Dielectric dispersion of Ag/PAN nanocomposites

M A Kudryashov\textsuperscript{1*}, A A Logunov\textsuperscript{1} and L A Mochalov\textsuperscript{1,2,3}

\textsuperscript{1} Department of Nanotechnology and Biotechnology, Nizhny Novgorod State Technical University n. a. R.E. Alekseev, Nizhny Novgorod, 24 Minina Street, 606950 Russia
\textsuperscript{2} Department of Physics and Optical Science, University of North Carolina at Charlotte, Charlotte, 9201 University City Blvd, NC 28223-0001, USA
\textsuperscript{3} Sirius University of Science and Technology, Sochi,1 Olympic Avenue, 354340 Russia

\*mikhail.kudryashov1986@yandex.ru

Abstract. The dependence of the electric modulus of silver/polyacrylonitrile nanocomposites on the ac field frequency has been studied at different temperatures and AgNO\textsubscript{3} content in the base mixture. The observed relaxational maxima on the frequency dependences of the electric modulus’ imaginary part are connected with the interfacial polarization. It was shown that the frequency electric modulus’ experimental points are well-described by the Cole-Davidson model, correspondingly. The values of the relaxation times and the activation energies of these structures have been estimated by this model.

1. Introduction
Despite the fact that nanoscale impurities are sometimes destructive to definite optical materials, for example, chalcogenide glass [1-4], inorganic nanoparticles can be useful for various use, such as for biosensors, catalysis, optoelectronics, data storage, etc. Nanocomposites, consisting of dispersed conductive nanoparticles in a polymer matrix, draw a considerable interest of researchers due to their possible electrical and electromagnetic applications [5]. Some examples of the general use have to do with the screening of electromagnetic interference or radio interference and electrostatic charge dissipation. Recently, there has been a steadily growing interest in the composites based on a polymer matrix and metal nanoparticles [6-9].

By now a range of methods has been developed that allow obtaining nanoparticles in a polymer matrix [10-12]. It was found out that in polymers, containing metal nanoparticles, the dielectric permittivity is sufficiently high; this enables the use of such materials in electronics and microwave technical equipment. Furthermore, such materials can be used as electrically conductive adhesives and circuit elements in microelectronics. They also possess anti-corrosion properties and may be used as coatings for metal contacts.

In order to study the electrical properties of such systems, they are considered to be heterogeneous, and are described within the framework of effective media theories. Different ratios, based on the dielectric permittivity and specific electrical conductivity of the constituent parts, are used in these media [13]. Electrical characteristics of metal-polymeric nanocomposites depend on the inclusion volume fraction, size and shape of the metal nanoparticles.
Dielectric relaxations in metal-polymeric composites can be studied by using dielectric permittivity spectroscopy. However, researching such materials, in which the dielectric permittivity can reach the values over 1000 at low frequencies of the electric field, the problem of relaxations’ disclosure and identification exists. The thing is that in this case the relaxations are concealed due to the presence of electroconductive impurities in the dielectric matrix. Therefore, to detect the dielectric relaxations the reciprocal value of the complex dielectric permittivity, the electric modulus, is implemented [14].

In this study we investigated the frequency dependence of the electric modulus of silver/polyacrylonitrile nanocomposites (Ag/PAN) synthesized at the stage of simultaneous processes of acrylonitrile polymerization and silver ions reduction.

2. Experimental part
Ag/PAN nanocomposite films were obtained by photopolymerization of silver nitrate (AgNO₃) solution in acrylonitrile (AN) in the presence of 2,2-dimethoxy-1,2-diphenylethane-1-one (IN) as a photo initiator. After mixing the monomer, IN and AgNO₃, the mixture was placed between two glass plates with a conductive ITO layer and polymerized by UV radiation with λ = 365 nm for 90 min. The concentration of the precursors varied in different experiments. The more detailed description of the nanocomposites synthesis is given in the papers [10, 15]. The AC-conductivity and capacitance were measured with the Hewlett-Packard 4284A LCR-meter; the resistor and the capacitor were connected simultaneously in the frequency range of 20 - 10⁶ Hz. The preset temperature of the sample was maintained in the frequency range of 285-333 K by using the LOIP LT-100 circulation thermostat with an external cooling. Correspondingly, the real and imaginary parts of the dielectric permittivity were calculated based on the capacitance and AC-conductivity measurements.

3. Results and discussion
Generally, dielectric relaxations exist in polymer composites; this is well-presented in the work [14]. In metal-polymeric nanocomposites the interfaces between the metal nanoparticles and the matrix cause the interfacial polarization (Maxwell-Wagner effect). The charge carriers migrate under the influence of the applied electric field and are accumulated on the interface between the phases with significantly different dielectric permittivity and conductivity. As a result, large dipoles are formed on the surface of metal nanoparticles, this leads to the interfacial polarization formation. This relaxation is determined by the dielectric permittivity and the specific electroconductivity of the components which are the part of the heterogeneous material. The formed dipoles are very inert in the polymer composites, that is why the relaxation, being the slowest of all the emerging dielectric processes, is observed in the low frequency range. The observed high values of the dielectric permittivity, which quickly decrease with the field’s frequency growth, in nanocomposite Ag/PAN films are exactly the result of Maxwell-Wagner effect.

When the electric modulus is used for the interpretation of the interfacial polarization, the sharp jump of the dielectric permittivity is minimized. In this respect, the usual difficulties, related to the influence of the electrode nature, the contact ohmicity and the space charge injection which conceal the relaxation on the dielectric permittivity dispersion, can be resolved or even ignored [16].

The electric modulus (the reciprocal complex dielectric permittivity) $M^*$ is calculated by the following equation:

$$
M^* = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - j\varepsilon''} = \frac{\varepsilon'}{\varepsilon' + \varepsilon''} + j\frac{\varepsilon''}{\varepsilon' + \varepsilon''} = M' + jM'' ,
$$

where $M'$ and $M''$ are the real and the imaginary parts of the electric modulus, and $\varepsilon'$ and $\varepsilon''$ are the real and the imaginary parts of the dielectric permittivity, respectively.

Figures 1 and 2 show the composites’ electric modulus frequency dependences, obtained by Equation 1 at different concentrations of silver nitrate in the initial mixture (1 – 2, 2 – 10, 3 – 20, 4 – 30wt.%) and different temperatures of measurements (1 – 285, 2 – 293, 3 – 303, 4 – 313, 5 – 323, 6 –
333 K), respectively. As a result of the real part’s dielectric permittivity increase, the real part of the electric modulus ($M'$) decreases unevenly with the growth of silver nitrate nanoparticles content (the concentration of the metal salt in the base mixture) and with the increase of the temperature. Similar frequency dependence has been observed in other researches on composite materials on the basis of polymers with conductive impurities [17-19]. A sharp transition from low to high values assumes the relaxation process which is evident in the dispersion of the electric modulus imaginary part ($M''$) as the maximum losses (see Figure 1 and Figure 2).

The relaxational peak shifts to high frequencies with the temperature increase. At the same time, the maximum's intensity tends to decrease with the growth of nanoparticles’ inclusion volume fraction in the polyacrylonitrile matrix. Such an electric modulus frequency dependence demonstrates the interfacial polarization; this conforms both to the theory published in [20, 21] and other experimental works on similar materials’ dielectric properties [18, 22].

The shift of the peak towards high frequencies with the increase of the silver inclusion volume fraction in polyacrylonitrile (the content of silver precursor in the base mixture) can be attributed to the probable growth of the intrinsic conductivity of metal nanoparticles [20, 21]. While researching the morphology of nanocomposite films Ag/PAN [10, 15] it was found out that, increasing the amount of metal salt in the reactionary solution, we obtain silver nanoparticles of a bigger size. In turn, the electroconductivity of nanoparticles may differ from the conductivity of bulky silver and can be dimensionally-dependent. Thus, the growth of the metallic nanoinclusions may lead to the growth of their conductivity.

The electric modulus’ dispersions are not described by the fundamental model of Debye [23]. The observed maximums’ losses are bigger and more intensive than during the Debye relaxation process. From the Maxwell-Wagner-Sillars equations [24], based on a simple Debye relaxation, narrower and more intensive peaks are also obtained [25]. Both the Debye model and the Maxwell-Wagner-Sillars equations describe the process only with one relaxation time; this appears not to be doing for the nanocomposite Ag/PAN films.

**Figure 1.** The dependences of the real (a) and imaginary (b) parts of the electrical modulus on AC frequency at $T = 333\text{K}$ in Ag/PAN nanocomposites, obtained from the mixture with different concentrations of silver nitrate.
Figure 2. The dependences of real (a) and imaginary (b) parts of the electrical modulus on AC frequency in Ag/PAN nanocomposite, obtained from the mixture with 20 wt.% AgNO₃ and 15 wt.% IN at different temperatures of measurements.

While analyzing the dielectric properties of polymeric materials, the models of Cole-Cole [26], Cole-Davidson [27], Havriliak-Negami [28] and Kohlrausch-Williams-Watts [29] are often used. All these approaches view the processes with some distribution of relaxation times. Based on the results of the works [17, 18], to explain the electric modulus’ dispersion we used the Cole-Davidson model to present M. According to this model, the imaginary part ($M''$) and the real part ($M'$) of the electric modulus are as follows:

$$M' = \frac{M_s M_c [M_s + (M_c - M_c)(\cos \varphi)\cos \gamma \varphi]}{M_s^2 + (M_c - M_c)(\cos \varphi)'[2M_c \cos \gamma \varphi + (M_c - M_c)(\cos \varphi)']},$$  \hspace{1cm} (2)

$$M'' = \frac{M_s M_c (M_c - M_c)(\cos \varphi)' \sin \gamma \varphi}{M_s^2 + (M_c - M_c)(\cos \varphi)'[2M_c \cos \gamma \varphi + (M_c - M_c)(\cos \varphi)']},$$  \hspace{1cm} (3)

where $M_s$ and $M_c$ are the values of $M'$ when $\omega \to 0$ and $\omega \to \infty$, respectively,

$$0 < \gamma \leq 1, \quad \tan \varphi = \omega \tau, \quad \omega_{\text{max}} \tau = \tan \left( \frac{1}{\gamma + 1/2} \right),$$  \hspace{1cm} (4)

where $\omega_{\text{max}}$ is the frequency of maximum loss on the dependence $\varepsilon''(f)$ ($\omega_{\text{max}} = 2 \pi f_{\text{f, max}}$), and $\tau$ is the relaxation time, connected with the electrostatic field (often designated as $\tau_\varepsilon$). The relaxation time, connected with the constant displacement vector, is calculated as $\tau_M = (M_s/M_c)\tau_\varepsilon$, and the position of the relaxational peak on the $M''$ curve is calculated as $f_{M,\text{max}} = (M_s/M_c) f_{\text{f, max}}$ [25]. The index $\gamma$ determines the width of the maximum relaxation times’ distribution; at the value of $\gamma = 1$ only one relaxation time is observed (purely Debye relaxation process).

Figure 3 shows the dependences of the imaginary part of the electric modulus on the real part (the Cole-Cole equations) at different concentrations of silver nitrate in the initial mixture (1 – 10, 2 – 20, 3 – 30 wt.%, Figure 3a) and different temperatures of measurements (1 – 293, 2 – 313, 3 – 333 K, Figure 3b). Slightly squeezed, half-circles correspond to the processes with little distributions of relaxation times.
Almost for all the samples, the experimental points originate from the reference point; this proves the absence of any other relaxation process in the area of lower frequencies in the nanocomposite films. The changes in the radius of half circles demonstrate the impact of the inclusion volume fraction of silver nanoparticles in the PAN matrix.

The Cole-Davidson model describes the experimental curves well (the solid lines in Figure 1, 2 and 3). By the approximation of the experimental points we have estimated the indices $\gamma$ and $\tau_M$. All the values of $\gamma$ are higher than 0.59, this indicates a very narrow distribution of relaxation times. With the increase of the silver inclusion volume fraction in the polymeric matrix $\gamma$ tends to the growth, this indicates the approximation of the relaxation process to the purely Debye one. The growth of the measurement temperature causes the relaxation time’s decrease for all the samples. This is evident as the thermal energy facilitates the movement of the dipoles, having formed on the surface of silver nanoparticles in the ac field. With the increase of silver nanoparticles’ inclusion volume fracture of PAN we observe the decrease in the relaxation time as a result of the maximum losses’ position shift to higher frequencies.

Figure 4 shows the dependences of the relaxation time on the temperature’s reciprocal value; the dependences are approximated well by the straight lines in the Arrhenius coordinates. According to the work [18], the relaxation time can be represented as follows:

$$\tau = \tau_0 \exp \left( \frac{\Delta E}{kT} \right),$$

where $\Delta E$ is the relaxation process’s activation energy, $k$ is the Boltzmann constant, and $T$ is temperature. The values of $\Delta E$, obtained from the linear approximation and the equation (5), were 1.41 and 1.28 eV for the films, got at 20 and 30 wt.% of silver nitrate, respectively.

In the high frequencies area the experimental points diverge from the theoretical curves, obtained by the Cole-Davidson model; this can be explained by a probable emerging of another relaxation process. Such behaviour was observed at all the measurement temperatures and in all the nanocomposite films. It is necessary to mention that the type of the frequency dependence of the electric modulus’ imaginary part at nanocomposites’ high frequencies is similar to the dependence $M''$ for the polymer without silver nanoparticles. In polyacrylonitrile there are polar functional groups CN which create their own dipole moments. That is why the polymer may manifest dipole polarization [20]. The sharp increase of the electric modulus’ imaginary part (Figure 1 and 2) in the high frequencies’ range for the polyacrylonitrile with and without silver nanoparticles is, probably, connected with the low-frequency edge of the maximum losses during this polarization.
4. Conclusions
The analysis of the electric modulus frequency dependences demonstrates the relaxation behaviour in Ag/PAN nanocomposites, which is due to the interfacial polarization (Maxwell-Wagner effect). The Cole-Davidson model, that assumes the distribution of relaxation times, conforms to the experimental results. In the high-frequency range the dielectric properties of Ag/PAN nanocomposites are determined by the polymer matrix.

5. References
[1] Mochalov L, Logunov A, Kitnis A, Prokhorov I, KovalevA, Yunin P, Gogova D and Vorotyntsev V 2020 Sep. Purif. Technol. 238 116446
[2] Mochalov L, Logunov A, Vorotyntsev A, Vorotyntsev V and Mashin A 2018 Sep. Purif. Technol. 204 276
[3] Vorotyntsev V M, Malyshev V M, Mochalov L A, Petukhov A N and Salnikova M E 2018 Sep. Purif. Technol. 199 214
[4] Mochalov L, Kornev R, Logunov A, Kudryashov M, Mashin A, Vorotyntsev A, Vorotyntsev V 2018 Plasma Chem. Plasma Process. 38 587
[5] Luo X and Chung D D L 1999 Composites Part B: Engineering 30 227
[6] Bazarov V V, Bumai Y A, Valeev V F, Golovchuk V I, Lukashevich M G, Nuzhdin V I, Odzhaev V B, Kharchenko A A and Khaibullin R I 2020 J. Appl. Spectrosc. 87 476
[7] Kudryashov M, Logunov A, Gogova D, Mashin A, and De Filpo G 2020 Opt. Mater. 101 109746
[8] Kudryashov M A, Mashin A I, Nezhdanov A V, Logunov A A, Gracheva T A, Kuz’micheva T A, Chidichimo G and De Filpo G 2016 Technical Physics 61 1684
[9] Asmussen S V, Vallo C I 2018 Sol. Energy 174 640
[10] Kudryashov M A, Mashin A I, Tyurin A S, Fedosov A E, Chidichimo G and De Filpo G 2011 Technical Physics 56 92
[11] Kashihara K, Uto Yand Nakajima T 2018 Scientific Reports 8 14719
[12] Nuzhdin V I, Valeev V F, Galyautdinov M F, Osin Yu N and Stepanov A L 2018 Quantum Electronics 48 82
[13] Du H, Chen H, Gong J, Wang T G, Sun C, Lee S Wand Wen L S 2004 Appl. Surf. Sci. 233 99
[14] Raptis C G, Patsidis A and Psarras G C 2010 Exp. Polym. Lett. 4 234
[15] Kudryashov M A, Mashin A I, Tyurin A S, Chidichimo G and De Filpo G 2010 J. Surf. Invest.: X-Ray, Synchrotron Neutron Tech. 4 437
[16] Abu Bakr A, North A M and Kossmehl G 1977 Eur. Polym. J. 13 799
[17] Psarras G C, Manolakaki E and Tsangaris G M 2002 Composites Part A: Appl. Sci. Manufact. 33 375
[18] Psarras G C, Manolakaki E and Tsangaris G M 2003 Composites Part A: Appl. Sci. Manufact. 34 1187
[19] Baziard Y, Breton S, Toutain Sand Gourdeenne A 1988 Eur. Polym. J. 24 521
[20] Blythe T and Bloor D 2005 Electrical properties of polymers (Cambridge University Press, New York) p.480
[21] Wagner K W 1914 Electr. Eng. (Archiv fur Elektrotechnik) 2 371
[22] Tsangaris G M, Kouloumbi N and Kyvelidis S 1996 Mater. Chem. Phys. 44 245
[23] Debye P 1929 Polar molecules (The Chemical Catalog Company, Inc., New York) p. 172
[24] Sillars R W 1937 J. Inst. Electr. Eng. 80 378
[25] Tsangaris G M and Psarras G C, Kouloumbi N 1998 J. Mater. Sci. 33 2027
[26] Cole KS. and Cole R H 1941 J. Chem. Phys. 9 341
[27] Davidson D W and Cole R H 1950 J. Chem. Phys. 18 1417
[28] Havriliak S and Negami S 1966 J. Polym. Sci., Part C: Polym. Symp. 14 99
[29] Williams G and Watts D C 1970 Trans. Faraday Soc. 66 80

Acknowledgments
The research was funded by RFBR, Sirius University of Science and Technology, Public Company “Russian Railways” and Educational Fund “Talent and success”, Project № 20-38-51003.