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MODELING OF ELECTRICAL CONDUCTIVITY OF GRAPHENE-BASED POLYMER NANOCOMPOSITES

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Abstract: The use of nanocomposite materials has led to progress in the creation of new electronic devices (minitransistors, sensors, micro-drives, which are used to build artificial muscles, and supercapacitors. Nanocomposites occupy a special place with magnetosensitive fillers, particularly successfully used in medicine. Nanocomposites are also used for a protective coating. Depending on the operational functions, achieving a specific conductivity value and its change with temperature is necessary for such a coating. In the work, a conductivity model of polymer nanocomposites based on graphene (Gr/PS) was obtained using experimental data. The largest relative deviation between the conductivity surface and experimental data does not exceed 9.5%. The expression was obtained for the graphene concentration 1 < C(Gr) < 30 wt % and the temperature range 20 < T < 100 °C. The dependence of the specific electrical conductivity on the filler concentration and temperature obtained in the work will allow the researchers to select a nanocomposite with the required conductivity and evaluate the temperature effects on it for the conditions to which the material will be exposed.

Keywords: polymer nanocomposites based on graphene, nanocomposite conductivity, mathematical model of conductivity.

1. Introduction

The creation and use of nanocomposites today means a new step in the search for materials with the desired predetermined properties. In particular, nanostructured polyaniline, the synthesis of which is described in [1], is used for the manufacture of various electronic devices: mini-transistors [2], sensors [3,4], microdrives used to build artificial muscles [5], supercapacitors [6,7], anti-corrosion coatings [8]. A special place is occupied by nanocomposites with magnetosensitive fillers, which are of particular importance in medicine: recognition of biological formations in biological media, the target delivery of drugs to biological sites, adsorption of cell decomposition residues and their removal from the body due to the application of a magnetic field [9, 10].

In [11], an experimental study of the specific electrical conductivity of polymeric nanocomposites based on graphene was carried out. Such materials are used for protective coatings against electromagnetic irradiation and must have certain conductivity values to remove the statistical charge. In polymers, certain conductivity values are achieved by the introduction of conductive filler nanoparticles into a dielectric polymer material. In particular, in [12], a polymer nanocomposite with soot is considered, the introduction of which distorts the technological qualities of the material. A number of works, in particular [13], are devoted to the use of single- and multi-walled carbon nanotubes as a filler, but the cost of such material remains high. Technologically, the use of graphene has an advantage [14] due to the fact that this nanomaterial is obtained from inexpensive graphite by simple chemical processing.

Regarding the conductivity of Gr/PS, we find a certain discrepancy in data provided in the literature. In particular, [14] shows a change in conductivity by 9 orders of magnitude (from 10-8 to 10 C/sm). In [11], a 740-fold change (at 20 °C) is declared: from 0.128 to 95 C/sm. The dependence of the specific electrical conductivity on the concentration of the filler and on the temperature obtained in the work will allow experimenters to choose a nanocomposite with the required conductivity and to evaluate temperature effects on it for the conditions to which the material will be exposed.

2. Dependence of Gr/PS conductivity on filler concentration and temperature

In this paper, a model of the conductivity of polymeric nanocomposites based on graphene as a function of graphene concentration and temperature was created, in which experimental data from Fig. 3 [11] were used. Fig.3 [11] shows that

- Gr/PS conductivity slightly changes at low concentrations (up to 20 wt%);
- Even a small introduction of graphene (1 wt. %) leads to the formation of a percolation network, whose creation was proved by atomic force microscopy;
- Temperature change has little influence on the specific conductivity of the nanocomposite at filler concentration up to 20 wt. %;

− Nanocomposites with a concentration of 30 wt % were considered to be the most sensitive to temperature.

In [11], electrical conductivity was measured for concentrations: 1, 10, 20, 30 mass % and at temperatures of 20, 30, 50, 70, 100 °C. The shown dependence of conductivity on Gr concentrations for different temperatures (Fig. 3 in [11]) visually resembles a parabola. At zero concentration of the filler, the conductivity is considered equal to 0. Therefore, we carried out a linear decomposition of the conductivity function into polynomials up to the 3rd order without a free term.

$$\sigma(C)=\sum_{k=1}^{3}a(k)C^{k}\,. \qquad (1)$$

The obtained coefficient values are shown in Table 1.

Fig. 1 displays the obtained function of conductivity versus concentration, where experimental data are indicated by dots

Table 1

Coefficients of the linear decomposition of the conductivity function into polynomials of the third order for different temperatures

T (^{0}C)	20	30	50	70	100
Coef. $\begin{pmatrix} a(1) \\ a(2) \\ a(3) \end{pmatrix}$	$\begin{pmatrix} 6,791 \\ -1,303 \\ 0,053 \end{pmatrix}$	$\begin{pmatrix} 5,093 \\ -1,084 \\ 0,045 \end{pmatrix}$	$\begin{pmatrix} 3,071 \\ -0,738 \\ 0,032 \end{pmatrix}$	$\begin{pmatrix} 1,238 \\ -0,455 \\ 0,021 \end{pmatrix}$	$\begin{pmatrix} -0,554 \\ -0,161 \\ 0,00966 \end{pmatrix}$

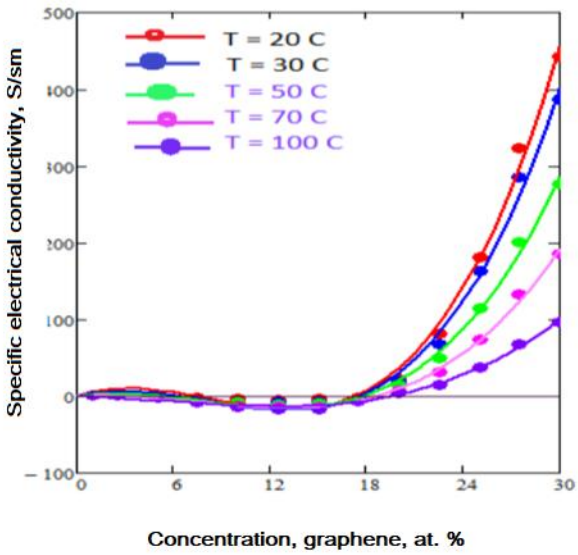

Fig. 1. Dependence of the specific electrical conductivity of Gr/PS on the concentration of graphene for different temperatures. Solid lines show the obtained functions, points correspond to the results of the experiment in [11].

As it can be seen from Fig.1, interpolation of conductivity by third-order polynomials describes the functional dependences for different temperatures satisfactorily. At low graphene concentrations, small values of negative conductivity are observed, inherent in nanocomposites even with a composition of 1 wt. %, which indirectly indicates the formation of a percolation network even at low concentrations. The presence of negative conductivity for all nanocomposites at low concentrations for all analyzed temperatures can be explained by the peculiarity of the electronic spectrum in graphene, which does not contain a forbidden band. It is important that our simulation and the obtained dependences reflect all these features: weak dependence on temperature and negative values of the specific conductivity at low concentrations and the subsequent rapid increase in the specific heat capacity with increasing concentration for all analyzed temperatures. Let us analyze the change in the decomposition coefficients (1) with increasing temperature, shown in Fig.2.

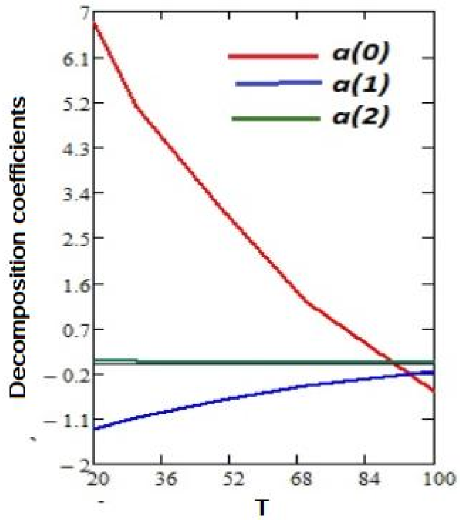

Fig. 2. Temperature dependence of decomposition coefficients obtained using the equation (1)

As we can observe, the coefficients of linear dependence are the most significant and most havily depend on temperature. The coefficients of quadratic dependence are small and always negative. These coefficients are characterized by inverse dependencies: the first coefficient decreases with increasing temperature until it reaches negative values at high temperatures (red line in Fig.2). The coefficients of the quadratic dependence acquire only negative values, increasing with increasing temperature. The coefficients in cubic dependence are practically independent of the temperature and their absolute value is very small. All our dependences are monotonic functions with small deviations from linearity. Therefore, to describe the dependence of the coefficients on temperature, we performed linear interpolation by second-order polynomials.

$$a(i,T)=\sum_{j=0}^{2}a(i,j)T^{j} \qquad (2)$$

The obtained values of the coefficients are given in Table 2.

Table 2

Coefficients of decomposition (2), for describing the temperature dependence of specific conductivity

a(0,j)	a(1,j)	a(2,j)
$\begin{pmatrix} 9,732 \\ -0,167 \\ 0,00064 \end{pmatrix}$	$\begin{pmatrix} -0,761 \\ 0,025 \\ -0,00009 \end{pmatrix}$	$\begin{pmatrix} 0,07 \\ -0,00094 \\ 0,0000033 \end{pmatrix}$

3. Results and discussion

Fig. 3 shows the surface of specific conductivity of nanocomposites with graphene content depending on the filler concentration and temperature. The surface is described by equation (3) with the coefficients given in Table 2.

$$\sigma(C,T)=\sum_{k=1}^{3}\left(\sum_{j=0}^{2}a(k,j)T^{j}\right)C^{k} \qquad (3)$$

Separate points indicate the experimental values of the specific conductivity of nanocomposites obtained experimentally in [11]. Bright red dots correspond to data that are in front of/on the surface, dim dots - values that are behind the surface.

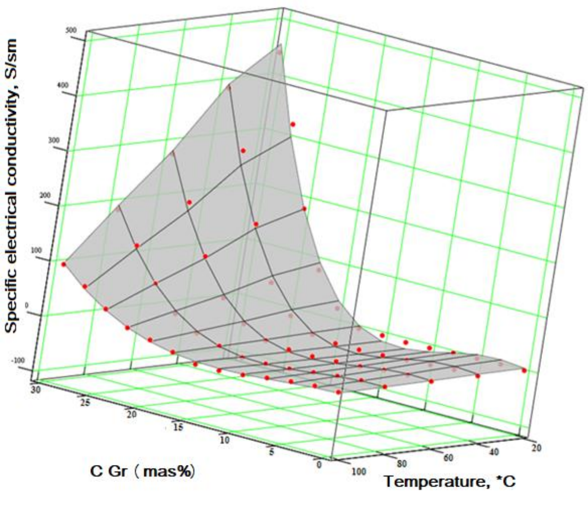

Fig. 3. The conductivity surface described by expression (3).

The largest relative deviation of calculated and experimental values does not exceed 9.5%. As it can be seen, the provided surface reflects all features obtained experimentally. At low concentrations, a weak dependence on temperature and concentration can be observed. There are regions of negative specific conductivity, and there is a rapid increase in conductivity with temperature for nanocomposites with a graphene concentration higher than 20 wt. %. The highest conductivity values characterise nanocomposites with 30 wt. % of graphene at 100 ^{0}C. The experimental values obtained in [11] are shown by dots in Fig. 3. As we can see from Fig. 3, the points do not significantly deviate from the obtained surface, which indicates the closeness of the compared calculated and experimental values. It should be noted that the resulting model is designed for the following constraints:

1. 1< C(Gr) < 30 (wt.%)
2. 2. 0 °C < T < 100 °C.

4. Conclusions

In this work, a simple model of the conductivity dependence of graphene nanocomposite on filler concentration and temperature is obtained. The model is valid for the region: 1 < C(Gr) < 30 wt. %; 20 < T < 100 °C. The relative deviation of the calculated and experimental values does not exceed 9.5 %. The simplicity of the model is an attractive option for estimating the filler content and operating temperatures of the material based on its desired specific conductivity.

5. Literature

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МОДЕЛЮВАННЯ ЕЛЕКТРОПРОВІДНОСТІ ПОЛІМЕРНИХ НАНОКОМПОЗИТІВ НА ОСНОВІ ҐРАФЕНУ

Корнелія Товстюк

Використання нанокомпозитних матеріалів привело поступу у створенні нових електронних пристроїв (мінітранзисторів, сенсорів, мікроприводів, які використовують для побудови штучних м`язів, надконденсаторів. Особливе місце посідають нанокомпозити з магнеточутливими наповнювачами, які особливо успішно використовують в медицині. Нанокомпозити також використовують для захисного покриття. До такого покриття, залежно від функціональних функцій, виникає потреба досягнення певного значення провідності та її зміни з температурою. В роботі отримано модель провідності полімерних нанокомпозитів на основі графену (Gr/PS), на основі експериментальних даних. Найбільше відносне відхилення між поверхнею провідності та даними експерименту не перевищує 9,5 %. Вираз отриманий для концентрації графену $1 < C(Gr) < 30$ мас. % та інтервалу температур $20 < T < 100\ ^{0}$ C. Отримана в роботі залежність питомої електропровідності від концентрації наповнювача та від температури дозволить експериментаторам підібріти нанокомпозит із потрібною провідністю і оцінити температурні впливи на неї для умов, в яких буде знаходитися матеріал.

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