Electrical conductivity of polymer/carbon nanofillers composites

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Abstract. Using a broadband dielectric spectrometry we studied the effect of carbon nanofillers (CN) with various aspect ratio (fullerene C_{60}, multi-walled carbon nanotubes (MWCNT), reduced graphene oxide (rGO) and hybrid rGO:MWCNT nanofillers) on the electrical conductivity of the polyazomethine-based nanocomposites. One-dimensional MWCNTs with high aspect ratio were shown to be the most effective CN for fabrication of polymer-based nanocomposites with enhanced electrical conductivity.

1. Introduction
Nanocomposite materials are increasingly used in different areas. Since the requirements for such materials are permanently increasing, there is a need to create new functional materials with superior properties. In particular, the development of flexible conductive materials for electronics, optics, and devices for energy conversion and storage, much attention is paid to the creation of electrically conductive polymer-based nanocomposites.

Performance of polymer materials is known to be substantially improved by loading even a small quantity of nanofillers [1,2]. Carbon nanofillers (CN) demonstrate excellent physical and chemical properties and could effectively be used for fabrication of high performance materials [3-5]. Thus, the polymer/CN nanocomposites have proved to be effective high performance materials in different engineering application, such as energy conversion, harvesting and storage (batteries, supercapacitors, and solar cells), anti-static agents, electromagnetic interference shielding, coatings and corrosion mitigation, sensors (chemical and biological), optical, and electroactive devices [6].

According to the generally accepted classification [7], carbon nanofillers available for polymer loading can be divided into several types depending on their dimensionality:

- **zero-dimensional** (0D) carbon black (CB), fullerenes and their derivatives,
- **one-dimensional** (1D) carbon nanotubes (CNT), including single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT), and functionalized CNT, and
- **two-dimensional** (2D) graphene (G) and its derivatives including graphene oxide (GO), reduced graphene oxide (rGO), and graphene nanoribbons (GNR).

As follows from CN classification, particularly carbon allotropes that mainly consist of sp²-hybridized carbon atoms are used for production of electrical conductive polymer nanocomposites. This is due to the formation of the extended π-conjugated system in their structures. The presence of numerous defects and sp³-hybridized carbon atoms and various functional groups in the CN structure decreases their intrinsic conductivity [5]. Development of methods for the CN production provides a decrease in their cost and the ability to produce sufficient quantity of CN [8]. By the moment, a variety of methods for CN producing from different sources has been elaborated [7]. This provides the CN availability for nanocomposites preparation in quantum satis. The most widely used methods of nanocomposites producing are as follows: solution/emulsion mixing, self-assembly, in situ polymerization, and electrospinning. The last, being a promising versatile and scalable technique allows producing polymer-based nanostructures including nanofibers varying in morphology, size
(diameter), and aspect ratios [9]. The efficiency of these methods is ensured due to the uniform distribution of CN particles in the polymer matrix and higher values of mechanical strength and electrical conductivity of the obtained nanocomposites. To enhance interaction with polymer chains for better distribution of nanofillers in the polymer matrix, functionalization of the surface of the CN particles or an addition of surfactants can be used. Yet, an excess amount of functional groups may decrease the intrinsic electrical conductivity of CN and consequently decrease the final conductivity of the nanocomposite [10]. Besides, the type of CN and their interactions with polymer matrix as well as the nanocomposites morphology exhibits a great influence on the electrical conductivity of the polymer nanocomposites [7].

Several common polymers such as polymethylmethacrylate (PMMA), polycarbonate (PC), polyimide (PI), polypropylene (PP), polystyrene (PS), polyurethane (PU), polydivinylbenzene (PVDB), and others have been used as polymer matrices. Individual types of CN and their derivatives, as well as mixtures of different CN types, were used as fillers for nanocomposites. Table 1 presents the data available in literature and concerning electrical conductivity of some polymer-based nanocomposites depending on polymer matrix, type of carbon nanofiller, way of preparation, and filler loading.

| Polymer | Filler | Fabrication technique | Filler content | Conductivity, S m\(^{-1}\) | Ref. |
|---------|--------|-----------------------|----------------|-----------------------------|------|
| PMMA    | rGO    | In-situ polymerization| 0.5–2 wt%      | 3.8×10\(^{-4}\) – 9.9×10\(^{3}\) | [11] |
| PC      | GO     | Solution mixing       | 1.09 vol%      | 4.1×10\(^{-2}\)            | [12] |
| PVA     | rGO    | Solution mixing       | 4–14 wt%       | 6.0×10\(^{-3}\) – 5.9       | [13] |
| PS      | rGO    | Self-assembly         | 0.2–0.9 vol%   | 7.0×10\(^{-7}\) – 2.0×10\(^{-2}\) | [14] |
| PI      | rGO    | In-situ polymerization| 0.5–2 wt%      | 2.1×10\(^{-11}\) – 8.5×10\(^{-9}\) | [15] |
| PS      | functionalized rGO | Solution mixing | 0.11–0.69 vol% | 1.4×10\(^{-10}\) – 9.2×10\(^{-2}\) | [16] |
| PS      | functionalized G | Solution mixing | 0.1 vol% | 13.84 | [17] |
| PI      | GNR + MWCNT | Electrospinning | 9 wt% | 8.3 | [18] |
| PS      | MWCNT | Electrospinning | 5 wt% | 5.3×10\(^{-3}\) | [19] |
| PS      | SWCNT | Electrospinning | 5 wt% | 3.7×10\(^{-2}\) | [19] |
| PMMA    | SWCNT | Solution mixing | 10 wt% | 1.7×10\(^{3}\) | [20] |
| PMMA    | SOCl\(_2\)-treated SWCNT | Solution mixing | 13 wt% | 1.0×10\(^{4}\) | [21] |
| PVDB    | Fullerene C\(_{60}\) + polyamiline | Solution mixing | 0.1–0.5 wt% | 0.35 – 47 | [21] |
| PU      | CB     | Electrospinning      | 7.87 wt% | 6.8×10\(^{5}\) | [23] |
| PMMA    | CB     | Solution mixing      | 1–10 wt%      | 1.5×10\(^{-12}\) – 2.2×10\(^{-3}\) | [24] |
| PP      | CB     | Melt mixing          | 0–5 wt%       | 1.0×10\(^{-14}\) – 1.0×10\(^{-4}\) | [25] |

As can be seen from the data presented in Table 1, one- and two-dimensional particles with a high aspect ratio, such as carbon nanotubes and graphene, seem to be the most effective nanofillers for polymer matrices. It is important to note that when using particles with a high aspect ratio (graphene, nanotubes), the percolation threshold is reached at lower concentrations of nanofiller in the polymer. As follows from Table 1, even a small loading with CNT or graphene-like nanofiller (about 1 wt%) in polymer matrix enhances electrical conductivity of the polymers.
In this work, for the first time, we studied and analyzed the effect of carbon nano-fillers with various aspect ratio (zero-, one-, and two-dimensional) on the electrical conductivity of the conjugated polymer, polyazomethine (PAZ). Thus, using a single polymer as a matrix, we can compare the effect of the carbon nano-filler type on the percolation threshold and electrical conductivity of the nanocomposites. Moreover, we can trace the change in the properties of the nanocomposites when using hybrid fillers that simultaneously combine particles of different topology: one-dimensional MWCNT and two-dimensional rGO nanoplatelets.

2. Materials and Methods

2.1. Nanocomposites preparation

For preparing nanocomposites, we used a conjugated polymer, PAZ with azobenzene side chains, as a matrix material. Its chemical structure is depicted in Figure 1. Detailed information on its synthesis and properties is available in Refs. [26,27].

As the matrix fillers, nanofillers of different dimensions: 0D (fullerene C₆₀), 1D (MWCNT), 2D (rGO), and 1D/2D hybrid (MWCNT/rGO) were chosen. Notably, electrical conductivity of the CN mentioned is quite different: for C₆₀ it is about zero, for rGO $\sigma \approx 35$ S m$^{-1}$ [28], whereas for MWCNT $\sigma = 10^7$ S m$^{-1}$ (as the producer declares).

Fullerene C₆₀ was purchased from ZAO ILIP (St. Petersburg, Russia). For obtaining rGO, we first produced GO from graphite powder (purchased from Sigma-Aldrich) following the Hummers method [5] and then GO was subjected to thermal reduction at 800 °C [28]. MWCNTs (Baytubes C150P) were purchased from Bayer Material Science. Both C₆₀ and MWCNTs were used as received. The hybrid rGO/MWCNTs nanofillers were used in the following proportion: 75:25, 50:50, and 25:75 wt%. We varied the carbon nanofillers content in the matrix up to the maximum loading $\varphi_{\max}$. The last was chosen to be close but a bit below the percolation threshold of the nanocomposites under study ($\varphi_{\max} = 2.5$ wt% for PAZ/C₆₀ [29-31], $\varphi_{\max} = 1.5$ wt% for PAZ/MWCNT [32], $\varphi_{\max} = 1.5$ wt% for PAZ/rGO [28,33], and $\varphi_{\max} = 1$ wt% for PAZ/MWCNT:rGO [34-37]).

For nanocomposites preparation, we used a solution mixing method. First, we dissolved a portion of PAZ in DMF by its sonication for 30 min at mild heating (40 °C). Then the PAZ solution was mixed with a specified quantity of nanofillers also dispersed in DMF for 30 min. For more accurate dispensing of filler amount, it was first dispersed in a solvent, and then a certain volume of the dispersion was added to the polymer solution depending on the dispersion concentration. To remove the solvent, we distillated PAZ/CN mixtures in vacuum and further dried the nanocomposites samples in vacuum at 60 °C.

For hybrid nanofiller preparation, rGO and MWCNT were first dispersed separately in dimethylforamide (DMF) and then the resulting dispersions were mixed in a certain proportions depending on their concentrations.

2.2. Nanocomposites investigation

The components of the complex dielectric permittivity, dielectric constant $\varepsilon'$ and dielectric loss $\varepsilon''$, of the nanocomposites were measured using broadband dielectric spectroscopy (BDS) technique with a
Novocontrol Alpha dielectric spectrometer (Novocontrol Technologies) in the frequency \( f \) range from \( 10^0 \) to \( 10^6 \) Hz and in the temperature \( T \) range from -150 to 170 °C (-100 to 170 °C for the PAZ/C\(_{60}\) ). Thin layers of the samples (a thickness of 50 μm) were placed in the measuring cell and subjected to alternate voltage with amplitude 1 V in nitrogen atmosphere. We derived the electrical conductivity \( \sigma \) data from the dielectric loss \( \varepsilon'' \) data using a relation

\[
\sigma(f, T) = 2\pi\varepsilon_0 f\varepsilon''(f, T)
\]

where \( \varepsilon_0 \) is the permittivity of the free space.

3. Results and discussion

3.1. General conductivity behavior

In Figure 2, electrical conductivity of the PAZ/CN nanocomposites as a function of temperature and frequency at different CN concentrations \( \phi \) is presented in 3D form. Generally, conductivity of all the PAZ/CN nanocomposites tends to increase with increasing temperature and frequency because of enhanced charge carrier mobility. When a CN concentration is low (0 – 0.5 wt.%), an increase in \( \sigma \) with increasing \( \phi \) is small. Moreover, when fullerene C\(_{60}\) is used as a filler in a concentration of up to 1%, a slight decrease in conductivity of PAZ/C\(_{60}\) nanocomposite can be recognized [31]. We believe that the uniform distribution of the zero-dimensional C\(_{60}\) nanoparticles in the polymer matrix prohibits the formation of conductive network and results in decreasing of dielectric loss in the PAZ/C\(_{60}\) nanocomposite [38]. It is manifested as a slight decrease in electrical conductivity. At the maximum C\(_{60}\) concentration (\( \phi = 2.5 \) wt%), the electrical conductivity increases significantly due to a percolation network formation. However, for other nanocomposites at high CN concentration (\( \phi > 1 \) wt.%) an increase in \( \sigma \) is noticeable. Finally, at \( \phi = \phi_{\text{max}} \) the PAZ/CN conductivity achieves a maximum value. When \( \phi \) is equal or exceeds the percolation threshold, the difference between conductivity of the PAZ/CN composites becomes minimal.

Comparing conductivity of the PAZ/CN composites family at \( \phi = \phi_{\text{max}} \), we can conclude that the PAZ/MWCNT nanocomposite exhibits a superior conductivity. This is because of strong interfacial interaction between MWCNT and the PAZ chain, which was proved with Raman spectroscopy technique [32]. Besides, interfacial interactions favor the MWCNT bundles disentanglement and prohibit their association [32,35].

The electrical conductivity of the PAZ/MWCNT nanocomposite exceeds that of PAZ for 7 orders \((1.54 \times 10^{-8} \text{ S cm}^{-1} \text{ vs. } 5.68 \times 10^{-15} \text{ S cm}^{-1}) \) at \( f = 1 \text{ Hz and } T = -150 \text{ °C and for 6 orders (1.01 \times 10^{-8} \text{ S cm}^{-1} \text{ vs. } 1.63 \times 10^{-14} \text{ S cm}^{-1}) \) at \( f = 1 \text{ Hz and } T = 20 \text{ °C} \) [36]. This is a reason, why the polymer-based composites filled with MWCNT could be treated as the most effective materials, particularly in the sense of electrical conductivity.

The PAZ/MWCNT:rGO nanocomposites demonstrate a bit reduced conductivity as compared with PAZ/MWCNT conductivity. However, hybrid MWCNT:rGO nanofiller exhibits improved particles dispersion in the polymer matrix [34-36], which is favorable for the nanocomposite application.

3.2. Conductivity components behavior

In Figure 3, frequency dependent conductivity of the PAZ/CN nanocomposites at 1% CN content is depicted at different temperatures. As generally accepted, the experimental electrical conductivity \( \sigma \) of any material should be considered as an additive characteristics constituting \( \sigma_{\text{ac}} \) (alternate current) conductivity \( \sigma_{\text{ac}} \) and \( \sigma_{\text{dc}} \) (direct current) conductivity \( \sigma_{\text{dc}} \):

\[
\sigma(f, T) = \sigma_{\text{ac}}(f, T) + \sigma_{\text{dc}}(T)
\]
As follows from eq. (2), $\sigma_{ac}$ depends on both frequency $f$ and temperature $T$, whereas $\sigma_{dc}$ depends on temperature only.

![Figure 2](image1.png)

**Figure 2.** Electrical conductivity of PAZ/CN nanocomposites with different concentrations of (a) fullerene $C_{60}$, (b) rGO, (c) MWCNT, and (d) different proportion of MWCNT:rGO hybrid nanofiller (at total concentration 1 wt.%). As a function of temperature and frequency.

Both $\sigma_{ac}$ and $\sigma_{dc}$ components of conductivity could clearly be recognized in Figure 3 for all the nanocomposites under investigation. Obviously, the $dc$ conductivity extension tends to increase with increasing temperature and at $T = 170 \degree C$ the $dc$ region spreads the frequency window from $10^3$ to $10^5$ Hz. Oppositely, at low temperatures, the $dc$ region is located mainly below frequency window available for instrumental analysis and we can recognize it only at low frequencies. This finding relates mainly to PAZ/C$_{60}$ nanocomposite. For PAZ/MWCNT nanocomposite, the $dc$ region is clearly recognized at all temperatures.

As can be seen from Figure 4, at low and moderate temperatures (-100 °C and 20 °C respectively) the $dc$ conductivity of PAZ/MWCNT nanocomposite significantly exceeds that of other nanocomposites and pristine PAZ. At high temperatures (160 °C) difference in the $dc$ conductivity of all samples becomes minimal. Moreover, as can be seen from Figure 3, PAZ/MWCNT nanocomposite exhibits the minimal variation of $dc$ conductivity depending on temperature (approximately 3 orders, from $10^{-8}$ to $10^{-5}$ S·cm$^{-1}$) in comparison with other samples.
Figure 3. Electrical conductivity of PAZ/CN nanocomposites with 1% loading of (a) fullerene C$_{60}$, (b) rGO, (c) MWCNTs, and (d) rGO:MWCNT (50:50 wt%) hybrid nanofiller as a function of frequency.

Figure 4. $dc$ conductivity of the nanocomposites containing 1% of CN at different temperatures.

We should emphasize that for PAZ/MWCNT nanocomposites particularly, the $dc$ region is coarsely rather than exactly constant because of appearance of interfacial polarization phenomenon, also known as a Maxwell-Wagner-Sillars (MWS) effect. This phenomenon is typical for nanocomposites with high CN loading and is manifested especially at high temperatures and low
frequencies. It is originated from high electrical heterogeneity between matrix and CN [39-41]. In polymer nanocomposites, the nanofiller particles are separated from each other by a thin polymer layer, which can be considered as a potential barrier for charge carriers, hindering their transfer between adjacent particles. This barrier could be overcome by charge carriers by their tunneling between adjacent conducting regions (nanofiller particles) [42].

The frequency dependence of $\sigma_{ac}$ conductivity can successfully be described with a power function:

$$\sigma_{ac} = A f^s$$

where $A$ and $s$ are the material’s characteristic constants. The power exponent $s$ was calculated for nanocomposites with maximum CN loadings as a slope of the curves depicted in Figure 3 at high frequencies. The parameter $s$ was found to decrease with increasing temperature while for a pristine PAZ this parameter remains almost unchanged (Figure 5). This finding allows suggestion that correlated barrier hopping (CBH) could be accepted as a reliable mechanism to specify $\sigma_{ac}$ behaviour of the PAZ/CN nanocomposites [29,36]. Pike [43] and Elliot [44] proposed the CBH model for explaining the ac conductivity of disordered solids. Later this model was successfully applied to polymer nanocomposites [36]. According to CBH model the power exponent $s$ may be calculated as follows:

$$s = 1 - \frac{6kT}{W_m},$$

where $W_m$ is a height of the energy barrier between localized states of charge carriers, $k$ is the Boltzmann constant.

We calculated values of the energy barrier, $W_m$, according to CBH model for all nanocomposites under study. As follows from Figure 6, $W_m$ decreases abruptly when CN are embedded into polymer matrix and its value is almost independent of CN species. A decrease in the potential barrier of PAZ/CN nanocomposites in accordance with the CBH model could be explained by either variation of the types of the transport centers or an increase in the transport centers density. It was previously shown that the temperature dependences of $\sigma_{ac}$ follow the Arrhenius equation [29,36].

![Figure 5](image1.png)  
**Figure 5.** Temperature dependences of power exponent $s$ for nanocomposites under study.

![Figure 6](image2.png)  
**Figure 6.** Activation energy $W_m$ depending on composition of nanocomposite.
4. Conclusions
Polymer-based nanocomposites containing CN were produced and their electrical conductivity was measured with BDS. As a matrix we used a conjugated polymer, PAZ. As fillers, we used CN of different dimensions to recognize the influence of their topology on nanocomposites conductivity.

We discovered that PAZ/MWCNT nanocomposite at the maximum loading $\varphi_{max}$ exhibits the highest electrical conductivity as compared with other PAZ/CN nanocomposites. Therefore 1D topology of MWCNT could be treated as the most suitable for fabrication of high-performance polymer-based nanocomposites with enhanced electrical conductivity.

Two components of conductivity, $\sigma_{ac}$ and $\sigma_{dc}$, were recognized and analysed. Both components were found to increase significantly with temperature. The frequency dependence of $dc$ conductivity was shown to be disturbed by the MWS effect, particularly for PAZ/MWCNT nanocomposites. The frequency dependence of $ac$ conductivity follows a power law, whereas its temperature dependence obeys the Arrhenius equation.

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