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Charge transport in an epoxy composite under coupled temperature and water uptake effects

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Abstract— During use, electrical equipment are subjected to changes in temperature and humidity. The impacts of temperature and water absorption on the conduction properties of epoxy composites have been well documented in the literature, but they are usually assessed separately. This work aims to gather current-voltage characteristics of epoxy composites filled with silica under various temperatures and water uptake levels to build a single physicochemical model. Current measurements were conducted at various temperatures (20, 40, 60, and 80°C), electric fields (1, 2, 3, 4, 5, and 10 kV/mm), and water uptakes (dried, 50% RH and 90% RH). Samples of silica-filled epoxy resin (63% in weight), 1 mm thickness, were used. Dried samples were conditioned at 70°C under vacuum conditions, and moist samples were obtained via conditioning at 50% and 90% RH at the temperatures of interest. The total amount of water uptake varies with temperature. The dried samples showed a clear threshold between a linear and a non-linear regime. The moist samples showed a non-linearity with a slope 2 in log-log scale, for all voltage and temperature levels. Furthermore, for the same voltage level, the conductivity is able to increase up to five orders of magnitude according to the RH of conditioning. In the non-linear regime, the slope in log-log of the current - voltage characteristics falls from 2.6 or above in dried conditions to 2 under moist conditions. This evolution corresponds to a decrease from several to a single level of the traps. This highlights the influence of water in the evolution of the energetic level of the traps for the electronic mobility. Furthermore, assuming a second regime of SCLC, it is shown that increasing the water content does not increase the number of charge carriers but their mobility. According to this approach, the number of charge carriers paradoxically decreases with the water content. This decrease explains the overlay of the current of the second regime on that of the ohmic regime.

Keywords—epoxy, water, traps, electronic mobility, conductivity, insulation, MVDC.

I. INTRODUCTION

As a consequence of recent developments in HVDC, the interest in MVDC for distribution of power systems has considerably increased. Some successful cases include applications in railways, shipboard systems, distribution grids and offshores [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 electrical insulation 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 mentioned:

- As in many other polymeric materials, conduction in epoxy, being filled or not, is ohmic at low fields. Above a threshold field, steady-state currents follow a power law with the applied field. A space charge limited current (SCLC) has been proposed under T_g [2]. Many

other studies explored different conduction mechanisms to different epoxy composites.

- It has been observed that the temperature effects on DC conduction of epoxies 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.

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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 moist samples is discussed.

II. MATERIALS AND METHODS

A. Framing the Material

Anhydride-based epoxy resins filled with microsilica ($T_g = 115^\circ\text{C}$) 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 Fig. 1, underlines a good dispersion and distribution of particles in the matrix, so as the variability of filler sizes (from mesoparticles to $100\ \mu\text{m}$). From these plates, disks of 70 mm of diameters are obtained.

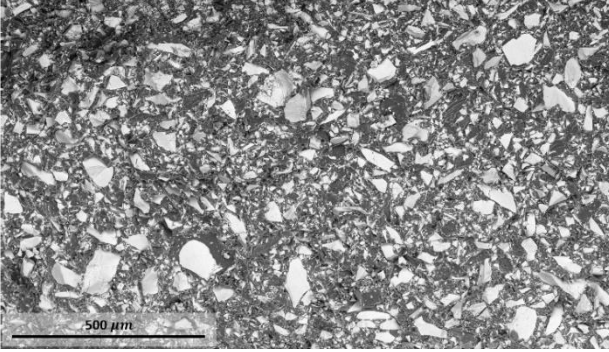


Fig. 1 Scanning electron microscope of an epoxy sample obtained from cryogenic cut.

B. 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 have not 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 were 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. Electrodes consist of 200 nm thick gold layers.. It is considered that the sample can lose some water during the process, so after installation into the test

cell, they are conditioned again in temperature and humidity for 4 hours at the same time as they are discharged.

C. I-V Measurements

Current measurements have been performed in a plane-plane configuration. The electrode system is installed in the sealable vessel, where vacuum or pressure can be applied, and equipped with temperature and %RH sensors. Samples are installed between main electrodes with a 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). All measurements have been done at isothermal conditions (20°C , 40°C , 60°C and 80°C). The RH inside the climatic chamber is controlled to reproduce the same value of conditioning. Applied electric fields were from 0.25 to 10 kV/mm.

The test consists of 1 hour of polarization and 1 hour of depolarization, starting from lower voltages and lower temperatures. The signal measured during the polarization step is the absorption current (i_{abs}), and the one at the depolarization step, the desorption current (i_{des}). 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 and under 2 bars of dried nitrogen to avoid breakdown into the air at high voltage values.

For moist samples, the cell is opened at low voltages so that the environment inside the vessel is identical to that in the climatic chamber. During measurements above 3 kV, the cell is closed and filled with pressurized nitrogen. Between measurements, the cell is opened during 4 h to allow samples to reach again equilibrium with the surrounding environment.

The conduction current (i_c) is obtained by the sum of i_{abs} and i_{des} as in equation 1. The current is later divided by the equivalent surface according to the standards to obtain the current density.

$$i_c = i_{\text{abs}} + i_{\text{des}} \quad (1)$$

D. DMA analysis

The dynamic mechanical analysis (DMA) measures were carried out using a 3-point bending device in a TA Instruments' DMA Q800 V21.3. The rectangular samples ($50 \times 10 \times 1\ \text{mm}$) were exposed to air and submitted to a fixed frequency of 1 Hz. The temperature was raised at 3K/min from -40 to 150°C .

III. RESULTS

A. Water Uptake in Equilibrium

In this study, we are not interested in the diffusion mechanism of water absorption but in 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 Fig. 2. Only the water absorption reported to the matrix is computed, and a total amount of 1.4% of water has been identified.

The mass ratio of water within a polymer at equilibrium may be represented by equation 2. It is related to the relative humidity RH, with two parameters: a constant κ that represents the mass ratio of water at saturation and depends on the nature of the polymer and the temperature, and an exponent α usually close to unity (as for Henry's law in liquids).

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

Aiming to obtain these coefficients, the data applied to build Fig. 2 is replot as a function of relative humidity in Fig. 3. The lines can be fitted with power laws, but for physical reasons, α is taken equal to unity, even if the fit is not as good. Ascending values of κ are found, as seen in Table I. Remark that constant or slightly decreasing values of κ with temperature are mainly reported [10].

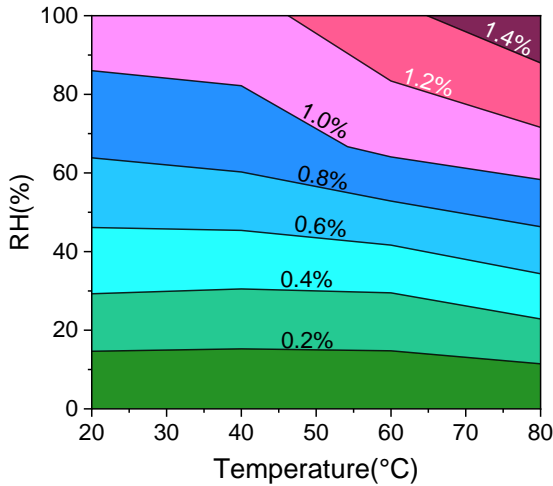


Fig. 2 Chart of water content (%) at equilibrium reported to the matrix as a function of temperature (T) and relative humidity (% RH).

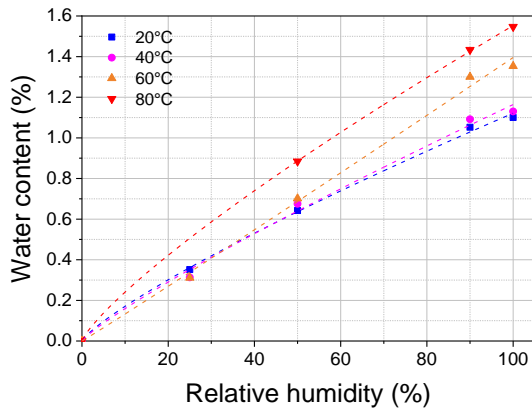


Fig. 3 Water content reported to the matrix as a function of the relative humidity.

Table I
Values of κ if $\alpha = 1$

20°C	40°C	60°C	80°C
$1.16 \cdot 10^{-2}$	$1.19 \cdot 10^{-2}$	$1.39 \cdot 10^{-2}$	$1.59 \cdot 10^{-2}$

Fig. 3 and Table I show that the absorbed water content depends not only on the RH but also on the temperature. For a better understanding of this unexpected behaviour, DMA tests were performed on samples after 3 different conditionings. Fig. 4 shows the evolution with temperature of the mechanical losses $\tan \delta$.

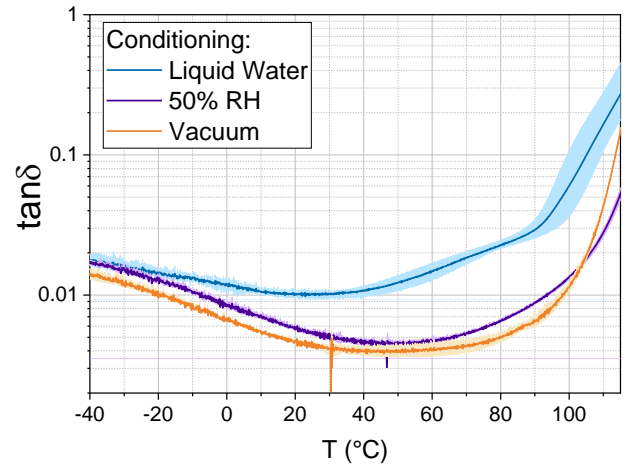


Fig. 4 Mechanical losses $\tan \delta$ with temperature depending on the samples conditioning: deionized water at 40°C, 50% RH at 40°C, drying under vacuum at 70°C.

B. I-V Measurements

For dried samples, the current density profiles as a function of electric field is displayed in Fig. 5. Two main regions for each isotherm can be distinguished: a domain at low voltages, in which the slope is equal to 1, and another one at high voltages, with slopes of 2.17 at 80°C and 2.62 at 60°C. Missing values between 5 and 10 kV/mm does not allow the calculation of the slope at 20 and 40°C.

A threshold has been identified at fields in the range of 3-5 kV/mm for the temperatures of the study.

For samples conditioned at 50% RH, a similar profile has been found (Fig. 6), but three main differences can be highlighted:

(1) Compared to dried samples, the current densities presented an increase of several orders of magnitude depending on the field and temperature;

(2) The threshold decreased, appearing between 1-2 kV/mm for measures at 20-60°C. Therefore, 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 at low fields, so that no threshold was identified.

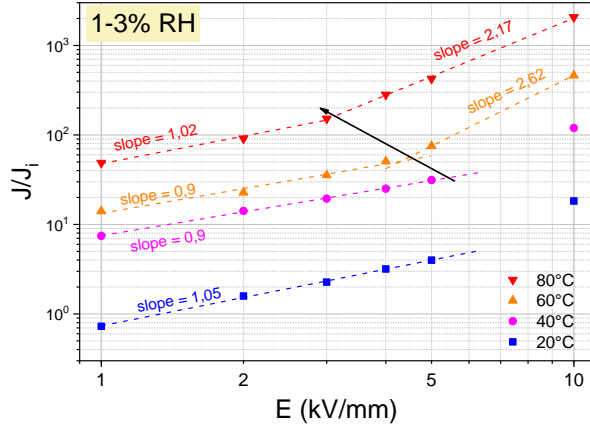


Fig. 5 Relative current densities as a function of electric field for samples conditioned at 70°C under vacuum and tested at 1-3% RH.

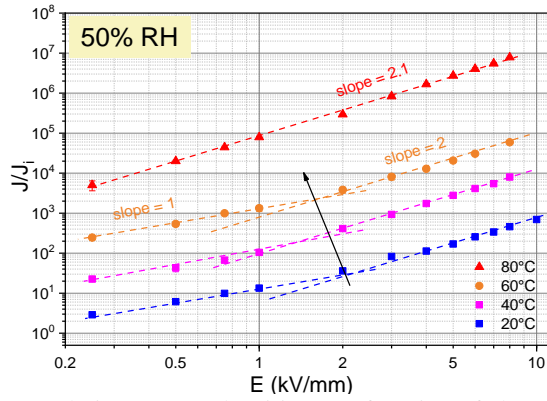


Fig. 6 Relative current densities as a function of electric field for samples conditioned at 50% RH.

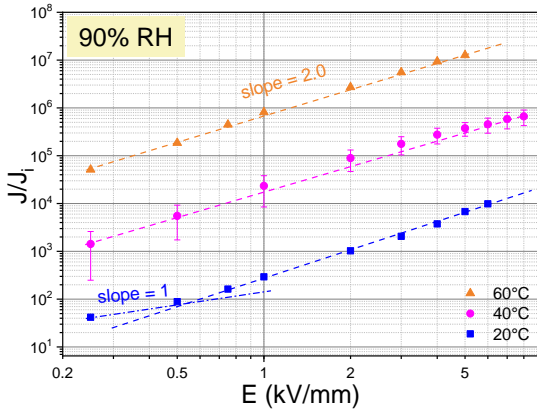


Fig. 7 Relative current densities as a function of electric field for samples conditioned at 90% RH.

When conditioned at 90% RH, a regime with a slope 2 is observed throughout the voltages and temperatures (20-60°C) investigated, as pictured in Fig. 7. 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 5 orders of magnitude can be found (as, for example, if we compare the values of J at 5 kV/mm and 60°C between 1-3% RH and 90% RH conditioning).

IV. DISCUSSION

A. The Hygroscopic Law

Fig. 4 showed that in wet condition, the losses at 20 and 40 °C were similar whereas they increased at 60 and again at 80°C. In Fig. 3 at RH=100%, the water contents are similar at 20 and 40°C and increased at 60 and again at 80°C. These observations seems correlated and the mechanical analysis provides explanations. As a matter of fact, increasing losses attested by $\tan\delta$ are allowed by the loss of secondary bonds inside the material. It is known that water breaks existing Van Der Waals bonds between polymer chains and substitutes molecules on each part of the former bond. This contributes to a larger plasticization, which itself leads to larger mechanical losses due to the decrease of the viscosity component. Correlation also appears for a 50% conditioning. In Fig. 4, losses due to plasticization are larger at 80°C than at the 3 lower temperatures and in Fig. 3, the water contents are similar at 20, 40 and 60°C and increased only at 80°C.

B. Model of J vs water uptake and temperature

With regard to the thermal behaviour, many studies have already pointed out to an Arrhenius-like validation. The Arrhenius law is described in equation 3.

$$J = J_c \exp\left(\left(-\frac{E_a}{k}\right)\left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \quad (3)$$

Where J_c represents 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. Fig. 8 shows that data fit an Arrhenius law no matter the conditioning parameters. The deduced activation energies are given in Table II. Remark that these activation energies depend mainly on the water content and much less on the electric field. This activation energy can be interpreted in the following way: for the same variation of temperature, e.g. from 20 to 40°C or 40 to 60°C, the increase in current is all the larger as the water content is high.

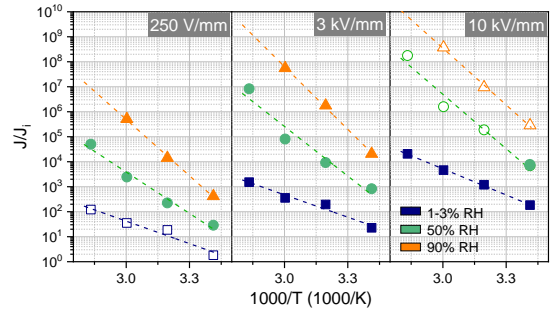


Fig. 8 Relative current densities as a function of the inverse of the temperature in the range of temperature 20-80°C. Open icons represent datapoints obtained from an extrapolation of measured datapoints.

Table II
Activation energies E_a calculated from Fig. 8

	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

C. Models of J vs electric field

As mentioned before, two domains have been identified on I-V curves. The first one is undoubtedly ohmic and, as many authors, we will assume a space charge limited current (SCLC) for the second regime.

The ohmic conduction with the assumption of a single species of charge carrier is given in equation 4:

$$J = nq\theta\mu E \quad (4)$$

It is directly related to the volume concentration of charge carriers n , their electric charge q , and their mobility μ , θ being the ratio of electrons available for conduction.

The SCLC (Equation 5), on the other hand, is not proportional to n . It is related to the square of the electric field E^2 , with the vacuum permittivity ϵ_0 , relative permittivity ϵ_r , mobility μ , and the insulation thickness s .

$$J = (9/8) \epsilon_0 \epsilon_r \theta \mu E^2/s \quad (5)$$

From equations 4 and 5, the voltage threshold V_{th} between SCLC and ohmic regimes can be deduced (Equation 6):

$$V_{th} = (8nes^2)/(9 \epsilon_0 \epsilon_r) \quad (6)$$

The experimental values of V_{th} are listed in Table III 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} m^{-3} can be deduced at $T= 20^\circ\text{C}$ and $\text{RH}= 50\%$.

Table III
Approximate 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	-

D. Evolution of the trap levels with water content

An exponent of 2 of the electric field in equation 5 corresponds to a single level of traps whereas values larger than 2 reveal a distribution of traps levels [11]. As

the water content increases, Fig. 5 to 7 show that the exponent, i.e. the slope of the second regime, decreases from 2.62 or above to a constant value of 2. This evolution highlights the influence of water in the evolution of the energetic level of the traps. At low water content, various levels can be found whereas a higher water content leads to a single level. Remark that the missing slopes at 40°C and 20°C are expected to overpass the value at 60°C , at least to be clearly larger than 2. Complement experiments are scheduled to bring confirmation.

E. Charge carriers

The increase of conduction with increasing water content could at first be interpreted in terms of conduction due to the migration of ions issued from water dissociation. However, such an ionic conduction constitutes a mass transfer towards the electrode, which naturally cannot be permanent [12, 13]. However, here, we could imagine that electrochemical reactions would occur at the electrodes generating oxygen and hydrogen gases. The water content inside the material could be regenerated by the humid environment. Contrary to usual ionic conduction phenomena, a stabilized situation could be imagined.

Water ions are probably present as space charges but their contribution to the conduction is probably negligible, which can be rather attributed to electron mobility.

Data show that J increases exponentially with the water content w_h (not displayed above). In these conditions, considering equation 4, $n\theta\mu$ should increase exponentially and considering equation 5, $\epsilon_r \theta\mu$ should also increase exponentially. The dielectric constant is known to increase with water content, and with temperature in the case of epoxy. However, variations of ϵ_r with T and w_h are much smaller than the variations of the current here and cannot explain them. Then, the only possible explanation is the increase of the apparent mobility $\theta\mu$. Using equation 5 at the highest T and RH investigated, apparent mobility $\theta\mu$ would reach $10^{-9} \text{ m}^2/\text{V.s}$. This order of magnitude is well below the minimum electron mobility in solids [13]. The model is consistent with low values of θ of the order of $10^{-5} - 10^{-6}$.

Let us consider the concentration of charge carriers n . As shown in Table III, V_{th} decreases with RH at constant T and vice versa. In Fig. 9, V_{th} decreases linearly with the water uptake at 20°C (the only temperature at which a threshold has been identified at 90% RH). There is a factor of 10 between dried and wet samples at 20°C . Considering equation 6, this evolution of V_{th} can be attributed either to n or to ϵ_r . Since the dielectric constant cannot increase that much, the only possible explanation is the decrease of n . This leads to admit paradoxically a decrease in charge carriers with increasing water content.

The water-induced mobility may be explained by several reasons. The concentration of deep traps is

decreased thanks to the water molecules that filled them in a more or less ionized and/or clusterized form. Shallow traps, from which electrons can easily escape thanks to low energy phonons, are either pre-existing traps from the epoxy matrix or, more probably, traps provided by water molecules, loosely bonded to the polymer matrix or the silica fillers. From a structural point of view, the swelling and plasticization of the polymer system induced by the water ingress should facilitate the jumps from one trap to another.

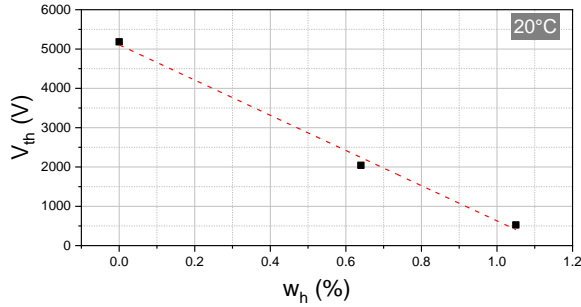


Fig. 9 Voltage threshold V_{th} between ohmic and SCLC at 20°C as a function of water uptake.

F. Evolution of the currents with T and RH

Comparison of equations 4 and 5 allows to justify the shift of the two lines of each regime. With increasing water content and temperature, both lines are translated upward but the line of the second regime is shifted towards left inducing a decreasing of V_{th} . As a matter of fact, both currents are proportional to the apparent mobility $\theta\mu$ but the ohmic current is also proportional to n which decreases. The increase of the ohmic current is then not as large as the one of the current of the second regime. That is why the current of the second regime overlay on that of the ohmic regime

V. CONCLUSION

In this study, I-V measurements of a silica-filled epoxy composite have been performed as function of temperature and water uptake. The main conclusions are:

- Samples were able to uptake up to 1.5% of water, reported to the matrix.
- The current density increased exponentially with the water uptake.
- A model of the current density was proposed. It is based on the Arrhenius law. Based on the data, the water content is taken into account in the activation energy.
- The water absorbed in the polymer reduces the distribution of the energy levels of the charge carrier traps to a single level.
- Assuming a second regime of SCLC, it was shown that increasing the water content does not increase the number of charge carriers but their apparent mobility. The number of charge carriers paradoxically decreases with the water content.

- This decrease explains the overlay of the current of the second regime on that of the ohmic regime.

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