 h for the curing process at room temperature, and finally for 4 h in an oven at 353 K. When the process was completed the samples were removed from the molds.

The complex dielectric permittivity ε^* was measured with a LCR HP4284A meter (Fig. 1). At low temperatures (below room temperature), the samples were placed in a closed cycle cryostat and cooled down to the lowest temperatures. In high temperature measurements, the samples were placed in a furnace and heated up to 500 K and then cooled down to room temperature. The equivalent electrical circuit was selected as capacitance and tangent of losses. From these quantities, according to planar capacitor formula, complex dielectric permittivity was calculated. All measurements were performed at constant temperature change rate of 0.5 K/min. Square-like samples with typical thickness about 2 mm and area of 20 mm^2 were investigated. Silver paste was used for contacting. The electrical conductivity σ was calculated according to equation $\sigma = i\omega\varepsilon_0\varepsilon''$, where $\omega = 2\pi\nu$ and ν is the measurement frequency. Up to 10 samples were tested for each type of carbon black type and each concentration measured under the same heating/cooling conditions, from which the average values were calculated and are those reported in the present paper.

III. RESULTS AND DISCUSSION

A. Low temperature region

The investigations of room temperature dielectric properties of carbon black-based composites indicate that the percolation threshold in CBH composites is close to 1 wt. %, while for CBL composites, its value is close to 2 wt. %. Both dielectric permittivity ε' and electrical conductivity σ have a maximum close to temperature T = 170 K for the composite with 2 wt. % of CBH filler (Fig. 2). A similar behavior was observed in all other composites with carbon black

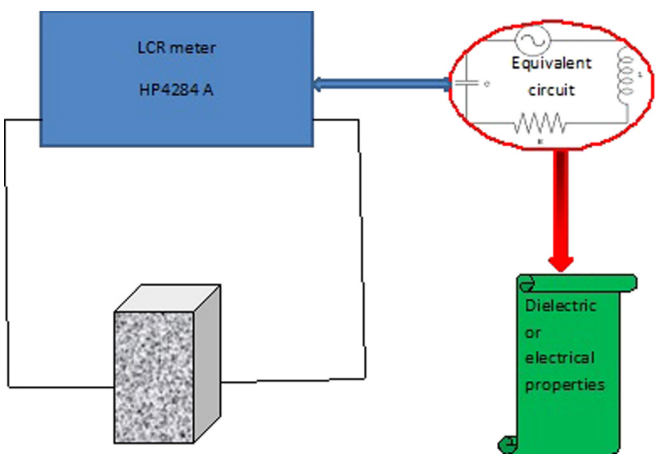

FIG. 1. Schematic set-up of the dielectric/electrical measurements. The sample can be placed into home-made furnace or closed cycle cryostat.

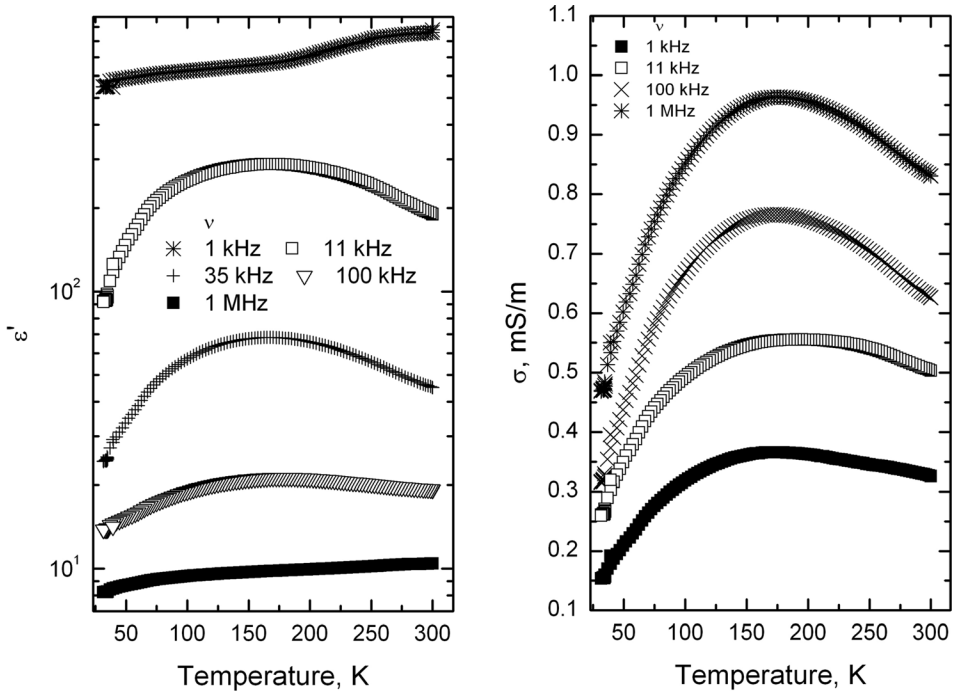

FIG. 2. Dielectric permittivity and electrical conductivity of epoxy resin composite with 2% high surface area-carbon black filler as a function of temperature and frequency.

concentrations above the percolation threshold. The increase of dielectric permittivity ε' and electrical conductivity σ on cooling is related to thermal shrinkage of polymer matrix. Such increase vanishes close to the polymer matrix glass transition temperature.

With such a high value of conductivity (Fig. 2), the blocking contact effect can play an important role.[26] To separate volume conductivity from contact effect, we calculated the specific resistance

$$\rho^* = \rho' - i\rho'' = 1/(i\omega\varepsilon_0\varepsilon^*). \quad (1)$$

The half circle at higher frequencies and lower values of ρ^* is caused by the volume conductivity of composite, and the higher values of ρ^* are already influenced by contacts (Fig. 3). The contact influence is playing an important role at higher temperatures and at low frequencies. So, it is extremely important to extract bulk or volume conductivity from the experimental data.

For better understanding the phenomena, we have plotted the frequency dependence of electrical conductivity at various temperatures (Fig. 4). The conductivity is frequency-independent at low frequencies (below 1 kHz) and at higher frequencies (between 10 kHz and 100 kHz). According to the aforementioned specific resistance formalism, the frequency-independent conductivity plateau at higher frequencies indicates dc volume conductivity, while at lower frequencies, the conductivity is driven by contacts. The same procedure was applied to other composites in order to determine their dc volume conductivity.

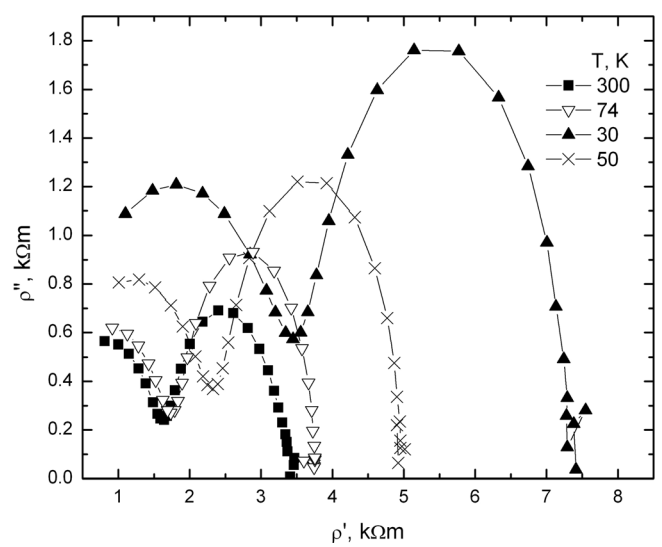

FIG. 3. Cole-Cole diagram of $\rho^* = \rho' - i\rho''$ for composite with 2% high surface area-carbon black filler at different temperatures.

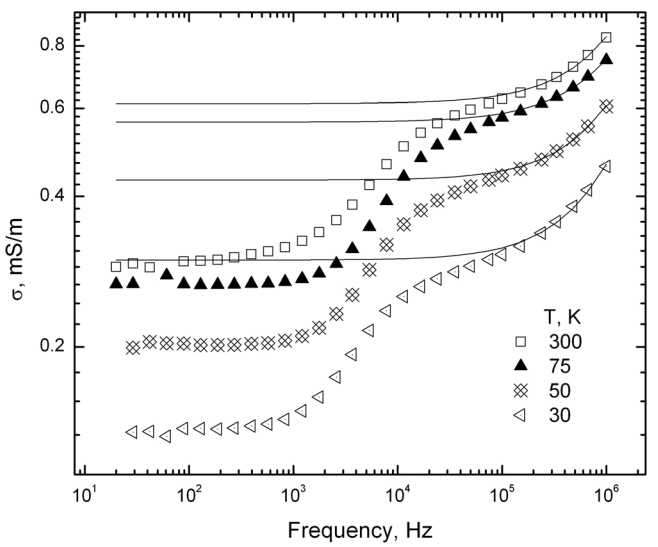

FIG. 4. Frequency dependence of the electrical conductivity of epoxy resin composite with 2% high surface area-carbon black filler.

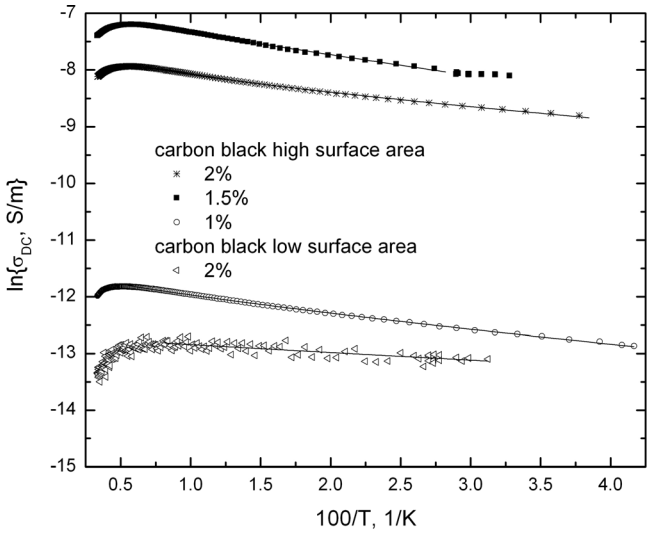

FIG. 5. Mott's law fit for dc conductivity of carbon black composites (low temperatures region).

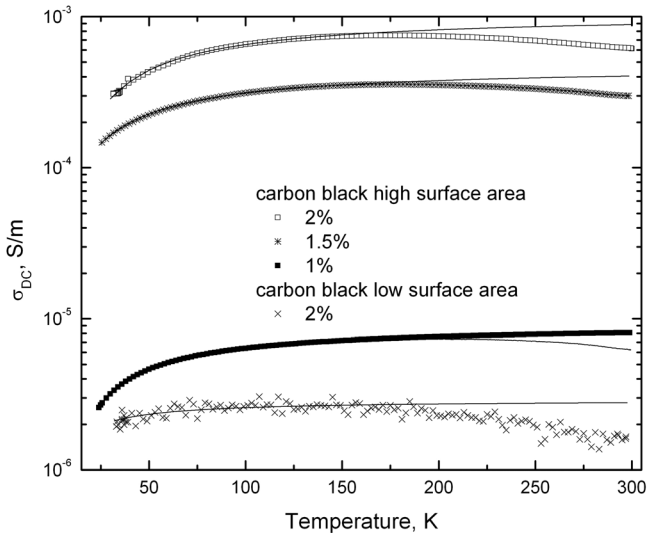

FIG. 6. Temperature dependence of dc conductivity of carbon black-based composites with tunneling model fit (low temperatures region).

The 1/T dependence of $\ln\sigma_{dc}$ is presented in Fig. 5. It is clearly observed that no Arrhenius law is valid at low temperatures for dc conductivity of investigated composites. We assumed that the temperature dependence of dc conductivity can be fitted by the general Mott expression for variable range hopping[11]

$$\sigma_{dc} = \sigma_0 \exp(-(T_M/T)^{1/n}), \tag{2}$$

where T_M is a constant depending on the density of state and localization length of the system, $n = 1 + d$ (d is dimensionality of the system). Obtained parameters are summarized in Table I. All parameters (except dimensionality d) strongly increase with carbon black concentration and are higher in CBH-based composites than in CBL ones. The value of dimensionality d is rather low, but in good agreement with the data presented in Ref. 12 and thus can be explained by ES-VRH model. According to this model, the wave functions of vibrational states and of electronic states (strongly) localized at the Fermi level decay with distance R as $\exp[-(R/L)^{\xi}]$, with $\xi > 1$ and L being the localization length. According to Ref. 12

$$\xi = 1/d, \tag{3}$$

thus, for example for CBH 2 wt.%, $\xi = 10$. The hopping dimensionality is lower in CBL composites.

The temperature dependence of dc conductivity (Fig. 6) was also fitted with fluctuation-induced tunneling model[15]

$$\sigma_{dc} = \sigma_0 \exp(-(T_1/(T + T_0))), \tag{4}$$

where T_1 represents the energy required for an electron to cross the insulator gap between conductive particles aggregate, and T_0 is the temperature above which thermally activated conduction over the barriers begins to occur. According to the tunneling model,[15]

$$T_1 = wA\beta_0/8\pi k, \tag{5}$$

$$T_0 = 2T_1/\pi\chi w, \tag{6}$$

where $\chi = (2mV_0)^{0.5}/h$ and $\beta_0 = 4V_0/ew$, m and e being the electron mass and charge, respectively, V_0 the potential barrier height, w the interparticle distance, and A the area of capacitance formed by the junction. Obtained parameters are listed in Table II. A detailed comparison between Figs. 5 and 6 gives evidence that dc conductivity of carbon black composites can be described with the same accuracy and in the same temperature range with variable range hopping model[11] and fluctuation-induced tunneling model.[15] Therefore, from these results we cannot conclude which mechanism—tunneling or hopping— is dominant at low temperatures. The mechanism of conductivity can be rather mixed, i.e., based on carriers tunneling through insulating polymer matrix and hopping inside carbon black clusters, with dominant role of hopping mechanism and electron localization at low temperatures.[12,27] We will further discuss about low-temperature conductivity

TABLE I. Mott's law parameters of carbon black-based composites.

	$\ln\{\sigma_0, S/m\}$	d	T_M, K
CBH 2%	−6.9	0.1	40.8
CBH 1.5%	−7.54	0.51	38.5
CBH 1%	−11.5	0.31	36.3
CBL 2%	−12.68	0.07	13.4

TABLE II. Fluctuation-induced tunneling model parameters of carbon black-based composites.

	$\ln\{\sigma_0, S/m\}$	T_1, K	T_0, K
CBH 2%	−6.86	52.2	10.1
CBH 1.5%	−7.6	47	14.7
CBH 1%	−11.6	38.4	6.4
CBL 2%	−12.7	12.5	7.3

mechanism in subsection about low-temperatures properties of annealed samples (below).

B. High temperature region

dc conductivity was also calculated at higher temperatures (above room temperature) (Fig. 7). The pure epoxy resin is not conductive at room temperature. No dc conductivity can be estimated for pure resin at room temperature and slightly above (above glass transition temperature). At higher temperatures, dc electrical conductivity of pure epoxy resin increases according to Arrhenius law

$$\sigma_{dc} = \sigma_0 \exp(-(E/kT)), \quad (7)$$

where E is the activation energy. There is some difference in the dc conductivity of pure resin upon heating and cooling (Fig. 7(a)). A similar increase of dc conductivity at higher temperatures (above glass transition temperature) was observed also in composites with 1 wt. % CBH and 2 wt. % CBL filler. At the same time, dc conductivity of composite with 2 wt. % of CBH starts to increase at higher temperatures (at approximately 440 K). Such a behavior was correctly fitted by Arrhenius law (7) and obtained parameters are listed in Table III. The activation energy is lower in composites than in pure polymer matrix and is lower in CBH-based composites than in CBL ones. Obtained conductivity activation energy values are substantially higher than those reported in Ref. 28 obviously due to lower CB concentration. When the concentration of carbon black increases, the activation energy decreases. In composites after annealing, the activation energy decreases while it increases in pure resin.

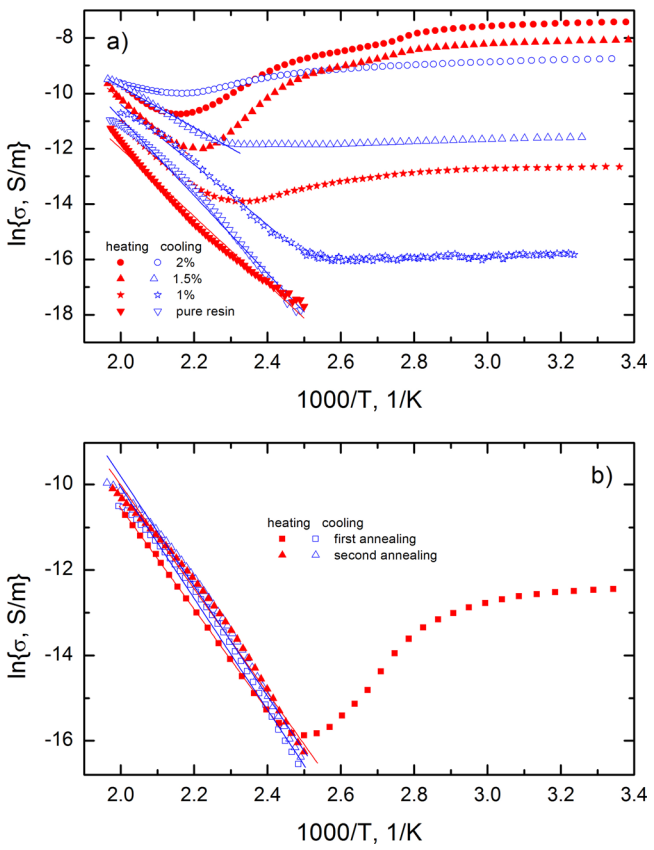

FIG. 7. Temperature dependence of dc conductivity of composites (high temperatures region) with (a) high surface area carbon black and (b) low surface area carbon black.

TABLE III. Arrhenius law parameters of carbon black-based composites in high temperature region.

	$\ln\{\sigma_0$, S/m$\}$	E/k_B, K (eV)
CBH 2% heating	9	9380 (0.808)
CBH 2% cooling	3.82	2911 (0.25)
CBH 1.5% heating	11.48	10844 (0.93)
CBH 1.5% cooling	5.11	7430 (0.64)
CBH 1% heating	10.98	11071 (0.95)
CBH 1% cooling	11.36	10881 (0.94)
CBL 2% heating (1 annealing)	13.1	11827 (1.01)
CBL 2% cooling (1 annealing)	16	13034 (1.12)
CBL 2% heating (2 annealing)	14.2	12145 (1.05)
CBL 2% cooling (2 annealing)	15.9	12866 (1.11)
pure resin heating	12.51	12253 (1.05)
pure resin cooling	17.1	14000 (1.2)

At lower temperatures (below 400 K), the dc conductivity decreases upon heating due to different thermal expansion properties of pure epoxy and carbon black (Fig. 7). In contrast, upon cooling after annealing, no increase of dc conductivity is observed in composites with 1 wt. % of CBH. In these composites, the low value of dc conductivity remains almost temperature-independent. So, after annealing at room temperature, the dc conductivity of composites with 1 wt. % of CBH decreases by several orders of magnitude and vanishes for composites with 2 wt. % of CBL filler. Such decrease is related to the rearrangement of gaps between the carbon black aggregates.[15] According to Ref. 15, the crossover frequency ω_s denoting the crossover from the low-frequency dc-plateau of the conductivity to high-frequency-dependent ac behavior, the dc conductivity σ_{dc} and static permittivity ε_s read as

$$\omega_s = \sigma_{dc}/(\varepsilon_0 \varepsilon_s), \quad (8)$$

$$\omega_s \approx \sigma^z{}_{dc}, \quad (9)$$

where the exponent z characterizes the relation between conductivity and capacitance networks.[15] For the samples under consideration, we have obtained the value $z = 1$, that denotes that the capacitance network remains unchanged when the conduction network is changed. The decrease of dc conductivity is less pronounced in composite with 2 wt. % of high surface area-carbon black. In this composite, a minimum of conductivity remains upon cooling, close to a temperature of 444 K.

The decrease of conductivity after annealing is related to very different carbon black and epoxy resin thermal expansion properties. As a result, epoxy resin shrinks more rapidly on cooling and displaces carbon black clusters. Finally, carbon black conductivity network was partially (for composites with CBH filler) or fully (for composites with 2 wt. % CBL filler) damaged. The physical meaning of such a damage is related to the increase of the mean distance between carbon black clusters and to the decrease of tunneling conductivity. In damaged samples, the second annealing does not recover initial values of conductivity at the previous

stage (Fig. 7(b) with 2 wt. % of CBL filler), but only slightly increases activation energy, see Table III.

Moreover, we have performed annealing of composites with 2 wt. % of CBL inclusions at different temperatures as presented in Fig. 8 in order to explain the effect of annealing temperature on dielectric properties of composites. It is evident that annealing decreased the dc conductivity of carbon black composites (Fig. 8). However, the most pronounced decrease appeared after annealing at temperatures slightly above the glass transition temperature, and finally the dc conductivity vanished after annealing at temperatures higher than the glass transition temperature. This conductivity decrease is related to the fact that all polymers exhibit changes in the slope of specific volume versus temperature close to the glass transition temperature on cooling.[29] Thus, a rapid decrease of polymer matrix volume close to the glass transition temperature has a more pronounced effect on the decrease of dielectric properties of composites and on CB network damage.

At higher temperatures (above glass transition of pure epoxy resin matrix), the electrical conductivity is possible via transport through conductive epoxy resin (σ_{ep}), tunneling between carbon clusters (σ_{CB}) and carbon clusters-epoxy resin series transport ($\sigma_{CBep)}$. Thus, the total conductivity of composite reads:

$$\sigma_{tot} = \sigma_{ep} + \sigma_{CB} + \sigma_{CBep.} \quad (10)$$

The tunneling conductivity σ_{CB} occurs also at lower temperatures, however, its temperature dependence is much lower in comparison to that of σ_{ep}, according to the parameters presented in the Tables II and III. Thus, this conductivity cannot change significantly the activation energy of the total conductivity at higher temperatures. Therefore, the main mechanism responsible for conductivity changes at higher temperatures is the carbon clusters-epoxy resin series transport, where important contribution occurs from electron tunneling through Schottky contact between carbon black and epoxy resin. A simple quantum mechanics analysis of such a barrier[30] shows that this potential barrier is inversely proportional to the carriers' concentration in completely depleted areas. This phenomenon can explain the decrease of conductivity activation energy with CB concentration and account for lower activation energy for CBH in comparison to CBL-based composites. Besides, when the CB concentration increases, the contribution of σ_{CB} to the total conductivity σ_{tot} increases, and therefore the conductivity minimum (denoting the crossover from electrical conductivity inside and between CB clusters to the CB-epoxy resin serial conductivity) is observed at higher temperatures (Fig. 7).

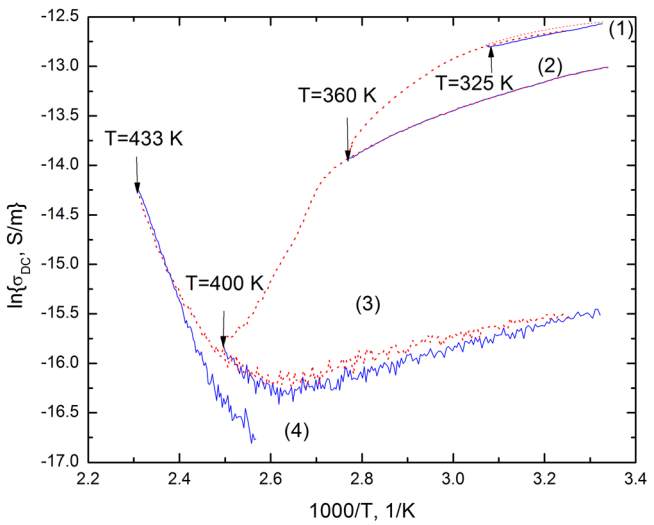

FIG. 8. Temperature dependence of dc conductivity of carbon black-based composites with 2% of low surface area-carbon black filler annealed at different temperatures. The most pronounced effect is observed after annealing slightly above glass transition temperature (400 K). The heating-cooling cycles are consistently numbered. The red dot line represents heating data and the blue solid line represents cooling data.

C. Low temperature properties of annealed samples

The decreased conductivity of composites after annealing was studied by cooling composites with 1.5 and 2 wt.% of CBH filler down to 25 K (Figs. 9 and 10). For composites with 1 wt. % of CBH and 2 wt. % of CBL fillers, the conductivity after annealing becomes non-measurably small and therefore cannot be investigated at low temperatures. The conductivity dependence of annealed composite was also fitted with Mott's law (2) (Fig. 9). The obtained parameters are $\sigma_0 = 9.6\,\mu$S/m, $d = 0.84$, $T_M = 58.7$ K for composite with 1.5 wt. % CBH filler and $\sigma_0 = 6.7\,\mu$S/m, $d = 0.8$, $T_M = 62.1$ K for composite with 2 wt. % CBH filler. At low temperatures, the tunneling model (4) is valid for annealed samples conductivity (Fig. 10). Obtained parameters are $\sigma_0 = 7.5\,\mu$S/m, $T_1 = 58.6$ K, $T_0 = 19.6$ K for composite with 1.5 wt. % of CBH filler and quite similar values $\sigma_0 = 5.2\,\mu$S/m, $T_1 = 58.6$ K, $T_0 = 17.3$ K for composite with 2 wt. % of CBH additives. Compared to those of non-annealed samples, the values of T_1 and T_0 are higher whereas that of σ_0 is lower. The effect of annealing can be twofold: increasing the average distances between CB clusters and as a result increasing the potential barrier for current carriers tunneling in annealed samples, or damaging CB

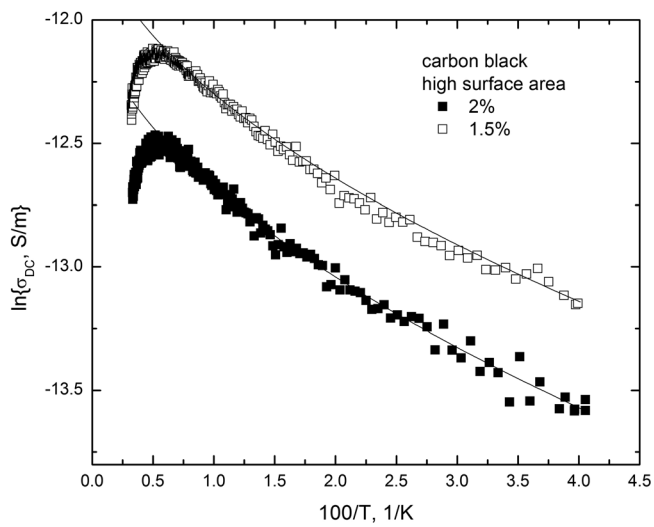

FIG. 9. Mott's law fit for dc conductivity of annealed carbon black-based composites (low temperatures region).

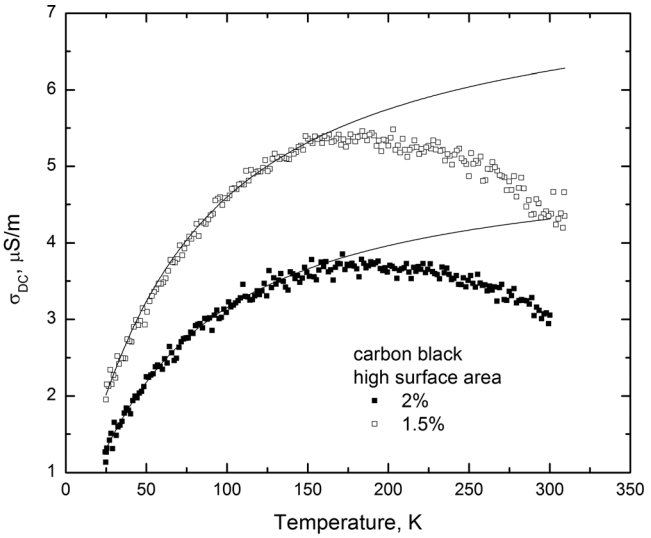

FIG. 10. Temperature dependence of dc conductivity of annealed carbon black-based composites with tunneling model fit (low temperatures region).

network for carriers hopping. The damages can be broken connections between CB clusters due to rapid thermal expansion of polymer matrix on heating and (or) cooling. In any case, these damages cannot increase dimensionality for hopping, therefore, the main conductivity mechanism at low temperatures is electron tunneling between CB clusters.

IV. CONCLUSIONS

Both kinds of commercially available ENSACO carbon black investigated, characterized by high and low surface area, CBH and CBL, can have a broad technological impact in the field of fabrication of conductive composites above the percolation threshold on the basis of epoxy resin for a wide range of electrical applications. The influence of the CB surface area on the broadband dielectric characteristics should be exploited for the production of effective low-cost electromagnetic materials working at different temperatures. The following peculiarities in electrical/dielectric properties of different surface area-carbon black/epoxy resin composites above the percolation threshold have been discovered by broadband electric/dielectric spectroscopy in a wide temperature range (500–25 K):

(i) At higher temperatures (above glass transition of epoxy resin matrix $T_g = 393$ K), the electrical conductivity of composites is governed by electrical transport in polymer matrix and current carriers tunneling from carbon black clusters to polymer matrix. The activation energy of conductivity in this temperature range decreases with current carriers' concentration, i.e., with carbon black concentration, and is higher for CBL-based composites.

(ii) In intermediate temperature range (393–150 K), the electrical conductivity is mainly governed by electron tunneling. In this temperature range, the electrical conductivity slightly increases on cooling due to the different thermal expansion coefficients of polymer matrix and carbon black.

(iii) At lower temperatures, the electrical conductivity is governed by electron tunneling and hopping. The electrical conductivity and dielectric permittivity of composites strongly decrease after composites annealing at high temperatures (500 K); at the same time potential barrier for carriers tunneling strongly increases. The percolation threshold increases in carbon black composites after annealing.

To conclude, according to observed frequency dependence of their electrical conductivity, epoxy resin composite filled with 2% of CBH filler can be suitable for producing electrodes in polymer light-emitting devices as well as for solar cells. At room temperature, 2 wt. % of CBL and 1 wt. % of CBH within epoxy resin might be investigated for active layer production for electroluminescent displays. At relatively high temperatures (above 400 K), epoxy with 2 wt. % of CBH embedded can be used as electrostatic dissipation and antistatic coatings.

ACKNOWLEDGMENTS

This research was funded by the European Social Fund under the Global Grant measure (Lithuanian team). Belarusian, Italian and French teams are partly funded by EU FP7 projects FP7-266529 BY-NanoERA, PIRSES-2012-318617 FAEMCAR, FP7-PEOPLE-2013-IRSES-610875 NAmiceMC, and BRFFI project F13F-004.

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