Relations between microstructure, electrical percolation and corrosion in metal—insulator composites

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Received 17 October 2000; received in revised form 31 May 2001

Abstract

Five series of compacted granular metal—polymer composites were prepared in a wide range of metal volume fractions. The metals are Al, Fe, Ni, W and Zn powders. The polymer in powder form is the poly-phenylsulfur \(-C_6H_4S-_n\), noted as PPS. Using electrical complex impedance spectroscopy (ECIS) measurements, the a.c. electrical properties of these composites were analyzed as a function of metal volume fraction and of working frequencies. Each material was characterized by scanning electron microscopy to determine the distribution and morphology of the particles. Close to the percolation threshold, abnormal electrical behavior was observed and interpreted using scanning electron microscopy (SEM) analysis. Two types of modeling calculation are proposed to describe the electrical properties. A model inspired by the Effective Medium Approximation (EMA) improves the modeling approach: the mechanically induced modification of grain size and distribution is interpreted in terms of new modeling parameters governing the evolution of the conductance. A description of electrical behavior close to the percolation threshold is proposed using percolation theory. Critical exponents are determined above and below the percolation compositions. Finally, a study of corrosion behavior for Zn based composites is presented and correlated with the initial electrical behavior of these composites. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Metal/insulator composites; Transport properties; Electrical complex impedance spectroscopy; Effective medium approximation; Percolation theory; Grain size, Corrosion

1. Introduction

Much of the recent progress in industry (aeronautics, electronics, corrosion protection…) is the result of the use of both structural and functional composite materials. These composites can be made of insulating and conducting particle mixtures, which are subjected to both mechanical and thermal treatment during the manufacturing process. To obtain electrical components that might be good conductors, which are simultaneously chemically and mechanically stable, the classical manufacturing process consists of compacting powders of metal and polymer constituents. Below a certain volume fraction of metal defined as the critical threshold \(\Phi_c\), the composite is an insulator, while above this composition it becomes an electrical conductor. If electrical currents can percolate through the bulk material, then varying degrees of corrosion may occur along the electrical paths existing in the composite. To limit this corrosion and increase the lifetime of the material one can manufacture conducting composites having metal compositions, \(\Phi\), just above the critical threshold. Previous works have described the transport properties in composites and discussed the various modeling approaches that allow the interpretation of the sigmoid electrical responses in these composites [1–10]. To optimize the properties of these composite systems, it is necessary to model the theoretical dependencies linking the concentration, the particle size and the composite conductivity. A review on various models was given by Clerc [11]. The effect of particle size on the electrical properties...
properties was previously determined by using percolation theory [12,13].

In compacted composites, it is well established that, for a given composition, the electrical properties strongly depend on grain size, morphology and applied pressure [14–18]. The calculation of the equivalent conductivity necessarily involves all of the neighboring particles, too [19].

Three major models have been developed previously to make predictions on the electrical behavior of ideal composites: (i) the Effective Medium Approximation (noted as the EMA model) [11,20,21], (ii) percolation theory [1,11], (iii) the micro-structural approach (noted as the EMA model) [11,20,21], (ii) percolation theory [12,13].

The conductivity of a composite can be described by Bruggeman [25] symmetric and asymmetric medium equations. The symmetric expression forms the basis for the effective medium approximation, which will be represented in Section 3. The classical EMA model gives a global description of the electrical properties, however, it involves a critical composition $\Phi_{\text{perc}}$ which is different from the effective percolation composition $\Phi_{\text{perc}}$. This theory is used usually to describe the properties of binary mixtures far from the percolation threshold when the ratio $\sigma_{\text{insulator}}/\sigma_{\text{conductor}}$ is sufficiently high [26,27]. In the case of the classical EMA approach, the major difficulty resides in the fact that the final granulometry and texture are never well known, and that this model itself is based on simple and regular distributions of ideal particles. This is not the case in ‘real’ materials.

Percolation theory delivers a good description of the percolation features near the threshold $\Phi_{\text{c}}$ but does not explain the experimental data far from the percolation fraction $\Phi_{\text{perc}}$. This model gives a good description of a composite system when the $\sigma_{\text{insulator}}/\sigma_{\text{conductor}}$ ratio is very small [26]. In our case, we are trying to describe the conductor/insulator system for volume fractions $\Phi$ ranging from 0 to 1.

The classical EMA and a modified EMA model are used first to determine the parameters governing the conductor to insulator transition. Then a comparison between the EMA and percolation theory parameters is presented.

2. Experimental

2.1. Sample preparation

Poly-dispersed metal/polymer composites were prepared by mixing powdered metallic (Al, Fe, Ni, W and Zn) particles with an insulator polymeric matrix of poly-phenylsulfur $[-\text{C}_6\text{H}_4\text{S}-]_n$, PPS. This polymer used in powder form is a chemically inert insulating material. All composites were prepared under the same conditions: the constituents were mixed in well-defined proportions and pressed in a cylindrical 13-mm die under a uniaxial pressure of 10 ± 1 kbar. Both the initial PPS and the metal constituents are granular. Hence, for all volume fractions the composite pellets present residual cavities ($\Phi_{\text{cavities}}$). Finally, the macroscopic properties will be functions of the volume fractions ($\Phi$, $\Phi_{\text{PPS}}$, $\Phi_{\text{cavities}}$), where:

$$\Phi + \Phi_{\text{PPS}} + \Phi_{\text{cavities}} = 1.$$ 

The cavities are insulating regions for electron currents; hence we will not distinguish between PPS and cavities. The metal volume fractions $\Phi$ after pressing were then calculated taking into account these cavities. The volume fractions are then calculated using the initial weights of the constituents, the individual density of each constituent and the effective volume of the cylindrical pellets. Different metal/PPS composites were prepared with metal compositions $\Phi$ ranging from 0 to 1. Increments of $\Delta\Phi = 0.10$ were chosen; however, near the inflexion threshold, samples are prepared with variable metal compositions where $\Delta\Phi = 0.01$. For each composite, two sets of samples were prepared to avoid discrepancies in measurement.

2.2. Grain size

The initial grain size (before compaction) was controlled using a Malvern sizermeter in polyphase mode analysis. Using spherical particle approximation, particle size analysis was performed in the 0.3–300 μm range, using pure water as a solvent.

2.3. Electrical Complex Impedance Spectroscopy (ECIS)

Each sample was subjected to electrical complex impedance measurements 10 min after pressing, for frequencies ranging from $10^{-1}$ to $10^7$ Hz. The electrical complex impedance was measured using a potentiostat/galvanostat Model 273A from EGG, coupled with a HF frequency response analyser SI1255 from Schlumberger. Each sample was placed between two gold electrodes under a constant pressure of 50 mbar at ambient temperature (20 °C). Results are usually plotted either as a (log $\Sigma_{\text{real,part}}$, $\Phi$) graph or as a Nyquist graph ($X=Z’$, $Y=-Z’$), where the complex impedance is $Z = 1/\Sigma = Z’ + jZ’$. Nyquist representations show clearly the difference between the insulating and conducting state responses. In the [log$\Sigma$, $\Phi$] plots, two critical volume fractions ($\Phi$) are defined: the inflexion point of the EMA model $\Phi = \Phi_{\text{inf}}$ (see annex) and the point $\Phi = \Phi_{\text{c}} < \Phi_{\text{inf}}$, where a rapid evolution of log$\Sigma$ starts. This inflexion point is defined as corresponding to the maximum of $\frac{d^2 \log \Sigma}{d\Phi^2}$. These two critical volume
fractions are discussed in the modified EMA model. It can be determined either by calculating the maximum of \( \frac{d^2 \log \Sigma}{d \Phi^2} \), see Fig. 1b, or from the strong changes in the Nyquist representation: a significant change from an insulating (pseudo-linear curve) to a conducting (circular curve) behavior occurs over a very small composition range.

Such a critical value \( \Phi_c \) might be associated strongly with the percolation threshold of percolation theory (see Fig. 1a). In this theory, only the percolation threshold is clearly defined.

2.4. Scanning electron microscopy

Scanning electron microscopy (SEM) was carried out on a Philips XL30 microscope to determine grain morphology and size distribution after the compaction process. These observations showed the evolution of grain size as a function of metal concentration in the samples. The microscope was linked to an EDS X-ray microanalysis system, which allowed to investigate the microstructure (composition and distribution of the clusters) of the samples. In the case of corroded electrodes, the sample was dried before analysis.

2.5. Corrosion analysis

A simple electrochemical device associated with the impedance spectroscopy analyzer was used (Fig. 2). The corrosion of Zn/PPS composite electrodes in hydrochloric acid solution at constant pH (pH 2) and under an alternating potential was analyzed as a function of the working time \( t \) and of the Zn volume fraction in the composite. This device consisted of two electrodes A and B connected to the analyzer. The two electrodes were identical (dimensions, shape and composition). All the experiments were performed at room temperature. The working frequency \( \nu \) varied automatically between 1 and \( 10^6 \) Hz. The applied a.c. voltage was \( V = 100 \) mV.

3. Results of the modeling approach

3.1. Initial EMA model

In real compacted composites, the critical composition and the evolution of impedance can differ from one composite system to another. To understand better the conductivity of our metal/polymer composites, two types of modeling approach were proposed: a modification of the EMA model and the application of percolation theory. Generally, these models are valid for ideal composites in which all constituents are characterized by a unique size. It is well known, however, that the experimental percolation threshold depends on the particle size distribution in the composite.

<table>
<thead>
<tr>
<th>Composition of samples</th>
<th>Al</th>
<th>Fe</th>
<th>Ni</th>
<th>W</th>
<th>Zn</th>
<th>PPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_{10} (µm)</td>
<td>14.5</td>
<td>23.1</td>
<td>4.6</td>
<td>14.1</td>
<td>2.6</td>
<td>7</td>
</tr>
<tr>
<td>D_{50} (µm)</td>
<td>31.4</td>
<td>42.9</td>
<td>20.7</td>
<td>34.8</td>
<td>5.5</td>
<td>35.9</td>
</tr>
<tr>
<td>D_{90} (µm)</td>
<td>62.9</td>
<td>80.2</td>
<td>57.9</td>
<td>109.5</td>
<td>12.6</td>
<td>88.3</td>
</tr>
<tr>
<td>Span</td>
<td>1.54</td>
<td>1.33</td>
<td>2.58</td>
<td>2.74</td>
<td>1.81</td>
<td>2.27</td>
</tr>
</tbody>
</table>

Note: \( D_{10} \) is the value of the particle size that separates the distribution in 10/90%. \( D_{50} \) is the value of the particle size that separates the distribution in 50/50%. \( D_{90} \) is the value of the particle size that separates the distribution in 90/10%. Span: breadth of the distribution. \( \text{Span} = |D_{90} - D_{10}|/D_{50} \).
where \( \Phi_1 \) and \( \Phi_2 \) are the volume fractions of the two constituents with \( \Phi_1 + \Phi_2 = 1 \) and \( \Sigma_{1,2} = \sigma_{1,2} + (d-1)\Sigma \), where \( d \) is a dimensional parameter associated with the connectivity of the system [11]. Generally, using this EMA model, the inflexion point of the curve (log\( \Sigma, \Phi \)) is characterized by a composition noted as \( \Phi_{\text{infl}} \) with \( \Phi_{\text{infl}} = 1/d \) in the case of an ideal two-phase composite. This composition differs considerably from the critical composition \( \Phi_c \).

Using the ECIS measurements represented in Nyquist diagrams, the conductance value for each composite was determined. In the case of insulating mixtures, the circles can be modeled by an RC parallel circuit. For conducting mixtures, the adequate model is an RL series circuit. In all cases, it is possible to evaluate the resistance and the conductance of the samples. Fig. 3a and 3b show a selection of results below and above the percolation threshold, for some Fe/PPS composites. The experimental and theoretical conductances (for all composites) calculated with the EMA model are represented in Fig. 4a–4e, where the \( d \) values represent a mean value according to \( d = 1/\Phi_{\text{infl}} \).

As expected, we note that this simple EMA model fits the data well when far from the percolation (or inflexion) compositions; however no good fit is obtained close to these compositions. This can be observed for the Al, Fe, Ni and Zn/PPS composites. Even if the \( \Phi_{\text{infl}} \) critical composition can be simulated, the experimental evolution close to this critical composition differs greatly from the calculated curves. Generally, the experimental insulator–conductor transition is less steep than the calculated transition predicted by the
3.2. New fitting parameters for EMA model

The laser grain size analysis (Table 1) showed a relatively high dispersion of particle sizes. Moreover, it has been previously demonstrated [12, 13] that particle size is an extremely important parameter in conduction. Therefore, it is clear that the classical EMA model fails. It was therefore necessary to control this particle size dispersion to improve the model.

In the elaboration of the modified EMA model, we first assume that the composites are composed of couples: metal/metal, polymer/polymer and metal/polymer. Then each couple could give its own contribution to percolation.

To take into account the distribution of metal particle sizes, the complex medium was modeled as follows:

- The composite was first divided into elemental sections or layers having the same composition;
- The thickness of these sections is linked to the size of the largest particles after compaction;
- In each section, the effective medium approximation can be applied: each metal particle is supposed to be coupled to polymer particles only. This means that, after compaction each metal/metal couple is changed into one unique particle, and that the notion of metal particle pairs ‘in contact’ vanishes. As a result, it is possible to distinguish independent regions in the sample in which each population of grains has its own connectivity parameter d.

- Due to surface contributions (partial oxidation), the metal grain conductances can depend strongly on grain size. Due to these surface effects, in compacted samples, the smallest isolated particles have the highest resistance. This is the reason why we have assigned a σ value to each particle. This last value is determined by computation.
- The mechanical effects involved in the compaction process condition the final grain size distributions (after compaction) which depend strongly on the initial total volume fraction of metal. The last major fact is that the ‘final’ grain size of the composite, involved in the compaction process, depends on the total volume fraction of the metal (Φf). Actually, the more the volume fraction of the metal increases, the more the small grains agglomerate. The proportion of large particles increases with the volume fraction. This volume fraction depends on the extent of metal particle clustering. In Fig. 5 the formation of agglomerates of metal particles due to the compaction process is shown.

However all these hypotheses are also questionable because they cannot take into account the statistical notion of percolation. Fig. 6 summarizes our various hypotheses schematically.

The modified equation we propose is:

$$\frac{\sum - \sigma_1}{\Phi_1} + \frac{\sum - \sigma_2}{\Phi_2} + \ldots + \frac{\sum - \sigma_n}{\Phi_n} = 0$$  \hspace{1cm} (2)

with $$\Sigma_i = \sigma_i + (d_i - 1)\Sigma$$; $$\Phi_1 + \Phi_2 + \ldots + \Phi_n = 1$$; $$d_n = \frac{\sum_{i=1}^{n-1} d_i \Phi_i}{\sum_{i=1}^{n} \Phi_i}$$

Each d value will represent the ‘effective dimensionality’ for a metal couple (i):PPS and will be associated with a size, a volume fraction Φi of the metal and its conductivity σi. In our case, we arbitrarily divided the grain size diagrams into three parts. This implies that, from Eq. (2), we have to refine six parameters: d1, d2, d3, σ1, σ2, σ3. The parameter σ4 is the conductivity of PPS. In our approach d4 is obtained arbitrarily from the inflexion point (see Appendix) by assuming that: $$d_4 = 1/\Phi_{inf}$$.

Such a choice is coherent with the initial EMA model applied to an ideal two-phase system.

The initial Φi values are determined from grain size measurements.

Fig. 5. SEM micrograph showing the formation of a metal cluster due to compaction.

Fig. 6. Model of composite divided into sections.
Fig. 7. SEM micrograph (over-exposed) of a Zn/PPS composite: the metal particles appear in black. (a) Below critical threshold, $\Phi_v = 16\%$. (b) Above critical threshold, $\Phi_v = 20\%$.

The evolution of particle size distribution after compaction depends on the total volume fraction of the metal and might be described as follows:

- Below the critical threshold, the particles are farther apart. Therefore, after compaction, the grain size will be roughly the same as the initial grain size.
- Near the critical threshold (5% below and above), the metallic particles are more and more in contact: the grain size is modified. The number of smaller grains decreases while the number of larger ones increases very quickly.
- Above the critical threshold the particle distribution stays unchanged irrespective of $\Phi_v$ because a major part of the smaller particles has disappeared during compaction.

A fairly good approximation of the critical threshold can be determined from SEM analyses. Despite the fact that SEM gives a two-dimensional representation of the material, this approximation should be acceptable because of the very high homogeneity of the samples. Fig. 7 shows the distribution of the metal particles in the matrix (for Zn/PPS composites in the present case) below the critical threshold (Fig. 7a) and at the critical threshold (Fig. 7b). This micrograph is overexposed so as to distinguish clearly the black particles of metal from the white polymer.

The critical threshold as defined in this work is the composition from which an idealized first conducting line (the so-called infinite cluster) should appear through the composite (first conducting path from one electrode to the other). In Fig. 7a, one can observe that no continuous black line exists: this explains the fact that no percolation of electrical current is observed in this sample. In Fig. 7b we can observe continuous metallic lines, which indicates that percolation occurs in this sample. This volume fraction is associated well with the range of definition of $\Phi_c$.

The SEM observation permits us to observe the characteristic evolution of the initial grain size: the fraction $\Phi_i$ of each grain size family depends on the total metal volume fraction presently noted as $\Phi_v$. The values $\Phi_i$ have been adapted to the experimental data. For Al, Fe, Ni and Zn based composites, Fig. 8 shows the functions used to refine the grain size. These functions are obtained from measurements.

- For $0 < \Phi_v < (\Phi_{\text{infl}} - 0.05)$, the fractions $\Phi_1$ (smallest particles), $\Phi_2$ and $\Phi_3$ (largest particles) are the same as the fractions initially determined from laser grain size analyses (Table 1).
- For $(\Phi_{\text{infl}} - 0.05) < \Phi_v < (\Phi_{\text{infl}} + 0.05)$, the smallest particles agglomerate, $\Phi_1$ decreases and $\Phi_3$ increases.
- For $\Phi_v > (\Phi_{\text{infl}} + 0.05)$, there is a complete change in the particle size distributions because of the agglomeration of the smallest particles: however, each fraction $\Phi_i$ becomes constant again.

For each composite, the initial and final grain sizes (as a percentage of the total metal volume fraction) are presented in Table 2.

For the W based composites, the $\Phi_i$ are always found to be equal to $1/3$ (measurements).

The new modified equation now is:

Fig. 8. Functions used for grain size parameter definitions. $\Phi_{1,2,3}$ are variable parameters.
Table 2
Weighted grain size $\Phi_1$ and $\Phi_3$ (as a percentage of $\Phi_3$) used in Eq. (3)

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Fe</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_3 &lt; \Phi_{infl} - 0.05$</td>
<td>8</td>
<td>35</td>
<td>10</td>
<td>51</td>
</tr>
<tr>
<td>100. $\Phi_1$</td>
<td>5</td>
<td>11</td>
<td>27</td>
<td>6</td>
</tr>
<tr>
<td>$\Phi_3 &gt; \Phi_{infl} + 0.05$</td>
<td>5</td>
<td>20</td>
<td>6</td>
<td>20</td>
</tr>
<tr>
<td>100. $\Phi_1$</td>
<td>40</td>
<td>30</td>
<td>55</td>
<td>35</td>
</tr>
</tbody>
</table>

Note: $\Phi_2$ is always equal to $1 - \Phi_1 - \Phi_3$.

In Fig. 9a–9e, the experimentally obtained curves of all metal/polymer composites can be compared to the calculated curves obtained from Eq. (3). One can see that close to the critical threshold, a better agreement between calculated and observed data is obtained than before (Fig. 4a–4e).

We can also note the following features:

1. For the W composites, the calculation of $\log$ gives $d_1 = 4.06$, $d_2 = 2.96$, $d_3 = 1.38$ and a quite good agreement between the calculated and measured curves; this may be attributed to the hardness of each W grain and also the initial grain size. Under the compaction process, the grains cannot agglomerate and the final grain size is close to the initial one (Table 1).

Fig. 9. Modified EMA model. Experimental and theoretical conduction of metal/PPS composite as a function of metal volume fraction $\Phi$. Conductance $\Sigma$ in logarithmic scale. (a) Al/PPS; (b) Fe/PPS; (c) Ni/PPS; (d) Zn/PPS; (e) W/PPS.

Table 3
New modeling parameters for a modified effective medium approximation

<table>
<thead>
<tr>
<th></th>
<th>Al/PPS</th>
<th>Fe/PPS</th>
<th>Ni/PPS</th>
<th>W/PPS</th>
<th>Zn/PPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_1$ ($\Omega^{-1}$)</td>
<td>52</td>
<td>416</td>
<td>1069</td>
<td>55.8</td>
<td>0.553</td>
</tr>
<tr>
<td>$\sigma_2$ ($\Omega^{-1}$)</td>
<td>148</td>
<td>881</td>
<td>863</td>
<td>34.1</td>
<td>0.015</td>
</tr>
<tr>
<td>$\sigma_3$ ($\Omega^{-1}$)</td>
<td>159</td>
<td>1063</td>
<td>694</td>
<td>11.6</td>
<td>0.092</td>
</tr>
<tr>
<td>$d_1$</td>
<td>2.03</td>
<td>4.05</td>
<td>2.96</td>
<td>4.06</td>
<td>5.45</td>
</tr>
<tr>
<td>$d_2$</td>
<td>1.62</td>
<td>2.00</td>
<td>2.15</td>
<td>2.96</td>
<td>3.32</td>
</tr>
<tr>
<td>$d_3$</td>
<td>1.53</td>
<td>1.50</td>
<td>1.40</td>
<td>1.38</td>
<td>1.17</td>
</tr>
<tr>
<td>$&lt;d&gt;$</td>
<td>1.70</td>
<td>2.10</td>
<td>2.16</td>
<td>2.70</td>
<td>5.00</td>
</tr>
<tr>
<td>Quadratic error $^a$</td>
<td>0.13</td>
<td>0.043</td>
<td>0.027</td>
<td>0.022</td>
<td>0.019</td>
</tr>
<tr>
<td>$\Phi_{inh}$ (obs.)</td>
<td>0.588</td>
<td>0.474</td>
<td>0.463</td>
<td>0.370</td>
<td>0.200</td>
</tr>
</tbody>
</table>

$^a$ This term indicates the quality level of the refinement.
2. For Al, Fe and Ni composites the $D_{50}$ values are roughly similar and similar mean $d$ values (from 1.7 to 2.2) and similar $\Phi_{\text{ins}}$ values (from 0.588 to 0.463) (see Table 3) are observed.

3. For Zn composites, the grain sizes are much smaller than for the other composites ($D_{50} = 5 \, \mu m$); $\Phi_{\text{ins}}$ is smaller, too.

4. In the case of Al and Zn composites, the ductility of the metal grains may be the origin of the observed progressive evolution of the conductivity just above the critical threshold which can result from the agglomeration of ductile grains during the compaction process.

The main conclusion must be that there is a strong correlation between the initial mean size and the critical composition (the $D_{50}$ and the $\Phi_{\text{ins}}$ values). In addition, the three parameters ‘$d$’ depend on the grain size distribution after the compaction process (including the volume fractions associated with each size), and on the hardness of the metal grains. Moreover, conduction is characterized by the three $d$, and three $\sigma$, values. Finally, we can conclude that the proposed model should improve significantly the initial EMA model even though a small discrepancy persists close to the critical threshold.

3.3. Percolation theory

The main result of percolation theory [11,26,28] resides in the fact that a transport property (conduction in our case) can be developed close to the percolation threshold, $\Phi_{\text{perc}}$ as follows:

$$\Sigma_{\text{tot}} = A(\Phi - \Phi_{\text{perc}})^{c} = A (\Delta\Phi)^{c} \quad \text{for} \quad \Phi > \Phi_{c} \quad (4a)$$

$$\Sigma_{\text{tot}} = B(\Phi_{\text{perc}} - \Phi)^{-s} = B (\Delta\Phi)^{-s} \quad \text{for} \quad \Phi < \Phi_{c} \quad (4b)$$

where $\tau$ and $s$ are the two classical critical exponents linked to the formation of continuous clusters through the composite above and below the $\Phi_{\text{perc}}$ volume fraction. $A$ and $B$ are constants linked to the $\sigma_{\text{conductor}}$ and $\sigma_{\text{insulator}}$ values. The exponents $\tau$ and $s$ can be determined by plotting log $(\Sigma)$ versus log $\Delta\Phi$ below and above the percolation threshold.

3.3.1. Determination of the critical volume fractions $\Phi_{c}$

To determine the most probable $\Phi_{\text{perc}}$ value we proceed as follows:

- The initial $\Phi_{\text{perc}}$ value is calculated as predicated in Section 2.3. from the maximum of the derivative $d\log \Sigma / d\Phi^{c}$. As a first approach we considered that $\Phi_{\text{perc}} = \Phi_{c}$.

- This $\Phi_{\text{perc}}$ value is then modified to obtain an ideal linear correlation $\log(\Sigma) = k \log(\Delta\Phi)$.

- The final $\Phi_{\text{perc}}$ values were found to be close to the initial $\Phi_{c}$ values.

The measured values of $\Phi_{c}$ ranged between 0.190 and 0.588. The evolution of this critical volume fraction can be explained by the microstructure of the conducting powders and the insulating polymer. Kussy [29] argues that in a mixture made up of small conducting and large insulating particles, the smallest particles will tend to coat the larger ones. This is the case with our Zn/PPS composites. The mean size of Zn grains is about seven times smaller than that of the PPS grains. A three-dimensional conductance can occur. It is interesting to note that the experimental value of $\Phi_{c} = 0.190$ is in good agreement with the theoretical value of 0.198 for a face centered cubic lattice [26,28].

For the Al, Fe, Ni and W/PPS composites, the mean sizes of the conducting and insulating grains are quite similar. The different values of $\Phi_{c}$ suggest that conduction should be associated with a configuration intermediate between a 2D and a 3D system.

3.3.2. Determination of the exponents $s$ and $\tau$

It has been previously demonstrated in [29–32] that the nature of the powder, the cavities and the microstructure of a composite have a strong influence on the critical exponents. In our composites, the $\tau$ values range between 1.45 ± 0.29 for the W/PPS composites and between 2.07 ± 0.21 for the Zn/PPS composites. It seems that the grain size dispersion and the nature of the material have a relatively small influence on $\tau$. Like the critical volume fraction, the observed $\tau$ seem to be related to systems ranging between 2D to 3D dimensions. Nevertheless, a comparison between $\tau$ and the particle size can be done: Table 1 shows the particle size distribution of the conducting particles. If we consider the $D_{50}$ characteristic, we observe that the smaller the particle, the higher is $\tau$. As previously proposed by Wu and McLachlan [33], such an evolution of $\tau$ could be explained by the increase of contact resistance between the grains.

Table 4 summarizes $s$ and $\tau$ calculated from the best Log–Log plots. It can be seen that a very wide range of calculated $s$ values is obtained ($s = 0.832; s = 2.282$), and that no connection can be established between the $s$, $\tau$, $\Phi_{c}$ values and the particle sizes. The values $s = 0.832$, $s = 0.992$ and $s = 1.028$ respectively found for the Ni, W, Al/PPS composites are in quite good agreement with the values measured for other composites ($s = 0.73$ for Ag/KCl mixture [34]). They are also congruent with the 2D and 3D values obtained from simulations [26,35–37]. However, the very high values of $s$ for Zn and Fe/PPS composites cannot be explained.

From $s$, $\tau$ and $\Phi_{c}$ one can calculate the conductance using the normalized percolation equations [38]:

$$\Sigma = \sigma_{\text{conductor}} \left[ (\Phi - \Phi_{c})/(1 - \Phi_{c}) \right]^{\tau} \Phi > \Phi_{c} \quad (5a)$$

$$\Sigma = \sigma_{\text{insulator}} \left[ (\Phi_{c} - \Phi)/\Phi_{c} \right]^{-s} \Phi < \Phi_{c} \quad (5b)$$
Table 4
Critical volume fraction and critical exponents of percolation theory. The r value represent the linearity coefficient of the linear regression used for the Log–Log plot calculations

<table>
<thead>
<tr>
<th>Refined values of, $\Phi_{perc}$</th>
<th>Al/PPS</th>
<th>Fe/PPS</th>
<th>Ni/PPS</th>
<th>W/PPS</th>
<th>Zn/PPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refined values of, $\Phi_{perc}$</td>
<td>0.56</td>
<td>0.47</td>
<td>0.44</td>
<td>0.37</td>
<td>0.19</td>
</tr>
<tr>
<td>Percolation approach: critical exponent $\tau$</td>
<td>$1.602, \pm 0.214, \ 1.643, \pm 0.150,$</td>
<td>$1.900, \pm 0.225, \ 1.140, \pm 0.131,$</td>
<td>$1.970, \pm 0.159,$</td>
<td>$r = 0.984$</td>
<td>$r = 0.981$</td>
</tr>
<tr>
<td>Percolation approach: critical exponent $s$</td>
<td>$1.028, \pm 0.141, \ 2.282, \pm 0.203,$</td>
<td>$1.987, \pm 0.172, \ 0.992, \pm 0.073,$</td>
<td>$0.832, \pm 0.112,$</td>
<td>$r = 0.988$</td>
<td>$r = 0.976$</td>
</tr>
</tbody>
</table>

Fig. 10. Plot of the conductance of metal/PPS composites using percolation theory. Conductance $\Sigma$ in logarithmic scale. (a) Al/PPS; (b) Fe/PPS; (c) Ni/PPS; (d) Zn/PPS; (e) W/PPS.

In Fig. 10a–10e, the experimental data and the conductances calculated from Eq. (5a) and Eq. (5b) are represented as a function of the metal volume fractions $\Phi$. It can be observed clearly, that such a percolation model fits the data well. For the W/PPS composites (and partly for the Al/PPS composites) $\tau$ and $s$ are both close to 1. These results are in agreement with Bruggeman’s symmetric theory.

4. Percolation and corrosion

Often metal–insulator composites are intended to function in aggressive environments over a period of many years. To connect the percolation compositions found for electron currents with the percolation paths available for corrosion currents, we carried out a corrosion study for Zn composites in acid media. The mea-
measurements were carried out using the electrochemical device described in the experimental section. From these ECIS measurements (see Fig. 11), the complex conductance modulus $|\Sigma|$ was determined at each frequency $\nu$. Its variation as a function of time and composition is conditioned by the evolution of the internal electrical circuits subjected to corrosion.

In Fig. 12a–c, the complex conductances $|\Sigma| = 1/|Z|$, obtained for a fixed frequency of 10 Hz, are reported as a function of time. In Fig. 12d, the conductances are reported as a function of the Zn concentration at a fixed frequency of 10 Hz for 30, 200 and 400 min. $|\Sigma|$ is linked directly to the corrosion current. In Fig. 12a–c, different types of behavior are observed:

- For $t < 400$ min, a decrease of the conductance modulus is observed in all cases, due to the surface corrosion of the Zn metal by the $H^+$ ions.
- For $400 < t < 500$ min, a plateau is observed in each experiment. This is probably due to the formation of hydrated species (including ZnO oxide) on the surface and in the cavities close to the surface of the composite. The infiltration of the $H^+$ ions is then stopped because the precipitated species act as insulating barriers thus lowering corrosion.
- For $t > 500$ min, different types of behavior are observed:
  - At Zn concentrations below the percolation threshold (Fig. 12a), the conductance increases which might be due to the fact that the Zn based species have gone and that the acid solution can again reach the interior of the composite. But due to the low Zn concentration, corrosion phenomena are quite limited.
  - At Zn compositions above the percolation threshold (Fig. 12c), the conductance decreases again. $H^+$ ions infiltrate and the Zn particles are corroded due to their high concentration (Fig. 13). After a long period of time the acid solution infiltrated all the bulk. Since no Zn cluster are found, conduction due to electrons ceases.
  - For compositions near the percolation threshold (Fig. 12b), conductance becomes stable since the infiltration of the acid solution is compensated for by the formation of insulating Zn based species.

The hypothesis concerning the infiltration of acid solution into the bulk is confirmed in Fig. 13a–c. For a Zn/PPS (30/70) working electrode, these micrographs show the interface between the parts of the electrode which is in the acid solution and that which is not. The part immersed in the acid solution has been attacked by corrosion. After corrosion the Zn particles (white in Fig. 13) are replaced by cavities into which the acid solution can easily penetrate.

![Fig. 11. Nyquist plots for a series of Zn/PPS composites as a function of corrosion time. (a) 10/90; (b) 15/85; (c) 20/80.](image-url)
Fig. 12d shows that close to the inflexion threshold and for a fixed time \( t \), the increase of \( |\Sigma| \) is very sharp. As the electron currents circulating through the composite electrodes are in series with the ionic currents migrating through the acid solution, such a strong variation can be ascribed to the appearance of a corrosion current \( I \) (defined as \( I = U/|\Sigma| \)).

To describe better the correlation between the electrical percolation composition \( (\Phi_{\text{perc}} = 0.19 \) for the Zn composites) and the percolation composition linked to corrosion currents, we have determined the time-dependent critical exponents \( s \) and \( \tau \) from the conductance curves obtained after corrosion. These critical exponents were calculated for each working time \( t \), and after having determined the corresponding percolation thresholds, \( \Phi_{\text{corr}} \). The \((s, \tau)\) couples and the corresponding \( \Phi_{\text{corr}} \) values were found to be:

\[
\Phi_{\text{corr}} = \Phi_{\text{perc}} = 0.19; \quad (1.45 \pm 0.24; \quad 2.07 \pm 0.12) \quad \text{for } t = 0 \text{ min},
\]

\[
\Phi_{\text{corr}} = 0.17; \quad (1.31 \pm 0.17; \quad 1.40 \pm 0.09) \quad \text{for } t = 30 \text{ min},
\]

\[
\Phi_{\text{corr}} = 0.15; \quad (0.68 \pm 0.18; \quad 0.26 \pm 0.13) \quad \text{for } t = 100 \text{ min}
\]

\[
\Phi_{\text{corr}} = 0.14; \quad (0.65 \pm 0.16; \quad 0.18 \pm 0.21) \quad \text{for } t = 400 \text{ min}.
\]

It is interesting to note that these \( s \) and \( \tau \) values decrease as the corrosion time increases. The interpretation of this evolution is not clear. In such granular composites, several phenomena could be considered. Due to corrosion (see Fig. 13), the metallic particles are first dissociated into ions that can migrate through the aqueous acidic solution; then, this dissociation involves the formation of additional cavities into which the aqueous solution can infiltrate increasingly. Finally, the composite medium transforms into a more complex four-phase system (i.e., metal, PPS, cavities and solution): at this stage, the classical two-phase percolation theory probably fails. From these results, we can conclude that there is a satisfactory correlation between the percolation of ‘electron currents’ and the percolation of the currents due to corrosion. However, it should be remarked that \( \Phi_{\text{corr}} \) is somewhat smaller than the initial \( \Phi_{\text{perc}} \) value. Even though the correlation is not perfect, the percolation paths for acid solutions are well correlated with the percolation of metal circuits in the composites. In other terms, the residual cavities that can facilitate corrosive solution penetration are mainly associated with metal particles.

### 5. Discussion and conclusion

It has been demonstrated already [39] that the effective medium approximation will generally fail in granular materials. In this paper, we have proposed a modified model that should improve strongly the agreement between experimental and calculated data. In Table 3, the main results of this paper are gathered. It was shown clearly that the introduction of several \( d_i \), \( \sigma_i \) values and \( \Phi_i \) linked to the metal grain size improves the agreement between calculated and experimental logarithmic conductances. In other terms, a distribution of connectivity parameters associated with different sizes should be at the origin of the variation of \( \Sigma \) close to the percolation threshold. The proposed model allowed us to determine a set of different values for \( d_i \) and \( \sigma_i \).

The evaluation of the percolation exponents \( \tau \) and \( s \) permits us to better define the values of \( \Phi_i \). A marked
Fig. 13. SEM (back scattered electron) micrographs of a Zn/PPS (30/70) composite electrode. (a) magnification 150; (b) magnification 350; (c) magnification of delimited section. The section of the electrode out of the acid solution is not attacked (the Zn particles are white). The section immersed in the acid solution is corroded (absence of white particles, presence of black cavities). The arrows show some cavities.

correlation between particle size, percolation composition $\Phi_{\text{perc}}$, percolation exponents $s$ and $\tau$ and material hardness can be noted. However, a small discrepancy persists close to the percolation threshold: it is mainly due to the fact that the EMA approach cannot account for the probability of creating percolation paths through the sample. The calculated curves obtained either from our modified EMA approach or from percolation theory, both fit the data in a satisfactory way. Nevertheless, the correlation defined as:

$$R = \sqrt{\frac{\sum_{n=1}^{N}(\text{Experimental}-\text{Calculated})^2/(\text{Calculated})^2}{n-1}}$$  \hspace{1cm} (6)$$

shows that percolation theory always fits better the systems than the EM model (see Figs. 9 and 10). The main interest of the present EM model resides in the fact that microstructural parameters can be taken into account directly, thus allowing a better description of the real heterogeneous material. This approach might be improved by increasing the number of $d_i$ values that are associated with the grain size distribution.

Acknowledgements

The authors gratefully acknowledge Professor J.P. Clerc (IUSTI, Marseille, France) for helpful discussions during this study. They also thank the ‘Conseil Régional Provence Alpes Côte d’Azur’ for financial support.
Appendix A. Percolation threshold and inflexion point determination

Eq. (1) gives

\[ \Sigma = \frac{(d\Phi_1 - 1)\sigma_1 + (d\Phi_2 - 1)\sigma_2 \pm \Delta^{1/2}}{2(d-1)} \]

where

\[ \Delta = (d\Phi_1 - 1)^2 \sigma_1^2 + (d\Phi_2 - 1)^2 \sigma_2^2 + 2(d-1 + \Phi_1\Phi_2 d^2)\sigma_1\sigma_2 \text{ with } \Phi_1 + \Phi_2 = 1. \]

The calculation of \( \frac{d^2(\log\Sigma)}{d\Phi_1^2} = 0 \) presents only one solution:

\[ \Phi_{\text{inf}} = -\frac{\sigma_1 - \sigma_2 + \sigma_2 d}{(\sigma_1 - \sigma_2)d} \quad \text{or} \quad \Phi_{\text{inf}} \]

\[ = -\frac{\sigma_2}{\sigma_1 - \sigma_2} + \frac{\sigma_1 + \sigma_2}{(\sigma_1 - \sigma_2)d} \]

In the case of an insulator/metal composite, \( \sigma_2 \) is negligible as compared to \( \sigma_1 \). The solution is then:

\[ \Phi_{\text{inf}} = \frac{1}{d} \]

where \( \Phi_{\text{inf}} \) is the inflexion threshold of the \((\log \Sigma, \Phi)\) representation. The \( \Phi_0 \) value can be determined from the maximum of \( \frac{d^2(\log\Sigma)}{d\Phi_1^2} \), which is very close to the \( \Phi_{\text{perc}} \) value.

References