"All science requires mathematics".

Roger Bacon *(1220?–1292), English monk,*
philospher, and scientist.
Opus Majus.

CHAPTER 8

MODELLING OF THE CONDUCTIVITY

8.1 INTRODUCTION.

This chapter is intended to analyse the behaviour of the conductivity with respect to the content of conductive complex. As has been seen in the previous chapter, the measurement of the conductivity was only achieved for the extruded blend with the highest content of PANIPOL^{TM}. Therefore, the analysis concentrates on the conductive behaviour of the compression moulded blends (refer to section 6.3). For the analysis, two approaches were followed. The first one was the percolation theory and the second one was a generalisation of effective media theories. As will be seen in the relevant section, both approaches require expressing the conductivity of the composite as a function of the volume fraction of the conductive phase. Literally, the term conductive phase refers, in the case of the present work, to the conducting polyaniline salt, whose content in the as-received pellets of PANIPOL^{TM} is about 25 wt.% (refer to sections 3.2 and 4.3.1). However, in this particular study the entire PANIPOL^{TM} complex was regarded as the conductive phase, whose volume fraction in the blends (Table 8.1) was calculated using *Eq. 5.3a* (refer to section 5.2.4) and the density values of 1100 and 940 kg/m^3 corresponding to the PANIPOL^{TM} and SBS, respectively (refer to the relevant sections in chapter 3). The average volume conductivity of each compression moulded blend is also presented in Table 8.1 (refer to Table 6.5 in section 6.3). Similarly to the previous chapters, general conclusions are presented in the final section.

Table 8.1. Volume fraction of PANIPOL^{TM} in the compression moulded blends and their corresponding average volume conductivity (σ).

Wt.% in the blend	**Volume fraction in the blend**	**Average σ (S/cm)**
0	0.0000	1.00×10^{-14} *
5	0.0430	7.27×10^{-11}
10	0.0867	3.50×10^{-6}
15	0.1310	4.26×10^{-5}
20	0.1760	2.10×10^{-4}
35	0.3151	5.32×10^{-4}
50	0.4608	7.61×10^{-4}
100	1.0000	2.57×10^{-3} **

* σ of the SBS (refer to section 3.3.1)
** σ of the PANIPOL^{TM} pellets (refer to Table 4.5 in section 4.7)

8.2 PERCOLATION THEORY APPROACH.

The percolation theory has been used to interpret the behaviour of conductivity in mixtures of conducting and non-conducting particles [22,57,62,78,79,189,193,194]. The sudden transition in such materials from insulator to conductor is evidence of a percolation threshold. As has been seen in chapter 2, the percolation equation (i.e., *Eq. 2.1* from section 2.4.2) describes the relationship between the composite conductivity and conductive filler concentration in the vicinity of the percolation threshold. To facilitate following the sequence of the present analysis, the percolation equation, together with the definition of its terms is presented again in this section. The equation is referred to as *Eq. 8.1*.

$$\sigma_m = \sigma_h(\phi - \phi_c)^t \text{.....} Eq.\ 8.1.$$

σ_m = conductivity of the composite.

σ_h = conductivity of the conductive filler.

ϕ = volume fraction of the conductive filler.

ϕ_c = percolation threshold.

t = critical exponent.

Equation 8.1 is valid at concentrations above the percolation threshold, that is, when $\phi > \phi_c$. The critical volume fraction and the exponent t are used to classify the microstructure of percolating systems. They are sensitive to various factors, one of the more important being the relative size of the conducting and insulating particles. Therefore, *Eq. 8.1*, can be used to fit experimental data and find values of ϕ_c and t which can be compared with previous model predictions. However, some researches, for example McLachlan et al. [80], argue that the percolation theory is also limited in that the percolation equation is valid near the threshold, only when the ratio of the conductivities of the two components is infinite. This can be a problem when dealing with real systems where all components have finite conductivities. Strictly speaking, the percolation theory only applies when either the conductivity of the low conductivity filler (σ_l) is equal to zero or when the resistivity of the high conductivity filler ($1/\sigma_h$), with conductivity σ_h, is also equal to zero. In spite of its limitations, the percolation theory can help to elucidate the mechanisms and microstructure that control the conductivity process in conductive composites.

In principle, to predict the conductivity of the composite, a non-linear iterative fitting method should be used to evaluate the unknown parameters ϕ_c and t in *Eq. 8.1* from experimental $\{\phi, \sigma_m\}$ pairs. Then the predicted and experimental data can be correlated, and the maximum value of the squared correlation coefficient [195], r^2, is searched for. However this method implies that it is necessary to exclude the experimental $\{\phi, \sigma_m\}$ pairs for which $\phi \leq \phi_c$ because the condition $\phi > \phi_c$ must be fulfilled to evaluate the term $(\phi - \phi_c)^t$ in *Eq. 8.1* for any given value of t. This reduces the data set and usually distorts the results as r^2 may reach several maximum values even at ϕ_c far from the percolation region. A more suitable method is to express *Eq. 8.1* in the following form:

$$[\sigma_m]^{1/t} = [\sigma_h(\phi - \phi_c)^t]^{1/t},$$

which reduces to:

$$\sigma_m^{1/t} = \sigma_h^{1/t}(\phi - \phi_c) = \sigma_h^{1/t}\phi - \sigma_h^{1/t}\phi_c.$$

Rearranging the above expression, the following equation is obtained:

$$\sigma_m^{1/t} = -\sigma_h^{1/t}\phi_c + \sigma_h^{1/t}\phi \text{ .....Eq. 8.2.}$$

Eq. 8.2 has the mathematical form of the equation that describes a straight line with the intercept on the axis y and also allows including all the experimental $\{\phi, \sigma_m\}$ pairs to determine the unknown parameters. Therefore, by plotting $\sigma_m^{1/t}$ vs. ϕ for a varying exponent t and applying a linear regression analysis to find the plot with the maximum r^2, it is possible to find the best estimate of the value of t. Moreover, this analysis also aids in finding the equation that describes the plots making it possible to estimate the value of ϕ_c and predict a value for σ_h, which can be compared with the actual value.

Accordingly, all the equations obtained by applying the regression analysis will have the form of the equation of a straight line, which is:

$$y = -a + bx \text{ .....Eq. 8.3.}$$

Therefore, by comparing *Eq. 8.2* with *Eq. 8.3*, it is possible to realise that in *Eq. 8.3*, y will correspond to a predicted value of $\sigma_m^{1/t}$, and that x will correspond to the

actual value of ϕ. Additionally, the terms a and b in *Eq. 8.3* will correspond to expressions from which the values of ϕ_c and σ_h can be predicted (equations 8.3a to 8.3d).

$$a = \sigma_h^{1/t}\phi_c \text{ .....Eq. 8.3a}$$

$$b = \sigma_h^{1/t} \text{.....Eq. 8.3b}$$

$$\phi_c = a/b \text{.....Eq. 8.3c}$$

$$\sigma_h = (b)^t \text{.....Eq. 8.3d}$$

8.2.1 EVALUATION OF THE CRITICAL PARAMETERS.

Following the method previously described, several plots of $(\sigma_m)^{1/t}$ vs. ϕ were performed by varying the value of the exponent t (the values of σ_m and ϕ are presented in Table 8.1). A linear regression analysis was applied to each plot, and an iterative process was performed in order to find the value of the exponent t that yielded the maximum r^2. As a mere example, one of the several plots obtained is presented in fig. 8.1. The regression analysis was carried out using the statistics package of the software Microsoft Excel 2000.

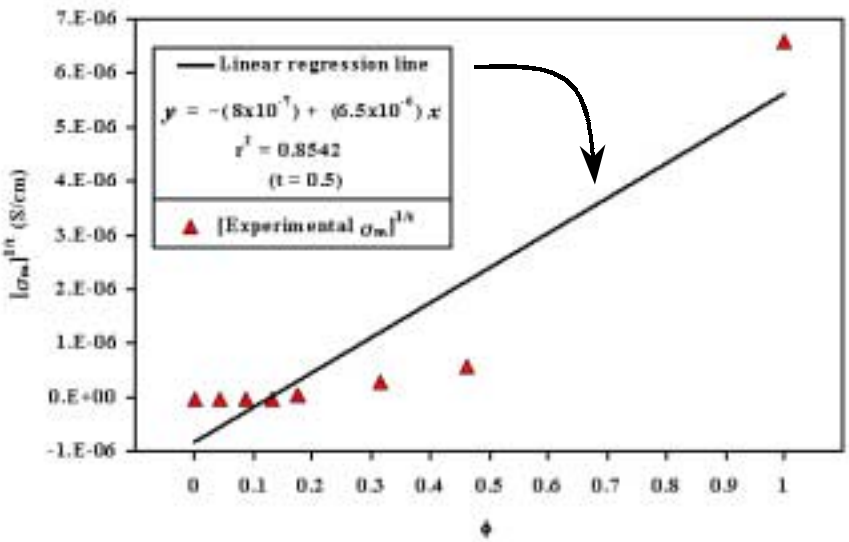

Figure 8.1. Plots of $(\sigma_m)^{1/t}$ vs. ϕ for $t = 0.5$.

The results from the iterative process are presented in fig. 8.2. Note that fig. 8.2b corresponds to the data between the broken lines in fig. 8.2a, but plotted reducing the scale of the main axes. Figure 8.2 also presents the predicted values of ϕ_c for each value of t that were obtained by using the equation of the regression lines (*Eq. 8.3*) and *Eq. 8.3c*.

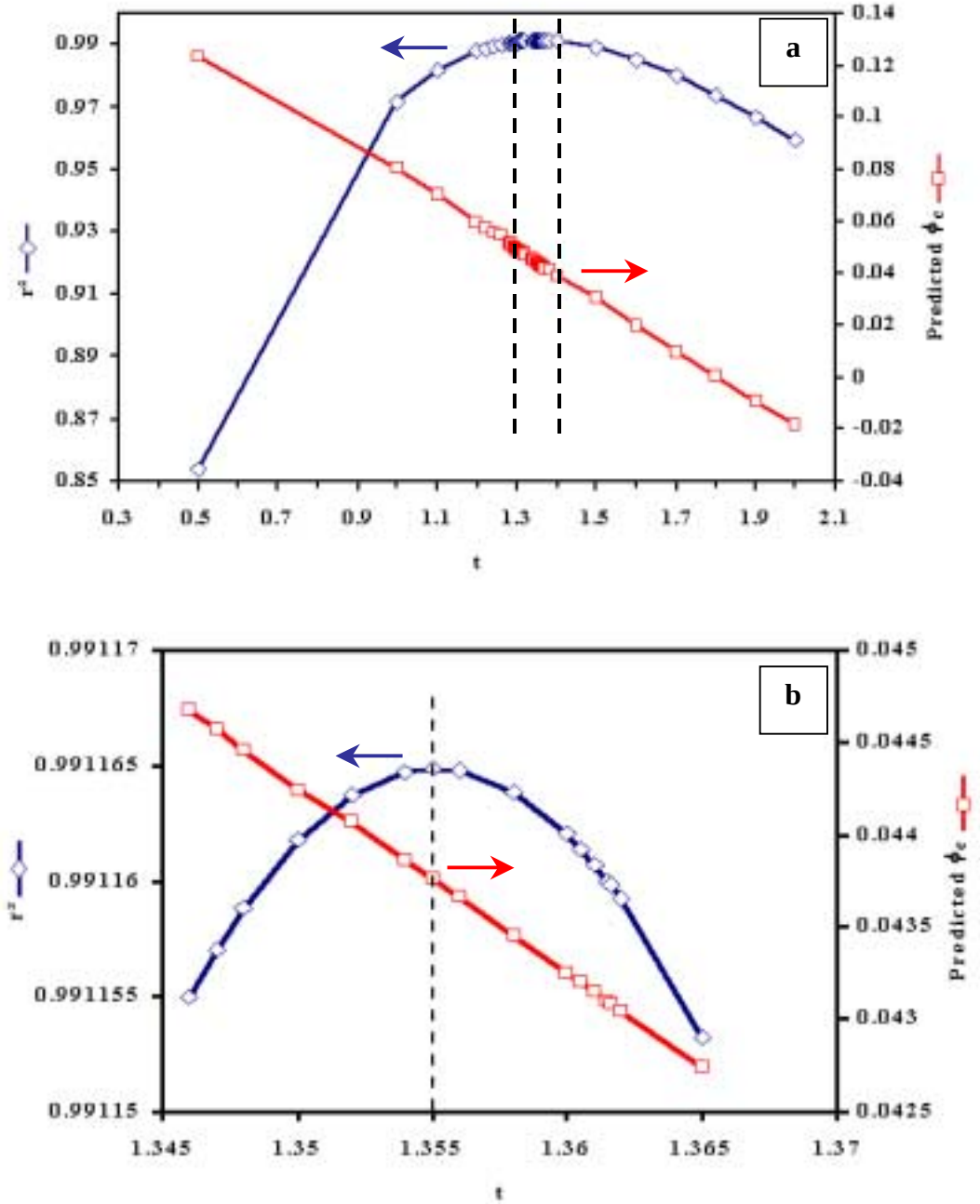

Figure 8.2. Variation of r^2 with respect to the value of the exponent t in the $\sigma_m^{1/t}$ vs. ϕ plots. The values of ϕ_c were obtained for each value of t using equations 8.3 and 8.3c.

From fig. 8.2b it can be observed that the maximum value of r^2 (i.e., 0.99117) was obtained for a value of t equal to 1.355, while the corresponding value of ϕ_c was 0.04376 (note the broken line in fig. 8.2b). Figure 8.3 presents the $(\sigma_m)^{1/t}$ vs. ϕ plots using the previously obtained value of t. This figure also shows the equation of the regression line, with the values of a and b equal to 5.571 x 10^{-4} and 1.273 x 10^{-2}, respectively. As commented before, these values were used in *Eq. 8.3c* to estimate the value of ϕ_c. It can be observed that this value (i.e., 0.04376) compares very well with that of 0.0430 corresponding to 5 wt.% of PANIPOL™ in the blends (refer to Table 8.1), which was originally estimated as the percolation threshold (refer to fig. 6.2 in section 6.3). The predicted value for σ_h was obtained using the values of b and t in *Eq. 8.3d*. This was equal to 2.7 x 10^{-3} S/cm, which is also in well agreement with the experimental value for the PANIPOL™ pellets of 2.57 x 10^{-3} S/cm. It should be stressed that the value of the critical parameters depends on the number of experimental data available to perform the curve-fitting method. However, the more experimental data available, the more accurate the method is to evaluate the critical parameters.

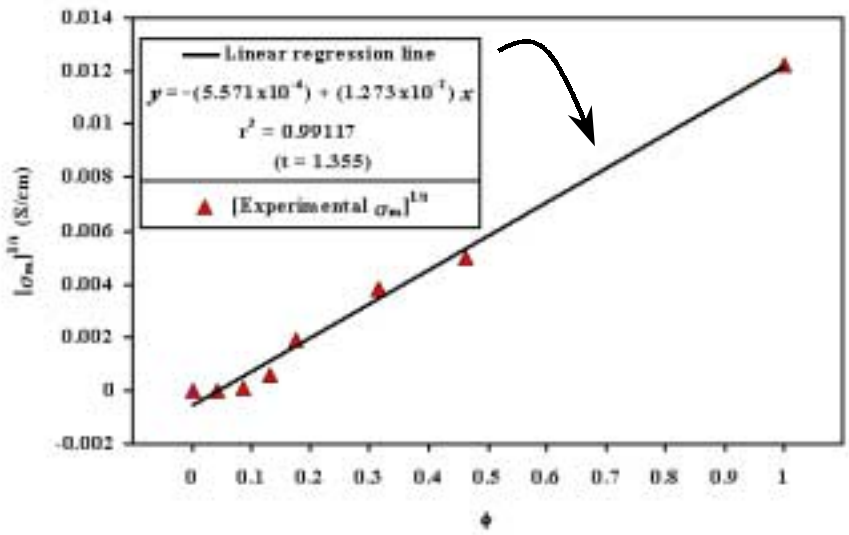

Figure 8.3. Plots of $(\sigma_m)^{1/t}$ vs. ϕ for t = 1.355.

The values of t = 1.355 and ϕ_c = 0.04376 were used in *Eq. 8.1* to predict the conductivity of the blends (σ_m) at each PANIPOL™ volume fraction (ϕ). In *Eq. 8.1*, the experimental value of 2.57 x 10^{-3} S/cm for the conductivity of the PANIPOL™ pellets (σ_h) was used. For the reasons already discussed, the predictions only included the

experimental $\{\phi, \sigma_m\}$ pairs for which $\phi > \phi_c$. The results are presented in Table 8.2 and the predicted and experimental ϕ vs. σ_m curves are presented in figure 8.4 for comparison. The predicted and experimental data were correlated with the value of the squared correlation coefficient equal to 0.99687.

Table 8.2. Predictions of σ_m using *Eq. 8.1* with $t = 1.355$ and $\phi_c = 0.04376$. Percolation theory approach.

ϕ	**Experimental σ_m* (S/cm)**	**Predicted σ_m (S/cm)**
0.0000	1.00×10^{-14}	----
0.0430	7.27×10^{-11}	----
0.0867	3.50×10^{-6}	3.61×10^{-5}
0.1310	4.26×10^{-5}	9.43×10^{-5}
0.1760	2.10×10^{-4}	1.66×10^{-4}
0.3151	5.32×10^{-4}	4.39×10^{-4}
0.4608	7.61×10^{-4}	7.86×10^{-4}
1.0000	2.57×10^{-3}	2.42×10^{-3}

* Average values (refer to Table 8.1)

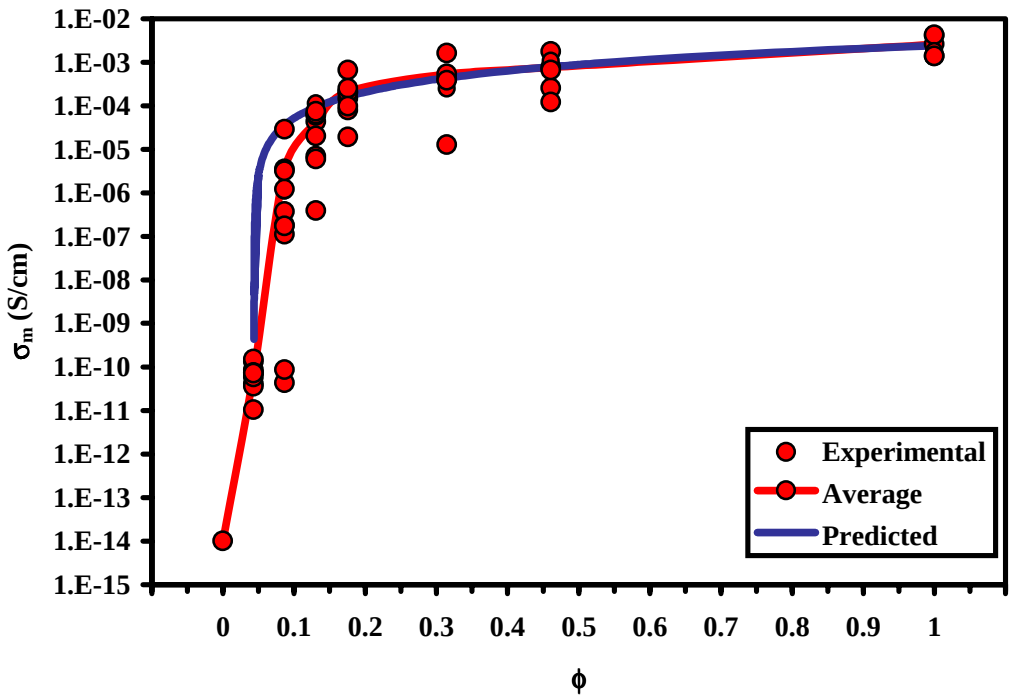

Figure 8.4. The predicted and experimental ϕ vs. σ_m curves ($t = 1.355$ and $\phi_c = 0.04376$ in *Eq. 8.1*). Percolation theory approach.

As has been observed, the value obtained for the critical exponent t is below the theoretical value for composites, which is most often found to lie in the range 1.65 to 2 [79,80]. However, values of t are reported to be below those limits, and sometimes values in excess of 2.0 have also been obtained. It should be stressed however, that the values of t (and the corresponding values of ϕ_c) are strongly dependent on the systems involved and on the blending techniques used to produce them. Additionally, the value of the critical parameters also depends on the mathematical form in which the percolation equation is used to perform the predictions [22,57,62,189,193,194].

As has been mentioned before, the percolation threshold (i.e., around 5 wt.% of conductive filler, or ϕ_c = 0.0430) was calculated based on the content of the PANIPOL^{TM} pellets in the blends. Now, in view of the fact that the content of the conducting PANI salt in the pellets is about 25 wt.%, the percolation threshold, based on the PANI salt content would be around 1.25 wt.%. The company supplying the pellets did not provide any specific information about the respective density values for the polyaniline salt and zinc compound that could have been used to calculate the correct volume fraction of the PANI salt in the blends. However, an approximate estimation, assuming that the density of the aforementioned compounds is the same as that of the pellets (i.e., 1100 kg/m^3), yields a ϕ_c equal to 0.01076 corresponding to 1.25 wt.% of the conducting polyaniline salt in the blends. Irrespective of the accuracy of this estimation, it is clear that the value of ϕ_c based only on the content of the PANI salt should be lower than 0.0430.

The critical parameters calculated for the present compression moulded PANIPOL^{TM}-SBS system are consistent with those calculated by Křivka et al. [194], who followed a similar method to the one used in this work. Křivka and co-workers studied mechanically blended mixtures (obtained with a pestle and mortar) of conducting PANI with potassium bromide and ammonium sulphate salt, respectively, which were subsequently pressed in a manual hydraulic press into small pellets. The values for the exponent t were also below the theoretical ones, being equal to 1.43 and 1.53, respectively. Moreover, the critical volume fractions obtained for those composites were respectively 0.016 and 0.023. Křivka et al. observed that at ϕ_c, their materials showed a morphology of segregated conducting PANI domains within the

matrix phase. This observation is also in good agreement with the morphology observed in the present PANIPOL^{TM}-SBS system at ϕ_c, in which the conducting PANI particles are segregated into small clusters that were formed into layered structures during the compression moulding process (refer to fig. 6.15 in section 6.4.3). Therefore, the conductivity at ϕ_c may be attributed to the incipient formation of very long layers of PANI in the direction of the current flow.

8.3 GENERALISED EFFECTIVE MEDIA THEORY APPROACH.

As explained before, experimental and theoretical data can be correlated to explain how the volume fraction and the morphology of the components affect the electrical behaviour of the composites. In general, previous theoretical work has only relied on percolation and effective media theories. As discussed before, the percolation theory is limited. Effective media theories (refer to section 2.4.3 in chapter 2, or to references [80] and [85]) are used to try to predict the effective or large-volume average of the electrical conductivity of composites. As explained in chapter 2, there are two special cases for which effective media theories exist, the symmetric and asymmetric cases. As has been seen in the relevant section, when one component is a perfect insulator, the symmetric media theory contains a conductor-insulator transition at a specific conductor volume fraction, which depends on the shape of the particles, whereas the asymmetric theory does not contain a transition. In practice, conductor-insulator transitions occur over a wide range of volume fractions.

A generalized effective media (GEM) equation that describes the conductivity of binary mixtures as a function of the conductivity of the components, the volume fraction of each, and the two percolation parameters, has been proposed by McLachlan [80,85,86]. One parameter is the critical volume fraction, ϕ_c, the other is the exponent t which depends on ϕ_c and a characteristic depolarisation coefficient, L, for the dispersion (refer to section 2.4.3). This coefficient depends on the shape of the particles and whether the dispersion is oriented, partially oriented or random. The equation, which was derived as an interpolation between the symmetric and asymmetric effective media theories, is valid for all volume fractions. Furthermore, the shape of the conducting and

insulating particles in the media can be deduced by analysing the experimental results. The GEM equation written in terms of the electrical conductivity is

$$\frac{(1-\phi)\left(\sigma_l^{1/t}-\sigma_m^{1/t}\right)}{\sigma_l^{1/t}+\left(\frac{1-\phi_c}{\phi_c}\right)\sigma_m^{1/t}}+\frac{\phi\left(\sigma_h^{1/t}-\sigma_m^{1/t}\right)}{\sigma_h^{1/t}+\left(\frac{1-\phi_c}{\phi_c}\right)\sigma_m^{1/t}}=0 \quad \text{.....Eq. 8.4,}$$

where:

ϕ = volume fraction of the higher conductive component (filler),

ϕ_c = critical volume fraction of the higher conductive component (percolation threshold),

σ_l = conductivity of the lower conductive component (matrix),

σ_h = conductivity of the higher conductive component (filler),

σ_m = conductivity of the medium (composite),

t = critical exponent.

Equation 8.4 reduces to the symmetric and asymmetric theories and has the mathematical form of the percolation equation in the appropriate limits. Accordingly, in the appropriate limits, and depending on the spatial distributions of the composite's phases, *Eq. 8.4* reduces to the equations given below. In those equations, $f = 1 - \phi$ and $f_c = 1 - \phi_c$ are the volume and critical volume fractions of the lower conductive component, respectively.

- *For oriented ellipsoids.*

When $\sigma_l = 0$,

$$\sigma_m = \sigma_h\left(1-\frac{f}{f_c}\right)^{f_c/(1-L_f)} \quad \text{.....Eq. 8.5a,}$$

and when $\rho_l \approx 0$,

$$\rho_m = \rho_h\left(1-\frac{\phi}{\phi_c}\right)^{\phi_c/L_\phi} \quad \text{.....Eq. 8.5b,}$$

In the previous equations, L_f and L_ϕ are the depolarisation coefficients for the lower and higher conductive phases, respectively. *Eqs. 8.5a* and *8.5b* reduce to the

equations from the symmetric theory when $f_c = 1 - L_f$ or $\phi_c = L_\phi$. In the equations given above and in the following ones, the terms ρ_m ($1/\sigma_m$), ρ_l ($1/\sigma_h$) and ρ_h ($1/\sigma_l$) stand for the resistivities of the composite, the lower and higher resistive phases, respectively. Also, it is clear that $\rho_l \approx 0$ when $\sigma_h = \infty$.

- *For randomly oriented ellipsoids.*

When $\sigma_l = 0$,

$$\sigma_m = \sigma_h \left(1 - \frac{f}{f_c}\right)^{m_f f_c} \text{.....}Eq.\ 8.6a,$$

and when $\rho_l \approx 0$,

$$\rho_m = \rho_h \left(1 - \frac{\phi}{\phi_c}\right)^{m_\phi \phi_c} \text{.....}Eq.\ 8.6b,$$

In equations 8.6a and b m_f and m_ϕ are exponents for the randomly oriented ellipsoids of the lower and higher conductive phases, respectively.

Equations 8.5a to 8.6b take the form of the equations from the asymmetric theory when $f_c = 1$ or $\phi_c = 1$. In general, the equations given above take the mathematical form of the percolation equation as follow:

When $\sigma_l = 0$,

$$\sigma_m = \sigma_h \left(1 - \frac{f}{f_c}\right)^{t} \text{.....}Eq.\ 8.7a,$$

and when $\rho_l \approx 0$,

$$\rho_m = \rho_h \left(1 - \frac{\phi}{\phi_c}\right)^{t} \text{.....}Eq.\ 8.7b.$$

Therefore, the GEM equation (*Eq. 8.4*) can also be viewed as a matched asymptotic expression as it interpolates between the equations given above (*Eqs. 8.7a* and *8.7b*), from which the relationship of the exponent t with the parameters L_f, L_ϕ, f_c, ϕ_c, m_f and m_ϕ can be deduced as follow:

- *For oriented ellipsoids.*

$$t = \frac{f_c}{1 - L_f} = \frac{\phi_c}{L_\phi} \text{.....}Eq.\ 8.8a.$$

- *For randomly oriented ellipsoids.*

$$t = m_f\, f_c = m_\phi \phi_c \text{ .....} Eq.\ 8.8b.$$

Equations 8.8a and 8.8b can be solved together with the relation $f_c = 1 - \phi_c$ to give:

$$t = \frac{1}{1 - L_f + L_\phi} = \frac{m_f m_\phi}{m_f + m_\phi} \text{ .....} Eq.\ 8.9.$$

Accordingly, these equations can be used to deduce the particles shapes and their spatial distributions in composites, for which values of the involved parameters can be found in the literature [84,85]. Although the morphological analysis performed on the compression moulded blends suggested that the morphology responsible for the conductivity mainly consisted of layered structures of the conductive filler within the insulating matrix (refer to section 6.4), for the purpose of the present modelling it will be assumed that the PANIPOL^{TM}-SBS blends are similar to a system containing oriented spheroids. Therefore, *Eq. 8.8a* will be appropriate to deduce the morphology of the blends. For this, typical values of L for spheroids (of different shapes) oriented in the direction of the current flow are presented in Table 8.3 [84]. Defining the three principal axes of the spheroid as a, b and c, the values of L are for particles in which two of the axes are of equal length (that is, $b = c$). The term L is purely numerical and depends only on the axial ratios of the dispersed particles [84,181].

Table 8.3. Values of L for spheroids in which $b = c$.
(from Meredith and Tobias [84]).

Shape	**b/a**	***L***		**Shape**	**b/a**	***L***
Rods	0	0.5000		Oblate spheroids	2	0.2383
Prolate spheroids	1/6	0.4784			3	0.1823
	1/5	0.4720			4	0.1477
	1/4	0.4624			5	0.1245
	1/3	0.4465			6	0.1077
	1/2	0.4134				
Spheres	1	0.3333		Disks	∞	0.0000

8.3.1 EVALUATION OF THE CRITICAL PARAMETERS.

The GEM equation (*Eq. 8.4*) was written as a quadratic equation as follows:

$$\alpha\sigma_m^{2/t} + \beta\sigma_m^{1/t} + \gamma = 0 \text{ .....} Eq.\ 8.10.$$

Solving *Eq. 8.10* for σ_m, the true solution for any given value to the variables is found to be

$$\sigma_m = \left(\frac{-\beta + \sqrt{\beta^2 - 4\alpha\gamma}}{2\alpha} \right)^t \text{ .....} Eq.\ 8.11,$$

where:

$$\alpha = A(1+B)$$

$$\beta = (B-A)\sigma_h^{1/t} + (1-AB)\sigma_l^{1/t}$$

$$\gamma = -(1+B)\sigma_h^{1/t}\sigma_l^{1/t}$$

$$A = \frac{1-\phi_c}{\phi_c}$$

$$B = \frac{1-\phi}{\phi}$$

To predict the conductivity of the blends (σ_m), an iterative process was performed in which the parameters ϕ_c and t were varied freely in *Eq. 8.11*. The values of ϕ used for the predictions are those presented in Table 8.1. On the other hand, σ_h and σ_l correspond to the volume conductivity of the PANIPOL™ pellets (i.e., 2.57 x 10^{-3} S/cm) and SBS (i.e., 1 x 10^{-14} S/cm), respectively. For each $\{\phi_c, t\}$ pair, the predicted data were correlated with the experimental ones in order to find the maximum value for r^2, which would suggests the correct values for the parameters ϕ_c and t. The results from the iterative process are presented in fig. 8.5, which shows that the highest values for r^2 were obtained for $\{\phi_c, t\}$ pairs corresponding to {0.03, 1.4} and {0.06, 1.3}. This is observed more clearly in fig. 8.6 (note the broken arrows), in which the scale of the main axes was reduced. These results suggested that the correct values of t and ϕ_c should be in the intervals $1.3 \leq t \leq 1.4$ and $0.03 \leq \phi_c \leq 0.06$, respectively. To increase the accuracy of the calculations, a similar iterative process to the previous one was performed for $\{\phi_c, t\}$ pairs in the intervals $1.3 \leq t \leq 1.4$ and $0.03 \leq \phi_c \leq 0.064$. The

results are presented in fig. 8.7, which suggests that the correct values for t and ϕ_c should lie in the intervals $1.34 \leq t \leq 1.36$ and $0.044 \leq \phi_c \leq 0.050$, respectively (note the broken arrows in the figure). Accordingly, the values calculated for t and ϕ_c are, respectively, 1.35 ± 0.010 and 0.047 ± 0.003, although it must not be assumed that these values should be exactly halfway between the limits above quoted. These values are, however, in good agreement with those obtained from the percolation theory approach (i.e., 1.355 and 0.04376, respectively). Moreover, the numerical quantity of 0.047 assigned to ϕ_c, also compares well with that of 0.0430 corresponding to 5 wt.% of PANIPOL™ in the blends (originally estimated as the percolation threshold). The predicted conductivities, using the values obtained for t and ϕ_c in *Eq. 8.11*, are presented in Table 8.4 together with the experimental results. The value for r^2 was 0.99724. The predicted and experimental ϕ vs. σ_m curves are presented in figure 8.8 for comparison.

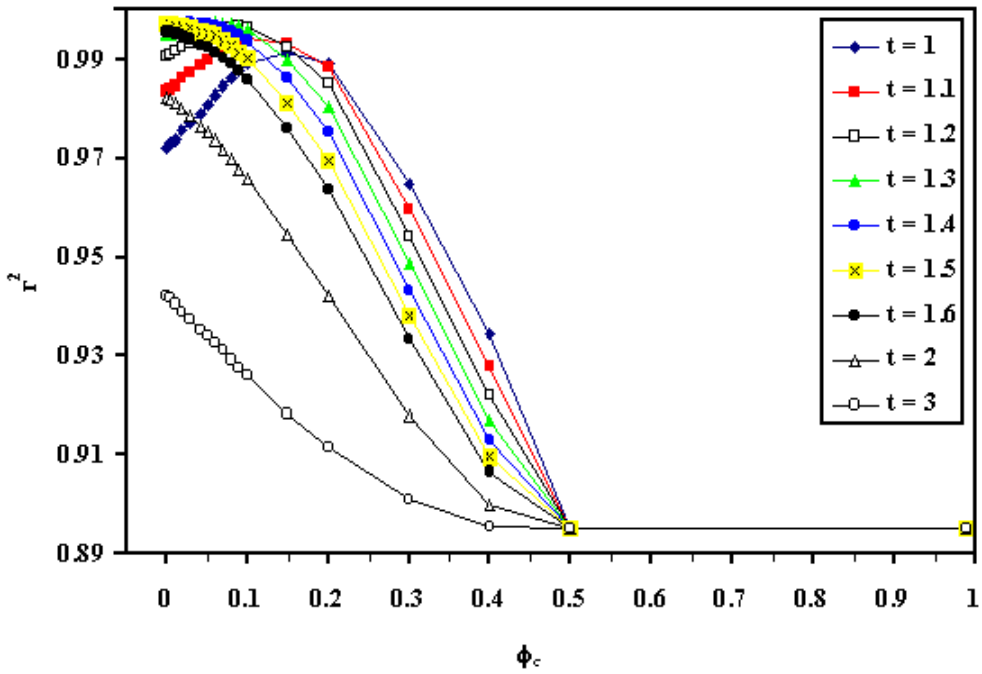

Figure 8.5. Results from the iterative process followed by using *Eq. 8.11* for different $\{\phi_c, t\}$ pairs.

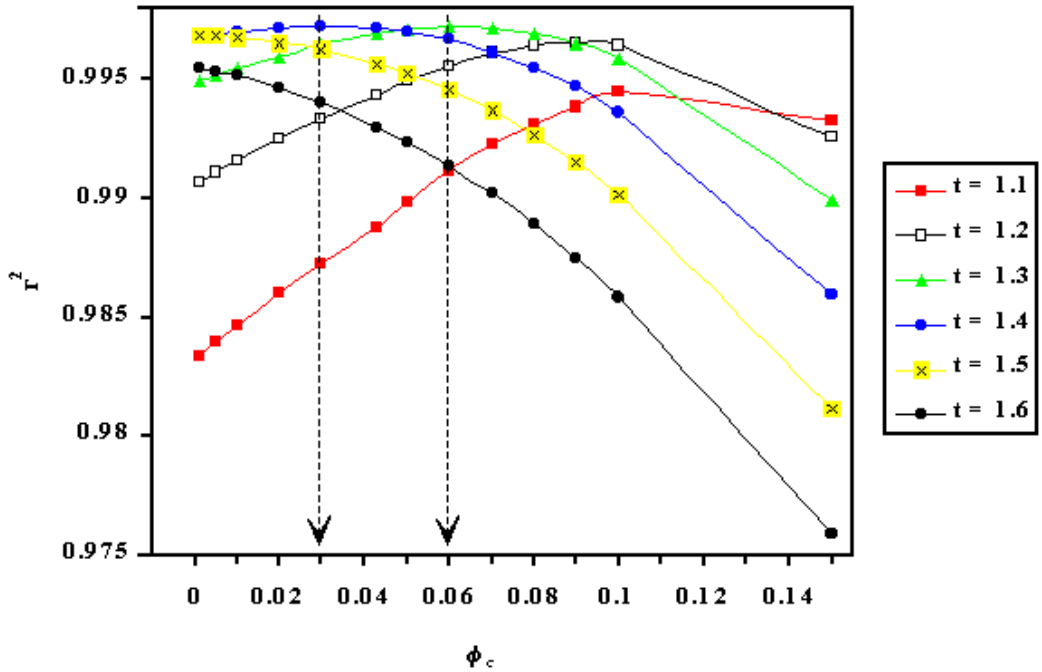

Figure 8.6. Results from the iterative process followed by using *Eq. 8.11* for different $\{\phi_c, t\}$ pairs. As fig.8.5 but with a reduced scale for the main axes.

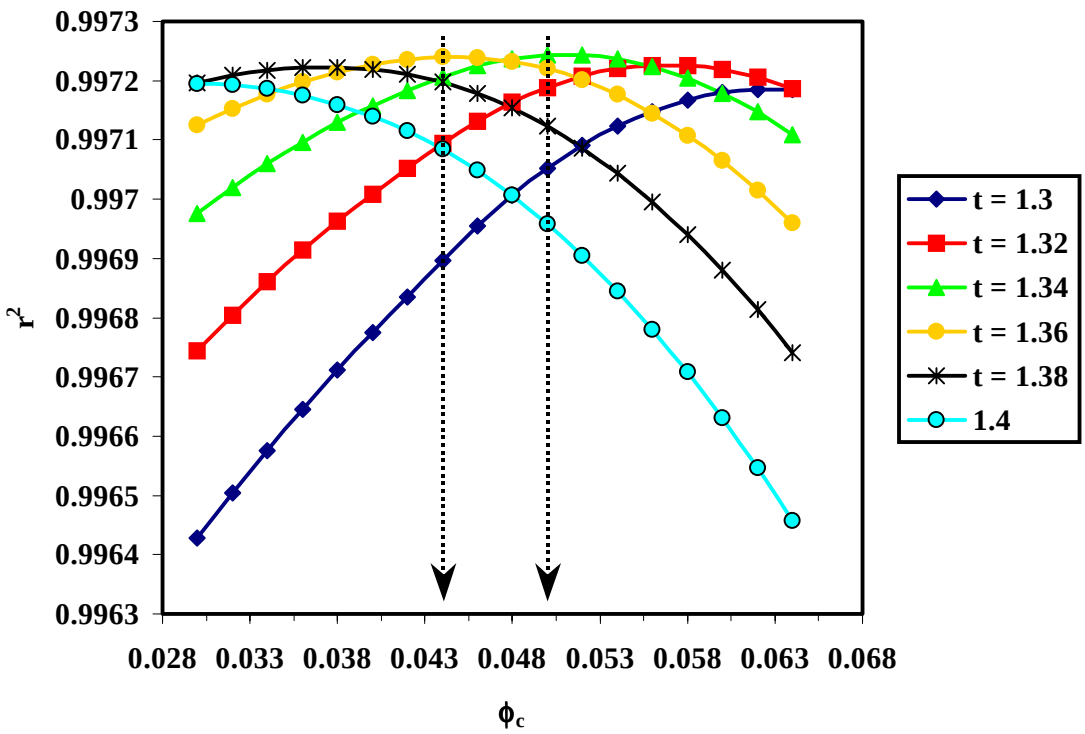

Figure 8.7. Results from the iterative process followed by using *Eq. 8.11* for $\{\phi_c, t\}$ pairs in the intervals $1.3 \leq t \leq 1.4$ and $0.03 \leq \phi_c \leq 0.064$.

Table 8.4. Predictions of σ_m using *Eq. 8.11* with t = 1.35 and ϕ_c = 0.047. GEM approach.

ϕ	Experimental σ_m* (S/cm)	Predicted σ_m (S/cm)
0.0000	1.00×10^{-14}	1.00×10^{-14}
0.0430	7.27×10^{-11}	2.78×10^{-13}
0.0867	3.50×10^{-6}	3.52×10^{-5}
0.1310	4.26×10^{-5}	9.68×10^{-5}
0.1760	2.10×10^{-4}	1.73×10^{-4}
0.3151	5.32×10^{-4}	4.64×10^{-4}
0.4608	7.61×10^{-4}	8.33×10^{-4}
1.0000	2.57×10^{-3}	2.57×10^{-3}

* Average values (refer to Table 8.1)

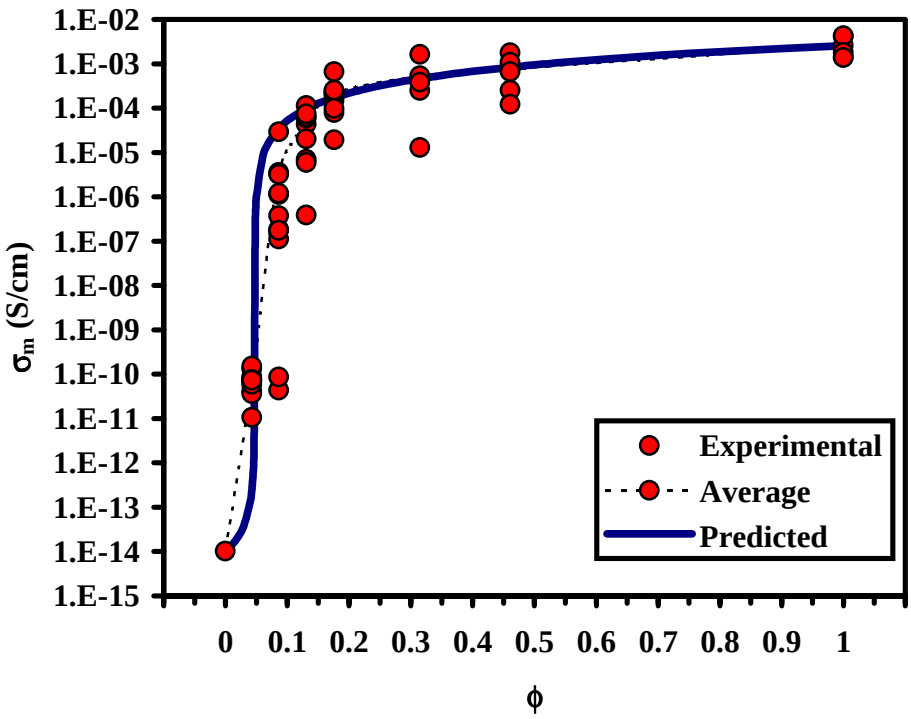

Figure 8.8. The predicted and experimental ϕ vs. σ_m curves (t = 1.35 and ϕ_c = 0.047 in *Eq. 8.11*). GEM approach.

The values of t and ϕ_c obtained were used in equations 8.8a and 8.9, to calculate the values for L_ϕ and L_f, being these equal to 0.0348 and 0.2941, respectively. It should be stressed however, that the previous values were calculated based on the content of

the PANIPOL^{TM} pellets in the blends, which is not strictly correct. As has been mentioned before, the evaluation of the critical parameters and other ones derived from them should have been performed taking into account the content of the conducting polyaniline salt in the blends. Assuming that the value calculated for L_ϕ corresponds to the depolarisation coefficient for the PANI salt would suggest that, at the percolation threshold, the polyaniline particles would exhibit a morphology of extremely flattened spheroids as indicated in Table 8.3 for spheroids with $\infty > b/a > 6$. This is in agreement with the morphology observed for the compression moulded blend with 5 wt.% of PANIPOL^{TM} complex, which is being regarded as the percolation threshold. As has been seen, the aforementioned blend displayed a morphology of layered structures of the conductive filler (refer to fig. 6.15 in section 6.4.3), which now could be visualized as aggregates of flattened polyaniline particles within the SBS matrix. Again, the incipient formation of very long layered structures of the conductive phase in the direction of the current flow may be responsible for the conductivity at ϕ_c.

8.4 CONCLUSIONS.

Percolation theory and a generalisation of effective media theories were used to model the conductivity behaviour in the compression moulded PANIPOL^{TM}-SBS blends. Both approaches yielded similar values for the critical parameters, these being $t = 1.355$ and $\phi_c = 0.04376$ from the percolation theory, and $t = 1.35$ and $\phi_c = 0.047$ from the GEM approach. The values calculated for ϕ_c are in good agreement with that of 0.0430 corresponding to the compression moulded blend with 5 wt.% of PANIPOL^{TM}, which was initially suggested as the percolation threshold.

The critical parameters calculated from the percolation theory are consistent with those calculated by other researchers for other PANI-based systems following a similar method to that employed in this work. The morphology observed in those composites at ϕ_c consisted of segregated conducting PANI domains within the matrix phase, which is also consistent with the morphology observed in the PANIPOL^{TM}-SBS blend with 5 wt.% of conductive filler.

The low value of the depolarisation coefficient calculated through the GEM approach for the PANIPOL^{TM} phase suggests that, at the percolation threshold, the

polyaniline particles would exhibit a morphology of extremely flattened spheroids, which is in well agreement with the layered structures of the conductive filler observed in the compression moulded blend with 5 wt.% of PANIPOL^{TM} complex. This enables us to visualize the morphology of the composite at the percolation threshold as aggregates of flattened polyaniline particles within the SBS matrix.

The conductivity at the percolation threshold may be attributed to the incipient formation of very long layers of polyaniline in the direction of the current flow.