=========================== **POLYMERS** ===========================

Effect of Electrode Material on Impedance Spectra of Metal−Polyethylene Structures with Carbon Nanotubes

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Abstract—The effect of an electrode material on electrical properties of a composite material based on super-high-molecular polyethylene (SHMPE) filled with carbon nanotubes has been studied using impedance spectroscopy. Using the method of replacing the sample by an equivalent electric circuit, it has been found that, depending on the electrode material, a blocking barrier with high active resistance and a space charge region adjacent to it arise in the interface region. It has been shown that the barrier height is controlled by surface electronic states of SHMPE and weakly depends on the electron work function of metal electrodes (Bardeen barrier). The characteristic times of electrical relaxation characterizing bulk and interface regions of the composite under study have been determined.

1. INTRODUCTION

Composites based on the polymer matrix with carbon nanotubes (CNTs) belong to a specific class of materials combining lightness and flexibility of polymers with high strength, electrical conductivity, and thermal conductivity. The long length and small diameter of tubes result in that the nanotubes form an integrated network in the polymer matrix even at their minimum concentrations (1−2 wt %), which makes the material conductive. CNTs have long been considered as an effective tool for increasing consumer characteristics of polymeric materials; however, the efficient solution of this problem faces some difficulties. One of them is associated with achieving good coupling (bond) of the nanotube surface with molecular chains of the polymer. Otherwise, physicomechanical properties of the composite can degrade [1]. Another problem arises since the uniformity of the nanotube distribution in the polymer structure is typically low even when primary components are well mixed. Therefore, high-conductivity regions appear in the object; however, they are isolated from each other and do not form an integrated conductive network. As a result, the through conductivity behaves unpredictably or even contradictorily, depending on the filler concentration, the conductivity varies in response to temperature or mechanical stresses [2].

We note that impressing results are already achieved on the way of quality improvement of such composites obtained using chemical activation of nanotubes by attaching various functional groups to their surface [3, 4]. As a result, CNTs are bound with polymer molecular chains, which causes an increase in mechanical and strength parameters of the composite material and an improvement of the uniformity and reproducibility of electrical characteristics. However, the value and behavior of the conductivity of even such composites can be significantly distorted by processes at the electrode−sample boundary. This contact region is often called the interface at which the conductive structure integrity can be violated due to electrode gaps with the sample and the specificity of electronic state changes on the polymer surface. There is a variety of phenomena which can affect the electronic structure of the contact. Among them are the appearance of space charges at localized surface levels, electrostatic barrier formation, the shift of levels of occupied and unoccupied electronic states in the polymer, and others [5, 6]. At present, the discussed mechanisms of charge transfer through the interface and composite material bulk are speculative to a large extent, which complicates calculations of electronic structures of actual interfaces. Therefore, currently, experimental methods for studying interface features and electrical characteristics of conductive composite materials are most commonly used.

In this work, the impedance spectroscopy method is applied to study the effect of electrode materials on

electrical properties of the structure of metal–polymer composites based on the SHMPE matrix with multi-walled CNTs in the frequency range from 100 Hz to 100 MHz. The use of this method is caused by that the polymer composite contains not only resistive phases consisting of contacting tubes, but also capacitive elements near contacts and in the form of conductive clusters in the bulk, separated by polymer interlayers. Therefore, it becomes possible to measure the frequency behavior of active and reactive impedance components and to determine characteristic times of electrical relaxation, which implicitly characterize the interface, material bulk properties and homogeneity. As for the practical applicability of polymer composites, the data on the distribution of electrical relaxation times are necessary to estimate the response rate of the obtained composite.

2. SAMPLES AND MEASUREMENT RESULTS

The choice of SHMPE as a matrix to obtain the object of study is explained by its applications in many industry fields as a structural material with unique physicomechanical properties [7]. In particular, SHMPE is characterized by a low friction coefficient, an increased rigidity, fiberizability, and the efficient interaction of macromolecules with CNTs. Nanotubes were separated from a carbon condensate produced in atmospheric-pressure carbon–helium plasma of the high-frequency arc discharge with nickel introduced as a catalyst [8]. The CNT separation and functionalization were performed by boiling the condensate in a concentrated nitric acid for 3 h. An acid-insoluble precipitate was rinsed in distilled water and dried under standard conditions; in this case, additional hydroxyl groups were formed on the nanotube surface. The content of separated CNTs was 76 wt % of the initial carbon condensate. The electron microscopy study of the separated product showed that multi-walled CNTs with a diameter of 20–40 nm and an average length of 5–15 μm were fabricated. SHMPE powders with a molecular mass of 1.5×10^6 g/mol and CNTs were mixed in an ultrasonic disperser in ethanol. Then the dried mixture was placed into a compression mold and heated to 140°C with a rate of 0.5°C per minute under a pressure of 60 bar. As a result, samples shaped as disks 12-mm-diameter and 0.2–0.4 mm thick, containing 4 wt % of CNTs, were obtained.

To perform impedance measurements, electrodes made of aluminum, copper, or indium foil 10 μm thick were pressed to sample face surfaces. The foil was pressed to the surface through soft silicon gaskets to provide stability of the direct current through the sample. The metal electrode area was 1.13 cm². The experiment was performed using WK4270 and BM538 Tesla impedance spectrometers allowing measurements of frequency dependences of the impedance magnitude and the phase shift angle of between current and volt-
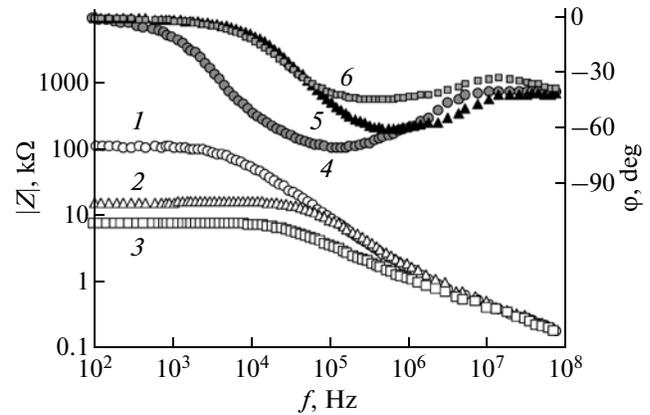

Fig. 1. Frequency dependence of (*1–3*) |Z| and (*4–6*) angle φ for the studied composite with (*1, 4*) Al, (*2, 5*) Cu, and (*3, 6*) In electrodes.

age in the frequency range from 100 Hz to 100 MHz at room temperature. The ac voltage at the device output was $U_{ac} = 0.1$ V; furthermore, dc bias voltages from 0 to 10 V could be applied to the sample. The relative error of impedance measurements did not exceed 5%.

Many modern devices measure the impedance magnitude |Z| and the angle φ of the phase shift between current and voltage, and then transform them to desired electrical characteristics for parallel or series equivalent circuits replacing the sample. Figure 1 shows the experimentally measured frequency dependences of |Z| (curves *1–3*) and the angle φ (curves *4–6*) of the composite under study with Al, Cu, and In electrodes. We can see that the highest impedance is observed in the case of Al electrodes, |Z| = 110 kΩ at $f \longrightarrow 0$ (*1*); in the measurements with Cu and In electrodes, the impedance decreases to 17.8 and 7.8 kΩ, respectively (*2, 3*). The frequency dependence of the impedance has dispersion, decreasing with the electric field frequency. In the low-frequency region, the angle φ is almost zero, which indicates the dominance of the active conductance at which the current coincides in phase with the effective voltage. However, the phase shift angle becomes negative with increasing frequency, which is characteristic of the bias current varying with frequency. The impedance dispersion is characterized by the electrical relaxation time typically determined by the semigraphical method using the Nyquist locus. To this end, the dependence of the imaginary component $Z''(f) = |Z|\sin\varphi$ of the impedance on the real component $Z'(f) = |Z|\cos\varphi$ is constructed. As seen in Fig. 2, the impedance loci with Al, Cu, and In electrodes are shaped as semicircles whose center is shifted downwards with respect to the horizontal axis. The right-hand side of semicircles resting against the Z' axis corresponds to the static resistance of the composite with corresponding electrodes. The left-hand side of semicircles points to the high-frequency impedance which is almost independent of the
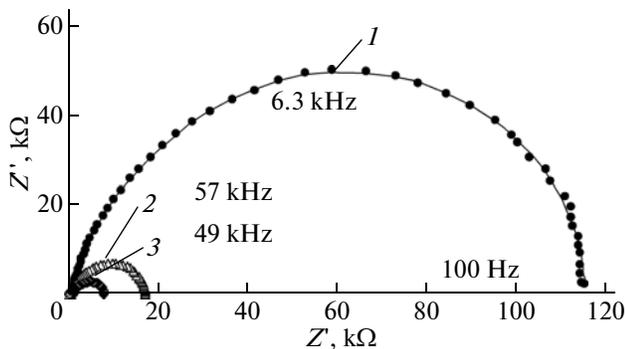
Fig. 2. Impedance loci for the structures with (*1*) Al, (*2*) Cu, and (*3*) In electrodes. Frequencies of the positions of locus maxima are indicated.

Fig. 3. Equivalent circuit.

electrode material, $|Z| \approx 180\ \Omega$ at $f = 100$ MHz. The locus maxima correspond to the largest values of the imaginary component of the impedance, reached at characteristic frequencies f_{max} indicated in Fig. 2. The electrical relaxation times calculated from the relation $\tau_0 = 1/2\pi f_{max}$ for Al, Cu, and In contacts is $\tau_0 = 2.52 \times 10^{-5}$, 2.79×10^{-6}, and 3.25×10^{-6} s, respectively. The fact that the center of locus semicircles is shifted with respect to the $Z'(f)$ axis indicates the existence of several relaxation times in the metal–polymer composite system. Therefore, the values of τ_0 should be considered as a certain averaged value. From the physical point of view, the existence of several relaxation times in this material can be caused by the complex electronic structure of the interface, and numerous relaxation processes in the material bulk can result from structural and electrical inhomogeneities.

Such complex heterogeneous media including the composite under study can be analyzed using dispersion relations for the impedance, containing a function of a continuous or discrete (with small step) relaxation time distribution, which is defined analytically or is reconstructed from experiment by numerical methods [9, 10]. However, there are serious problems not only with the choice of an adequate model for the analytical description of the sample, but also with the choice of a numerical method for determining the relaxation time distribution function. Therefore, in this study, to analyze the impedance spectra, we used the sample replacement by the equivalent circuit (Fig. 3) containing series RC parallel units each describing mutually causal relaxation processes in sample regions with various polarization and conductance. The subscript i indicates the number of used units. The calculation and analysis of such self-similar electrical circuits for heterogeneous materials are presented in [11, 12]. However, because of complexity and awkwardness of calculations, in this study, we restricted the analysis of impedance spectra to a six-unit circuit whose parameters were determined using a
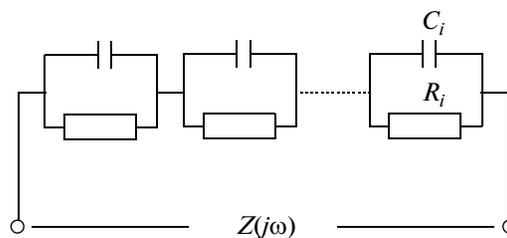
special program for simulating impedance spectra (EIS–Spectrum Analyzer). Such a number of units caused no problems when operating with this program and allowed good enough approximation of experimental frequency dependences of $|Z|$ and impedance loci in the frequency range from 100 Hz to 100 MHz. As a result, the values of R and C were determined for each unit with an accuracy of ~5%.

Figures 4a–4c show histograms for the sample with Al, Cu, and In electrodes, in which black and gray columns correspond to determined values of R and C of each circuit unit as functions of the dimensionless quantity $\log(\tau/\tau_0)$. Here $\tau = RC$ is the time constant of each unit and τ_0 is the average impedance relaxation time of samples with Al, Cu, and In electrodes, determined by the frequency of locus maxima. The results presented in such a form allow the consideration of the determined RC characteristics of the material relative to the dimensionless time of electrical relaxation. For example, several left columns of histograms in Figs. 4a–4c in the region $\tau \ll \tau_0$ characterize probably the bulk material regions in which the determined values of RC are independent of electrode material. A certain difference in these values for various histogram columns indicates the CNT distribution heterogeneity in the composite bulk. Based on the averaged capacitances in last three left columns (C_x), the average relative permittivity of the composite was determined using the relation $C_x = \varepsilon C_0$ as $\varepsilon = 7.0 \pm 0.5$. Here C_0 is the capacitance of the measuring cell without sample.

The two rightmost histogram columns which are in the electrical relaxation range $-0.2 \le \log(\tau/\tau_0) \le 0.3$ most likely describe the interface resistance and capacitance. A comparison of histograms in Fig. 4 shows that one of these columns fixes the considerable capacitance $C \sim 8$ nF for all electrodes and a relatively small resistance R which varies from 1.5 to 5.0 kΩ for Al, Cu, and In electrodes. On the contrary, another column shows large resistances $R = $ (a) 70, (b) 14, and (c) 4.3 kΩ for Al, Cu, and In electrodes; however, the capacitance appears significantly smaller and varies from 150 to 700 pF. To clarify the features of RC characteristics of the interface, the impedance spectra were studied under a dc bias voltage U_{dc} at the sample. As an example, Fig. 5 shows the modification of impedance
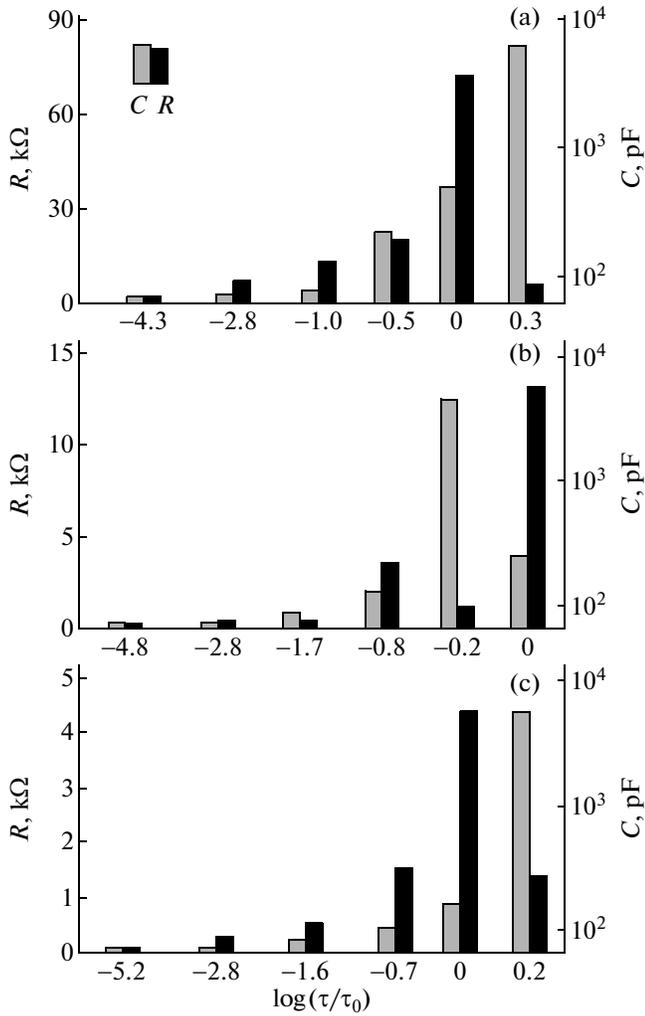
Fig. 4. Histograms of the dependences of R and C of each unit of the equivalent circuit (black and gray columns) on $\log(\tau/\tau_0)$ for the composite with (a) Al, (b) Cu, and (c) In electrodes.

Fig. 5. Impedance loci for the sample with Al contacts as a function of the bias voltage $U_{dc} = $ (*1*) 0, (*2*) 1, (*3*) 3, (*4*) 5, and (*5*) 6 V. The frequencies of the locus maxima are $f_{max} = $ (*1*) 6.3, (*2*) 7.2, (*3*) 12.5, (*4*) 14.4, and (*5*) 30.0 kHz.

3. RESULTS AND DISCUSSION

The experimental data obtained in this study show the significant effect of the electrode material on the surface electrical characteristics which differ from the bulk ones. The experiment shows that, depending on the electrode material, a blocking barrier and an adjacent near-contact region with high capacitance and conductance arise in the interface region. According to the existing physical concepts, the barrier height should be defined by the difference between of the metal electron work function and the polymer electron affinity. The band structure of polymers as unordered materials is often identified with the band structure of amorphous materials in which edges of the valence and conduction bands are spread, and the Fermi level is at the band gap center. Furthermore, the band gap contains surface deep and shallow states resulting from surface structural defects, polymer chain breaks, and other causes. Due to the significant gap between the valence and conduction bands (3 eV and more), caused by overlapping σ- and π-electron shells of macromolecules, the intrinsic carrier concentration in such materials is low. However, charges can be injected from electrodes under an electric field and be trapped by surface traps. The further transport of the injected charge can occur along the edges of valence or conduction bands via multiple carrier trapping by energy-distributed shallow traps until reaching conductive CNTs responsible for the sample conductance as a whole. Within such a concept, it was found [13] that, for polymer samples of the poly(arylenephthalide) class, i.e., poly(diphenylenephthalide) (work function is 4.2 eV), the barrier for the Cu electrode (work function is 4.4 eV) is 0.2 eV; in the case of the Al electrode (Al work function, taking into account surface oxide, is 4.7 eV), the barrier is 0.5 eV.

For polymers with saturated chemical bonds, among which polyethylene is, the energy of the σ-electron bond of chain molecules is such that the band gap appears comparable to the best solid-state dielectrics (diamond, quartz). Currently, there is certain

loci as a function of the bias voltage U_{dc} for the sample with Al contact. We can see that the real and imaginary components of the impedance decrease with voltage, whereas the frequency at which the locus maximum is reached shifts to higher frequencies. The histograms constructed in a similar way for various bias voltages show that the active resistance R in the near-contact region decreases from 70 to 16 kΩ as U_{dc} increases, while capacitance characteristics of the interface are almost unchanged. At the voltage $U_{dc} = 6$ V, the histogram for the sample with Al contacts becomes approximately identical to the histogram shown in Fig. 4b for the sample with Cu contacts. As the voltage U_{dc} increases above 6 V, current fluctuations appear, and the sample is switched to the high-conductivity state. At the bias voltage is removed, the initial impedance values are restored.
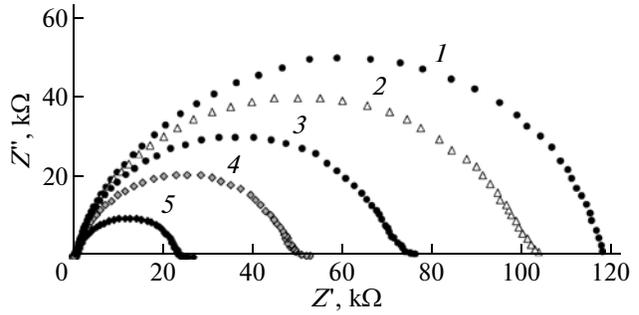
ambiguity in the determination of the Fermi level position and the polyethylene band gap (~7.6–9.1 eV) [14]. Nevertheless, the calculations performed suggest that surface states arranged below the vacuum level in the band gap exist in polyethylene as well [15]. Unfortunately, the problem of the trap nature in polyethylene is almost unexplored. Published data are reduced to only enumeration and classification of possible causes facilitating the formation of electron trapping centers. However, it should be considered that they can partially or completely compensate for the charge induced at surface levels from the metal side at high densities of surface states. In this case, the surface barrier height caused by traps themselves can be independent of or only partially depend on the metal electron work function (Mott–Bardeen barrier). It is quite probable that exactly such a barrier arises in the material under study. This circumstance explains the fact that, when using Cu and In electrodes instead of Al, the rather significant change in the electron work function (from 4.7 eV taking into account the oxide layer for Al to 4.4 and 3.8 eV) only slightly decreases the surface resistance (from 70 to 14 and 4.3 kΩ, respectively), and slightly affects the capacitance component of the interface.

We note that the interface notion includes the polymer–metal interface itself and the adjacent inner layer, where the space charge is accumulated. It seems that this is exactly the cause of the appearance of two columns in histograms, one of which characterizes the boundary barrier with high active resistance, the second characterizes the inner region of the space charge with low resistance and high capacitance. Under dc bias voltage, the experimentally observed change in the impedance points to the decrease in the active resistance of the contact due to the increase in carrier injection from the electrode. This results in an increase in the filling factor of deep traps. Upon reaching the voltage corresponding to complete filling of deep traps, injected charges cannot be trapped, which explains the experimentally observed effect of the sharp increase in the sample current and its fluctuations due to shallow-trap conduction activation.

4. CONCLUSIONS

Currently, a large number of studies are devoted to electrical metal–polymer structures, in which an important role is paid to polymer surface states and conduction mechanisms in the material bulk. However, the physical processes of charge transfer through such structures are still under discussion. In this study, it was shown that the metal–composite interface can be considered as the Mott–Bardeen barrier formed by the space charge of electrons trapped by traps in the material surface region. This barrier only partially depends on the metal electron work function. In the methodological aspect, this study can be considered as the demonstration of the capability of the impedance spectroscopy method which makes it possible to obtain important information on electrical properties of the interface and material.

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