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## DC CONDUCTION OF EPOXY COMPOSITES UNDER COUPLED TEMPERATURE AND WATER UPTAKE EFFECTS

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### INTRODUCTION

As a consequence of recent developments in HVDC, the interest in MVDC for distribution of power systems have been considerably increased. Some successful cases comprehend applications in railways, shipboard systems, distribution grids and offshore [1]. As a branch of these studies, the validation and improvements of insulating materials have been imposing itself as a mandatory step to ensure the reliability and the safety of such systems.

Epoxy resins have been widely applied in electrotechnics for decades, and studies about their potential HV/MVDC applications aren't new. They are used in all kinds of insulators, bushings, spacers, and any structural element that demand dielectric and mechanical performance. As a so well-studied material, extensively literature can be found about conduction mechanisms, the impact of temperature, and water absorption. Some facts merit to be cited:

- Guillermin [2] has found that, under  $T_g$ , epoxy composites with silica presented ohmic conduction at low fields and space charge limited current (SCLC) at high ones. Ohmic and SCLC are distinguished between themselves by relating differently with the electric field, the first being linear  $J(E)$ , and the second by the square  $J(E^2)$ . Many other studies explored different conduction mechanisms to different epoxy composites.

- It has been commonly accepted that the temperature effects on DC conduction of epoxies are likely to follow an Arrhenius mechanism that relates the current with the exponential of the inverse of the temperature  $J(e^{1/T})$ .

- The general impact of water absorbed in AC electrical properties, as well as the diffusion mechanisms [3]–[7] is equally well understood. Epoxies following Fickian, Langmuir, or anomalous diffusions mechanisms have been identified.

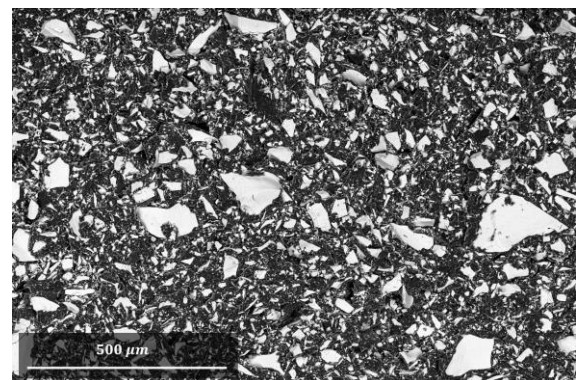
If studies of DC current and temperature effects of epoxies have been reported without the control of water uptake, the role of water absorption and diffusion mechanisms have been exhausted explored for mechanical, thermal, and AC electrical properties, but less for DC conductivity. Some attempts were found with the objective to quantify the humidity effects on DC conductivity

or resistivity. Gonon [8] has found an increase of several orders of magnitude on I-V measurements when epoxy laminated composites have uptaken water. Lutz and Kindersberger [9] went further by identifying an increase of 7 orders of magnitude on the electrical current of a mineral-filled epoxy resin. Zou [6] made many progresses by correlating water uptake, microstructural changes, and electrical properties. The author also compared the impact of micro and nanofillers on these dynamics. This article aims to complement the progressive comprehension mentioned above, associating the water uptake with DC conductivity, and with the conduction mechanisms of an epoxy composite filled with silica. Voltage levels have been limited to those of MV electric fields. Indeed, the contribution of temperature both into the water uptake at equilibrium and DC conduction of wet samples is discussed.

### MATERIALS AND METHODS

#### Framing the Material

Anhydride-based epoxy resins filled with microsilica have been reticulated and shaped into plates of 1 mm of thickness. A view from Scanning Electron Microscope (SEM) through the thickness, as the one in **Figure 1**, underlines a good dispersion and distribution of particles in the matrix, so as the variability of filler sizes (from mesoparticles to 100  $\mu m$ ). From these plates, disks of 70 mm of diameters are obtained.



**Figure 1** Scanning electron microscope of an epoxy sample obtained from cryogenic cut.

### Framing the Initial Conditions

Prior to electric tests, all samples are dried at 70°C under vacuum conditions for as at least 2 weeks until stabilization in weight. The weight is considered stable when the same value is measured for 3 consecutive days.

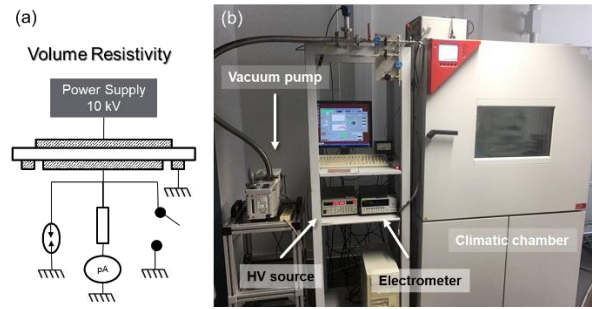
Once dried, samples are installed in climatic chambers under controlled temperature and relative humidity (%RH). The water uptake is computed based on the gravimetric method, and samples are considered stable when their weights haven't been changing for at least 3 consecutive days. Temperatures selected were 20, 40, 60, and 80°C. Relative humidity have been set at 50% and 90%. Dried samples are tested without this conditioning step. Additional conditioning at 25% RH at all temperatures of the study have been performed to enrich data of total amount of water absorption in equilibrium.

After conditioning, the samples' surfaces are sputter-coated using a turbomolecular pumped coater Quorum Q150T ES. The end specimens possess a 200-nm layer of gold on both sides, disk-shaped with 50mm of diameter on one side and 54 mm on another. It's considered that the sample can lose some water during the process, so after installation into the test cell, they are exposed again T/%RH of conditioning for 4 hours at the same time they're discharged.

### I-V Measurements

Current measurements have been performed in a plane-plane configuration (**Figure 2-a**). The electrode system is installed in the vessel able to be closed, and that is associated to a vacuum or gas pump, temperature and %RH sensors. Samples are installed between main electrodes and guard electrode. The vessel is placed in a climatic chamber and connected from one side to a high-voltage source (PS365 SRS High Voltage Power Supply) and on the other side to an electrometer (Keithley 6517B Electrometer/High Resistance Meter). The final set-up is seen in **Figure 2-b**. All measurements have been done at isothermal conditions (20°C, 40°C, 60°C and 80°C). The RH inside the climatic chamber is regulated to reproduce the same value of conditioning. Electric fields have varied between 1 to 10 kV/mm.

The test consists of 1 hour of polarization and 1 hour of depolarization, starting from lower voltages and lower temperatures. At the end of an isothermal test, temperature is dropped and the sample is discharged for at least 4 hours. Tests with dried samples are performed with the vessel closed, RH regulated between 1-3%, and 2 bars of dried gas (nitrogen) to avoid breakdown into the air at higher values of voltage.



**Figure 2** Configuration of plane-plane electrodes (a) and I-V measurement set up (b).

For wet samples, the cell is opened at low values of voltages so as the environment inside the vessel is equals to the one set up for the climatic chamber. For tests when  $V > 3000V$ , the cell is closed and dried air is pumped, followed by a reconditioning step where it's expected that the sample reabsorbs some water content that have been eventually lost during the test.

The current density ( $i_c$ ) is obtained by the sum of the currents of polarization ( $i_p$ ) and depolarization ( $i_{dp}$ ) as in equation 1, and later divided by the surface of the electrodes to obtain the current density. All values of  $J$  are represented relatively with  $J_1$  that it the lowest value among all datapoints. No relevant offset has been detected.

$$i_c = i_p + i_{dp} - 2 i_{offset} \quad [1]$$

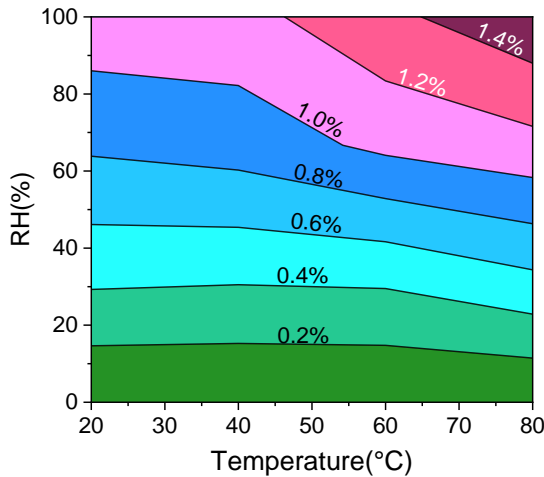
## RESULTS

### Water Uptake in Equilibrium

For this study, we are not interested in explore the diffusion mechanism of water absorption but the relationship between the total amount of water absorbed and the conductivity. To do so, a qualitative chart of water uptake has been designed based on gravimetric measurements, and presented in **Figure 3**. Only the water absorption reported to the matrix is computed, and a total amount of 1.4% of water has been identified.

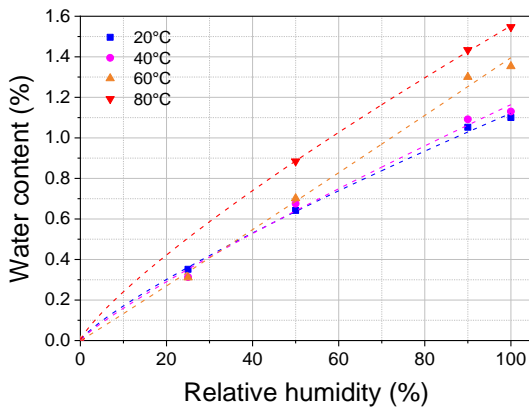
The water concentration within a polymer at equilibrium may be represented by equation 2, which relates this concentration to the relative humidity RH, with two parameters: a constant  $\kappa$  that depends on the nature of the polymer and the temperature and an exponent  $\alpha$  usually close to unity (as for Henry's law in liquids).

$$w_h = \kappa(RH)^\alpha \quad [2]$$



**Figure 3 Chart of water content (%) at equilibrium reported to the matrix as a function of temperature (T) and relative humidity (% RH).**

According to [10], in the particular case of epoxies,  $\kappa$  is usually constant or can slightly decrease with temperature. Aiming to obtain these coefficients, the data applied to build **Figure 3** is replot as a function of relative humidity in **Figure 4**. The coefficients are given in **Table 1**. The value of  $\kappa$  seems to oscillate around an average of  $2.45 \cdot 10^{-4}$ , but we have the impression that it decreases between 20°C and 60°C and jump at 80°C. Because of the particularity of the power model, as water contents are relatively close among different temperatures, when  $\kappa$  decreases,  $\alpha$  increases, so the inverse phenomena is observed for  $\alpha$ . If an  $\alpha = 1$  had been chosen, a descending value of  $\kappa$  should be found, as seen in **Table 2**, which is mostly in accordance with theory, even if the fitting is less precise than with the power law.



**Figure 4 Water content reported to the matrix as a function of the relative humidity.**

**TABLE 1 COEFFICIENTS OF HYGROSCOPIC ABSORPTION OBTAINED FROM FIGURE 9.**

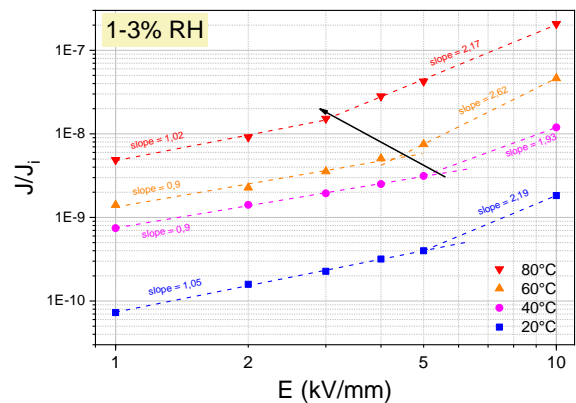
Temperature (°C)	$\kappa$	$\alpha$
20°C	2.60 E-4	0.82
40°C	2.19E-4	0.86
60°C	1.26E-4	1.02
80°C	3.74E-4	0.81

**TABLE 2 VALUES OF  $\kappa$  IF  $\alpha = 1$**

20°C	40°C	60°C	80°C
1.16E-4	1.19E-4	1.39E-4	1.59E-4

**I-V Measurements**

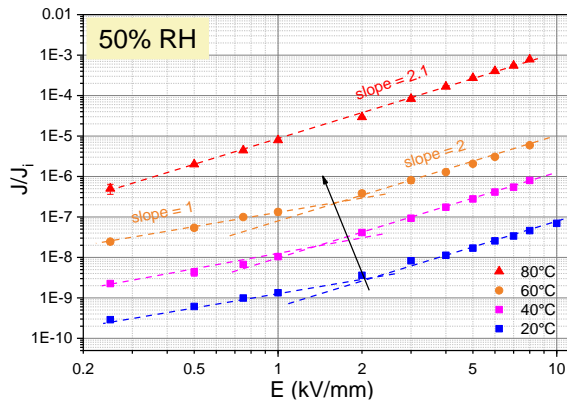
The current density profiles as a function of electric field for dried samples is illustrated in **Figure 5**. Two main regions for each isothermal can be distinguished: a domain in lower voltages, in which the slope is equals to 1, and another at higher voltages, with voltages close to 2. A slope equals to 1 indicates a linear relationship between J and E; i.e. an ohmic behavior. A slope equals to 2 is in accordance with a space charge limited current model (SCLC). A threshold has been identified at fields in the range of 3-5 kV/mm for the temperatures of the study. The current density seems to increase exponentially with temperature, and the threshold increase linearly with it between 40°C and 80°C. These mechanisms are in accordance with previous studies, but the values of threshold have changed.



**Figure 5 Current density as a function of electric field for samples conditioned at 70°C under vacuum and tested at 1-3% RH.**

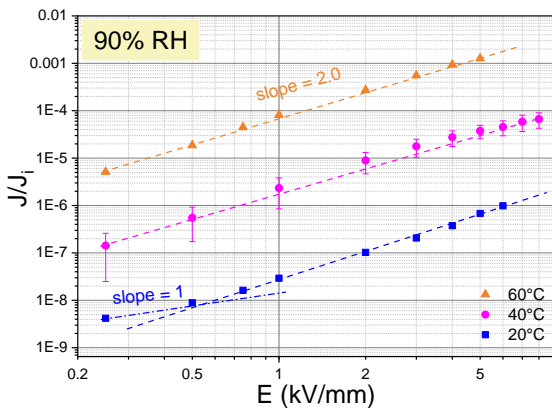
A similar profile has been found for samples conditioned at 50% RH (**Figure 6**), but three main differences merit to be highlighted:

- (1) Values of J presented an increase up to 1 order of magnitude;
- (2) The threshold also decreased, appearing between 1-2 kV/mm for measures at 20-60°C. Because of it, additional measures at lower fields were performed.
- (3) The conduction profile at 80°C presented a good fit with a slope = 2 for all data point, even for lower fields and additional measures, so no threshold has been identified.



**Figure 6** Current density as a function of electric field for samples conditioned at 50% RH.

When conditioned at 90% RH, a SCLC has been identified for all for voltage levels and temperatures (20-60°C) related to middle voltage fields, as pictured in **Figure 8**. Only the values at 20°C and 250-500 V suggests an ohmic mechanism. If compared to dried samples, J increased even more, and a difference of 4 orders of magnitude can be found (as, for example, if we compare the values of J at 5kV/mm and 60°C between 1-3% RH and 90% RH conditioning).



**Figure 7** Current density as a function of electric field for samples conditioned at 90% RH.

## DISCUSSION

### The Hygroscopic Law

An  $\alpha < 1$  indicates that the material is absorbing less water than it should be expected. Three hypotheses can be cited: (1) Exposition time were too short and samples haven't been humidified enough, (2) water absorption is related to exudation of additives, such as reminiscent plasticizers and stabilizers, misleading gravimetric measures, and (3) an eventual chemical degradation is related to a decrease of crosslinking degree. As Gonon observed [8], water absorption increases with the increase of the degree of curing in the first stages of ageing.

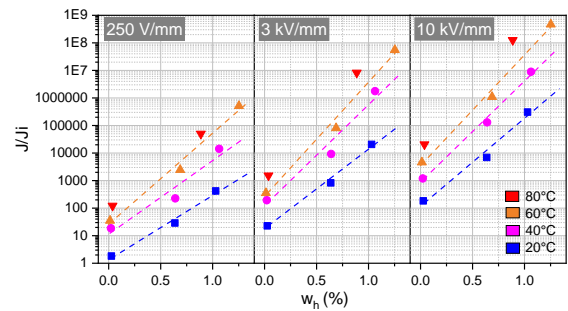
### Model of J vs water uptake and temperature

Hereafter is an attempt to model the impact of water uptake in conduction. **Figure 8** correlates

$\log(J)$  with  $w_h$  for different field levels (250 V/mm, 3 kV/mm, and 10 kV/mm). The linear fit in this semi-log scale leads to an exponential relation between  $\log(J)$  and  $w_h$  as shown in equation 3:

$$J = J_d e^{\beta w_h} \quad [3]$$

where  $J_d$  is the initial current measured for dry samples. Values of  $\beta$  are given in **Table 3**. This coefficient increases with field and temperature but remains within a factor of 2 in the investigated ranges of F and T. Remark that since only 2 data points were acquired at 80°C, no fitting was plotted.



**Figure 8** Current density as a function of water content for E = 250 V/mm, 3 kV/mm, and 10 kV/mm.

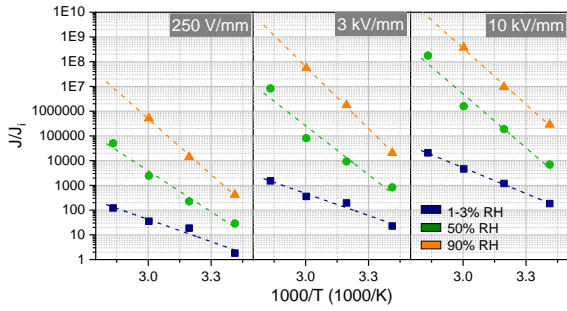
**TABLE 3** VALUES OF  $\beta$  OBTAINED FROM **FIGURE 8**.

E (kV/mm)	20°C	40°C	60°C
0.25	232	269	333
3	291	372	416
10	316	369	402

With regard to the thermal behavior, many studies have already pointed out to an Arrhenius-like validation. The Arrhenius law is described in equation 4.

$$J = J_c \exp\left(-\frac{E_a}{k} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right) \quad [4]$$

Where  $J_c$  representing the current at an initial temperature  $T_0$ ,  $T$  is the temperature of interest,  $k$  is the Boltzmann constant, and  $E_a$  an activation energy. **Figure 9** shows that data fit an Arrhenius laws no matter the conditioning parameters. The deduced activation energies are given in **Table 4**. Remark that these activation energies depends mainly on the water content and much less on the electric field.



**Figure 9** Current density as a function of the inverse of the temperature in the range of temperature 20-80°C.

**TABLE 4** ACTIVATION ENERGIES  $E_a$  CALCULATED FROM FIGURE 9.

	$E_a$ (eV)		
	0.25 kV/mm	3 kV/mm	10 kV/mm
1-3% RH	0.26	0.26	0.30
50% RH	0.47	0.57	0.62
90% RH	0.65	0.72	0.65

**Models of J vs electric field**

For a first approach, the impact of water will be evaluated based on the changes of charge carriers  $n$  and their mobility  $\mu$ . As mentioned before, two domains have been identified on I-V curves: ohmic and SCLC. The ohmic conduction with the assumption of a single species of charge carrier is given in Equation 5:

$$J = nq\mu E \tag{5}$$

It is directly related to the volume concentration of charge carriers  $n$ , their electric charge  $q$ , and their mobility  $\mu$ .

The SCLC (Equation 6), on the other hand, is not proportional to  $n$ . It is related to the square of the electric field  $E^2$ , with vacuum permittivity  $\epsilon_0$ , relative permittivity  $\epsilon_r$ , mobility  $\mu$ , and the insulation thickness  $s$ .

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{E^2}{s} \tag{6}$$

From equations 5 and 6, the voltage threshold ( $V_{th}$ ) between SCLC and ohmic regimes can be deduced (Equation 7):

$$V_{th} = \frac{8nes^2}{9\epsilon_0\epsilon_r} \tag{7}$$

The experimental values of  $V_{th}$  are listed in **Table 5** depending on T and RH. Taking a mean value of the relative dielectric constant  $\epsilon_r=4$ , values of the volumic concentration  $n$  of charge carriers of the order of  $10^{18} \text{ m}^{-3}$  can be deduced at  $T= 20^\circ\text{C}$  and  $\text{RH}= 50\%$ .

**TABLE 5** APPROXIMATIVE THRESHOLD VOLTAGES ( $V_{th}$ ) BETWEEN OHMIC AND SCLC

	$V_{th}$ (V)			
	20°C	40°C	60°C	80°C
1-3%RH	5180	5210	4350	3040
50% RH	2040	1750	1600	< 250
90%RH	525	< 250	< 250	-

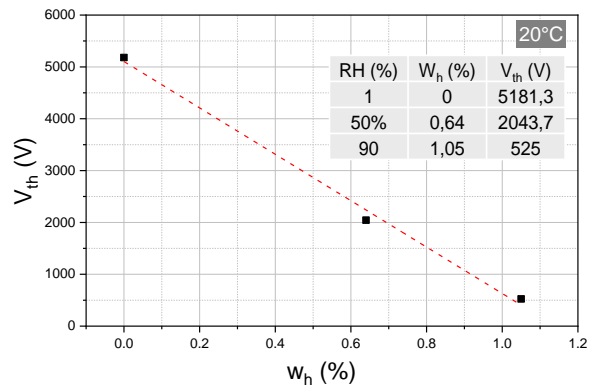
**Charge carriers**

Since the impact of water on J is exponential, considering equation 6,  $n$  and/or  $\mu$  should increase exponentially. An increase of  $n$  would suggest that water introduces new extrinsic charge carriers that will complement the conduction, by water dissociation, or chemical reactions, including hydrolysis. One other hypothesis is that water will detrapp intrinsic charges for the case of a trap-limited mobility.

However, considering equation 8, an increase of  $n$  would also lead to an increase of  $V_{th}$ . As shown in **Table 5**,  $V_{th}$  decreases with T and vice versa. In **Figure 10**,  $V_{th}$  decreases linearly with the water uptake at 20°C (the only temperature in which a threshold has been identified at 90% RH). Paradoxically, if we consider that  $\epsilon_r$  doesn't change with the same magnitude, this means a decrease in charge carriers with increasing water content.

Considering equation 8,  $V_{th}$  is inversely proportional to the dielectric constant, which increases with water and temperature. However, these variations of  $\epsilon_r$  with T and  $w_h$  are much smaller than the observed variations of  $V_{th}$ . Reduction of  $V_{th}$  could also come from the trapping of charge carriers by water.

In summary, according to this model, the variations of  $n$  across the T and RH ranges should not exceed one decade, as  $V_{th}$ . This is far too little to explain the number of decades of variations in J.



**Figure 10** Voltage threshold  $V_{th}$  between ohmic and SCLC at 20°C as a function of water uptake.

Finally, a last hypothesis is the increase of the mobility  $\mu$ .

Thanks to equation 8 and in the frame of the simple model considered in this discussion, mobilities can be inferred. At highest T and RH, calculated mobility does not exceed  $10^{-9}$  m<sup>2</sup>/V. This order of magnitude is well below the minimum electron mobility in solids [11]. Therefore, charge carriers are ionic species. We assume that ions H<sup>+</sup> and OH<sup>-</sup> from water dissociation, more or less surrounded by clusters of water molecules, play a major role in the conduction phenomena observed above.

This increased mobility may be explained by several reasons. The concentration of traps is decreased thanks to the water molecules that filled them. The swelling of the polymer system due to water ingress enlarge the free volumes allowing a decreasing of the ions interactions with the material.

## CONCLUSIONS

In this study, I-V measurements of an epoxy composite filled with silica as function of temperature and water uptake have been performed. It has been found that:

- Samples were able to uptake up to 1.5% of water.
- The current density increased exponentially with the water uptake.
- The water uptake being related to the RH, an equation of J as function of RH (conduction due to hygroscopic effects) has been fit from data.
- The Arrhenius-like contribution has been checked and added to the model.
- Conduction mechanisms lead to the conclusion that water will mostly increase the mobility  $\mu$  rather than the number n of charge carriers.
- Estimated values of mobility lead to discard electronic mobility in favor of ionic mobility. Space charge observations would be helpful to better evaluate the polarity of the charge carriers and the field distribution.

## ACKNOWLEDGEMENTS

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