JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 22, No. 11-12, November – December 2020, p. 629 - 634

Effect of filler/matrix interphase boundaries on the DC electrical conductivity of two- and three-dimensional composites

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A three phase predictive model is presented based on the generalized effective medium (GEM) modified equation which describes the DC electrical conductivity of a wide variety of binary mixtures. Six series of two- and three-dimensional composites have been investigated, at a constant temperature, taking into account the role of interphase zone existing between the macromolecular chains and the polypyrrole fillers. The fitting of experimental data using the GEM-modified model provides to estimate the volume, concentration and intrinsic conductivity of interphase zone, depending on macromolecular network chains used in each series.

(Received April 11, 2020; accepted December 7, 2020)

Keywords: Polymeric matrices, Polypyrrole, Percolation threshold, Generalized effective medium law, Interphase zone

1. Introduction

Conducting polymers have received lots of attention due to their potential applications such as gas separation membranes and electroluminescent diodes [1,2]. Polypyrrole (PPy) is one of the most interesting conducting polymers because it exhibits high conductivity [3], and can be easily introduced in a polymeric matrix. The composites formed with low contents of PPy demonstrate reasonable high conductivities [4]. Many studies showed that the electrical properties of heterogeneous materials are closely related to the composition of its constituents [5-7]. Several theoretical approaches have been developed to predict the DC electrical conductivity of composite materials. For very low particle concentrations, these laws give identical results, often in agreement with experiments. However, for concentrations higher than a few percent, they generally give different results, often in disagreement with the results [8, 9], because the morphological parameters such as particle size, their distribution, and mostly the interphase region between the components are not taken into account. To avoid this problem, the interactions between the conducting filler and the matrix, as well as filler–filler overlapping, Aribou et al. [10] recently presented a systematic investigation of electrical properties of two series of percolating systems, introducing three parameters characteristic of the interphase zone: the concentration, the conductivity and the volume fraction of the interphase zone on the generalized effective medium (GEM) model for DC electrical conductivities given by McLachlan. This study has proven the existence and the role of the interphase region on conduction mechanisms of a percolating system based on polymer loaded with conducting charges.

Our goal, in this paper, is to investigate the DC electrical conductivity of two dimension (2D) and three dimension (3D) composites using McLachlan model. We have considered that these composites contain two constituents (filler and matrix), and the modeling results show a remarkable disagreement with the experimental data. After that, we made small modifications on the McLachlan model in order to take into account the consideration of a third constituent which is the interphase zone that exists between matrix and filler. Six series of composite materials, based on six host matrices loaded with different fractions of PPy fillers, were investigated. The results show that the interphase zone has a significant influence on the electrical conductivity processes, and the present conclusions have important implications for the design of polymer loaded conducting filler composites.

2. Experimental techniques

2.1. Sample preparation

We used a polymethylmethacrylate (PMMA) insulating matrix with a DC electrical conductivity of the order of 3×10^{-15} $(\Omega.m)^{-1}$, glass transition temperature about 113 °C and density 1.14-1.20 g.cm^{-3}. The polypyrrole powder was obtained by doping intrinsic polypyrrole with tosylate anion (TS^-) (PPy). The doping rate was controlled by X-Ray Photoelectron Spectroscopy Technique (XPS) and was found to be of the order of one sulfur (S) for four nitrogen (N), i.e., one tosylate anion (TS^-) for four pyrrole monomers. Polypyrrole particles have a diameter 20-

40μm, DC electrical conductivity 54 $(\Omega.m)^{-1}$, and density 1.2 $g.cm^{-3}$. The samples investigated in this study were obtained by mixing the polypyrrole particles and the polymethylmethacrylate matrix. This mixture was heated at 150 °C and then pressed at 5 $ton.cm^{-2}$ to prepare solid disc-shaped samples. The percolation threshold ϕ_p for this series of samples is approximately 3.85 % [11].

2.2. Measurements

The DC conductivity measurements of PPy/PMMA composite materials were carried out using a 617 Keithley electrometer. The samples were prepared as discs of thickness about 1 mm, with aluminium electrodes of 10 mm diameter on the opposite sites of the sample. The electrical contacts were formed by silver paint. The experiment consists of measuring the electrical resistance of each sample in order to determine the DC conductivity of the different series of the composites at constant temperature (300 K). Reference [12] presented the measurement details of electrical conductivity.

3. Results and discussion

3.1. Generalized Effective Medium Approach (GEM)

The analysis of the electrical conductivity behaviour of percolating composites versus concentration of filler loaded in polymeric matrices allowed us to distinguish two remarkable domains of DC conductivity behaviour around the percolation threshold, ϕ_p. Below ϕ_p, the conductivity of the composite has no significant changes. When the concentration reaches the critical percolating threshold, the conductivity exhibits a sharp increase, attaining a value almost constant which characterizes the conducting charges behaviour. For modeling this behaviour, the Generalized Effective Medium Theory (GEM) was proposed by McLachlan et al. [13-15] which is a combination of both percolating and Bruggeman's effective medium model. The DC electrical conductivity, below and above the percolation threshold, is described by the mixture law [16]:

$$(1-\phi_f)\frac{\sigma_m^{1/t}-\sigma_c^{1/t}}{\sigma_m^{1/t}-A\sigma_c^{1/c}}+\phi_f\frac{\sigma_f^{1/t}-\sigma_c^{1/t}}{\sigma_f^{1/t}-A\sigma_c^{1/t}}=0 \qquad (1)$$

where σ_f and ϕ_f are the conductivity and concentration of filler, σ_m is the conductivity of host phases, and σ_{DC} represents the conductivity of the composite, as shown in Fig. 1. The exponent t characterizes DC conductivity, and its theoretical value is t =1.3 for 2D and t =2 for 3D [17-18], the constant A is described in terms of the percolation threshold, ϕ_p, and $A=(1-\phi_p)/\phi_p$. In this work, the DC electrical conductivity measurements; for all samples, show a percolating behaviour.

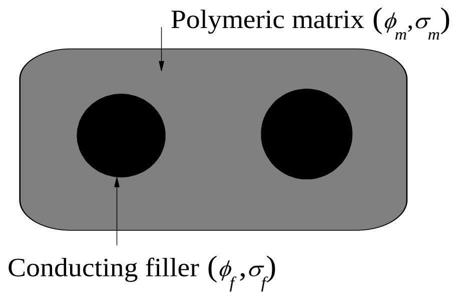

Fig. 1. Schematic representation for filler/polymer composite materials consisting of conducting filler and polymeric matrix

Figs. 2 and 3 show the calculation results using the GEM equation for the three dimension (3D) PPy/PMMA (our composite), polypyrrole/chitosan-g-polycaprolactone (PPy/CPC) [19], and polypyrrole/polystyrene (PPy/PS) [20] and for the two dimension (2D) polypyrrole/poly(2,6-dimethyl-1,4-phenylene Oxide) (PPy/PPO) [21], polypyrrole/sulfonated polycarbonate (PPy/S-PC) [22] and polypyrrole/polycarbonate (PPy/PC) [22], in order to follow the validity of the GEM equation. The solid lines correspond to the calculated conductivity using the equation (1) with universal values of parameter t. Those predicted by percolation theory, are t = 1.3 for 2D and t = 2 for 3D (solid line) and with the values of an adjustable parameter t those represented the best fit of the experimental data. It is clear that, the GEM equation of McLachlan is only valid for PPy concentrations below the percolation threshold ($\phi < \phi_p$) for both 2D and 3D series. On the other hand, a good agreement is shown with the values of adjustable parameter t which are greater than those of the universal values, as can be seen in table 1. These results seem to be in good agreements with the logical interpretation and validity of the McLachlan equation because the interzone separated the two phases does not have any effect since the PPy fractions loaded for ($\phi < \phi_p$) does not have a remarkable effect on the conductivity, and this prediction has been confirmed for PPy fractions ($\phi > \phi_p$) (Figs. 2 and 3).

Table 1. Fitting parameters of GEM model (Eq. 1) using the DC conductivity of two-dimensional (2D) and three-dimensional (3D) composite materials

Series		ϕ_P (%)	σ_m $(\Omega.cm)^{-1}$	σ_f $(\Omega.cm)^{-1}$	Theoretical values of t	Calculated value of t'
2D	PC/PPy	15	$3\ 10^{-5}$	0.23	1.3	1.76
	Sulfonated-PC/PPy	15	$8\ 10^{-5}$	0.82	1.3	1.80
	PPO/PPy	15	$7.5\ 10^{-6}$	0.82	1.3	1.96
3D	PS/PPy	12	$1\ 10^{-12}$	0.54	2	2.55
	CPC/PPy	1.5	$4\ 10^{-9}$	1.91	2	2.70
	PMMA/PPy	3.85	$2.2\ 10^{-8}$	0.54	2	2.31

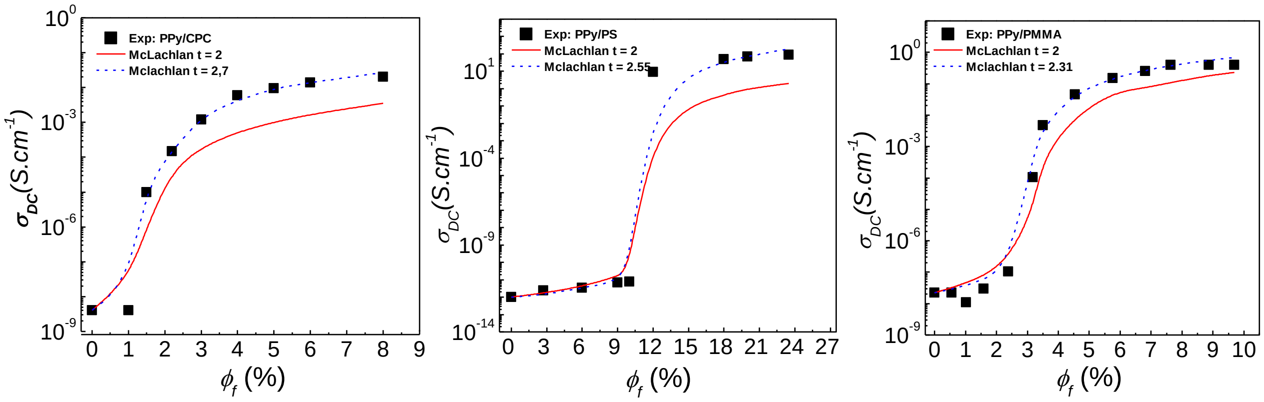

Fig. 2. DC electrical conductivity vs. PPy fractions at room temperature. Comparison between experimental data and 3D-theoretical results for three series of percolating composites (color online)

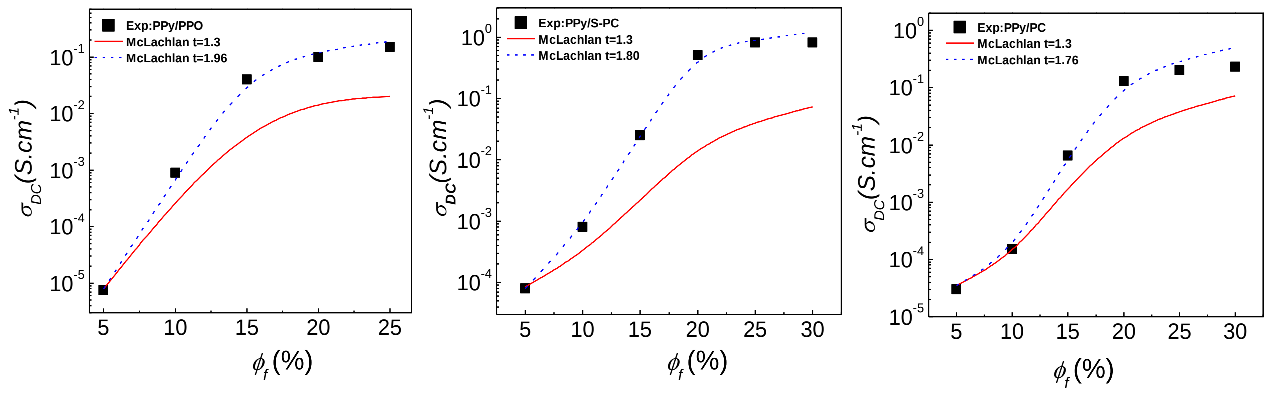

Fig. 3. DC electrical conductivity vs. PPy fractions at room temperature. Comparison between experimental data and 2D-theoretical results for three series of percolating composites (color online)

3.2. GEM with interphase approach (GEM-modified)

As seen in the previous section, the fitting with a universal value of the parameter t does not fit accurately with two constituent phases of composites. To solve this problem, we supposed that these composites contain a third region separating the two phases, macromolecular chain and conducting charges, the interphase zone as shown in Fig. 4. In this case, we made a modification on GEM using electrical conductivity, taking into account the volume, V_i, and concentration, ϕ_i, of the interphase zone. The modified-GEM equation for the electrical conductivity of a system with three components can then be written as:

$$(1-\phi_f-\phi_i)\frac{\sigma_m^{1/t}-\sigma_c^{1/t}}{\sigma_m^{1/t}-A\sigma_c^{1/t}}+\phi_i\frac{\sigma_i^{1/t}-\sigma_c^{1/t}}{\sigma_i^{1/t}-A\sigma_c^{1/t}}+\phi_f\frac{\sigma_f^{1/t}-\sigma_c^{1/t}}{\sigma_f^{1/t}-A\sigma_c^{1/t}}=0 \quad (2)$$

The volume of composite material V_c in this case (Fig. 4) can be expressed by the sum of the volume of the matrix V_m, filler V_f and the so-called interphase volume Vi as follows $V_c=V_f+Vi+V_m$. If it is divided by V_c we obtain the relationship between the volume fractions of each component written as $1=\phi_f+\phi_i+\phi_m$. Since ϕ_i must be zero when ϕ_f is zero, it is expected the existence of an interphase volume constant k which could be given as $\phi_i=k\phi_f\phi_m$ and the volume fraction of the matrix as $\phi_m=(1-\phi_f)/(1+k\phi_f)$ [23], and in this case, the volume fraction of interphase region is:

$$\phi_i = (k\phi_f)\frac{1-\phi_f}{1+k\phi_f} \tag{3}$$

This equation describes the concentration of an interphase zone of a heterogeneous mixture of composites in many studies and fits correctly the experimental data [1, 24,25]. The interphase volume is also dependent on the size of the filler, i.e. when k is close to zero the interaction between the macromolecular chains and conducting filler is negligible and high values of k indicate strong polymer-conducting filler interactions.

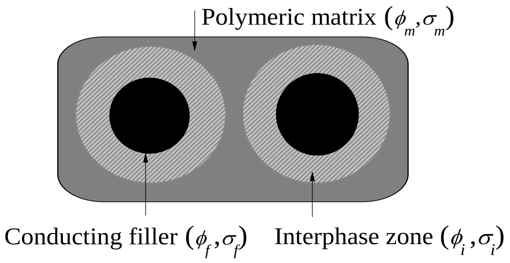

Fig. 4. Schematic representation for filler/polymer composite materials consisting of conducting filler particle, interphase zone and host polymeric matrix

To follow this prediction, we have extended such studies to investigate the effect of filler/polymer matrix interphase, based on GEM model, by taking into account the interphase zone effect on the DC conductivity. The results obtained from simulation of Eq. (1) (no interphase) and Eq. (2) (with interphase) are compared with the experimental data in Figs. 5 and 6, respectively, for 2D and 3D composites of studied series. As can be seen in these figures, considering the interphase zone parameters (intrinsic conductivity σ_i, fraction ϕ_i , and volume V_i) in the equation 2, the obtained results are in good agreement with the experimental data, indicating the significant role of the interphase zone on the conduction mechanisms of these percolating systems. Table 2 illustrates the values of interphase zone parameters for each series of composites, and comparing these values, it appears that the conductivity and the volume of the interphase zone of 2D composites are higher than those of 3D composites which show the effect of non-crystalline mesostructured organic networks on conduction mechanisms of the heterogeneous composites.

Table 2. Fitting parameters of modified-GEM model (Eq.2) using the DC conductivity of two-dimension (2D) and three- dimension (3D) composites materials

Series		Interphase conductivity $\sigma_i(\Omega.cm)^{-1}$	Interphase constant volume, k
2D	PC/PPy	$6\ 10^{-5}$	0.30
	Sulfonated-PC/PPy	$8\ 10^{-4}$	1.08
	PPO/PPy	$4.45\ 10^{-4}$	0.83
3D	PS/PPy	$6\ 10^{-11}$	0.098
	CPC/PPy	$2.5\ 10^{-7}$	0.077
	PMMA/PPy	$2\ 10^{-7}$	0.043

In order to analyse the PPy filler effect on the interphase zone concentration, we calculate ϕ_i versus ϕ_f of each series using the derived general equation (3), obtaining the results shown in Fig. 7. As can be seen in this figure, ϕ_i of both 2D and 3D composites increases with increasing of PPy fillers, and the same behaviour has been identified in a study presented by Gohil and Shaikh [26] based on interphase influence on the elastic behaviour of fiber reinforced composites. In addition, ϕ_i of 3D composites are superior to those of 2D which demonstrates a significant influence of composites dimensionality on intrinsic interphase zone fractions.

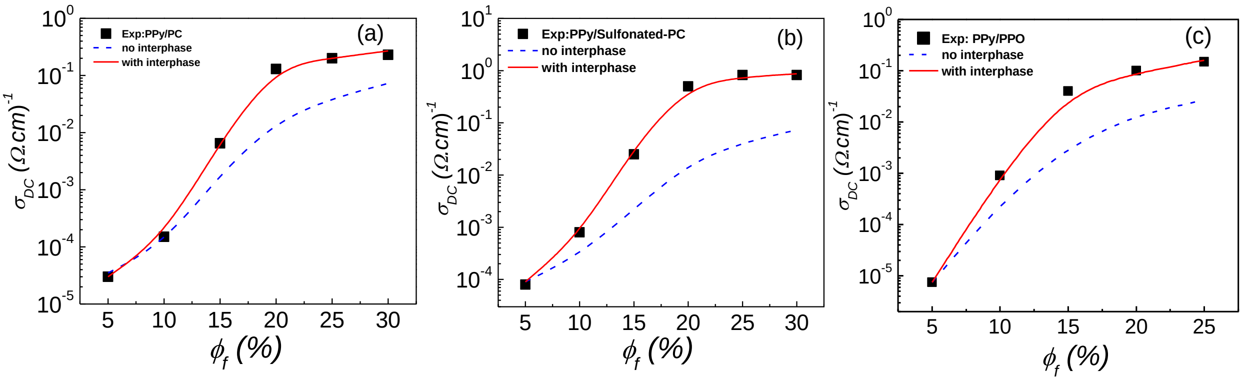

Fig. 5. DC electrical conductivity versus conducting particles fraction of 2D composite materials. Comparison between experimental data and theoretical results: (a) series PPy/PC,(b) series PPy/sulfonated-PC and (c) series PPy/PPO (color online)

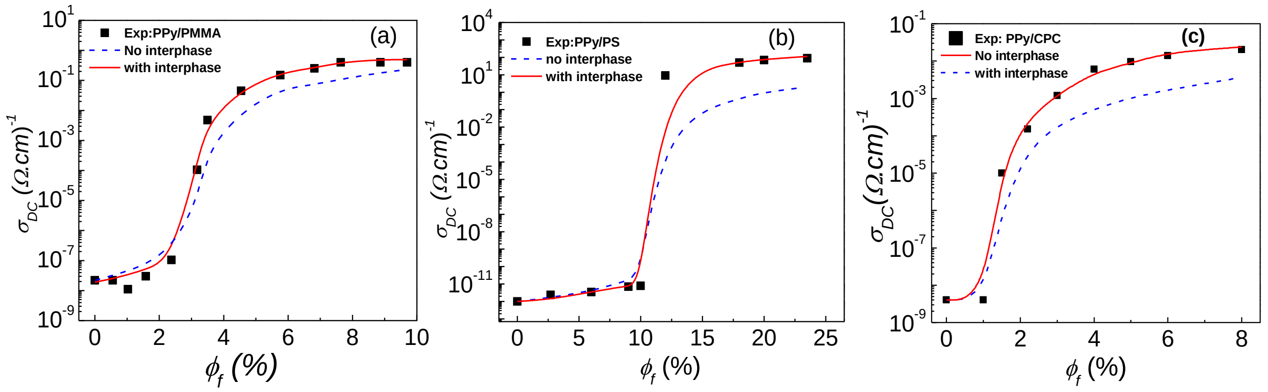

Fig. 6. DC electrical conductivity versus conducting particles fraction of 3D composite materials. Comparison between experimental data and theoretical results: (a) series PPy/PMMA, (b) series PPy/PS and (c) series PPy/CPC (color online)

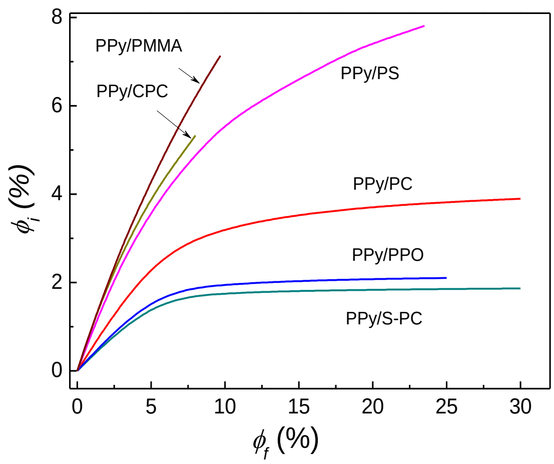

Fig. 7. The interphase concentration of 2D and 3D composites as predicted by equation 5 taking into consideration the obtained values of k for each series from Table 2 (color online)

4. Conclusions

In this work, we present a model for the electrical conductivity for composite systems considering the existence of an interphase zone between the conducting filler and the polymeric matrices. It provides a means to determine the volume, intrinsic conductivity and concentration of interphase zone in composites using advanced numerical results. It is obvious that the effect of the interphase zone has a significant influence on the electrical conductivity and diverts the conductivity distinctly from the mixture models without taking into account the interphase effect. Compared to other models, the GEM-modified model has proven to be a better fit with the available experimental data, demonstrating the reliability and universality of this model.

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