Sensing characteristic of GPCs induced by sliding of graphene flakes

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Abstract. The main aim of this paper is to investigate the effect of slide between overlapped graphene flakes on the sensing characteristic of graphene-based polymer composites (GPCs). During deformation process of GPCs, the position of the graphene flakes can be determined by using an affine transformation. The analytical solution is obtained based on the equivalent resistance formulas of series and parallel circuits. Meanwhile, the numerical simulation is also conducted through the finite element method (FEM). In addition, the consistence between the analytical solution and numerical result are proved by a simple model consisted of two-layer graphene flakes. The result shows that the gauge factor (GF) of the sensor is related to both the initial resistance and the length of the graphene flakes: the GF of the sensor decreases with the increase of the initial resistance, while the effect of the length of graphene flakes is less. Moreover, the pre-stretched GPCs have a larger sensing range which can improve the usability of the sensor.

Keywords: graphene-based polymer composites; piezoresistivity; FEM

1. Introduction

GPCs have recently attracted tremendous attention because of their excellent piezoresistivity and flexibility [1, 2]. Many researches have been conducted to investigate the preparation technology and sensing performance of GPCs fibers [3, 4], thin films [5, 6] and foams/aerogels [7]. These studies are mainly focus on innovating or improving the preparation methods in order to achieve massive and commercial production. The sensing mechanism of GPCs can only be inferred from experimental phenomena and results due to the limitations of the methods of observation and measurement.

The piezoresistivity of GPCs prepared by stacking graphene flakes onto the polymer substrate layer by layer depend on the following three factors [2, 8, 9]: (i) The slide of graphene flakes: due to the weak interfacial binding capacity between graphene flakes and the large stiffness mismatch between graphene flakes and stretchable substrate, graphene flakes will slide under an small mechanical strain. When GPC is stretched, the overlapped area between different graphene flakes decreases due to the horizontal slide of graphene flakes, thus the length of electron-migration path increase. (ii) Disconnection of graphene flakes and the crack within the graphene film: As the strain increase continuously, some overlapped graphene flakes disconnect or cracks within the film initiate and propagate, which reduce the number of electron-migration paths. (iii) The tunneling effects: An electron can migrate across the cut-off distance (i.e., 1 nm) between adjacent graphene flakes because of tunneling effects. Because graphene flakes are stacked randomly upon the substrate, all the three factors will affect the conductivity of the sensor simultaneously during the deformation process of GPCs.
Modeling and simulation based on the characteristics of GPCs can deeply understand the sensing mechanism and evaluate the contribution of various factors. Liu et al. [10] derived the relative resistance-strain relationship by only considering the contribution of contact resistance in the flake-flake junctions at small strains. To investigate the effect of the crack on the sensing characteristic, Li et al. [11] developed a program which can solve the equivalent resistor network and output the resistance. Hempel et al. [5] and Tian et al. [12] studied the piezoresistive behavior by simulating the percolation of current through a network of randomly positioned circular graphene flakes with a uniform size distribution. In addition, some researches were conducted to the contribution of the tunneling effect. Zhao et al. [13] explained the piezoresistive characteristics of nanographene films by a charge tunneling model. Oskouyi el al. [14] investigated the conductivity and piezoresistivity of graphene flakes composites based on the percolation theory and Monte Carlo method. Under the large strain, it is demonstrated that the sensors have a high sensitivity because the disconnection of graphene flakes, the generation and propagation of cracks and the tunneling effect play a dominant role in GPCs [5, 15, 16]. However, their relative resistance as a function of strain is usually non-linear which is only suitable for qualitative analysis. When the slide of graphene flakes plays a dominant role under a small strain, the relative resistance as a function of strain is linear [9, 10], which is convenient for quantitative evaluation. Thus it's more worth to study the sensing characters of GPCs under the effect of the slide of graphene flakes.

In this paper, a simulation model is established to investigate the effect of the slide of graphene flakes on the sensing characteristic of the GPC. The inherent resistance of graphene flakes is considered while the contact resistance is ignored. The analytical solution and numerical simulation result of GF during deformation of GPCs are obtained by using the equivalent resistance network and FEM, respectively. In addition, the effect of the initial resistance and the size of graphene flakes on the sensitivity of GPCs are investigated. Finally, the piezoresistive behavior of GPCs with a pre-stretched treatment is also explored in the present work.

2. A 2D model of GPCs with sliding graphene flakes

GPCs are composed of a few layers of stacked graphene flakes and a polymer substrate, as shown in Figure 1 [12]. The Young's modulus of graphene is 10^6 times higher than that of the polymer substrate [11], therefore, the graphene flakes are considered as rigid body during the present work. When a mechanical strain is applied on GPCs, the slide of overlapped flakes occurred because of the weak interfacial binding capacity between graphene flakes and the large stiffness mismatch between graphene flakes and the polymer substrate, as shown in Figure 2 [4, 10]. \( l_0 \) and \( s \) denote the effective initial length of GPCs and the thickness of the graphene flakes, respectively. Besides, the width of the graphene flakes is set to a unit length. Figure 3 shows the 2D model of GPCs sensor established by alternately stacking equal-size graphene flake. It should be noted that only the slide of the overlapped graphene flakes are considered while the other factors are ignored in the present work.

During the deformation process, the y coordinates of each graphene flakes keep unchanged while the x coordinates is calculated by the affine transformation formula:

\[
x'_i = x'_0 (1 + \varepsilon)
\]

where \( x'_0 \) is the initial center coordinates of \( i \)th graphene flake, \( x'_i \) is the center coordinates of \( i \)th graphene flake after deformation, \( \varepsilon \) is the applied strain on the model. Figure 4 shows the deformed configuration of each graphene flake in GPCs.

![Figure 1. Cross-sectional view of graphene film [17].](image)
Figure 2. (a) SEM image of an rGO-l-hair fiber in its initial state. (b) SEM image of an rGO-l-hair fiber after stretching to crack [4].

Figure 3. Initial configuration of the GPC model.

Figure 4. Deformed configuration of the GPC model.

The total resistance of the GPC model includes the inherent resistance of graphene flakes and the contact resistance between graphene flakes. To prevent the separation between graphene flakes and the polymer substrate during deformation, graphene is usually encapsulated by polymer. Instead of a perfect two-dimensional flat film, the soft graphene has many micro-wrinkles on its surface [17]. Therefore, there are many contact points between different graphene flakes. The contact resistance between graphene flakes is very small according to Holm Contact Resistance Model. Although the resistivity perpendicular to the crystal layers of graphite is about 150 times larger than that of graphene basal plane [10], the inherent resistance of graphene is much larger than the contact resistance because of the large aspect ratio of graphene. For example, if the length of graphene is 5μm [11] and the minimum overlap length is 1nm, the resistance parallel to basal plane of graphene is at least 148 times larger than that perpendicular to the crystal layers, in which the thickness of graphene is adopted as 0.335 nm [18]. Therefore, it can be concluded that the contact resistance can be ignored during the investigation of the present GPC model.

3. Analytical solution

Figure 5 shows the equivalent circuit which is developed by deformed configuration of the GPC model (see Figure 4). The resistance $R$ of the deformed model is determined by the equivalent resistance formula of series and parallel circuits:

$$
R = \frac{\rho l_0}{s} \left[ \frac{2n + (1-2n)e}{2(n_1 n_2) n} + \frac{(2n-1)e}{2n n} + \frac{(2n-1)e}{2n_2 n} \right]
$$

where $\rho$ is the resistivity of graphene, $n_1$ is the number of odd layer, $n_2$ is the number of even layer, $n$ is
the number of the graphene flakes in every layer, as shown in Figure 5.

![Image](image_url)

**Figure 5.** The equivalent circuit of the GPC model.

When the strain equal to 0, the initial resistance of this model \( R_0 \) can be depicted by equation as follow:

\[
R_0 = \frac{\rho l_0}{(n_1 + n_2)s}
\]  

(3)

Gauge factor \( \beta \) is an important factor to evaluate the sensing properties of the strain sensor, which represents the relative resistance with unit strain.

\[
\beta = \frac{R - R_0}{R_0} \frac{1}{\varepsilon}
\]  

(4)

\( GF \) of this model can be described as:

\[
\beta = (1 - \frac{1}{2n})(1 + \frac{n_1^2 + n_2^2}{n_1 n_2})
\]  

(5)

Because graphene flakes are stacked alternately in GPCs, \( n_1 \) equals to \( n_2 \) approximately. The expression of \( GF \) can be simplified as follow:

\[
\beta \approx 3 - \frac{3}{2n}
\]  

(6)

Because the value of \( n \) in Equation (6) is a very large number and thus the theoretical value of \( GF \) goes to 3 approximately.

The experimental sample of GPCs is obtained by stacking graphene flakes randomly on the substrate. Therefore when there is a small strain within the GPCs sensor, the slide of the graphene flakes is the main deformation form. The theoretical value of \( GF \) is consistent with the experimental result [6, 19], which can prove that the present model is reasonable.

4. Numeric simulation using finite element method

To obtain the resistance of the GPCs model during the deformation process, a constant current is applied on the two electrodes. The distribution of the potential \( \varphi \) can be calculated and the calculation formulas are as follows:

\[
\nabla \cdot \sigma \nabla \varphi = 0 \quad \text{(in } \Omega )
\]

\[
\varphi = \varphi_0 \quad \text{(on } \Gamma_1 )
\]

\[
\sigma \frac{\partial \varphi}{\partial n} = -J_n \quad \text{(on } \Gamma_2 )
\]

(7)

where \( \sigma \) is electrical conductivity, \( \varphi_0 \) is the potential at the boundary. \( J_n \) is the current density at the boundary. According to the Equation (7), the finite element equations can be obtained:
\[
\begin{bmatrix}
S_{11} & S_{12} & \cdots & S_{1n} \\
S_{21} & S_{22} & \cdots & S_{2n} \\
\vdots & \vdots & \ddots & \vdots \\
S_{n1} & S_{n2} & \cdots & S_{nn}
\end{bmatrix}
\begin{bmatrix}
\phi_1 \\
\phi_2 \\
\vdots \\
\phi_n
\end{bmatrix}
= 
\begin{bmatrix}
F_1 \\
F_2 \\
\vdots \\
F_n
\end{bmatrix}
\]  

(8)

Equation (8) can be written as:

\[ S\Phi = F \]  

(9)

where \( S = [S_{ij}] \), \( (i, j = 1, 2, \cdots, n) \) is global stiffness matrix; \( \Phi = [\phi_1 \ \phi_2 \ \cdots \ \phi_n]^T \) is vector of equivalent nodal potential, \( F = [F_1 \ F_2 \ \cdots \ F_n]^T \) is vector of equivalent nodal current. The potential distribution is calculated by the finite element method under a constant current. The model resistance can be obtained according to the Ohm's law.

5. Results and Discussion

The square resistance and thickness of graphene are 125 Ω/sq [20] and 0.335 nm respectively, then the resistivity of graphene is 4.1875×10^{-6} Ω•cm. The thickness of graphene is assumed to be 1 nm [13] due to the fact that graphene flakes encased in polymer is highly crumpled. The effective initial length of GPCs (\( l_0 \)) is 100 μm and the length of graphene flakes is 10 μm (i.e. \( n=10 \)). Based on above factors a two-layer sensor model of GPCs is developed. During deformation of GPCs, the theoretical value of GF calculated by equation (5) and the calculated value of GF obtained with FEM are plotted in Figure 6. The theoretical value of GF is 2.85. When the strain is less than 1%, the calculated value of GF is larger than the theoretical value, and the calculated value tends to the theoretical value gradually with the continuous increase of strain. When the strain is greater than 1%, the theoretical value and calculated value are consistent. This phenomenon is caused by the constriction resistance. As can be seen in Figure 7, a deflection occurs in the electron migration routes at the region of variable cross-section. The flake with a larger thickness (such as bilayer, trilayer, multi-layer graphene) lead to a greater constriction resistance, therefore, single-layer graphene is more suitable for the preparation of sensors than others. The constriction resistance is ignored in analytical solution, that’s the reason why the calculated value of resistance is larger than the theoretical value. With the increase of resistance in the model, the influence of constriction resistance on GF becomes smaller and smaller.

![Figure 6](image_url)

Figure 6. Gauge factor β as a function of strain
The density of graphene flakes is controllable during the preparation of GPCs, and the resistance increases with the decrease of the density [21, 22]. The graphene density of the model decrease gradually with the continuous increase of tension strain, as shown in Figure 4. Therefore, the GPCs model under different strain has different resistances, and a positive correlation between the strain of model and the resistance of GPCs can be found. The initial state of GPCs corresponds to a strain of $\varepsilon_0$ in the model. And the strain of GPCs is described as $(\varepsilon-\varepsilon_0)/(1+\varepsilon_0)$ when the strain of the model is equal to $\varepsilon$. The expression of GF of GPCs derived by equation (2) and equation (4) is obtained as follow:

$$\beta = 57(1+\varepsilon_0)/(20+57\varepsilon_0)$$

(10)

It can be seen in Figure 8 that the GF decreases with the increase of $\varepsilon_0$, that is, GF decreases with the increase of the initial resistance of GPCs. The decrease of GF attribute to the increase of the initial resistance of GPCs and the constant increment of resistance with unit strain.

When the initial strain $\varepsilon_0$ unequal to zero, the total resistance of the GPCs during deformation process consists of constriction resistance and the intrinsic resistance of graphene, in which the constriction resistance is constant and the intrinsic resistance of graphene increases linearly with elongation of the model. Thus the relative resistance as a function of strain obtained by FEM is linear as shown in Figure 9. Besides, the GF of the model with different configurations obtained by equation (3) is a constant as shown in Figure 10.

The theoretical values plotted in Figure 8 and calculated values plotted in Figure 10 of GF are basically consistent because the constriction resistance is small. According to Figure 10, it can be concluded that the GF and the sensing range of the sensor decreases with increase of initial strain. The reason is that the initial resistance increase and the overlap area of graphene flakes decrease as the increase of the initial strain of the model. This result is consistent with experimental result in the previous researches [3, 16].
Equation (6) shows that the theoretical value of GF increases slightly with the increase of $n$ (i.e. decrease of the length of graphene flake), and the maximum value of GF is 3. It can be explained by the large stiffness mismatch between graphene flakes and stretchable substrate. The slide of the graphene flakes during the deformation of the substrate is much easier within the GPCs with shorter graphene flakes. Therefore upon a tension strain, the GPCs have greater resistance when graphene flakes are shorter, which result in a larger theoretical value of GF as shown in Figure 11.

In addition, two models of double-layer graphene flakes with the effective length of 100 μm are constructed, in which the length of graphene flakes are 5 μm ($n=20$) and 2.5 μm ($n=40$), respectively. Figure 11 shows the GF as a function of strain of the models with different length of graphene flakes. Because the number of constriction resistance is positively correlated with the number of graphene flakes $n$ in the model, the calculated value of GF has larger increment than theoretical value with the increase of $n$ when the strain is less than 1%. The calculated value of GF is consistent with theoretical value when the strain is larger than 1%.

Furthermore, the GPCs model is established by stacking graphene flakes on a pre-stretched polymer substrate, as shown in Figure 3. Because graphene flakes are very thin and are stacked randomly, the overlap area of graphene flakes increases after the release of the substrate [9, 10], as shown in Figure 12. Theoretically, as the increase of the pre-strain of the substrate, the overlap area after releasing the GPCs film and the sensing range increase. A GPCs model with a length of 100 μm is established by
stacking two layers of graphene flakes on the pre-stretched substrate with a strain of 50% strain, in which the length of graphene is 10 μm. Figure 13 shows the linear sensing range of GPCs has been significantly improved because of the pre-stretched treatment. GF is equal to 2.72 in the range of pre-tension deformation (i.e. when the strain is less than 100%), as shown in Figure 14. GF and the slope of the relative resistance-strain curve increase due to the decrease of graphene layers when the strain is greater than 100%. GF tends to 4.5 because the increase rate of resistance is constant. In some experiments of the previous studies [9, 16], GF caused by disconnection of graphene flakes, cracking of the film and tunnel effect is much larger than that caused by slide of graphene flakes, so the change of GF in slide stage is usually neglected. It is considered that the relative resistance-strain curve is linear and GF is a constant in slide stage.

![Figure 11. Gauge factor β as a function of strain of the models with different length of graphene flakes](image1)

![Figure 12. Configuration of the model after releasing the pre-stretched strain](image2)

![Figure 13. Relative resistance-strain curve of pre-stretched model](image3)
6. Conclusions
In this paper, a two-dimensional model of GPCs is established according to the structural characteristics of GPCs. The effect of the slide of graphene flakes on the sensing characteristic was investigated. The position of deformed graphene flakes in GPCs is obtained by affine transformation. The model is simplified to a series-parallel circuit, and the analytical solution of model GF is obtained. Moreover, the numerical simulation results of relative resistance and GF are analyzed by finite element method.

The relationship between relative resistance and the applied strain is a linear function, and GF is a constant. GF and the linear range of relative resistance-strain curves decrease with the increase of initial resistance of GPCs. It can be concluded that the GF can slightly improve by reducing the length of graphene flakes. In addition, the result also shows that the pre-stretching treatment for GPCs can increase the linear range of relative resistance-strain curves. These results provide important fundamental insights for future experimental studies and applications of GPCs.

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