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# Characterization of the damage in nanocomposite materials by a.c. electrical properties: experiment and simulation

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Evolution of a.c. electrical properties under large strain of random nanocomposite materials made of a soft thermoplastic insulating matrix and hard conductive fillers is investigated. The transport properties are directly linked with the macroscopic mechanical strain on the composites during uniaxial tensile test or to the time under relaxation, meaning that the method is suitable for monitoring microstructural evolution of such composites. The real part of the conductivity indicated the breaking of the percolating network, while the imaginary part gave information on the possible "spatial correlation" of the damage events. Two different filler shapes were used, i.e. spherical and stick-like (aspect ratio about 15), leading to quantitatively different results. The microstructural evolution was simulated with the help of a resistance–capacitance (RC) model for the electrical properties and with finite element analysis for the mechanical properties. 

## 1. Introduction

Intrinsic conducting polymers have received much attention during the last decades, because of their interesting potential applications [1]. However, their poor mechanical properties constitute a major obstacle for a large-scale industrial use. To overcome this drawback, numerous polymer composites have been processed, in recent years, by mixing polypyrrole (PPy) conducting fillers with different kinds of polymer matrices [2, 3]. The aim being to obtain materials combining both the mechanical properties and processability of the matrix as well as the electrical properties of the fillers. The preparation and characterization of such materials, obtained by mixing an insulating latex of a styrene-butyl acrylate copolymer with a colloidal suspensions of PPy particles, have been recently reported [4]. The final composites films were prepared by freeze drying the suspensions and hot pressing the dried product. It was shown that the samples may be considered as model materials, as the fillers have a well-defined geometry and are randomly dispersed within the matrix. Thanks to different polymerization methods [4], the fillers can be chosen with either a spherical shape or an high aspect ratio (15), with nanoscale sizes. The d.c. electrical properties of the composite versus the filler content followed the well-known power law equation predicted by the statistical percolation theory [5, 6] and the percolation thresholds were found to be 3% and 13% for stick-like and spherical fillers, respectively.

It is well known electrical properties of binary mixture depend strongly on their microstructures. In particular, the dispersion [7], the aspect ratio of the fillers [8] or the filler–filler [9] and filler–matrix [10] interactions affect directly the electrical properties. It has also been shown, with carbon fibre reinforced polymers (CFRP), that electrical transport properties are very sensitive to microstructural changes. For instance, Schulte [11] has proven that electrical measurements can be a very efficient way for monitoring damage of CFRP. These authors [12] related fibre breaking or delamination with an increase in the electrical resistivity. A similar method has also shown to be relevant for detecting failure of CFRP at high strain rates [13]. Ceysson *et al.* [14] found good relationships between the evolution of the resistivity with the number of events in acoustic emission. Further investigations, dealing with a.c. electrical conductivity [15] correlated the dissipation factor with the macroscopic stress on CFRP. Despite of the accuracy of the method demonstrated with CFRP, it appears to have been seldom applied to thermoplastic particulate composites. Pramanik *et al.* [16] and Radhakrishnan *et al.* [17] reported the evolution of the conductivity under large strain of insulator-conductor composites above the glass transition temperature ($T_g$) of the matrix.

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However, these experiments were performed with reticulated matrices and only with d.c. measurements.

The present paper deals with the use of a.c. electrical measurements as a probe for monitoring *in situ* the damage of homogeneous nanocomposite materials made of electrically conductive fillers dispersed in a thermoplastic insulating matrix. Measurements under large strain were performed above the $T_g$ of the matrix in order to obtain a composite having a strong contrast from the viewpoint of both electrical and mechanical properties. The variations in the complex electrical conductivity $\sigma^*$ are compared with the predictions of a numerical simulation based on a resistance–capacitance (RC) model [18].

## 2. Experimental procedure

A schematic representation of the experimental setup is shown in Fig. 1a. Parallelepipedic samples with initial length $L_0$, width $W_0$ and thickness $T_0$ equal to 3, 1.5 and 0.5 cm, respectively, were used. During the uniaxial tensile tests, the specimen's length $L$ was determined from the displacement of the crosshead of a conventional Instron machine (4301). All the experiments were performed at room temperature, i.e. 30 K above the glass transition temperature of the matrix. A constant crosshead speed was maintained with an initial strain rate of $\dot{\varepsilon} = 10^{-3}\,\mathrm{s}^{-1}$. In order to obtain complementary information, three different tests were performed on the samples, namely: (i) uniaxial extension up to a true deformation $\varepsilon = \ln(L/L_0) = 0.2$ to characterize the damage in the percolating network; (ii) relaxation test by stopping the machine at $\varepsilon = 0.2$ and recording stress and conductivity versus time, to characterize the damage recovery and (iii) cyclic strain to quantify hysteresis effects.

The samples (Fig. 1b) were coated at their ends with silver paint, so as to insure a good electrical contact. Electrodes and sample were electrically isolated from the tensile machine. a.c. complex conductivity measurements were carried out for various frequencies in the range of 1 kHZ to 1 MHz using an HP 4248A bridge from Hewlett Packard with a low applied field of 1 V cm$^{-1}$.

The sample length $L$ and the complex admittance $Y^*$ as well as the applied strength $S$ data were recorded versus time. Upon large deformation the length and the cross-section of the sample vary and the admittance

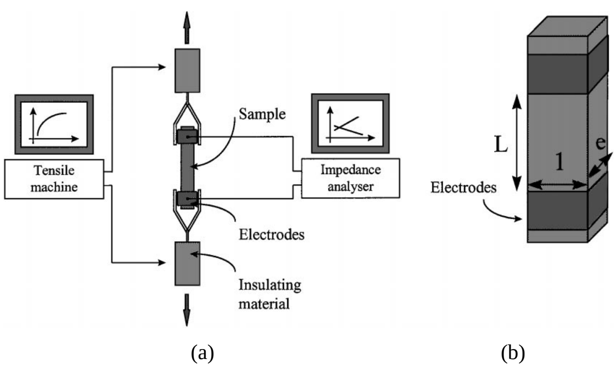



*Figure 1* Schematic representation of (a) the experimental setup and (b) electrodes and sample arrangement.

decreases, for geometrical reasons. However, the conductivity is an intrinsic parameter that should remain constant unless changes in the arrangement of the conductive component occur. For thermoplastic polymers, above $T_g$, the Poisson's ratio value is close to 0.5, meaning a conservation of the volume $V_0$ of the sample under large strain. Assuming that the damage in the network does not induce a strong variation of $V_0$ (i.e. that the volume of the holes is negligible), the mechanical stress $\Sigma_m$ and electrical conductivity $\sigma_e^*$ are governed by

$$\Sigma_m = \frac{S}{W \times T} = S\frac{L}{V_0} \tag{1}$$

and

$$\sigma_e^* = Y^*\frac{L}{W \times T} = Y^*\frac{L^2}{V_0} \tag{2}$$

With $W$, $L$ and $T$ the width, length and thickness of the sample during the test, and $V_0 = L_0 \times T_0 \times W_0$. The electrical and mechanical data were obtained tacking into account the geometrical evolution using Equations 1 and 2 with a minimum time step (including acquisition and data treatment) of 1.

## 3. Results and discussion

It is important to note that the deformation of the sample remained homogeneous and that, more specifically, no necking appeared in the samples during the deformation process. As the fillers used in the present work have a tensile modulus much greater than the one of the matrix, one can assume that the filler does not break and, thus, that the local events consist of filler–filler interaction breakage. Such a microstructural evolution, if it occurs, will lead to a decrease of the macroscopic conductivity, which results from the continuous network of filler within the matrix. Thus, the d.c. conductivity can be used as a direct probe for monitoring *in situ* the damage of such composites. Nevertheless, the a.c. conductivity gives more information than the static one. As the evolution of the permittivity is not easy to understand, the use of a numerical simulation that forecasts the influence of the network breakage on the macroscopic a.c. electrical properties was required.

### 3.1. Real part of the conductivity at low frequency

Typical data for real part of the conductivity ($\sigma'$) at low frequency (1 kHz) for composites filled with spheres (20%) and sticks (10%) up to a deformation of 0.2 and under relaxation are shown in Fig. 2a and b, respectively. For comparison, the true stress is also displayed. It is clear that the conductivity depends directly on the strain on the composite and on the time, during the tensile and relaxation tests, respectively. Moreover, both conductivity and mechanical stress exhibit a smooth evolution during the experiment, contrarily to similar measurements performed on CFRP [12, 14]. Such a continuous evolution is to relate to the large number

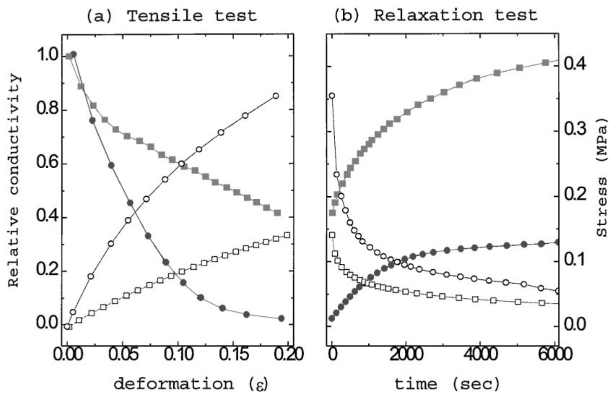



*Figure 2* Evolution of the normalized real conductivity at low frequency (1 kHz) under tensile and relaxation tests for composites containing 10% of stick-like filler (■) and 20% of spherical filler (●) and corresponding mechanical stress (opened symbols).

of fillers in each composite film. Indeed, as already mentioned, the composites are filled with nanoscopic particles, thus each sample contained a huge number of conducting fillers (in the order of $10^{11}$) and the macroscopic properties may be seen as an average response of local events.

### 3.1.1. Tensile test

It is striking that $\sigma'$ began to decrease as soon as the sample was deformed meaning, in other words, that the damage in the network occurs at very low applied stress. This corresponds to weak filler–filler interactions within the matrix. This compares well with the low deformation measurements [4] on these composites that showed that the reinforcement effect is much lower than the one predicted by the mechanical percolation theory [19, 20] and thereby that the filler–filler interactions are weak. Thus, some contacts between filler were broken at low applied stress, and accordingly the conductivity decreased. The damage may be quantified by the evolution of the relative conductivity from the initial state to a given deformation. Fig. 3 displays the average evolution (on six different samples), versus the volume fraction, of the relative conductivity

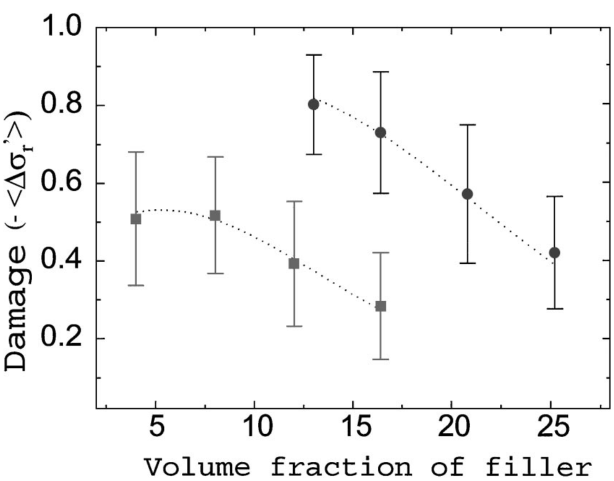



*Figure 3* Variation of the relative d.c. conductivity versus volume fraction for spherical fillers (●) and stick-like fillers (■).

for a true deformation between 0 to 0.2. This quantity dropped steadily with increasing volume fraction of fillers, irrespectively of the aspect ratio. However, the composites containing spherical fillers were more damaged than the ones filled with sticks. Comparable observations [16] have been interpreted by a reorientation effect of the fibres during the deformation, inducing a conservation of the percolating network.

### 3.1.2. Relaxation test

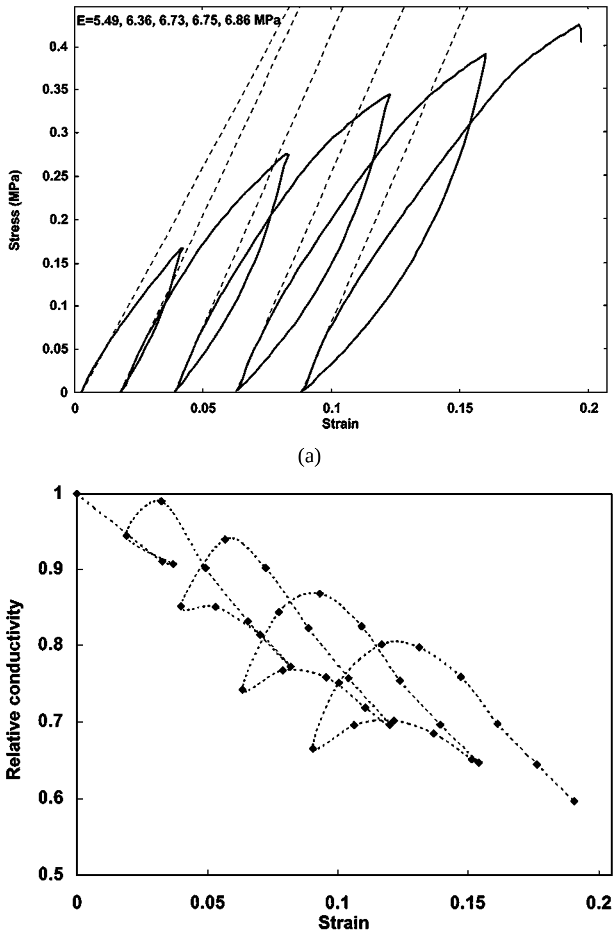
During the stress relaxation, the viscolelastic properties of the matrix leads to the well-known behaviour for the macroscopic stress versus time. More interesting is the direct influence of mechanical relaxation on $\sigma_e'$, which increased in a monotonic manner, proving that the holes in the network, appearing during a tensile test, are recoverable during a relaxation test. This implies that, in this experimental condition, the matrix does not fill the holes in the network. The aspect ratio influenced also quantitatively the recovery of the electrical conductivity: the composites filled with sticks exhibited a stronger recovery than the ones filled with spheres. The evolution of the electrical and mechanical quantity versus time can be fitted with a stretched exponential law as

$$\frac{\Delta X}{X} = \left[1 - \exp\left(\frac{-\Delta t}{\tau}\right)^{b}\right] \tag{3}$$

where $\Delta X/X$ is the relative variation of either the conductivity or the mechanical stress versus time, $\tau$ is a time characterizing the relaxation process and $b$ is an exponent describing the width of the distribution in relaxation time. The stress relaxation process described with shorter characteristic times ($\tau \approx 700$ s) than the electrical relaxation process ($\tau \approx 1200$ s) and with a broader time distribution as the value of b was equal to about 0.7 for the mechanical properties and to about 0.5 in the electrical case. This results, are linked with the local behaviour of the matrix surrounding the fillers where the damage events occurred, and difficult to interpret quantitatively. However, the experimental data may be qualitatively understood by considering that the macroscopic stress evolution is continue, even at a very small scale. On the contrary, the electrical conductivity between to fillers can be considered, in a first approximation, as a binary event (electrical contact or not), leading to longer characteristic time with a narrower distribution. We should notice that the distribution in relaxation time also depends on the stress distribution in the composite that is not easy to forecast.

### 3.1.3. Cyclic deformation

In the above section, it as been shown those both electrical and mechanical properties depend on time during the stress relaxation. Such a time-dependent phenomenon is a typical consequence of the viscoelastic behaviour of the matrix. Another way for characterizing this viscoelasticity is to perform cyclic deformation. It is of interest, in particular, to quantify the




(a)

(b)

*Figure 4* (a) Mechanical stress and (b) electrical conductivity for a composite containing 20% of stick-like filler under cyclic deformation.

electrical hysterisis and, thereby, hysterisis in the microstructural state. The mechanical stress and the relative conductivity for a composite filled with 20% of stick-like fillers under cyclic deformation is shown in Fig. 4a and b, respectively, Measurements were performed on four cycles and the maximum deformation was increased at each cycle up to 0.2. Again, the mechanical stress showed a typical behaviour for a polymer above its glass transition temperature. The electrical conductivity $\sigma'$ is directly dependent of the strain. The maximum value for $\sigma'$ decreased for each cycle, meaning that the network of hard fillers did not recover its initial state, even for zero stress. Nevertheless, a monotonic increase in the modulus of the composite with the number of cycles was observed, in apparent contradiction with the discussion concerning the relationship between the reinforcement and the filler fraction. An interpretation of such a behaviour can be given considering that a very high local deformation of the matrix must occur in a region where fillers are changing from a contact to a non-contact state. In other words (Fig. 5), a very high stretching of the macromolecules surrounding these filler should occur, and thereby an increase of the modulus of the composite.

From these experiments, it has been shown that the continuous network breaking in random insulator–conductor binary mixtures may be quantified by measuring the real part of the conductivity. Thus, both the

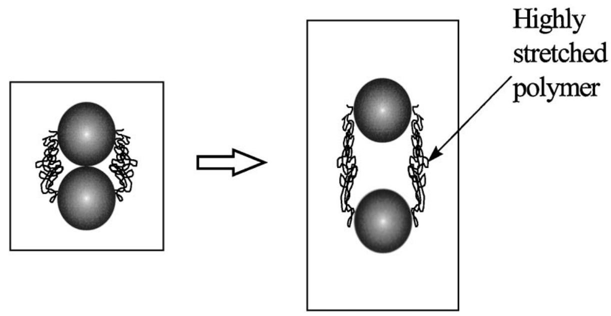



*Figure 5* Local stretching deformation of the matrix when the contact between two fillers is broken.

damage and the recovery of the network within composites can be monitored *in situ* by measuring the electrical resistivity. However, the a.c. measurements give more information than the d.c. ones, the next section describes the frequency dependence of the electrical result for both the real ($\sigma'$) and the imaginary ($\sigma''$) parts of the conductivity for tensile and relaxation tests, and thereby attempts to prove that $\sigma^*$ gives qualitative informations, when coupled with a numerical simulation, on the correlation between the damage events.

### 3.2. Frequency dependence

The composites were deformed under tensile tests and the electrical conductivity was recorded during both tensile and relaxation test, as described above. The experiments were carried out with volume fractions of 13% for spherical fillers and 4% for stick-like fillers, that means just above the percolation threshold in both cases [4]. This choice was motivated by the fact that the conductivity and the permittivity are very sensitive to the volume fraction of fillers close to the percolation threshold [6]. When two fillers are separated from each other during the tensile test, their electrical interaction should change from a resistor, describing the free carriers, i.e. the electrical contact, to a capacitor, modelling the trapped carriers, i.e. the polarization effects. Varying the frequency of the applied electrical field allows one to vary the relative importance of these two effects; at low frequency the electrical behaviour is dominated by the percolating network, while the polarization effects between clusters may have a great importance at high frequency, inducing an increase of the conductivity because of its imaginary part. Under such conditions, an increase of the relative permittivity was awaited during the tensile test, corresponding to the creation of capacities when the network was broken. The real and imaginary parts of the conductivity for different frequencies are shown in Figs 6 and 8 for spherical fillers and fibre, respectively. $\sigma'$ decreased during the tensile test, whatever the frequency and the aspect ratio of the filler, confirming the breaking of the network. Increasing the frequency decreased the amplitude of the variation both for $\sigma'$ and $\sigma''$. The permittivity increased just for frequency close to 1 MHz, in the case of stick-like fillers and close to the threshold and in both cases, at low frequency, $\sigma''$ decreased, contrarily to what was awaited.

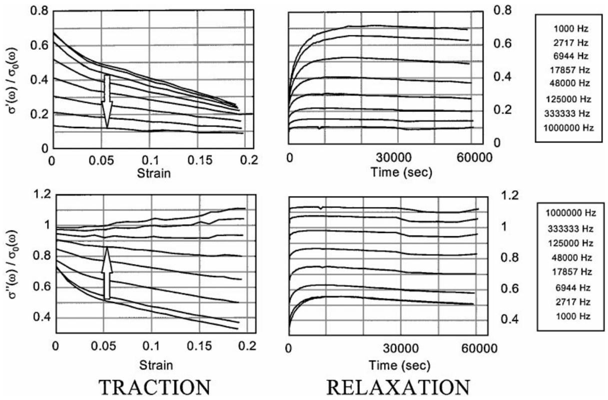



*Figure 6* Real and imaginary parts of the relative conductivity under tensile and relaxation tests for composites containing 4.5% of stick-like filler (the arrow indicates the increasing frequency).

The next section describes an attempt for modelling the microstructural evolution of the composites. Therefore two numerical simulations were used to determine the a.c. electrical properties on the one hand, and on the other hand, the mechanical stress at each node. These simulations are both, up to now, limited to the case of stick-like fillers. The aim is to determine the influence of the damage in the network and of the purely geometrical deformation on the macroscopic conductivity. After a brief introduction of the numerical methods, computed data will be shown. From these simulations and thanks to a comparison of the experimental data, a schematic representation of the composite behaviour under large strain may be given.

## 4. Numerical simulations

Two different simulations were used to describe the evolution, under tensile test of the mechanical and the electrical conductivity. The mechanical properties were determined with the help of a finite element simulation while the electrical properties were simulated with an RC type model. The aim of the finite element model (FEM) calculation is to determine the stress distribution on the nodes of a fibre tree under loading, while the electrical model relates the macroscopic properties with the microstructure.

### 4.1. Electrical modelling

The details of the electrical simulation used in this study are described elsewhere [21]. The macroscopic properties of the composites were related to the fillers' position and orientation thanks to an improvement of the called RC model developed by Clerc *et al*. [18] in which each resistor and capacitor value depends directly on both a simulated microstructure and the macroscopic properties measured for each component. Resistors describe the electron mobility between two fillers in geometrical contact while capacitors model the polarization effects between fillers that are not in contact. This numerical model, based on the construction of a resistors-capacitors network, computes the macroscopic electrical properties by accounting for the topology of fillers in the material. This method has shown [21] to be relevant for understanding the electrical properties of the composites described in this study, in the undeformed state. In this case [21] the microstructure was defined with the help of a random and uniform distribution of both particle position and orientation. This numerical simulation was, in the present work, used to estimate the macroscopic evolution of the conductivity whenever a local change in the arrangement of the fillers occurs. As for instance the evolution on the conductivity from the initial state to a deformed or damaged state.

### 4.2. Influence of the deformation

A first source of filler rearrangement is a purely geometrical effect due to the macroscopic deformation of the samples. As the modulus of the matrix (1 MPa) is much lower than the modulus the fillers (1 GPa), the fillers can be considered as not deformed during the tensile test. Thus, it is easy to compute the influence of the macroscopic deformation on the local behaviour, by applying a linear change of the fillers' centres of mass and orientation. Defining as $\boldsymbol{C}_i$ and $\boldsymbol{V}_i$ the centre of mass and the unitary vector, respectively for each filler $i$ in the underformed state, and as $\varepsilon$ the true deformation, the position and orientation fillers in the deformed state is governed by

$$\boldsymbol{C}_i(\varepsilon) = \boldsymbol{C}_i \times \exp(\varepsilon) \tag{4}$$

and

$$\boldsymbol{V}_i(\varepsilon) = \boldsymbol{V}_i \times \exp(\varepsilon) \tag{5}$$

in the direction of the tensile test and by

$$\boldsymbol{C}_i(\varepsilon) = \boldsymbol{C}_i \times \exp(-\varepsilon/2) \tag{6}$$

and

$$\boldsymbol{V}_i(\varepsilon) = \boldsymbol{V}_i \times \exp(-\varepsilon/2) \tag{7}$$

in the other directions (the vector $\boldsymbol{V}_i$ must be normalized after deformation). A representation of the filler rearrangement during the tensile test is displayed in Fig. 7a. With such evolution, the filler reoriented in the direction of the tensile test, i.e. in the direction of the conductivity measurement. The macroscopic conductivity was determined taking into account the geometrical change of the sample with the help of Equation 2. As depicted in Fig. 7b, the reorientation of the fillers in the direction of the macroscopic electric field induces a decrease of the value of each capacitor, describing the non-contact state, and thereby a decrease of the relative permittivity of the sample. However, with such a simulation, no damage in the percolating network is accounted for. Under such condition, the percolating volume fraction remains constant during the deformation and the real part of the conductivity rises, due to the correction with Equation 2. The influence of the damage of the network on the macroscopic conductivity is described in the next sections.

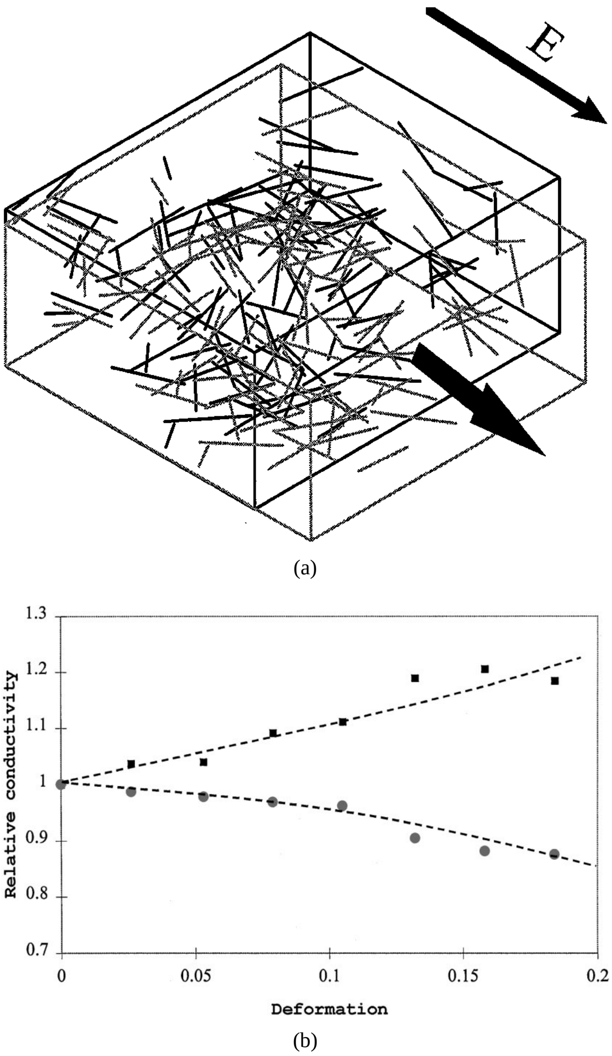



*Figure 7* (a) Schematic representation of the microstructural evolution of the composite under deformation: initial state (black) and with 20% of true deformation (gray) (b) corresponding evolution of the real and imaginary parts of the conductivity versus the deformation.

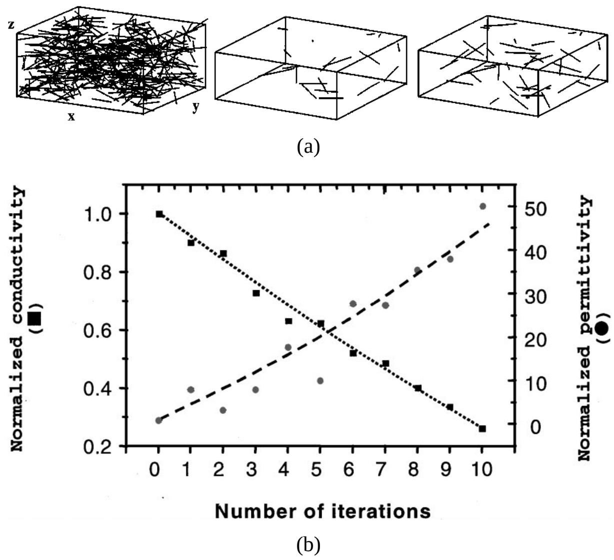



*Figure 8* (a) Simulated microstructure of a composite containing 15% of stick-like filler: initial state, damaged fillers after 5 steps and after 10 steps (b) corresponding evolution of the real and imaginary parts of the conductivity versus number of steps.

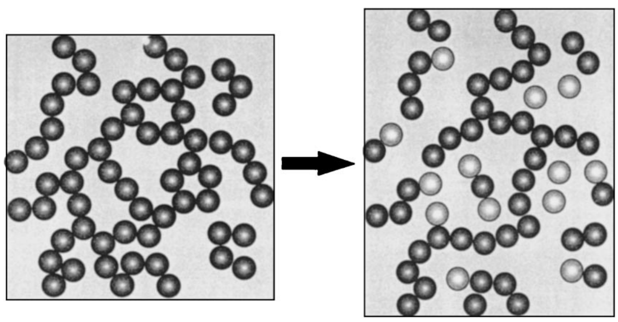


*Figure 9* Schematic representation of the damage mechanisms in the composite material, initial state (left) and deformed state (right). In the latter case, the fillers changing from a contact to a non-contact state were plotted in grey.

## 4.3. Mechanical and electrical modelling

The mechanical method, based on finite element simulation, has also been reported recently [19] and proven to be relevant to model the elastic modulus of a strongly contrasted composite materials, and its evolution with the volume fraction of filler. This simulation is suitable in the elastic domain (linear dependence) and does not account for the matrix behaviour but only considers the filler–filler interactions. In the present paper, the same simulation was used, but to determine the position of the more stressed nodes within the composite. These nodes were then supposed to be broken.

The electrical and mechanical simulations, with complementary roles, were combined together. Therefore, the resistors, accounting in the electrical simulation for the contact between two fillers, were changed to capacitors once they broke. Fig. 8a displays the microstructure in the initial state as well as the broken fillers increasing the number of steps, Fig. 8b shows the corresponding evolution for the electrical conductivity. $\sigma'$, of course, decreased as the number of conducting paths in the material was lowered. However, the relative permittivity was found to rise. This behaviour, in disagreement with the experimental observation, indicated that the experimental behaviour could not be explained only by the damage in the network.

With the help of the above-described results, a summarized representation of the probable microstructure evolution during a tensile test is proposed in Fig. 9. The percolating network has not been totally broken, as the conductivity never reached very low values with a homogeneous deformation. Thus, the real part of the conductivity indicates that, during the deformation process, the rearrangement of the fillers is so that a percolating volume fraction is kept. This is probably the results of two competitive strength within the material, namely: (i) the stress localization due to the difference between the behaviour of the matrix and of the filler, this stress localization tending to break the network; and (ii) to the attraction of the filler with each other, due to the high matrix deformation required to break a contact. These competitive strengths have been characterized by different tests under high deformation. The evolution of $\sigma''$ can be explained qualitatively by a general process of reorientation of the filler in the electric field (in the case of rod fillers) rather than by local phenomena, such as only the damage of the network. Even if this information is only qualitative, it is very interesting and in good agreement with the observation that the composites exhibited no necking during deformation. The weak filler–filler interactions probably also leads to the breakage of dead-ends and even of isolated cluster during the tensile test. This breakage would induce a further decrease of the permittivity, which cannot, however, be verified as the mechanical simulation failed to predict the stress on these elements.

## 5. Conclusions

This work has dealt with the a.c. electrical properties measurements under large strain of composites strongly contrasted in the viewpoint of their electrical and mechanical properties. A good correlation between electrical conductivity and mechanical stress with different kind of solicitation was measured. The macroscopic conductivity and stress evolution were very smooth, due to the nanoscopic size of the fillers. Real part of the conductivity at low frequency versus deformation is explainable in terms of damage in the percolating network, which is more important and less recoverable with spherical than with stick-like shaped fillers. Cyclic deformation tests have also been performed, which shed some light on the importance of the very high local deformation of the matrix on the macroscopic properties. The imaginary part of the permittivity was found to increase at high frequency close to the percolation threshold and in the case of high aspect ratio fillers. This is probably to relate to the formation of capacity with very high values when the network is broken. This phenomenon was, however, only measured in particular conditions, when the permittivity is very sensitive on the volume fraction of filler, and a decrease of the polarization effects is, on the contrary, measured in the other cases. Although the a.c. electrical behaviour of such composites under high deformation is very complex (a complete and comprehensive explanation of the measured data cannot, yet, be given), the coupling of a.c. electrical measurements and numerical simulation permitted to indicate that the damage mechanisms were not localized on the network. Such information is in agreement with the evolution of the conductivity from very low deformation levels, i.e. with low stress. This method is very powerful as it allows the understanding not only of the damage in the network but also the possible correlation of the network breakage. Different numerical tools have been developed during this work that may be applied to many composites materials. Further investigations with other kinds of filler that, in particular, present stronger interactions with each other would be very interesting.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