

# Numerical method to evaluate the influence of organic solvent absorption on the conductivity of polymeric composites

Antonio Carrillo<sup>1</sup>, Ignacio R. Martín-Domínguez<sup>1</sup>, and Alfredo Márquez<sup>1\*</sup>

Centro de Investigación en Materiales Avanzados, S. C. (CIMAV) Miguel de Cervantes  
120, Complejo Industrial Chihuahua 31109 Chihuahua, Chih., México.

## Abstract

A theoretical analysis that describes the change on electric properties of polymeric composites, filled with conductive aggregates, during organic solvent absorption processes is presented in this work. This methodology takes into account the moving boundaries typical of this phenomena; requiring simple numerical procedures to be solved. The results show no numerical instabilities during the calculation process. The obtained results correlate very close to the available experimental data; therefore could be very useful for chemical sensor design.

## 1. Introduction

The relationship between electrical resistivity and the volumetric fraction of conductive aggregates into a polymeric conductor composite, has been widely analyzed both theoretically and empirically [1-4], being the percolation theory the most accepted model to describe this phenomenon [5-12]. However, this relationship has always been studied on homogeneous composites, where distribution of the conductive fraction inside the composite is uniform. There are, nevertheless, a wide range of phenomena where the conductive fraction varies significantly with position, specially when gaseous or liquid solvents are being absorbed by the polymer matrix. This phenomenon has an important application on designing chemical sensors and artificial odor detection systems. In these devices the solvent presence is been detected when electric resistance of the composite changes due to the absorption of the solvent by the polymeric matrix. On previous works [13-15] a number of authors have been found that when a sensor, tailored with a polymer composite chemically compatible with the solvent to be monitored, is brought in contact with this solvent; a variation on the electric current circulating through the sensor is observed and, at the same time, an increase in volume occurred. This sample swelling occurs because the composite matrix absorbs the solvent, and consequently the volumetric fraction of the conductive aggregates changes; as a result the electric resistivity of the composite also changes [13-15], diminishing, if the solvent is a good electric conductor, or increasing, if it is a dielectric solvent. It is important to note that on this process the electric resistivity varies across the transversal section of the composite, because of the solvent diffusion. A model that describes such a phenomenon is presented on this work, for polymeric composites filled with conductive particles. The aim of the model is to connect the percolation theory with the solvent diffusion equation in amorphous polymers. Also, it must be mentioned that in this first paper we have restrict the analysis to dielectric solvents and polymers, however in a second paper we will generalize this approach to any arbitrary components. Finally, it is important stress out that to our knowledge no similar analysis has been previously reported in the literature.

## 2. Analysis

In order to exemplify the method, an axisymmetric geometry was selected to study the composite behavior. Main reason for this geometry selection is that modern sensors commonly have such configuration [13-15]. A simplified typical electric circuit arrangement, for the mentioned sample, is presented on Figure 1. On this configuration, the solvent diffusion process

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\* Corresponding author; e-mail address: alfredo.marquez@cimav.edu.mx

into the composite gradually changes its electric conductivity, following the solvent concentration profile along the sample radius over a time period. In order to model the previous situation, the following hypotheses were considered: a) Solvent diffusion process on the sample is one-dimensional, taking place only along the radial direction (axial diffusion is neglected); b) The polymeric matrix and the organic solvents are dielectric materials; c) Solvents are absorbed only by the polymeric matrix, and not by the conductive aggregates; d) Solvent diffusion into the composite follows Fick's Law (this is especially true on elastomeric matrix composites and copolymers).

Using those hypotheses it is possible to predict, at constant voltage, the variation of the electric current on the composite during the solvent diffusion process. First of all, Ohm's Law can be written as:

$$I(t) = \int_0^{a(t)} \frac{E}{\rho_m(t)l} dA(t) \quad (1)$$

where  $I(t)$  and  $\rho_m(t)$  are the instantaneous electric current on the sample and local composite resistivity.  $A(t)$ ,  $a(t)$  and  $l$  are the transversal section, external radius and longitude of the sample. Finally  $E$  is the applied voltage, which remains constant.

Eq. 1 can be normalized as:

$$\frac{I(t)}{I_0} = \frac{1}{r_0^2} \int_0^{a(t)} \frac{\rho_{m0}}{\rho_m(t)} r(t) dr \quad (2)$$

where  $r$  is the radial coordinate and variables indexed with zero represent the state of the composite before the solvent gets in touch with it. In order to calculate the electric resistivity, it is necessary to know its relationship with the solvent volumetric fraction. This can be done by modifying a model proposed by McLachlan [11], which describes the conductive composite electric resistance change as a function of its conductive and dielectric volumetric fractions. This equation, which is known as the generalized effective media (GEM) model, integrates two morphology parameters:  $f_C$  (the critical percolative value of the conductive fraction) and  $q$  (an experimental exponent). Previous equation can be written as:

$$\frac{(1-f)(\rho_L^{-1/q} - \rho_m^{-1/q})}{\rho_L^{-1/q} + f_R \rho_m^{-1/q}} + \frac{f(\rho_H^{-1/q} - \rho_m^{-1/q})}{\rho_H^{-1/q} + f_R \rho_m^{-1/q}} = 0 \quad (3)$$

where  $\rho_H$ ,  $\rho_L$  and  $\rho_m$  are the resistivities of the high and low resistive components and the composite resistivity respectively,  $f$  is the conductive fraction and  $f_R$  is given by the following expression:

$$f_R = \frac{1-f_C}{f_C} \quad (4)$$

Solving Eq. 3 for  $\rho_m$ , we have:

$$\rho_m = \{1/2 [B \pm (B^2 + 4C)^{1/2}]\}^{-q} \quad (5)$$

where;

$$B = f_R^{-1} [(f f_R + f - 1)\rho_H^{-1/q} - (f f_R + f - f_R)\rho_L^{-1/q}],$$

$$C = f_R^{-1} (\rho_L \rho_H)^{-1/q} \quad (6)$$

The positive sign of Eq. 5 is used to describe the behavior of a composite with larger conductive fraction than that of the percolation one, while the negative one is used for those with a smaller fraction [11,12]. Therefore, in this work we will use only the positive sign of the previous equation.

It is important to mention that the GEM equation was deduced for a composite of only two components. However, we can use it if considering the following approximation; since the polymer matrix and organic solvents are both dielectrics with a resistivity of the same order of magnitude and substantially different from that of the conductive fraction, we may treat both phases (polymer and solvent) as an unique phase. Therefore, the sum of the polymeric matrix fraction,  $f_p$ , plus the solvent fraction,  $f_s$ , will be named as the non conductive fraction in Eqs. 5 and 6. This last approximation is possible because the resistivity is one of the physical magnitudes that present the broader range of values. Indeed, the resistivity of common organic substances varies typically between  $10^{16}$  to  $10^8$  ohms-cm, while the conductive aggregates have conductivities between  $10^{-1}$  to  $10^{-7}$  ohms-cm.

To evaluate  $f(r,t)$  on each location as function of time, the following relation was considered:

$$f(r,t) = 1 - f_p(r,t) - f_s(r,t) = 1 - f_p(r,0) \frac{V_T(r,0)}{V_T(r,t)} - f_s(r,t) \quad (7)$$

$$f(r,t) = 1 - f_p(r,0)[1 - f_s(r,t)] - f_s(r,t)$$

where  $V_T(r,t)$  is the local volume as a function of time.

In order to determine the evolution of the solvent volumetric fraction  $f_s(r,t)$  it is possible to use Fick's Law<sup>14</sup>.

$$\frac{\partial f_s(r,t)}{\partial t} = D \nabla^2 f_s(r,t) \quad (8)$$

where D is the diffusion coefficient, related with the volumetric fraction. This last parameter, in the case of polymers, could become concentration dependent for large swelling levels; however in the present study we consider it as a constant. Taking into account the hypothesis number I, this last expression may be written as;

$$\frac{\partial f_s(r,t)}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r D \frac{\partial f_s(r,t)}{\partial r} \right) \quad (9)$$

To solve this equation, the following initial and boundary conditions apply:

$$f_s(r,0) = 0, \quad 0 \leq r \leq a(0) \quad (10)$$

$$f_s(r,t) = f_{s_{\max}}, \quad r = a(t), \quad t \geq 0$$

where  $f_{s_{\max}}$  is the maximal solvent volumetric fraction that the composite is able to absorb. There are two solutions of Eq. 9, subjected to conditions (10); the first one is valid for large times, and the second one for short times [16]. The first one has the following form:

$$f_s(r,t) = \left( 1 - \frac{2}{a(t)} \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t) J_0[r_n \alpha_n]}{\alpha_n J_1[a(t)\alpha_n]} \right) f_{s_{\max}} \quad (11)$$

where  $J_0$  and  $J_1$  are the first class Bessel functions, of zero and first order respectively, and  $\alpha_n$  are the positive roots of  $J_0[a(t)\alpha_n]$ . Whereas, the second one has the next structure:

$$f_s(r, t) = \left( \sqrt{\frac{a(t)}{r}} \operatorname{erfc} \frac{a(t) - r}{2\sqrt{Dt}} + [a(t) - r] \sqrt{\frac{Dta(t)}{4a(t)r^{3/2}}} \operatorname{ierfc} \frac{a(t)}{2\sqrt{Dt}} + \dots \right) f_{S \max} \quad (12)$$

Using the previous equations it is possible to calculate  $f(r, t)$ , using the value of  $f_s(r, t)$  in Eq. 7. Finally, to evaluate the increment of the filament external radius the following relation was deduced:

$$a^2(t) = a^2(0) + 2 \int_0^{a(t)} f_s(r, t) r dr \quad (13)$$

It is evident that it is not possible to get an explicit expression for  $a(t)$  using equations 11, 12 and 13, however it is possible to evaluate this parameter employing a numerical method.

#### 4. Results and discussion

In order to illustrate the use of this algorithm, experimental data from Márquez *et al* [14] and Carrillo [15], was used. This composite was elaborated using Polybutadiene (PB) as the polymer matrix. On Figure 3, it is shown its electric resistance evolution when prepared using different volumetric fractions of carbon particles. It can be noticed that the composite has a percolation composition of around 0.14 v/v of carbon particles. The parameters of Eqs. 4-6 were calculated using this correlation. Subsequently, concentration profiles were evaluated for five different hypothetical solvents, as a function of the radial coordinate at, different times. Figure 1 show the obtained results for a diffusion coefficient of  $D = 9 \times 10^{-6} \text{ cm}^2/\text{s}$ . The first curve on the graph corresponds to the first minute of contact with this solvent, while the subsequent ones are five minutes apart of each other. It is relevant to notice on these curves, how the external radius  $a(t)$  increases as a function of time, as dictated by Eq. 13. It also can be noticed that the line corresponding to the first minute presents some irregularities, due to the selection of the particular solution for the diffusion equation (Eq. 11). Indeed, when both solutions (Eq. 11 and 12) are used these irregularities are vanished.

Figure 7 illustrates how the electric current curve falls with the solvent contact time, for each different solvent. It can be noticed that, in general, the current diminishes rapidly with time, at the exception of the first solvent, which is in good agreement with experimental observations [4, 7, 10, 14, 15].

Finally, it is important to mention that this methodology may allow a more precise sensor design, based only on easy obtainable laboratory data.

#### 5. Conclusion

A methodology that describes the change on electric properties of polymeric composites, during solvent diffusion processes, is presented in this work. The equations that result from this methodology requires simple numerical procedures to be solved, and no numerical instability was observed during the process. The obtained results correlate very close the available experimental data, and therefore could be very useful for chemical sensor design.

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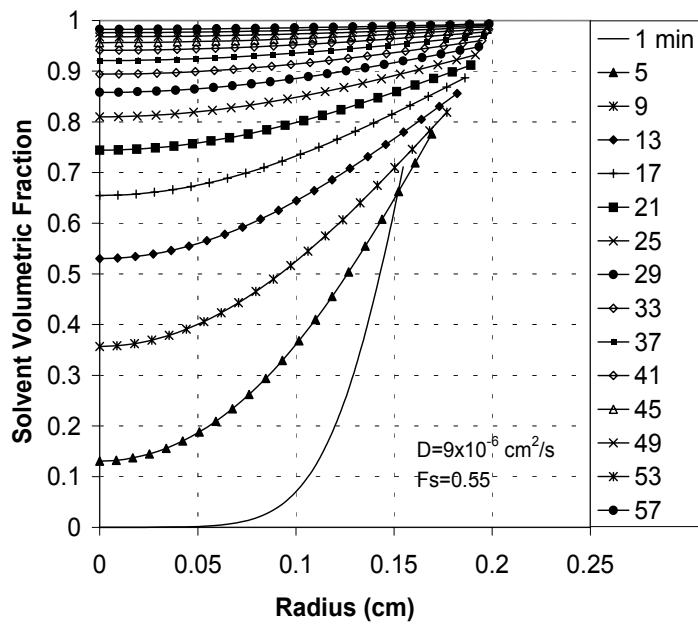


Figure 1.

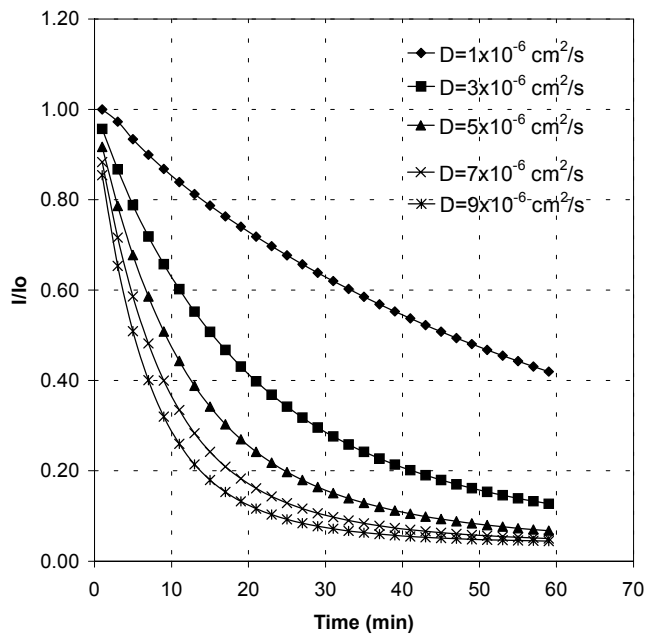


Figure 2.

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