

## **INFLUENCE OF THE GLASS TRANSITION ON THE DIELECTRIC PROPERTIES OF A RESIN.**

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**Summary:** The dielectric properties of a resin have been investigated over a wide range of frequencies (1mHz-1MHz), as a function of the temperature varying from 23°C up to 100°C, through the glass transition temperature, 65°C.

A net effect of the glass transition was observed, with a brutal occurrence of a dc-conduction phenomenon, a rapid and strong increase in the relative permittivity and an amplification of the dielectric losses as soon as the temperature reaches the glass transition value.

No relaxation phenomenon was clearly observed. In contrast, owing to its threshold temperature and the low-frequency domain within which it occurs, it was suggested that the strong increase in the relative permittivity is due to charges accumulation in the material consecutively to the dc-conduction. To clear up this assertion, dielectric data were analysed using, first the electric modulus formalism which is thought to suppress capacitive phenomena such as low-frequency dispersion (LFD) and amplify consecutive relaxation, then the discrimination method of Havriliak-Negami. A succession of two narrow peaks, attributed to relaxation of charges carriers accumulated in the material in two different types of sites was detected at low frequencies, below 1Hz, while a third one, broader and localised within the frequency range 10Hz-60Hz was referred as a  $\alpha$ -peak. The temperature dependences of the characteristic frequencies of these peaks were examined and discussed according to theoretical previsions. Their shape involves thermodynamic changes in the material above 80°C.

**Keywords:** Dielectric, relaxation, glass transition, polymer.

**Résumé :** Les propriétés diélectriques d'une résine à base de diglycidyl-éther de bisphénol A (DGEBA) ont été étudiées en fonction de la fréquence dans la bande (1mHz-1MHz) pour différentes valeurs de la température variant de 23°C à 100°C.

Un effet très net de la transition vitreuse a été observé. Il se manifeste par le déclenchement brutal d'un phénomène de conduction ohmique, une augmentation rapide de la permittivité relative et une amplification des pertes diélectriques dès que la température atteint la valeur de 65°C correspondant à la transition vitreuse du matériau.

Aucun phénomène de relaxation diélectrique n'a été clairement observé. Par contre, du fait que la conduction ohmique d'une part et la croissance rapide de la permittivité diélectrique d'autre part se déclenchent à la même température de seuil et sont observées simultanément dans le domaine des basses fréquences, on suggère que cette dernière est consécutive à une accumulation de charges dans le matériau. Pour vérifier et étayer cette hypothèse, les données diélectriques ont été analysées en utilisant comme outils, d'abord le module électrique dont l'une des propriétés est d'amplifier les phénomènes de relaxation à basses fréquences consécutifs à un empilement de charges, puis la méthode de discrimination d'Havriliak-Negami. Une succession de deux pics de relaxation ont été détectés à des fréquences inférieures à 1Hz. Ils révèlent l'existence de deux sites différents dans le réseau du matériau où des porteurs sont accumulés. Un troisième pic, plus élargi et localisé dans la bande (10Hz-60Hz) est attribué à un phénomène de relaxation de type  $\alpha$ . L'influence de la température sur la fréquence de relaxation de ces pics a été analysée à la lumière des prévisions théoriques. Les allures observées laissent envisager une transformation du comportement thermodynamique, probablement un changement de phase et une variation de la viscosité, dès que la température atteint 80°C.

**Mots-clés:** Diélectrique, relaxation, transition vitreuse, polymère.

## **I-INTRODUCTION**

Since a few decades, industrial applications of epoxy resins-based-polymeric materials have been expanded and diversified. In microelectronic industries for example, these materials are used as encapsulants for components protection from chemical and mechanical stresses<sup>[1]</sup>. The main role of a packaging material is to ensure the electrical insulation of the circuit pins. To achieve that aim some properties required for such materials are, for example, a very low conductivity to avoid currents leaks, low relative permittivity and loss factor to minimize capacitive effects and energy dissipation respectively, a thermal conductivity high enough to facilitate heat dissipation. The resin epoxy-based-dielectric materials are also used as high voltage insulators. For that purpose the resin is filled with silica, alumina or glass particles which reinforce the mechanical properties, improve the heat conductivity of the material and contribute to reduce the the manufacturing costs<sup>[2]</sup>.

Owing to the varied application fields of these materials, several works have been devoted to the study of their electrical and dielectric properties (conduction, energy storage and dissipation, polarisation under electric field...)<sup>[3,4,5]</sup>. One knows for example that anions penetration in composite films of PET/PANI (polyethylene terephthalate/polyaniline) consecutive to doping leads to additional loss peaks in comparison to non doped ones, high temperature treatment of the filler decreases interfacial polarisation in a composite and in a general manner the dielectric properties of composites strongly depend on the matrix.

The dielectric properties of polymeric materials are more and more studied by means of spectroscopic method. Dielectric spectroscopy is a rapid mean for the diagnosis of electric equipments insulation and its aging during operation. Relaxation

phenomena in solid dielectrics represent one of the most investigated topics in materials sciences area and generally the spectra of the complex permittivity (real and imaginary) are used to present most of the phenomena studied<sup>[6]</sup>. Kyritsis and al.<sup>[7]</sup> have associated to these parameters those of the impedance and the electric modulus to analyse the dielectric properties of poly (hydroxyethyl acrylates)/water hydrogels. Among these representations the one of the electric modulus remains the less frequently used although it was found well adapted for analysis of electric relaxation phenomena in ionic conductors and more generally those occurring at very low frequency consecutively to quasi dc-conduction<sup>[8]</sup>.

The dielectric spectra may not show evidence of relaxation phenomena. That is the case in ionic conductors such as silicon monoxide. For that material, within the wide range of frequency ( $10^{-3}$ Hz- $10^9$ Hz), the imaginary permittivity follows a power-type law  $\omega^m$ , where the value of m depends on the frequency domain ( $m \leq 1$ )<sup>[9]</sup>. In a recent paper we have observed similar behaviour on a DGEBA-based resin used for high voltage insulation<sup>[4]</sup>. The present work follows the latter. It is a contribution to the study of the dielectric properties in polymers by means of the dielectric spectroscopy method and has been carried out at L.E.M.D-C.N.R.S (Grenoble/France). The well known difficulty is related to the heterogeneous structure of the material which leads very often to complex dielectric polarisation processes owing to the major role of the interfaces polymer/filler<sup>[10]</sup>. Therefore the present paper only deals with the results on the filler-free resin. A next paper will show the effect of various parameters such as the nature of the filler, its thermal treatment and electric aging of the samples on the dielectric properties of the material.

## **II-EXPERIMENTAL**

The epoxy resin is a DGEBA (Diglycidyl Ether of Bisphenol A) cured with an acid anhydride. It is filler-free. Its glass transition temperature  $T_g$  is 65°C. The Samples were 0.5mm thick and moulded between two circular aluminium plane electrodes, 18mm diameter each. They were disposed for measurements into a heating box which temperature is calibrated with an accuracy of 0.5°C. Dielectric measurements were carried out in the range (10<sup>-3</sup>Hz-10<sup>6</sup> Hz) using a high-resolution impedance analyser (Novocontrol BDS 20).

### III-EXPERIMENTAL RESULTS

Figures 1a and 1b show the dielectric constant  $\epsilon'$  and the imaginary permittivity  $\epsilon''$  of the resin, as a function of the frequency, for the temperature varying from 23°C up to 100°C.

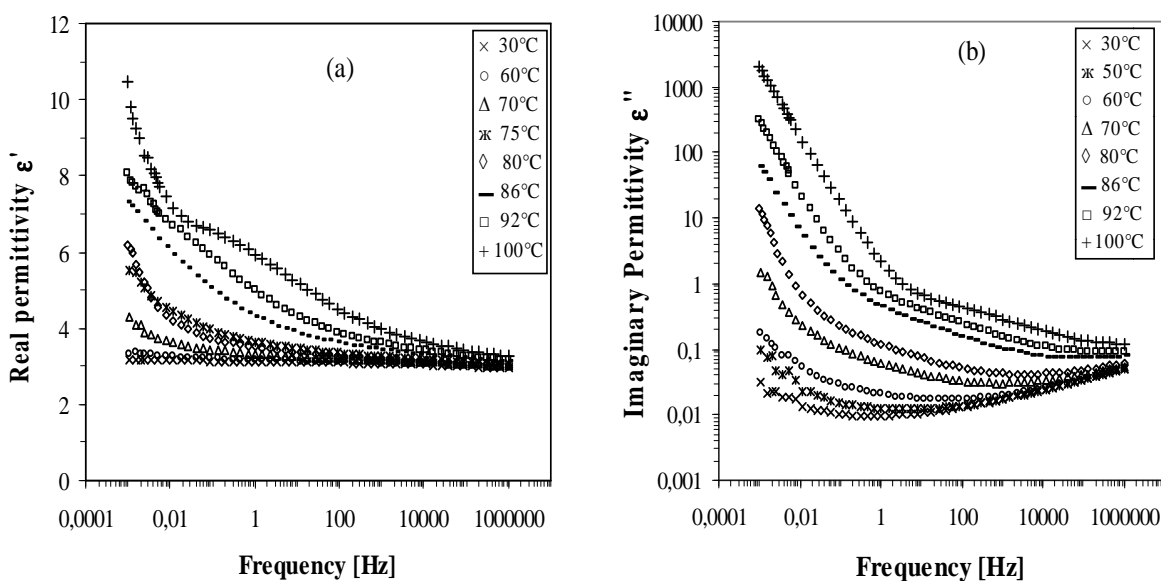
Below 60°C,  $\epsilon'$  remains close to the value 3.0 measured at high frequency (Fig. 1a). Above 60-70°C, the permittivity is no longer constant but increases as frequency decreases.

The loss factor  $\epsilon''$  vs. frequency increases with temperature, reaching very large values at low frequency for the highest investigated temperatures (Fig. 1b).

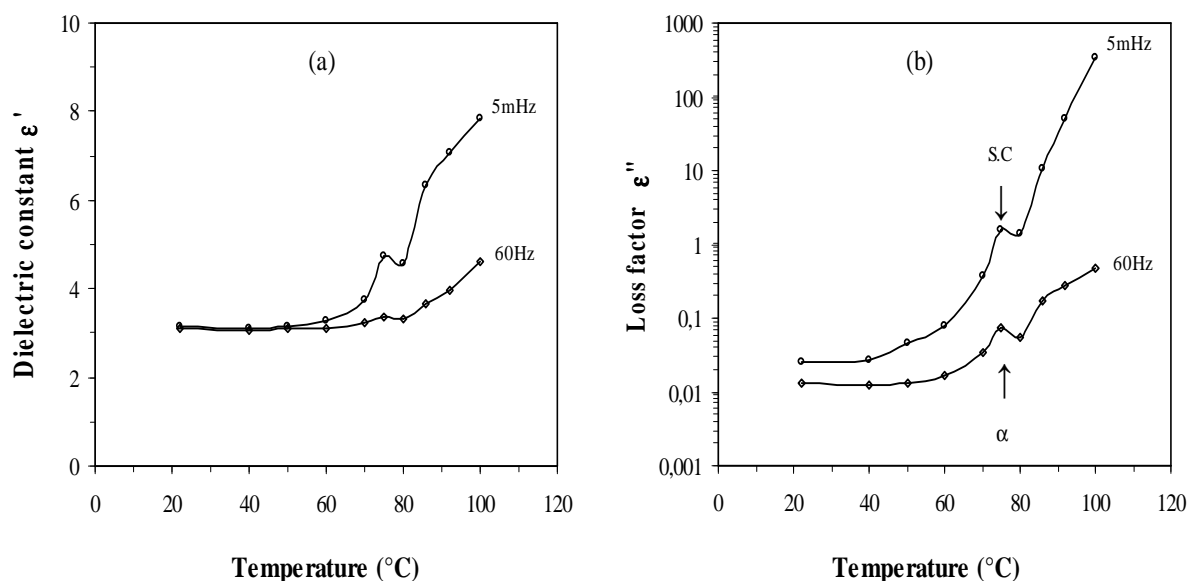
The curves are shifted to the right, i.e. towards the highest frequencies, as the temperature increases. They are also shifted upward by about a decade from 23°C to 100°C. The curves do not show loss peaks. However at low frequency and high temperatures, they exhibit a slope of about -1 indicating the dominance of an ohmic conduction mechanism. At mean frequency [1Hz-10 kHz] and temperatures lower than 90°C, their slope is about -0.25. Similar frequency dependences of the loss factor  $\epsilon''$  have been described and characterized with a power-type law  $\epsilon'' \sim \omega^m$  [9].

Figures 2a and 2b show the temperature dependences of the dielectric constant  $\epsilon'$  and the loss factor  $\epsilon''$  respectively, for two values of the frequency, i.e. 5 MHz and 60Hz.

As far as the temperature is lower than 60°C, the relative permittivity  $\epsilon'$  remains constant and its value, about 3.0, does not depend on frequency (fig. 2a). Above 60°C, a rapid increase is observed, mainly



**Figure 1:** Spectra of the real (a) and the imaginary (b) permittivity according to temperature.



**Figure 2:** Temperature dependences of the real (a) and the imaginary (b) permittivity.  
S.C: Space-charge relaxation  $\alpha$ :  $\alpha$ -relaxation peak

at low frequency and the relative permittivity reaches very high values. For example at 100 $^{\circ}\text{C}$ ,  $\epsilon'$  is about 8 at 5 MHz and about 4.2 at 60Hz. The loss factor  $\epsilon''$  varies similarly according to temperature (fig. 2b). However, its value is higher at lower frequency, whatever the temperature. Moreover, the relative permittivity  $\epsilon'$  shows two maxima. The first one is at 75 $^{\circ}\text{C}$  and the second one at about 86 $^{\circ}\text{C}$ . These maxima are correlated with two loss peaks on  $\epsilon''(T)$ . They are at low frequency (5MHz), mainly on the curve of the relative permittivity  $\epsilon'$ . In contrast, their magnitude seems to decrease with increasing frequency.

The precedent results show evidence of a threshold temperature, of about 60 $^{\circ}\text{C}$ . Indeed, above that temperature, a dc-conduction phenomenon releases in the material, the dielectric parameters  $\epsilon'$  and  $\epsilon''$  increase simultaneously and rapidly, two loss peaks in  $\epsilon''$  correlated with two maxima of the relative permittivity  $\epsilon'$  occur. This threshold temperature compares well with the glass transition temperature of our material ( $T_g \sim 65^{\circ}\text{C}$ ).

#### IV-INTERPRETATION AND DISCUSSION

The precedent conclusion suggests two phenomena to be invoked in the rapid increases of  $\epsilon'$  and  $\epsilon''$  and in the occurrence of peaks on these parameters, namely, an effect of the glass transition and the dc-conduction.

Above the glass transition temperature of a material, in the rubber state, rearrangement and local motions of polymer chains or chain fragments occur<sup>[11]</sup>. These changes increase with increasing temperature and can lead to a reinforcement of conduction<sup>[12]</sup>. Dipoles in the polymer chains can also orient in the applied electric field and contribute to the dielectric constant<sup>[13]</sup>. Both phenomena lead to a dielectric loss peak, referred as  $\alpha$ -relaxation peak, which causes a dissipation of electrical energy in the sample.

At sufficiently low frequencies and high temperatures, ions from the lattice of the material (intrinsic ions) or from impurities present in the material (extrinsic ions) may migrate due to applied electric field. This motion of charges gives rise to a dc-conduction phenomenon. The dc-conduction is a succession of hops of ions or other charge carriers along the lattice sites of the material over potential energy barriers in the direction of the electric field

<sup>[14]</sup>. The conduction process depends on the lattice structure, namely, the height of the free energy barriers and their distribution in the material. Indeed, in a material where all the lattice sites are equivalent (crystal for example), the free energy barriers are regularly spaced and of uniform height and charge carriers diffusion gives rise to a pure dc-conduction mechanism. In contrast in a material with disordered molecular structure (vitreous substances...), the free energy barriers can vary from site to site. Ions hop rapidly out of sites with low free energy barriers but tend to pile up at sites with high energy barriers. Diffusion of charge carriers over long distances in such material gives rise to conduction with charge accumulation which leads to polarisation of the material and to an increase in the relative permittivity. This phenomenon known as low frequency dispersion (LFD) <sup>[9]</sup> is responsible for dielectric relaxation in the sites where charges have accumulated. In materials with filler, charges pile-up due to dc-conduction occurs at the interfaces between the background material and the filler. The consecutive dielectric relaxation takes place at the interface and is known as Maxwell-Wagners-Sillars relaxation <sup>[15]</sup>.

When the spectra of the relative permittivity  $\epsilon'$  and the loss factor  $\epsilon''$  do not show evidence of dielectric relaxation phenomena, it is difficult to distinguish between the interfacial polarisation and the intrinsic dipolar relaxation contributions. However, in dielectrics for which the loss mechanism involves a series process such as dc-conduction (succession of hops of charge carriers over free energy barriers), it has been proposed to analyse data in terms of additive parameters (as impedances rather than admittances) <sup>[16]</sup>. The electric modulus, defined as the reciprocal permittivity  $M^* = \epsilon^{*-1}$ , has been found particularly well adapted for such data treatments. Using the formalism  $\epsilon^* = \epsilon' + i\epsilon''$  of the complex permittivity, the complex electric modulus  $M^*$  can be resolved into real and imaginary parts, respectively <sup>[7]</sup>:

$$M' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} \quad (1) \quad \text{and}$$

$$M'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \quad (2),$$

The formats of  $\epsilon^*$  and  $M^*$  differ in terms of how each highlights or conversely suppress observation of dielectric phenomena. As an example, for a conducting material with a relative permittivity  $\epsilon_s$  and a conductivity  $\sigma_0$  independent of frequency, namely  $\epsilon' = \epsilon_s$  and  $\epsilon'' = \sigma_0 / \epsilon_0 \omega$ , the real and imaginary modulus become respectively:

$$M' = \frac{M_s (\omega\tau)^2}{1 + (\omega\tau)^2} \quad (3) \quad \text{and}$$

$$M'' = \frac{M_s (\omega\tau)}{1 + (\omega\tau)^2} \quad (4), \text{ where}$$

$$\tau = \frac{\epsilon_0 \epsilon_s}{\sigma_0} \quad (5) \quad \text{and}$$

$$M_s = \frac{1}{\epsilon_s} \quad (6).$$

These expressions characterise the Debye-like relaxation dispersion and indicate that the modulus format describes the dc-conduction as a relaxation process with a characteristic time  $\tau$  called conductivity relaxation time. The  $\tau$  parameter determines the rate at which the electric field decays to zero in the dielectric under the constraint of a constant displacement vector <sup>[16]</sup>.

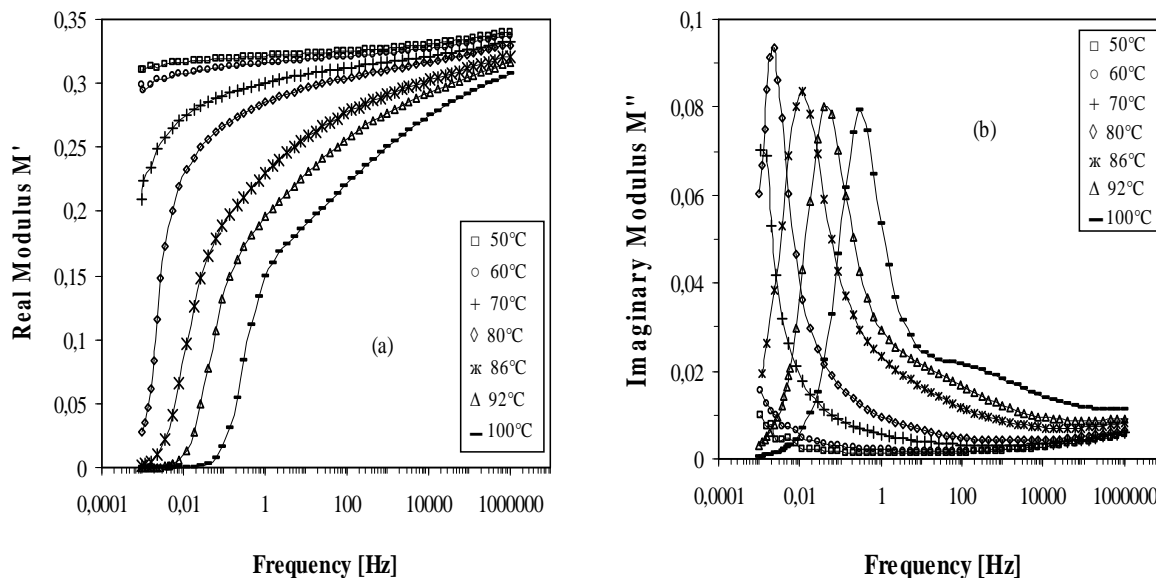
Highly capacitive phenomena are suppressed in the representation of  $M''$  vs. frequency, particularly when the ratio of the static to infinite relative permittivity is high. Consequently, low frequency dispersions (LFD) are suppressed while high frequency relaxations are amplified. This was verified when investigating dielectric properties of residual water in a mixture of sugar and drug. The peaks observed at low frequency on the spectra of the imaginary modulus revealed the existence of relaxation phenomena, non apparent on the spectra of the imaginary permittivity because masked by the importance of the LFD. Fitting the spectra of the complex permittivity with the

superposition of the Davidson-Cole process equation and the LFD power law led to separate the contribution of the space-charge relaxation from the whole loss-spectra [18]. The relevance of the electric modulus formalism has also been verified on a modified DGEBA-based epoxy resin, submitted to moisture, for which the spectra of the permittivity was futureless. In contrast the imaginary part of the modulus vs. frequency showed loss peaks. The frequency of the peaks and the glass transition temperature of the material were correlated according to time of exposure to moisture. This led to conclude that moisture absorption induced a plasticization of the polymer matrix and an enhancement of charge carrier mobility [19].

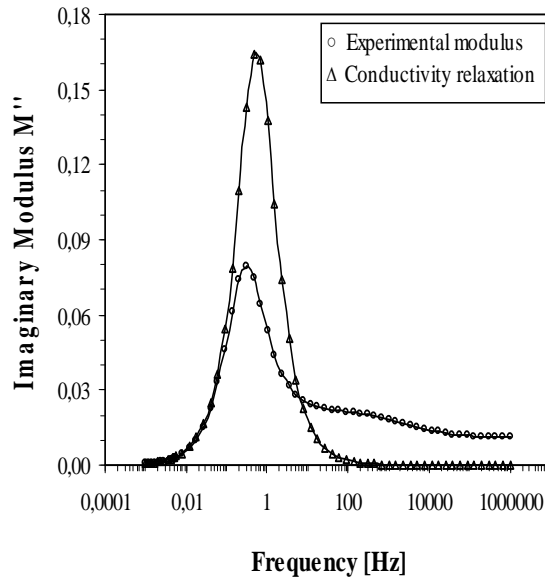
#### 4.2-Interpretation-Discussions

Now we consider figures 3a and 3b where we have reported the frequency dependences of the real and imaginary modulus for the temperature from 23°C up

to 100°C. At low temperature, the spectrum of the real modulus monotonously increases, then, reaches a plateau region. The magnitude of the plateau decreases with increasing temperature (fig. 3a). In the same temperature region, the imaginary modulus decreases with increasing frequency (fig. 3b). At temperature higher than about 60-70°C, in the low-frequency range (below 1Hz), the real and imaginary modulus show respectively an S-like shape and a narrow peak, characteristics of relaxation phenomena. At last, at 100°C for example, a second peak is observed, on the side of higher frequencies, at about 100Hz. This peak is broader and flattened and the corresponding S-like shape, on  $M'$  vs. Frequency (fig. 3a), is stretched and fairly observed. When the temperature increases, the peaks shift towards the high frequencies. This behaviour is characteristic of thermally activated processes [20,21].



**Figure 3:** Spectra of the real (a) and the imaginary (b) modulus according to temperature.



**Figure 4:** Comparison of the experimental imaginary modulus to the calculated conductivity relaxation at T=100°C

One has to notify here that both peaks on the imaginary modulus at low and higher frequencies (fig. 3b) arise at temperatures above 60-70°C. This confirms the glass transition effect described above. Concerning the narrow peak, it is located below 1Hz. Due to that very low frequency value it appears difficult to ascribe this peak to structural motions. In contrast, in that frequency range, one notices that the loss factor  $\epsilon''$  vs. frequency (fig. 1b) exhibits a dc-conduction phenomenon (slope  $\sim -1$ ). According to theoretical previsions, this peak may correspond to a simple conductivity-relaxation peak<sup>[16]</sup>, but it may also suggest a space-charge relaxation consecutive to LFD phenomenon<sup>[18]</sup> or imply the superposition of the two phenomena. In the latter case separation of the two components is necessary before individual analysis. Figure 4 compares the experimental imaginary modulus at 100°C to that simulated with expression (4) which gives the conductivity relaxation, using  $\epsilon_s=3$  (the characteristic value determined on figure 2a) and  $\sigma_0=1.81.10^{-12}\Omega^{-1}m^{-1}$  (typical value at 100°C) in expressions (5) and (6). The two curves are located in the

same frequency domain but the magnitude of the conductivity relaxation is about twice that of the measured modulus. This leads to conclude that the low-frequency narrow peak is not only due to a pure conduction phenomenon but suggests the contribution of charges accumulated in the material. We then have fitted the isothermal complex permittivity  $\epsilon^* = \epsilon' + i\epsilon''$  using the superposition of the Havriliak-Negami (HN) equation of multiple relaxation processes and the power law describing the LFD mechanism<sup>[6,17]</sup> namely:

$$\epsilon^* = \epsilon_\infty + \frac{\sigma_0}{\epsilon_0(i\omega)^n} + \sum \frac{\epsilon_s - \epsilon_\infty}{(1 + (i\omega\tau)^\alpha)^\beta} \quad (7)$$

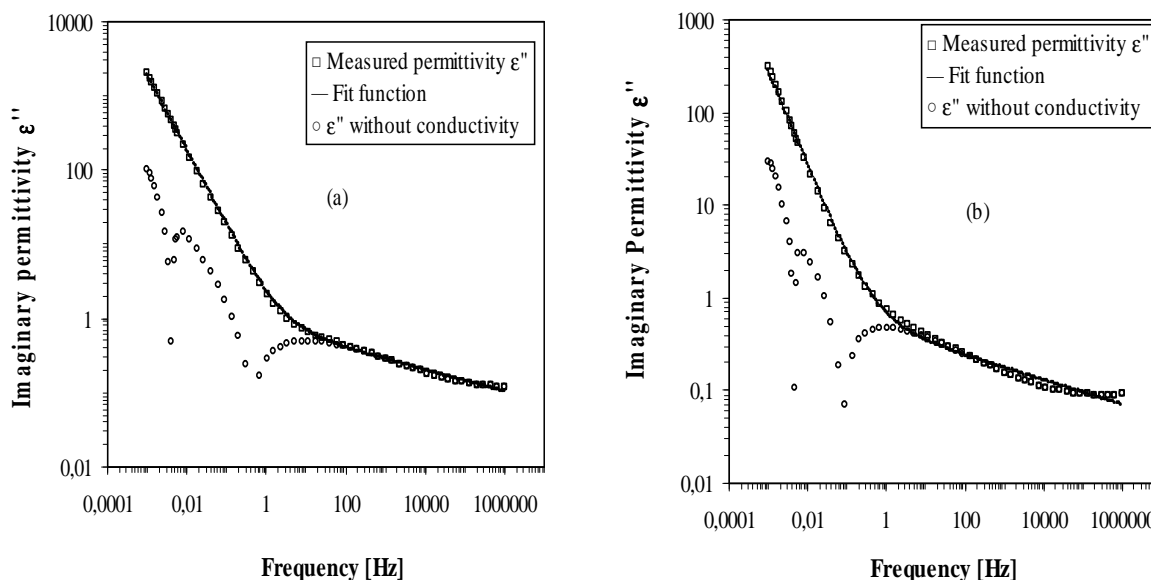
where  $\epsilon_\infty$  and  $\epsilon_s$  are respectively the high and low frequency limits of the dielectric permittivity,  $\tau$  is the characteristic relaxation time,  $\alpha$  and  $\beta$  are respectively symmetric and asymmetric form parameters of the relaxation curve ( $0 \leq \alpha, \beta \leq 1$ ),  $\sigma_0$  is the dc conductivity and  $n$ , a parameter which describes the low frequency charge transfer process ( $0 \leq n \leq 1$ ). Figure 5a shows for example the spectrum of the imaginary permittivity measured at 100°C together with the fitting curve. The

above fit function describes well the experimental data, particularly in the low-frequency part (below 3kHz). Figure 5a also shows the contribution of the HN process (data after subtraction of the LFD) to the whole spectrum. The curve is a succession of two peaks in the frequency domain where conduction dominates. The example of figure 5b for a temperature value of 92°C supports that observation and shows that the phenomenon is reproducible with varying temperature.

With the data of  $\epsilon''$  given by the HN process and using  $\epsilon'=3$  we have calculated the data of the imaginary modulus  $M''$  corresponding to the HN process using expression (2). On figure 6 we plot together, the spectrum of the experimental imaginary modulus  $M''$  at 100°C, with that corresponding only to the HN process. Here also the low-frequency part of the HN process is a succession of two peaks, narrow and juxtaposed, in agreement with the observations of figure 5.

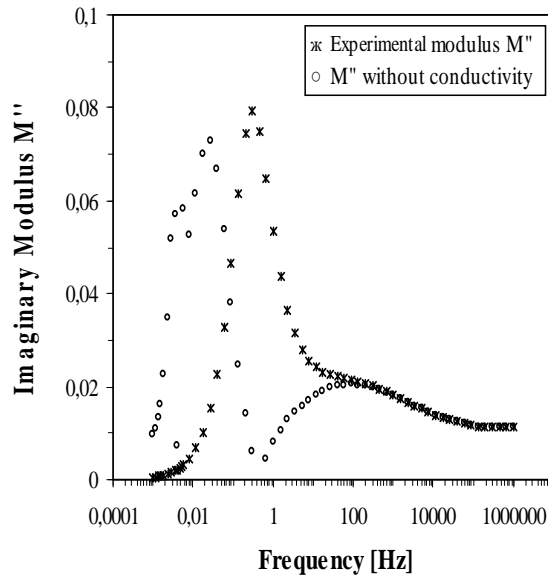
Moreover they are more clearly exhibited, with frequencies 4.7mHz and 27mHz respectively. These peaks show evidence of relaxation phenomena in the low frequency domain and consequently charge accumulation in the material and polarisation of the latter.

As already noticed the phenomenon is reproducible from one temperature to another. Accordingly the rapid increase in the real permittivity versus temperature, observed at low frequency above the glass transition (fig. 2a), suggests a reinforcement of the polarisation process probably due to thermally activated charge diffusion. As a consequence the maxima observed at 75°C and 86°C appear as polarisation peaks. An increase in the dielectric relaxation strength  $\Delta\epsilon=\epsilon_s-\epsilon_\infty$  with increasing temperature has been attributed to a reinforcement of the polarisation process in a mixture of sugar and drug [18].

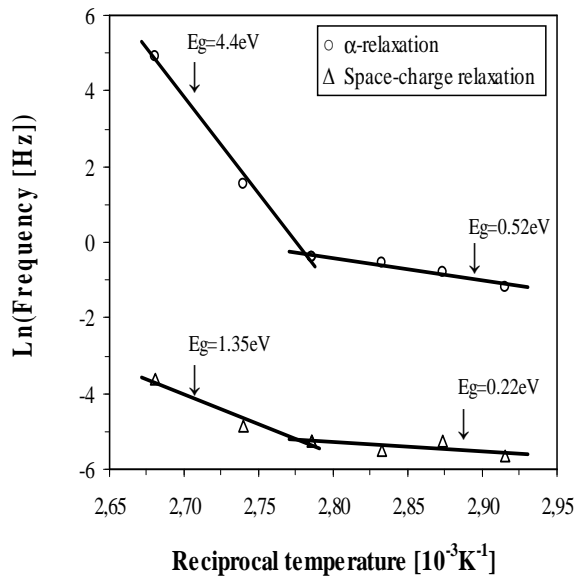


**Figure 5:** Detection of relaxation phenomena at T=100°C (a) and at T=92°C (b) using the permittivity formalism.

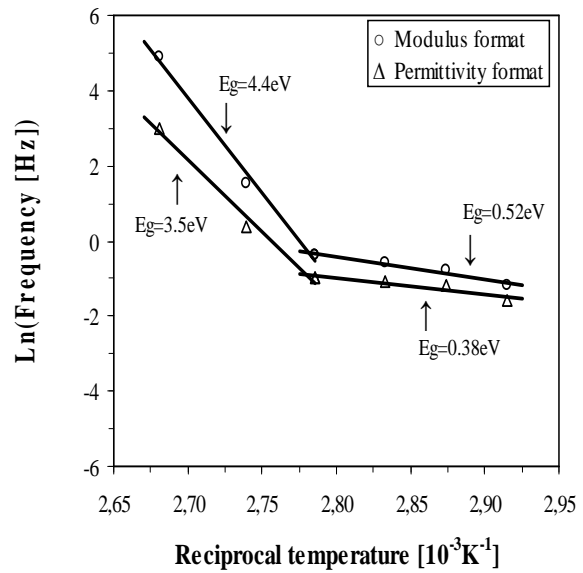




**Figure 6:** Comparison of the experimental modulus and the fit data.



**Figure 7a:** The Arrhenius laws of the low and the mean frequency peaks.



**Figure 7b:** Comparison of the Arrhenius laws in the modulus and the permittivity formats.

During long range diffusion, charge carriers hop over sites with low barrier height but pile up at sites with barrier height high enough until the electric field reverses. The characteristic time of the consecutive relaxation peak necessarily depends on that site and on the charge-carriers travel from the precedent blocking site. The conduction model of Stevels<sup>[14]</sup> implies a variation of the gap between two consecutive blocking sites from one micro-region to another, then a space distribution of the relaxation time. Therefore the number of relaxation peaks (or the number of relaxation times) gives an estimation of the number of particular micro-structures. From the preceding we conclude that, in our experience where two relaxation peaks are detected at low frequency, two distinct types of sites exist in the material. Ionic materials such as zeolites also contain several types of sites<sup>[22]</sup>. Figures 5a and 6 show also another peak, broader and more flattened than the low-frequency ones, at mean frequency, about 60Hz. This peak coincides exactly with that of the experimental spectrum (fig. 6) as was expected for that frequency range where conduction does not exist. According to the temperature region (above  $T_g$ ) and the frequency range where it occurs, although its magnitude is weak, we ascribe this peak to an  $\alpha$ -relaxation process. In other respects this peak is not symmetrical compared to the maximum frequency of 60Hz. The rising part below 60Hz is more abrupt than the decreasing one suggesting the superposition of at least two peaks in that frequency range. Similar frequency dependence of the imaginary permittivity has been observed and the mean frequency range [1-10 kHz] following the conduction domain has been described as a region of various dipolar relaxation processes which may some times overlap<sup>[9]</sup>. These peaks can be separated and analysed using the discrimination method based on the concept of relaxation-time distribution<sup>[22]</sup>.

Here we shall only investigate the global peak.

Now we study the temperature dependence of the characteristic times of the relaxation processes above. For that purpose we have collected the maximum frequency of each of the three relaxation peaks for different values of the temperature, above the glass transition. However we will not consider the peak of the lowest frequencies because, below 80°C, this peak is not entirely observed (the peaks shift on the lower frequencies as temperature diminishes) reducing thus the number of data for the curve.

On figure 7a we plot the maximum frequency of the two remaining relaxation peaks (determined from the modulus formalism) as a function of the reciprocal temperature in semi-logarithmic coordinates. Both curves of figure 7a are constituted of two linear parts on both sides of 86°C. The temperature coefficients of the segments below 86°C, of 0.22eV for the low-frequency peak and 0.52eV for the mean-frequency one, are within the range (0.2-1eV) and are compatible with activation energy generally determined in resins whatever the basic mechanism of the relaxation<sup>[20,21]</sup>, provided the latter is thermally activated and follows the Arrhenius law. As an example, in the case of dipolar relaxation process where the relaxing dipole is localized in a small volume with motion independent of the surrounding medium, such as dipole-groups, the characteristic activation energy is in the range (0.2-0.65eV)<sup>[11]</sup>. Figure 7a shows that above 86°C, the temperature coefficients are respectively 1.35eV for the low-frequency peak and 4.4eV for the mean-frequency one. These values, mainly the mean frequency one, are very high and show, at first sight that, only the rate process approach can not explain the rapid increase in the relaxation frequency observed above 86°C. One has to notify here that, in a general manner, temperature coefficient depends on various factors such

as the material, its state (crystalline, glassy, rubber) and for a same material, on the relaxing dipoles and on the kinetic state of the surrounding medium<sup>[23]</sup>. Indeed, above the glass transition temperature  $T_g$ , in the rubber state, temperature coefficient of dipolar relaxation process may be very high, between 1.3eV and 6.5eV as is the case when the relaxing dipole is connected with motion of the main chain of the polymer<sup>[11]</sup>. In our experiments, such mechanism would be invoked if only the mean frequency peak were concerned. However, one notices that the change in the slopes of the curves of figure 7a is independently observed on space-charge relaxation as well as on dipolar one. Therefore the phenomenon involved is not specific of the relaxing dipoles but necessarily characterizes the background structure of the material. We suggest an occurrence of thermodynamic processes such as phase change in the material and viscosity variation as soon as the temperature reaches 86°C. Such phenomena often occur above the glass transition temperature<sup>[13]</sup>. The 86°C temperature, then, appears as a threshold temperature at which the above changes release and contribute to the activation mechanism of these peaks.

We consider now, as an example, the mean-frequency peak in the permittivity and the modulus formats (fig. 5a and 6). In each format, we collect the maximum frequency of the peak according to temperature varying from  $T_g$  up to 100°C. On figure 7b we compare the corresponding Arrhenius laws. As was expected, the curve obtained with data of the permittivity format is below that of the modulus format (the modulus format shifts the relaxation peak towards the higher frequencies). It also shows two linear parts on both sides of 86°C, with temperature coefficients 0.38eV and 3.5eV close to those of the modulus format (0.52eV and 4.4eV). From the first agreement in the results of the fits of the permittivity and the modulus spectra, namely, evidence of a

succession of relaxation phenomena and from the last one, namely, the similar behaviour of the Arrhenius laws from the modulus and the permittivity formats, we confirm the relevance of the modulus formalism.

#### 4.3-Discussions

The three distinct relaxation phenomena were detected, together at every fixed temperature, above the glass transition (fig. 5a and 6). This suggests that in the ( $\epsilon''$ - $T$ ) coordinates-system, they all coexist on any temperature axis and can be distinguished only with their respective frequency. If we consider the temperature dependence of the imaginary permittivity (fig. 2b), the preceding means that, for example at the 75°C temperature of the maximum losses, the peak on the 5mHz frequency line corresponds to the space charge relaxation while that on the 60Hz line shows the  $\alpha$ -relaxation process. As already notified, each frequency line shows two loss peaks above the glass transition, on both sides of 80°C. This 80°C temperature compares well with the 86°C transition temperature between the two Arrhenius-laws of figures 7a and 7b. We conclude that the 80°C transition temperature divides the rubber region of our material into two temperature domains. The first domain spreads from the glass transition until 80°C. Here, the maximum losses locate at 75°C. The associated relaxation phenomena are thermally activated with energies of 0.22eV for the space-charge relaxation and 0.52eV for the  $\alpha$ -relaxation. The second domain begins at 80°C and spreads until 100°C. In that domain the maximum losses locate at about 86°C. The mechanisms of the relaxations associated to these losses (and the relaxing dipoles involved) seem to be the same as below 80°C but influenced by phase change and viscosity variation of the material which take place at 80°C. This leads to relatively high temperature coefficients of the characteristic Arrhenius-laws, about 1.35eV for the space-charge relaxation and 4.4eV for the  $\alpha$ -type

relaxation. However, the peak at 60Hz is more clearly exhibited than that at 5 MHz (fig. 2b) as was expected for that temperature domain where conduction is reinforced at low frequency, dominates the loss mechanisms and hides the space-charge relaxation.

The precedent loss peaks were also found correlated to two peaks of the relative permittivity on both sides of the 80°C threshold temperature. Figure 2a clearly shows that these peaks do not significantly exist at 60Hz but are preponderant in the frequency domain where polarisation of the material is observed. We ascribe these peaks to a reinforcement of the charge pile-up phenomenon at the glass transition and at the 80°C temperature of phase change and viscosity variation of the material.

## V-CONCLUSION

This paper deals with the study of the dielectric properties of a DGEBA-based resin as a function of the temperature varying from 23°C up to 100°C in the frequency domain [1mHz-1MHz].

First, the complex permittivity formalism was investigated. The usual loss factor could not detect relaxation phenomena. In contrast, as soon as the temperature reaches the glass transition, a dc-conduction phenomenon settles and a rapid and strong increase in the permittivity parameters ( $\epsilon'$  and  $\epsilon''$ ) occurs at low frequency (<1Hz). The three phenomena were correlated. Moreover, in the same frequency range, the permittivity parameters ( $\epsilon'$  and  $\epsilon''$ ) showed simultaneously two distinct peaks at 75°C and 86°C.

We analysed these tendencies using an association of the fit method of Havriliak-Negami and the electrical modulus formalism. We so detected:

-The existence of a succession of two relaxation phenomena at low frequencies. This reveals, on the one hand charge

accumulation in the material during the dc-conduction process and polarisation of the material, and on the other hand the existence of two types of sites occupied by the charges in the lattice of the material. The rapid increases in  $\epsilon'$  and  $\epsilon''$  are consecutive respectively to the polarisation of the material and to energy dissipated due to charges pile-up.

-A third peak, attributed to a  $\alpha$ -relaxation process, in the frequency range [10Hz-100Hz] according to the temperature of the material.

The temperature dependences of the characteristic frequencies of these three peaks were also investigated. This revealed two relaxation domains in the rubber state of the material. The transition from the first to the second domain occurs at about 80°C, probably due to phase change in the material and viscosity variation. These two domains were in accordance with the two relaxation peaks observed on  $\epsilon''$  vs. temperature. Both space-charges relaxation and  $\alpha$ -relaxation exist in the two domains, each with its characteristic frequency depending on the medium.

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