Electrical conductivity of polyazomethine/reduced graphene oxide nanocomposites

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Abstract. We produced nanocomposites comprised of polyazomethine and reduced graphene oxide by solution mixing. The nanofiller concentration ranged from 0.25 to 1.5 wt.%. Both neat polymer and nanocomposites samples were investigated using broadband dielectric spectrometry under the same conditions. The electrical conductivity $\sigma$ of the samples was examined as a complex value being a combination of two parameters: dc conductivity ($\sigma_{dc}$) and ac conductivity ($\sigma_{ac}$). The temperature dependences of $\sigma_{ac}$ were found to follow the Arrhenius equation, whereas the frequency dependences of $\sigma_{ac}$ were shown to obey a power law. We proposed that the correlated barrier hopping could explain behaviour of $\sigma_{ac}$ of the nanocomposites under study.

1. Introduction

Fabrication of polymer-based nanocomposites became an actual challenge of polymer science, which is determined by the engineering requirements for high performance materials. It is known that the presence of a small amount of nanofiller (a few percents or even less) in a polymer matrix can substantially improve performance characteristics of polymer-based materials [1,2].

Because of unique properties of carbon nanoparticles, they have been used extensively for the fabrication of polymer-based nanocomposites [3-5]. Graphene is known to exhibit superior physical and chemical properties. As a consequence, graphene and its derivatives seem to be effective carbon nanoparticles for creation of novel functional materials including stretchable electronic devices [6] as well as valuable nanofiller for polymer matrices [3,5,7].

The generally accepted method of graphene fabrication is graphene oxide (GO) reduction. Since GO initially contains significant amount of oxygen (in functional groups) on its surface and water residues within graphene layers, its intrinsic conductivity is quite low [5]. GO reduction decreases the amount of oxygen and removes water residues, thus enhancing its intrinsic conductivity. However, even reduced GO (rGO) often still contains oxygen-containing groups of GO, which could be favourable for chemical interaction with polymer matrix. Many conventional polymers have been used as matrices for production of nanocomposites comprising graphene or its derivatives. These nanocomposites demonstrate enhanced functional properties [5,7].

As a matrix, we chose polyazomethine. Polyazomethines are polymers exhibiting high mechanical
strength, thermal stability, film- or fiber-forming properties, and superior optical properties that specify their possible applications particularly in electronic and optical devices [8-10]. Polyazomethines are inherently insulators. Nevertheless, being filled with conductive nanoparticles, they exhibit enhanced conductivity [8].

When studying the polyazomethine/fullerene C₆₀ nanocomposites using a broadband dielectric spectroscopy (BDS), we found out an appreciable enhancing of the their electrical conductivity above C₆₀ percolation threshold (2 wt.%) [11,12]. The current study aims to fabrication of electroconductive polyazomethine/rGO nanocomposites varying in rGO loading and investigation of their electrical conductivity with BDS.

2. Materials and methods

2.1. Samples preparation

The chemical structure of the polymer which we used as a matrix for fabrication of electroconductive nanocomposites is presented in figure 1. It is polyazomethine (PAZ) with azobenzene side chains. Comprehensive information about its synthesis and principal characteristics can be found in [10,13]. GO was produced from graphite powder using a Hummers method [5]. Subsequently water dispersion of GO was used as a raw material for the rGO production.

![Figure 1. Chemical structure of PAZ.](image)

According to [14], we obtained rGO through thermal annealing of dried GO at high temperature. To prepare nanocomposites, we used the solution mixing method. For every sample we first prepared a PAZ solution in dimethylformamide (DMF) and mixed it with specified volume of rGO (similarly dispersed in DMF) to provide necessary rGO loading in nanocomposite. For effective elimination of solvent, we subjected the mixture to distillation in vacuum. Moreover, a continuous vacuum drying of the nanocomposites samples at 60°C was applied. Following this way, a set of PAZ/rGO nanocomposites samples varied in rGO concentration (0.25, 0.5 and 1.5 wt%) were produced for further research.

2.2. Broadband dielectric spectroscopy

Complex dielectric permittivity ε∗ of the nanocomposites was measured using a Novocontrol Alpha dielectric spectrometer (Novocontrol Technologies, Germany) in wide ranges of frequency (10⁰ – 10⁶ Hz) and temperature (-100 – 170°C). The temperature control accuracy was provided by using a Quatro cryosystem (Novocontrol Technologies, Germany). The samples under study were placed in the measuring cell where they were subjected to alternate voltage with amplitude 1 V in an inert (nitrogen) atmosphere. We collected and analyzed the results performed at sequential cooling of the measuring cell with a sample from 170°C to -150°C. For BDS measurements we used the nanocomposite samples in the form of thin layers with a thickness of 50 μm.

The dielectric loss ε” and electrical conductivity σ are known to be interrelated [15]:

$$\sigma(f, T) = 2\pi\varepsilon_0 f\varepsilon''(f, T)$$  \hspace{1cm} (1)

where ε₀ is the permittivity of the free space and ε″ is the imaginary part of the complex dielectric permittivity ε∗ = ε' - iε″.
3. Results and discussion

3.1. General conductivity behavior
Figure 2 demonstrates the electrical conductivity of the PAZ/rGO nanocomposites at different rGO concentration (\(\phi\)) depending on both temperature and frequency. At a low rGO concentration (0 – 0.5 wt.%), \(\sigma\) slightly increases with increasing \(\phi\). Nevertheless, higher rGO concentrations (\(\phi = 1.5\) wt.%) contribute to a more noticeable increase in \(\sigma\). The nanocomposite with \(\phi = 1.5\) wt.% exhibits the most significant \(\sigma\) growth. Anyway, electrical conductivity of the nanocomposites tends to increase with increasing both temperature and frequency.

![Figure 2. 3D representation of the electrical conductivity of the PAZ/rGO nanocomposites with different rGO concentration depending on both temperature and frequency.](image)

According to [15], we presented the measured electrical conductivity \(\sigma\) as an additive parameter comprising \(ac\) (alternate current) conductivity (\(\sigma_{ac}\)) and \(dc\) (direct current) conductivity (\(\sigma_{dc}\)):

\[
\sigma(f, T) = \sigma_{ac}(f, T) + \sigma_{dc}(T)
\]

We should emphasize that \(\sigma_{ac}\) depends on both frequency \(f\) and temperature \(T\), while \(\sigma_{dc}\) depends on temperature solely. Further the frequency and temperature dependences of conductivity and its components of the PAZ/rGO nanocomposites at different rGO concentration will be considered.

3.2. Electrical conductivity depending on frequency
Figure 3 depicts variation of the PAZ/rGO nanocomposites conductivity depending on frequency. It is clear that two components of electrical conductivity could clearly be recognized in accordance with equation (2): \(\sigma_{dc}\) and \(\sigma_{ac}\).

Obviously we can estimate the \(dc\) conductivity for investigated nanocomposites using figure 3 only at rather high temperatures (above 100°C) except nanocomposite with \(\phi = 1.5\) wt.% which exhibits \(dc\) conductivity in the whole temperature range. Consequently figure 4 shows variation of \(\sigma_{dc}\) with temperature in the range from 100°C to 170°C. Hereby, \(dc\) conductivity of all the nanocomposites tends to increase with increasing temperature. Apparently, the presence of rGO in small quantities (0.25 – 0.5 wt.%) increases \(\sigma_{dc}\) slightly because these amounts of rGO nanoparticles are not enough to form an extensive conductive network through the whole sample [16]. As the content of rGO becomes higher, \(\sigma_{dc}\) increases substantially as far as a percolation network of rGO nanoparticles is formed.
Below we will analyze variation of $\sigma_{ac}$ with frequency. As follows from figure 3, $\sigma_{ac}$ increases dramatically with increasing frequency presumably following to a power law [17]:

$$\sigma_{ac} = Af^{s}$$

where $A$ and $s$ are characteristic constants of material. Further we will analyze parameter $s$ as a function of temperature to clarify the mechanism of dielectric relaxation. In literature, two principal mechanisms of dielectric relaxation in solids are discussed. One mechanism is the quantum tunneling of either electrons or polarons through the barriers separating localized states. Another mechanism is electron hopping over the same barriers. Pike [18] modified the second mechanism and suggested the correlated barrier hopping (CBH) mechanism. Particularly he interpreted behaviour of $ac$ conductivity of disordered solids. Following Pike's model, the parameter $s$ in equation (3) could be presented as follows [19,20]:

**Figure 3.** Conductivity of exemplary PAZ/rGO nanocomposites with different rGO content ((a) $\phi = 0$, (b) $\phi = 0.5$ wt.%, and (c) $\phi = 1.5$ wt.%) vs. frequency. Dash-dot lines depict the conditional boundaries between $\sigma_{dc}$ and $\sigma_{ac}$.

**Figure 4.** $dc$ Conductivity of PAZ/rGO nanocomposites with different rGO loading vs. temperature.

**Figure 5.** Power exponent $s$ computed with equation (4) vs. absolute temperature.
\[ s = 1 - \frac{6kT}{W_m} \]  \hspace{1cm} (4)

where \( W_m \) is a height of the potential barrier between localized states to be overcome by the charge carrier. Reliability of equation (4) has been confirmed for polymers and polymer nanocomposites [19-21].

As follows from figure 5, the \( s \) parameter for all the samples (except neat polymer) goes down with increasing temperature rather in a linear manner, that is equation (4) is valid for the nanocomposites basically but neat polymer does not follow it. Therefore we can conclude that \( ac \) conductivity of the PAZ/rGO nanocomposites follows the CBH model. The energetic parameter of the CBH process, \( W_m \), was calculated for all the nanocomposites. Its values are listed in the box within figure 5. It is clear that rGO concentration in nanocomposites does not influence the \( W_m \) value.

3.3. Electrical conductivity depending on temperature

Figure 6 represents conductivity of the PAZ/rGO nanocomposites depending on reciprocal temperature. In the region of low and medium temperatures, the conductivity becomes actually the \( ac \) conductivity (\( \sigma = \sigma_{ac} \)). The growth of frequency rather than the growth of the temperature causes a more significant increase in \( ac \) conductivity. However, in the region of glass transition \( \sigma_{ac} \) grows intensively and achieves a maximum value. Above the glass transition temperature, \( \sigma \) becomes in fact equal to \( \sigma_{dc} \) (\( \sigma = \sigma_{dc} \)). As follows from figure 6, \( \sigma_{dc} \) is a frequency independent parameter.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Electrical conductivity vs. reciprocal temperature for exemplary PAZ/rGO nanocomposites with different rGO concentration (a) \( \phi = 0 \), (b) \( \phi = 0.5 \) wt.% and (c) \( \phi = 1.5 \) wt.%) at selected frequencies. Dash-dot lines depict the conditional boundaries between \( \sigma_{dc} \) and \( \sigma_{ac} \).}
\end{figure}

Since \( ac \) conductivity is a thermally activated process, it should follow the Arrhenius equation:

\[ \sigma_{ac} = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \]  \hspace{1cm} (5)

where \( E_a \) is the activation energy of the charge carriers, \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature.

Using figure 6 and equation (5), we computed the \( E_a \) values. The activation energy as a function of frequency is presented in figure 7. It is clear that \( E_a \) decreases with increasing frequency. Such a tendency in activation energy indicates an increase in probability of the electron jumps between the atom sites [22]. Besides, \( E_a \) decreases with increasing rGO content. This finding explains an increase
in $\sigma_{ac}$ with increasing nanofiller concentration.

![Figure 7. Activation energy of ac conductivity of PAZ/rGO nanocomposites with different rGO loading vs. frequency.](image)

4. Conclusions

The PAZ/rGO nanocomposites with different rGO content were prepared. Their electrical conductivity was investigated with BDS. Two components of conductivity, $\sigma_{dc}$ and $\sigma_{ac}$, were distinguished. We studied $\sigma_{dc}$ depending on temperature exclusively, whereas $\sigma_{ac}$ was analyzed depending on both temperature and frequency. It was shown that at small quantities (0.25 – 0.5 wt.%) of rGO, $\sigma_{dc}$ increases slightly because these amounts of rGO nanoparticles are not enough to form an extensive conductive network [16]. When the content of rGO becomes higher (> 0.5 wt.%), $\sigma_{dc}$ increases intensively due to percolation network formation. The percolation threshold of the PAZ/rGO nanocomposite ($\varphi \approx 1.5$ wt.%), was found to be lower as compared with that of PAZ/C$_{60}$ nanocomposite ($\varphi \approx 2$ wt.%) [11,12]. Summing up, we concluded that two-dimensional anisotropic rGO nanoparticles are more suitable for enhancing the electrical conductivity of polymers as compared with isotropic nanoparticles of fullerene C$_{60}$. We successfully described the temperature and frequency dependences of $\sigma_{ac}$ using the Arrhenius equation and a power function, respectively. The exponent $s$ in the power function was shown to decrease with increasing temperature. These data allowed us to suggest that the correlated barrier hopping is an appropriate mechanism for explaining the $\sigma_{ac}$ behaviour of the PAZ/rGO nanocomposites.

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