ELSEVIER

Polymer 43 (2002) 6307–6313

polymer

www.elsevier.com/locate/polymer

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

Antonio Carrillo[a], Ignacio R. Martín-Domínguez[a], Armando Rosas[b], Alfredo Márquez[a,*]

[a]*Centro de Investigación en Materiales Avanzados, S. C. (CIMAV) Miguel de Cervantes 120, Complejo Industrial Chihuahua,*
*31109 Chihuahua, Mexico*
[b]*Instituto Mexicano del Petróleo, E. C. Lázaro Cardenas No. 152, San Bartolo Atepeh., 07730 Distrito Federal, Mexico*

Received 20 March 2002; received in revised form 12 August 2002; accepted 12 August 2002

---

## Abstract

A theoretical analysis that describes the change in 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. © 2002 Published by Elsevier Science Ltd.

*Keywords:* Organic solvent absorption; Sensors; Liquid leakage

---

## 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, especially when gaseous or liquid solvents are being absorbed by the polymer matrix. This phenomenon has an important application in designing chemical sensors and artificial odor detection systems. In these devises the solvent presence is detected when electric resistance of the composite changes due to the absorption of the solvent by the polymeric matrix. In 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 in 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 in 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 restricted the analysis to dielectric solvents and polymers; however, in the second paper we generalize this approach to any arbitrary components. Finally, it is important to 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.

---

* Corresponding author. Fax: +52-614-439-1112.
*E-mail address:* alfredo.marquez@cimav.edu.mx (A. Márquez).

PII: S0032-3861(02)00558-X

## Nomenclature

| | |
|---|---|
| $I(t)$ | current intensity as a function of time |
| $E$ | applied constant voltage |
| $A(t)$ | transversal section area of the composite sample |
| $l$ | longitude of the composite sample |
| $a(t)$ | external radius of the composite sample |
| $r$ | radial coordinate |
| $\rho(t)$ | local resistivity of the composite |
| $\rho_H$ | resistivity of the dielectric component |
| $\rho_L$ | resistivity of the conductive component |
| $q$ | experimental percolation exponent |
| $f$ | volumetric fraction of the conductive component |
| $f_C$ | critical percolation value of $f$ |
| $f_R$ | $(1-f_C)/f_C$ |
| $f_P$ | polymer volumetric fraction |
| $f_S$ | absorbed solvent volumetric fraction |
| $f_{Smax}$ | maximum absorbed solvent volumetric fraction |
| $D$ | diffusion constant |
| $J_0$ and $J_1$ | zero and first Bessel functions |
| $\alpha_n$ | roots Bessel factor |
| $V_T(t)$ | total volume of the sample |

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 in Fig. 1. On this configuration, the solvent diffusion process 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:

(i) Solvent diffusion process on the sample is one-dimensional, taking place only along the radial direction (axial diffusion is neglected).
(ii) The polymeric matrix and the organic solvents are dielectric materials.
(iii) Solvents are absorbed only by the polymeric matrix, and not by the conductive aggregates.
(iv) Solvent diffusion into the composite follows Fick's law (this is especially true on elastomeric matrix composites and copolymers).
(v) The coefficient of convective transfer at the liquid–solid interface is infinite.

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

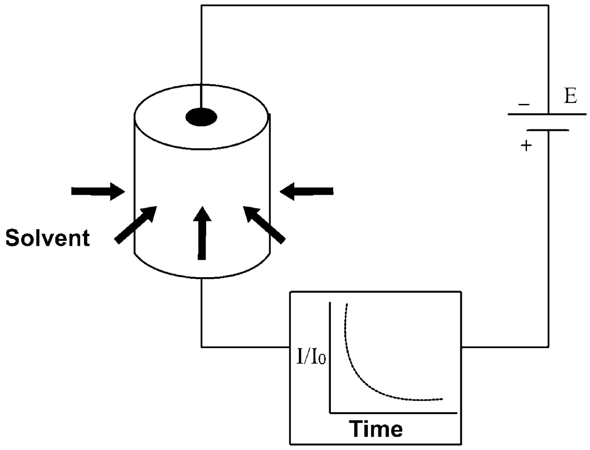

Fig. 1. Schematic of the solvent diffusion process.

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

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

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

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 McLachlang [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

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

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:

$$f_R = \frac{1-f_C}{f_C} \tag{4}$$

Solving Eq. (3) for $\rho_m$, we have

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

where

$$B = f_{\mathrm{R}}^{-1}[(ff_{\mathrm{R}} + f - 1)\rho_{\mathrm{H}}^{-1/q} - (ff_{\mathrm{R}} + f - f_{\mathrm{R}})\rho_{\mathrm{L}}^{-1/q}], \qquad (6)$$
$$C = f_{\mathrm{R}}^{-1}(\rho_{\mathrm{L}}\rho_{\mathrm{H}})^{-1/q}$$

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, $f_{\mathrm{P}}$, plus the solvent fraction, $f_{\mathrm{S}}$, 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 $10^{16}$ and $10^{8}$ Ω cm, while the conductive aggregates have restitivities between $10^{-1}$ and $10^{-7}$ Ω cm.

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

$$\begin{aligned} f(r,t) &= 1 - f_{\mathrm{P}}(r,t) - f_{\mathrm{S}}(r,t) \\ &= 1 - f_{\mathrm{P}}(r,0)\frac{V_{\mathrm{T}}(r,0)}{V_{\mathrm{T}}(r,t)} - f_{\mathrm{S}}(r,t) \qquad (7) \\ f(r,t) &= 1 - f_{\mathrm{P}}(r,0)[1 - f_{\mathrm{S}}(r,t)] - f_{\mathrm{S}}(r,t) \end{aligned}$$

where $V_{\mathrm{T}}(r,t)$ is the local volume as a function of time.

In order to determine the evolution of the solvent volumetric fraction $f_{\mathrm{S}}(r,t)$ it is possible to use Fick's law [17].

$$\frac{\partial f_{\mathrm{S}}(r,t)}{\partial t} = D\nabla^2 f_{\mathrm{S}}(r,t) + \nabla D \cdot \nabla f_{\mathrm{S}}(r,t) \qquad (8)$$

where $D$ is the diffusion coefficient related to the volumetric fraction. This last parameter, in the case of polymers, is normally concentration dependent for large swelling levels. The treatment of variable $D$ is mainly possible in closed form only if the variation of $D$ with $f_{\mathrm{S}}$ is known a priori, and if the variation can be expressed analytically [17]. Therefore, as a first approximation, in the present study we consider $D$ as a constant. Moreover, taking into account the hypothesis number (i), this last expression may be written as

$$\frac{\partial f_{\mathrm{S}}(r,t)}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD\frac{\partial f_{\mathrm{S}}(r,t)}{\partial r}\right) \qquad (9)$$

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

$$\begin{aligned} &f_{\mathrm{S}}(r,0) = 0, \quad 0 \le r \le a(0) \\ &f_{\mathrm{S}}(r,t) = f_{\mathrm{Smax}}, \quad r = a(t),\ t \ge 0 \end{aligned} \qquad (10)$$

where $f_{\mathrm{Smax}}$ 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

$$f_{\mathrm{S}}(r,t) = \left(1 - \frac{2}{a(t)}\sum_{n=1}^{\infty}\frac{\exp(-D\alpha_n^2 t)J_0[r_n\alpha_n]}{\alpha_n J_1[a(t)\alpha_n]}\right)f_{\mathrm{Smax}} \qquad (11)$$

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:

$$\begin{aligned} f_{\mathrm{S}}(r,t) = \Bigg(&\sqrt{a(t)/r}\,\mathrm{erfc}\frac{a(t)-r}{2\sqrt{Dt}} + [a(t) - r] \\ &\times\sqrt{\frac{Dta(t)}{4a(t)r^{3/2}}}\,\mathrm{ierfc}\frac{a(t)}{2\sqrt{Dt}} + \cdots\Bigg)f_{\mathrm{Smax}} \end{aligned} \qquad (12)$$

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

$$a^2(t) = a^2(0) + 2\int_0^{a(t)} f_{\mathrm{S}}(r,t)r\,\mathrm{d}r \qquad (13)$$

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

## 3. Algorithm for the numerical solution

In order to numerically evaluate Eqs. (11)–(13), the sample radius was divided into a number of segments, $n > 20$ (bi-dimensional rings), as shown in Fig. 2. Using

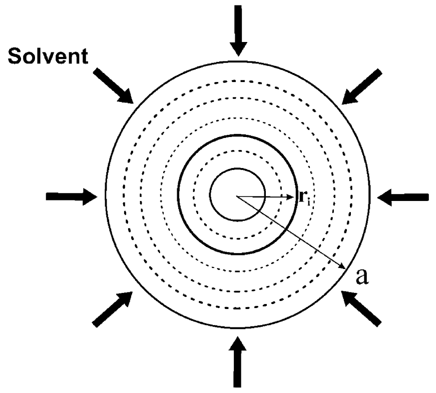

Fig. 2. Schematic of circuit for sensor testing.

Table 1
Experimental data from Márquez et al. [14] and Carrillo [15]

| | |
|---|---|
| Composite characteristics | |
| Resistivity of the dielectric component (Polybutadiene Solprene 200) ($\rho_H$) | $3.15 \times 10^{15}\ \Omega$ cm |
| Resistivity of the conductive component (carbon particles) ($\rho_L$) | $8.7 \times 10^{-2}\ \Omega$ cm |
| Experimental percolation exponent ($q$) | 3 |
| Critical percolation value ($f_C$) | 0.14 |
| Sample characteristics | |
| Cross-sectional area ($A_0$) | $6.514 \times 10^{-2}$ cm$^2$ |
| Length ($L$) | 30.0 cm |
| Test conditions | |
| Voltage ($E$) | 0–5 V |
| Temperature ($T$) | 25 ± 1 °C |

this partition, Eq. (13) can be expressed as

$$0 = a^2(0) - a^2(t) + \sum_{i=1}^{n} f_S(r_i^2 - r_{i-1}^2), \tag{14}$$

$r_n = a(t)$ and $r_0 = 0$

on which $a(t)$ is calculated by using a Newton–Raphson method, where Eq. (14) is linked to Eq. (11) for large times, or to Eq. (12) for short ones. Once that $a(t)$ was obtained with appropriated precision, the conductive volumetric fraction $f(t)_i$ at each radius $r_i$, is evaluated using the same previous Eq. (11) or (12). Electric resistivity at each location, $\rho_i$, is then calculated with the previous value and Eq. (5). The electric current intensity evolution, through the sample, can be evaluated with the following equation

$$\frac{I(t)}{I_0} = \frac{1}{a(t)_0^2} \sum_{i=1}^{n} \left(\frac{\rho_0}{\rho_i(t)}\right)(r_i^2 - r_{i-1}^2) \tag{15}$$

$r_n = a(t)$ and $r_0 = 0$

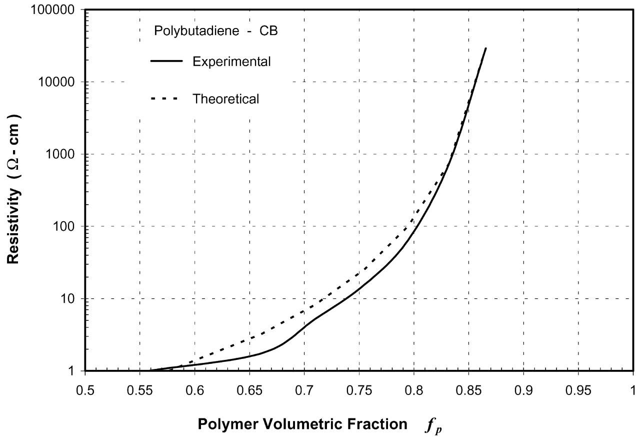

Fig. 3. Evolution of the resistivity of a PB/CB composite at different volume fractions of PB.

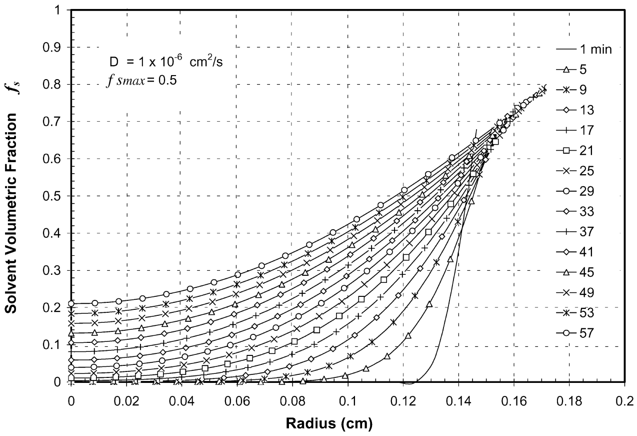

Fig. 4. Solvent diffusion with a $D = 1 \times 10^{-6}$ cm$^2$/s.

## 4. Results

In order to illustrate the use of this algorithm, experimental data from Márquez et al. [14] and Carrillo [15], was used. This data that is reported in Table 1, and correspond to a polymer composite with a carbon particles concentration larger than the critical percolation value, which represent the conductive fraction of the composite. This composite was elaborated using polybutadiene (PB) as the polymer matrix. In Fig. 3, electric resistance evolution when prepared using different volumetric fractions of carbon particles is shown. 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 (see Table 1). Subsequently, concentration profiles were evaluated for five different hypothetical solvents, as a function of the radial coordinate at different times. Calculations were performed on MS Excel spreadsheet, on a Pentium III based PC. The data were evaluated only for large times (corresponding to the validity range of Eq. (11)). Figs. 4 and 5 show the obtained results for a two particular solvents; one with a diffusion coefficient of $D = 1 \times 10^{-6}$ cm$^2$/s and another with a $D = 9 \times 10^{-6}$ cm$^2$/s. These values were chosen

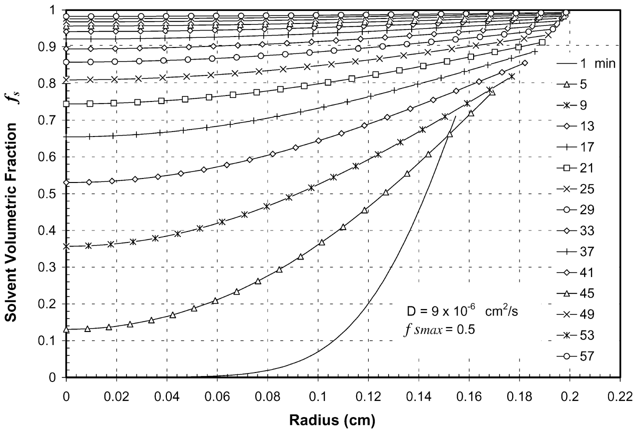

Fig. 5. Solvent diffusion with a $D = 9 \times 10^{-6}$ cm$^2$/s.

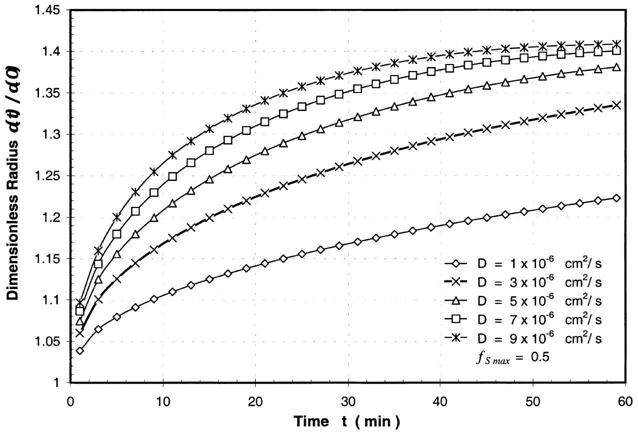

Fig. 6. Evolution of the normalized radii for different solvents.

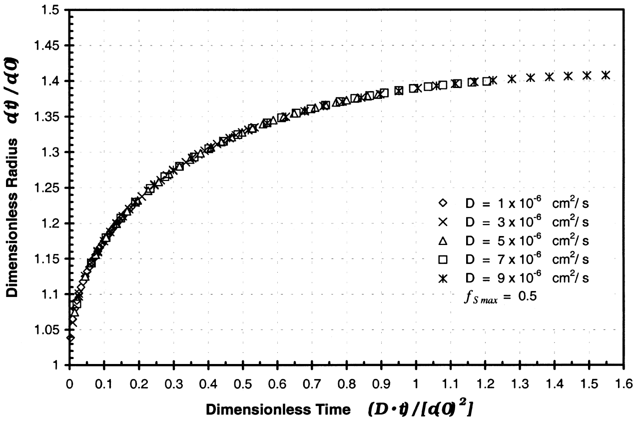

Fig. 8. Swelling master curve obtained by plotting the normalized radii against $Dt/a(t)^2$.

because they are very similar to actual values of hydrocarbons in an elastomer, as the PB [14,15]. The first curve in each 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 in these curves, how the external radius $a(t)$ increases as a function of time, as dictated by Eq. (13). It can also 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 (Eqs. (11) and (12)) are used these irregularities are vanished.

Fig. 6 shows the relationship between the instantaneous radii and the initial one, for a series of different solvents. First of all, it is interesting to observe that on the studied case the moving boundary exhibits a very large variation, as the radii increases more than 40%. As previously mentioned, for large swelling levels the diffusion coefficient may became concentration dependent, however, the results obtained with a constant coefficient correlate satisfactorily with the experimentally observed data [14,15].

Fig. 7 shows 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]. As expected, the current intensity drops faster for solvents that have larger diffusion coefficients on the composite than for those that have smaller ones. From a practical view, a more interesting fact is that; the rate at which the current intensity drops is different for different composites. Indeed, in previous works has been shown [14,15] that current intensity drop is significantly faster for PB than for SBR composites. It is important to mention that, by means of the evaluation of the difference between such drop rates, it is possible to identify what type of solvent is diffusing on the sensor's composites, in a relative inexpensive way.

Moreover, it is evident that the swelling curves of Fig. 6 could fit in a master curve, if one changes the contact time $(t)$ as the abscise variable by a dimensionless one as $Dt/a(t)^2$. For example, the result of this change is shown in Fig. 8, where one can see how they perfectly fit to a master curve. However, it is less evident that the curves corresponding to the current intensity also fit to a master curve. Fig. 9 shows these curves plotted versus the same last variable $Dt/a(t)^2$. It is amazing how they also fit to a perfect master curve.

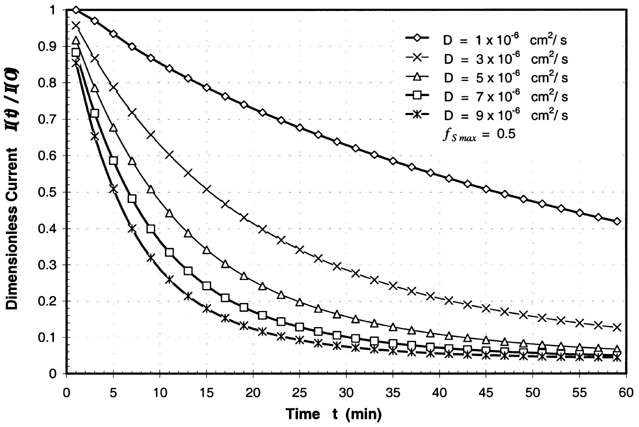

Fig. 7. Falling of the current intensity with the solvent contact time.

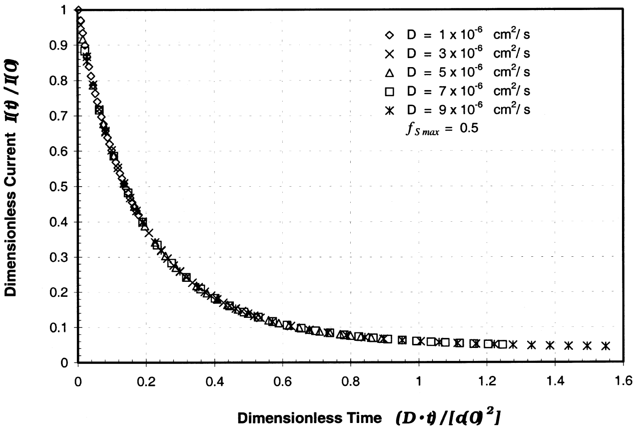

Fig. 9. Master curve obtained by plotting the current intensity against $Dt/a(t)^2$.

## 5. Discussion

As previously mentioned, the present analysis utilizes a number of approximations needed to obtain the results in a straightforward way. One of the more delicate approximations is the consideration of diffusion coefficient $D$ as a constant, when the radius increases until 40%, which means that the increase in volume is twice with a liquid volume fraction of 0.5. Generally, for such high concentration, $D$ is concentration dependent. However, it must be noted that the larger decrease in composite conductivity takes place at the first moments of the swelling, where the diffusion coefficient could be considered as a constant. Additionally, it is very difficult to find experimental data for this parameter when it becomes concentration dependent, therefore the use of such an analysis would become very limited for sensor designers. Indeed, as previously mentioned the treatment of variable $D$ is mainly possible, in closed form, only if the variation of $D$ with concentration is known a priori, and if the variation can be expressed analytically [17]. This last point is very important, because even though, a designer may find an analytical relation for $D(c)$, for a particular solvent in a polymer, it may change significantly for the doped composites of the same polymer. Moreover, we are currently developing a method to take into account this dependency. The method use the model of Philip [18,19], however, the calculations involved in this last method are significantly more complicated than in the present one, and the precision is almost the same, specially at the first stages of the swelling.

Another point to be signaled, in this analysis, is the use of the solvent volumetric fraction $f_S$ instead of the concentration $C$. We consider that the employ of the first parameter, for the present study, is better because it may be measured, in the actual experimental tests, in an easier and more precise way than the second one. For example, to measure the concentration it is necessary to weight continuously the sample, and as a consequence to interfere with the diffusion process. However, it is possible to measure the increase of the solvent volumetric fraction into the sample, by photographic means, with no interference during the test. Of course, it is possible to calculate the concentration from the volumetric fraction, however, in a number of polymers the relation between the solvent volumetric fraction and its actual concentration evolves with the swelling level, therefore the calculation of the concentration in basis of the volumetric fraction introduces a new uncertainty to the study of the phenomena, that is dictated mainly by the increase of dielectric volume into the sample.

Finally, it is important to mention that this methodology may allow a more precise sensor design, based only on easily obtainable laboratory data. Particularly, it provides a possibility to use complementary data, as for example the rate with which the current intensity falls, for the identification of a number of substances.

## 6. Conclusion

A methodology that describes the change in electric properties of polymeric composites, during solvent diffusion processes, is presented in this work. The equations that result from this methodology require 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.

## Acknowledgements

We are grateful to the ‘Instituto Mexicano del Petroleo’ and the ‘Consejo Nacional de Ciencia y Tecnologia’, for the award of the grants No. FIES 97-04-IV, and No. G 25866-A.

## Appendix A

In order to solve Eq. (3) for $\rho_m$, the next procedure was followed

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

Multiplying by the denominators both members we have:

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

Arranging:

$$\rho_m^{-2/q}-[ff_R+f-1)\rho_H^{-1/q}-(ff_R+f-f_R)\rho_L^{-1/q}]f_R^{-1}\rho_m^{-1/q}$$
$$-\rho_L^{-1/q}\rho_H^{-1/q}f_R^{-1}=0$$

The previous equation is a quadratic expression, which is straightforward solved by taking into account the parameters $B$ and $C$ defined by Eq. (6).

## References

[1] Miyazaka K, Watanabe K, Jojima E, Aida H, Sumita M, Ishikawa K. Electrical conductivity of carbon–polymer composites as a function of carbon content. J Mater Sci 1982;17:1610.
[2] Biing-lin L. Electrically conductive polymer composites. Polym Engng Sci 1992;32:36.
[3] Kortschot MT, Woodhams RT. Computer simulation of the electrical conductivity of polymer composites containing metallic fillers. Polym Compos 1998;9:60.
[4] Lux F. Percolation in electrical conductive polymer according to a new thermodynamic percolation model. Polym Engng Sci 1993;33: 334.
[5] Kirkpatrick S. Percolation and conduction. Mod Phys Rev 1973;45: 574.
[6] Beugtsson P, Kubát J. Electrical noise characteristics of carbon

black-filled linear low density polyethylene near to the percolation threshold. Polym Engng Sci 1993;33:573.

[7] Narkis M, Ram A, Stein Z. Electrical properties of carbon black filled crosslinked polyethylene. Polym Engng Sci 1981;21:1049.

[8] Sherman RD, Middleman LM, Jacobs M. Electron transport processes in conductor-filled polymers. Polym Engng Sci 1983;23:36.

[9] Yacubowicz J, Narkis M. Dielectric behavior of carbon black filled polymer composites. Polym Engng Sci 1986;26:1568.

[10] Hsu WY, Holtie WG, Barkley JR. Percolation phenomena in polymer/carbon composites. J Mater Sci Lett 1988;7:459.

[11] McLachlang DS. J Phys C 1987;20:865.

[12] Blazkiewcz M, McLachlang D, Newnham RE. The volume fraction and temperature dependence of the resistivity in carbon black and graphite polymer composites: an effective media-percolation approach. Polym Engng Sci 1993;32:421.

[13] Lonergan MC, Severin EJ, Doleman BJ, Beaber SA, Grubbs RH, Lewis NS. Array-based vapor sensing using chemically sensitive, carbon black-polymer resistors. Chem Mater 1996;8:2298.

[14] Márquez A, Uribe J, Cruz RJ. Conductivity variation induced by solvent swelling of an elastomer–carbon black–graphite composite. J Appl Polym Sci 1997;66:2221.

[15] Carrillo A. Caracterización eléctrica de un compuesto conductor sensible a disolventes orgánicos y temperatura. BSME Thesis. Mérida, Yucatán, México: Instituto Tecnológico de Mérida; 1997.

[16] Crank J. The mathematics of diffusion, 2nd ed. Oxford: Clarendon Press; 1967.

[17] Vieth WR. Diffusion in and through polymers: principles and applications. Oxford: Oxford University Press; 1991. ISBN 0-19-520906-0.

[18] Philip JR. Aust J Phys 1960;13:1–13.

[19] Philip JR. Aust J Phys 1963;16:287.