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AFM-based model of percolation in graphene-based polymer nanocomposites

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ABSTRACT

Here, we show that a prediction of conductivity in composites can be improved by replacing fitting parameters of the percolation models by information on composite's microstructure. The methodology was demonstrated on the modified McCullough's structure-oriented model combined with current maps obtained by Conductive Atomic Force Microscopy (CA-AFM). The approach was tested on nanocomposites with graphene nanoplatelets (GNPs/PS) and proved to be coherent with experimental conductivity measurements and able to predict a percolation threshold. For the composite GNPs/PS both experimental and calculated percolation thresholds are approximately equal to 0.9 wt.% of GNPs. The model can be used for a prediction of conductivity of different kinds of conductive–dielectric composites.

1. Introduction

Polymer composites have been used industrially for over 110 years [1]. The discovery of graphene [2,3], a light, stiff material with the unique conductive properties, gave a rise to a novel class of materials – polymer nanocomposites with graphene [4,5]. Graphene nanoplatelets (GNPs) are thin nanodisks with high aspect ratio consisting of up to 10 graphene monolayers stacked together [6,7]. The morphology of nanoplatelets allows the platelets to provide barrier properties efficiently, while their pure graphitic composition makes them excellent electrical and thermal conductors. Such composites have a tunable conductivity level in the range of 10^{-11}–10^{2} S/m and, as a result, can find different applications, for example as antistatic coatings [5,8,9].

At a certain loading of graphene the electrical conductivity of nanocomposites with graphene nanoplatelets (GNPs-NC) drastically grows up to thirteen orders of magnitude. This loading is called a percolation threshold, graphene in this case is a filler and a polymer is a matrix [10–12]. The percolation threshold is an indicator of quality and fine functionality of a composite. It should be as low as possible in order to reduce the use of graphene and reproducible in order to obtain the composite with a desired functionality. Nowadays, the lowest percolation thresholds for GNPs-NC are less than 0.5 wt.% and reach 0.1 wt.% [13]. The most important parameters influencing the percolation threshold are dispersion, a shape of the filler, physicochemical interactions between the matrix and the filler and a method used to obtain the composite. As there are so many parameters, the prediction of the conductive properties is critical.

Various models were proposed to predict the conductive behavior of composites. These models consider different assumptions and can be classified as statistical [10,14,15], thermodynamic [16–18] and structure-oriented [19]. The most conforming class of models is structure-oriented [19]. These models consider a microstructure of nanocomposites before or after the final processing. However, at the time they were developed the methods allowing realistic description of the composite's microstructure did not exist. Therefore, in the models mentioned above the composite's microstructure is replaced by fitting parameters.

Atomic force microscopy (AFM) became a powerful tool of investigation the morphology and electro physical properties of nanocomposites. In this study we propose a method allowing replacement the empirical fitting parameters by the information about the real morphology of the composite obtained with AFM. The method is demonstrated on the McCullough's structure oriented model [19].

2. The McCullough's model

In the McCullough's model [19] a microstructure of the composite and an orientation of the filler particles inside the composite are

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assumed to change with the concentration. Below the percolation threshold the filler particles aggregate in chains. The aspect ratio of the chains depends on a shape and a concentration of the filler in the composite. It is assumed that after the percolation threshold all smaller chains are connected in a conducting network. The formation of the chains is statistical in nature. Therefore, a distribution of chains' lengths will occur. The distribution can be described by a probability density function $n(v_f, a)$ resulting in a distribution of an effective aspect ratio a for a specified volume fraction v_f of the filler. Thus, the average value of the chain parameter $\langle\lambda\rangle$ is given by [19]:

$$\langle\lambda\rangle = \int_1^\infty n(v_f, a)\lambda(a)da, \tag{1}$$

where $\int_1^\infty n(v_f, a)\lambda(a)da = 1$ and $\lambda(a)$ is a chain parameter, depending on a filler shape. For the filler particles with an aspect ratio a exceeding 1, the chain parameter can be found as [19]:

$$\lambda(a) = 1 - A^2\left(1 - 0.5\left(A - A^{-1}\right)\ln\left(\frac{A+1}{A-1}\right)\right), \tag{2}$$

where $A^2 = \frac{a}{1-a^2}$.

The distribution $n(v_f, a)$, and hence $\langle\lambda\rangle$, is a function of concentration v_f. The final equation for the isotropic distribution of the filler particles appears as [19]:

$$\frac{\sigma_m}{\sigma} = \frac{v_m^2(1-\langle\lambda\rangle)}{V_m} + \frac{\sigma_m}{\sigma_f}\cdot v_f \cdot \frac{V_m^2 + v_m(1+V_m)\langle\lambda\rangle}{V_m^2}, \tag{3}$$

where $\frac{\sigma_m}{\sigma_f} << 1, \quad V_m = (1-\langle\lambda\rangle)v_m + \langle\lambda\rangle v_f$,

σ_m, σ_f, σ-electrical conductivities of the matrix, the filler and the composite respectively; v_f, v_m-volume fractions of the filler and the matrix. The complete characterization of $n(v_f, a)$ and the subsequent evaluation for $\langle\lambda\rangle$ is a tedious experimental task. However, λ and its average $\langle\lambda\rangle$ might be chosen as fitting parameters through the assumed aspect chain ratio a. An avoiding real microstructure of the composite brings a limitation to the model and a semi-empirical character of the Eq. (3). We have developed the technique of extracting the value for $\langle\lambda\rangle$ from the AFM-obtained data on composite's microstructure. The technique is demonstrated for the composite with polystyrene and graphene nanoplatelets (GNPs/PS).

3. A modification of the percolation model

A calculation of the chain parameter $\langle\lambda\rangle$ for ideal filler shapes (spheres, disks, ropes) according to the equations proposed in [19] allows to substitute $\langle\lambda\rangle$ by:

$$\langle\lambda\rangle \cong \lambda(\langle\grave{a}^2\rangle), \tag{4}$$

where $\langle\grave{a}^2\rangle$ – a mean-square value of the aspect ratio a of the conductive chain.

If the data on two-dimensional chain distribution is obtained (as it is possible with AFM in CA-AFM mode) the value of $\langle\grave{a}^2\rangle$ may be found as:

$$\langle\grave{a}^2\rangle = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{l_i}{d_i}\right)^2 = \left(\frac{\langle l\rangle}{\langle d\rangle}\right)^2 \tag{5}$$

where n – the number of conductive chains; l_i – the length of the ith chain; d_i – the diameter of the ith chain; $\langle l\rangle$ and $\langle d\rangle$ – the average length and diameter of the chain.

The evaluation of the right part of the Eq. (3) for the GNPs/PS composite shows that due to the low electrical conductivity of the matrix (10^{-9} S/m) and high conductivity of the filler (10^4 S/m), the first term is 5–7 orders of magnitude larger. Therefore, the Eq. (3) for the chosen type of nanocomposite can be reduced to:

$$\frac{\sigma_m}{\sigma} = \frac{v_m^2(1-\langle\lambda\rangle)}{V_m}, \tag{6}$$

where $\langle\lambda\rangle$ is described by Eqs. (4) and (5).

The density of the composite can be found as a sum of densities of the filler and the matrix taken according to their volume fractions:

$$\rho = \rho_f v_f + \rho_m(1-v_f), \tag{7}$$

where ρ – specific density of the composite, kg/m^3; ρ_f – specific density of the filler, kg/m^3; ρ_m – specific density of the matrix, kg/m^3.

When one uses GNPs as a filler, the resulting composite contains micro- and nanopores, influencing the bulk conductivity of the composite. We propose to consider the pores by using an apparent density ρ_{ap} connected with the specific density through the pores coefficient:

$$K_p = \rho_f/\rho_{ap}. \tag{8}$$

Assuming that the composites are produced by a reproducible technology (i.e. latex technology [20]) the K_p can be calculated only once from the measured properties of the produced nanocomposite and used for the conductivity prediction afterwards.

Then, Eq. (7) can be transformed to:

$$\rho = \rho_f v_f/K_p + \rho_m(1-v_f). \tag{9}$$

The coefficient K_p depends on geometry of the filler and on the technology of the composite's production. The value of ρ_{ap} can be defined experimentally if the sample's mass m, the volume V and the filler loading w are known

$$\frac{\rho_f}{K_p} = \frac{m\cdot w}{V - \frac{m(1-w)}{\rho_m}}. \tag{10}$$

From the Eq. (7) the volume fraction of the filler can be calculated as:

$$v_f = \frac{\rho - \rho_m}{\frac{\rho_f}{K_p} - \rho_m}. \tag{11}$$

Usually the loading of the filler in composites is expressed as a weight fraction (wt.%), therefore it is useful to change the volume fractions to weight fractions:

$$G = v_f/w_f, \tag{12}$$

where G – can be calculated by combining Eqs. (11) and (12).

$$\frac{\sigma_m}{\sigma} = \frac{G^2(1-w_f)^2(1-\langle\lambda\rangle)}{V_m}, \tag{13}$$

$$V_m = (1-\langle\lambda\rangle)G(1-w_f) + \langle\lambda\rangle G w_f, \tag{14}$$

the Eqs. (13) and (14) describe a conductivity behavior vs. filler loading. To solve these equations such known material properties and experimental parameters as the weight fraction of the filler w_f the mass of the sample m, the pores coefficient K_p, the specific density of the filler ρ_f, and the specific density of the matrix ρ_m should be used in a combination with the average chain parameter $\langle\lambda\rangle$.

4. AFM-based technique of $\langle\lambda\rangle$ evaluation

In order to obtain a value of $\langle\grave{a}^2\rangle$ and $\langle\lambda\rangle$ a technique based on analysis of an AFM-image obtained in the CA-AFM mode [23] was developed. A standard CA-AFM image should be imported to a software allowing for a statistical analysis. In the current experiment the scanning was performed with a probe station Ntegra Vita (NT-MDT, Russia) which goes together with Image Analysis