Conduction mechanism and dielectric properties of epoxy resins submitted to dc stress

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ABSTRACT

The electrical behavior of an alumina-filled epoxy resin highly used in ac applications is investigated to determine its suitability for high voltage dc applications. The conduction mechanisms of the as-received and cured material are analyzed under dc fields comprised between 1 kV/mm and 40 kV/mm, at different temperatures. The evolution of dielectric properties of the material submitted to dc ageing at high temperature (125℃) under fields of 4 kV/mm to 12 kV/mm is monitored and analyzed.

KEYWORDS

Dielectric, epoxy, dc stress, high voltage, conduction, space charge

INTRODUCTION

Epoxy resins are extensively being used as insulating materials in a wide range of ac electric power installations and equipments because of their good mechanical and electrical properties and its chemical stability. They are often used as a composite with mineral fillers, like silica or alumina, to form composites with appropriate mechanical and thermal properties. Within the context of a growing interest in high voltage dc current (HVDC) power transport, epoxy resins tend also to be used for this type of apparatuses. However, the development of HVDC equipment requires specific criteria (e.g., [1]) and specific materials with appropriate properties.

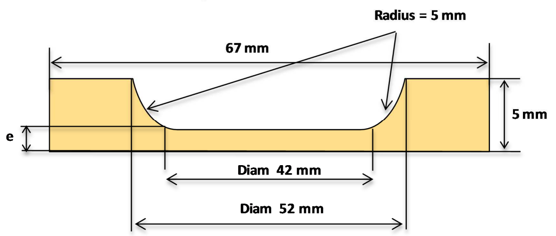
The electric field distribution across an insulator submitted to a high dc voltage differs greatly from that under ac voltage. The field distribution in dc is determined by the conductivity of the insulation, which is not constant and depends strongly on the temperature and on the applied voltage. Surface and volume space charges play an important role. Space charge may accumulate by processes like charge injection from electrodes and/or charge generation within the bulk. Due to the presence of trapped space charges, the electric field within the insulation may be significantly modified, thus accelerating ageing and increasing the risk of breakdown. The nature of electrodes and the dependence of the material conductivity with respect to temperature and electric field are key factors involved in dc field-related phenomena.

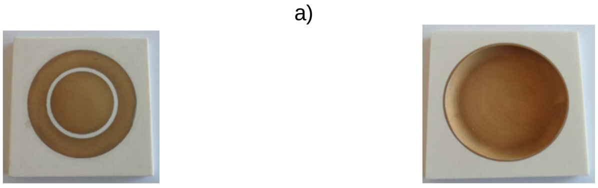
In service, the used insulating material must withstand high temperature and high dc stress. Long-term evaluation of its dielectric behavior under combined thermal and electrical stresses is therefore required for deriving information useful for component design, particularly because charge evolution in may occur with high time constants [2].

The present work deals firstly with conduction mechanisms of an alumina-filled epoxy resin under dc field. Results of conduction current experiments performed under fields up to 40 kV/mm at temperatures comprised between 20℃ to 105℃ are presented and discussed. The effects of the residual moisture are analyzed. The dielectric behavior of the material during thermo-electrical aging for several months at 125℃, under dc fields below and above the linearity threshold, is then addressed. The evolutions of the dielectric spectra and of the accumulated space charge are presented and discussed.

MATERIALS AND SAMPLES

The studied material is composed of a diglycidyl ether of bisphenol A type resin and an acid anhydride as hardener. The resin is filled with an alumina filler (66 wt%). Flat squared samples, with the characteristics shown in Fig. 1a, were machined from resin blocks manufactured for high voltage applications. The sample profile is thicker on the edge than in the center in order to provide uniform electric field in the center of the sample and to reduce field enhancement at the edges of the electrodes. Gold electrodes were applied on both sides by evaporation. The thickness of the samples in the central region was 0.7 mm. All the samples used for the study had the profile from Fig. 1a.





b)

Fig. 1. Profile of the used samples (a) and view of the electrodes deposited on the samples for current-voltage measurements (b)

A circular electrode of 30 mm in diameter, covering an area of constant thickness, was applied on one side of each sample used for conduction current experiments and served as measurement electrode. A grounded guard electrode was placed around the measurement electrode to collect the surface current (Fig. 1b). On the other side of each sample, a gold electrode of 50 mm in diameter was applied and used for applying the voltage. In order to extend the flashover lines, an insulating tube of 100 mm in height was stuck on each sample.

The samples submitted to ageing were provided with 50 mm diameter gold electrodes on both faces.

EXPERIMENTAL SET UP

Conduction current measurements

The experimental setup used for the conduction current measurements is shown schematically in Fig. 2. The samples were placed in a temperature-regulated oven. A low residual ripple 35 kV HVDC power supply (Fug HCP140-35000) and a Keithley 6517A electrometer have been used.

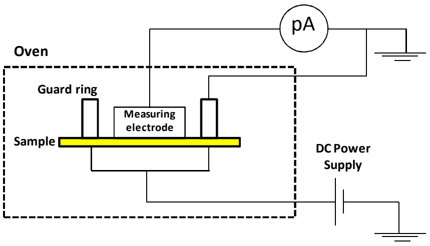


Fig. 2 Experimental set up for conduction current measurements

The charging currents were recorded for applied voltages up to 27 kV at 20℃, 60℃, 85℃ and 105℃. Quasi-ste ady state currents have been obtained after a transient regime of 10000 s. When the stable regime has been reached, the electric stress was removed. The samples were then short-circuited until the current has come down to a value below the noise level before the next voltage step.

Dielectric Spectroscopy

Capacitance and loss factor were determined by dielectric spectroscopy using a Solartron 1260 frequency analyser connected to a Solartron 1296 dielectric interface, under an RMS ac voltage of 2 V. Measurements were carried out at room temperature over a frequency range of 10^{-1} Hz to 10^{6} Hz.

Space charge measurements

The evolution of the space charge accumulated during ageing has been monitored by the thermal step method (TSM) [3-4]. The measurements have been made in short-circuit conditions, with a thermal step of -30K (25℃ to -5℃).

Ageing conditions and set up

15 samples have been aged during 70 days in a temperature-regulated oven at 125℃. To avoid flash over without immersing the samples in dielectric liquids, a specific N_2-pressurized ageing cell has been built (Fig. 3).

Fig.3 Photograph of the samples ready to be aged in the N_2 pressurized cell designed and built for the study before top closing, pressurization and voltage switch-on

A voltage divider coupled to the cell has allowed applying three different voltages across three groups of samples. Thus, sets of 5 samples have been submitted concomitantly to dc stresses of 12, 8 and 4 kV/mm respectively. The cell has been placed in an oven and pressurized at 1 bar during ageing. The pressure and the temperature were monitored all over the ageing period. Periodically, the voltage has been switched off, the cell cooled to room temperature and the samples removed from the cell for capacitance, dielectric loss and space charge characterization.

RESULTS AND DISCUSSION

Conduction mechanisms

Conduction current experiments enable to determine the conductivity, the main conduction mechanisms and the non-linearity threshold (i.e., the field value for which the conduction switches from a ohmic to a non-ohmic regime) from the current-voltage I(V) or current density-electric field J(E) dependence. Measurements have been first conducted on as-received samples, as HV apparatus parts can be manufactured in industry from resin blocks without prior drying to reduce time and power consumption. In a second step, samples have been dried and characterized to assess the effect of the moisture contained in the material.

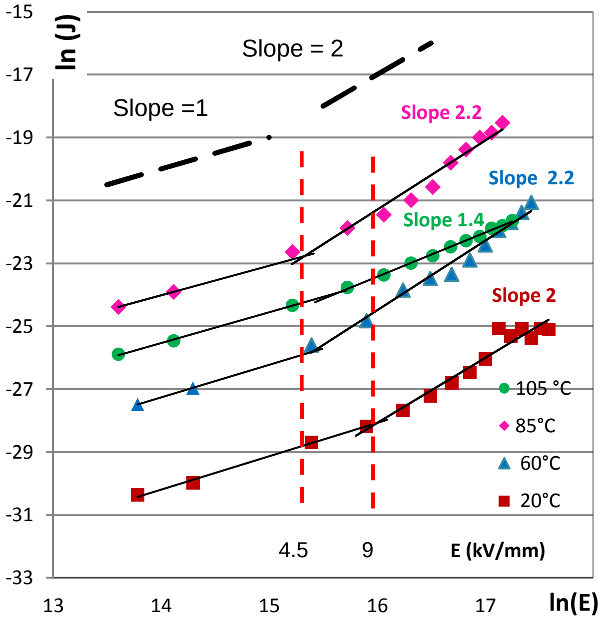


Fig. 4. Double logarithmic plot of the current density/applied field dependence of the as-received material [5]

From the conduction currents obtained on the as-received materials [5], an ohmic behavior has been identified at low field for all the studied temperatures. The volume conductivity values of the as-received material, calculated from the ohmic part of the J(E) characteristics, are in the range of 10^{-16} S/m (at 20℃) to 10^{-13} S/m (at 105℃). At high field, the experimental results allowed to identify a space charge limited current mechanism (SCLC) occurring for temperatures below 85℃ (Fig.4), i.e. a current-voltage dependence of the type [6]:

$$J = (9/8)\varepsilon_r\varepsilon_0\mu\left(V^{l+1}/d^{2l+1}\right) \quad (1)$$

where l ∈ [0, 3] with respect to the trap distribution, μ is the carrier mobility, V is the applied voltage, d is the sample thickness, ε_r is the relative permittivity of the material and ε_0 is the vacuum permittivity. The slope of the plot obtained at 20°C is very close to 2, which corresponds either to a lack of traps or to single-depth traps. At 60°C and 85°C, the slopes are equal to 2.2, corresponding to a distribution in the trap depths, which is characterized by slopes greater than 2. The threshold field delimiting the ohmic mode from the SCLC mode is in the range of 4 to 9 kV/mm, depending on the temperature.

At 105°C, the current appears to be controlled by injection at the electrode/insulator interface (Schottky-type injection):

$$J_S = A_s T^2 \exp[-(\emptyset_0 - \beta_S\sqrt{E_C})/kT] \qquad (2)$$

where A_s is the Richardson-Dushman constant for thermo-ionic emission, $\emptyset_0$ is the height of the potential barrier at the metal-dielectric interface without any applied field, $\beta_S = \sqrt{q^3/4\pi\varepsilon_0\varepsilon_r}$ is the Shottky constant and E_C is the field at the cathode. As the electric field at the cathode is often distorted by space charge [7-8], the electrical state at the contact can be quantified by a dimensionless parameter γ [8]:

$$E_c = \gamma(V/d) \qquad (3)$$

where $\gamma < 1$ for a contact dominant homocharge and $\gamma > 1$ for a contact dominant heterocharge. The expression of the Schottky current becomes, with the field distortion correction:

$$J_S = A_s T^2 \exp[-(\emptyset_0 - \beta_S\sqrt{\gamma V/d})/kT] \qquad (4)$$

TABLE I
Parameters related to the Schottky mechanism at 105°C in the as-received material

Slope of (LnJ_s) = f($(V/d)^{1/2}$)	β_{S_th}/kT	γ	$\emptyset_0$ [eV]
7 10^{-4}	5.4×10^{-4}	1.63	1.37

The parameters related to the Schottky mechanism in our case, where an involvement of heterocharges is put into evidence, are given above.

An increase in the conduction current with the temperature would be expected between 85°C and 105°C, especially at the approach of the glass transition temperature (~110°C for the studied material). In contrast, lower values of the conduction current are measured at 105°C with respect to 85°C. A probable reason for this behaviour is water elimination from the material. Indeed, significant volume resistivity decreases have been reported to occur in epoxy resins when the water contents increases [9-11]. In order to assess this hypothesis and, more generally, the impact of the absorbed moisture on volume resistivity and conduction mechanisms in the studied material, additional measurements were carried out on samples with the same characteristics as the previous ones, but which were dried in an oven at 100°C during 24 hours prior to the measurement. The drying conditions were determined by monitoring sample weight until no significant change has occurred. It came up that, after 24 hours at 100°C and a mass loss of 0.07%, the weight of the samples remained stable. Conduction current measurements have then been carried out at 60°C, 85°C and 105°C, and the results were compared to those obtained on the as-received material.

Fig. 5 shows an example of current/voltage characteristics measured at 85°C on as-received and cured samples, which put into evidence that the latter exhibits conduction currents 2 to 3 decades lower than the as-received one.

The values for the volume resistivity of the two types of samples, calculated for several temperatures from the ohmic region of the I(V) plot, are given in Table 2. As it can be seen, the resistivity of the cured samples is much higher compared to the uncured ones, especially for the temperatures below 105°C. In order to identify the main mechanisms which govern electrical conduction in the cured material, various representations of the J(E) characteristics have been set and analyzed with respect to conduction theories and models. Fig. 6 shows the J(E) characteristics plotted in a log-log representation.

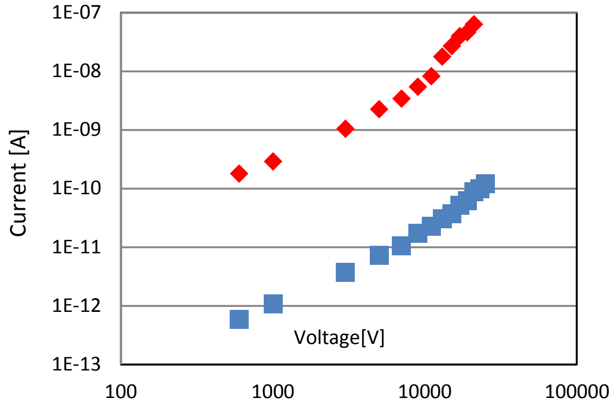


Fig. 5. Current/voltage characteristics measured at 85°C on as-received (♦) and cured (■) samples

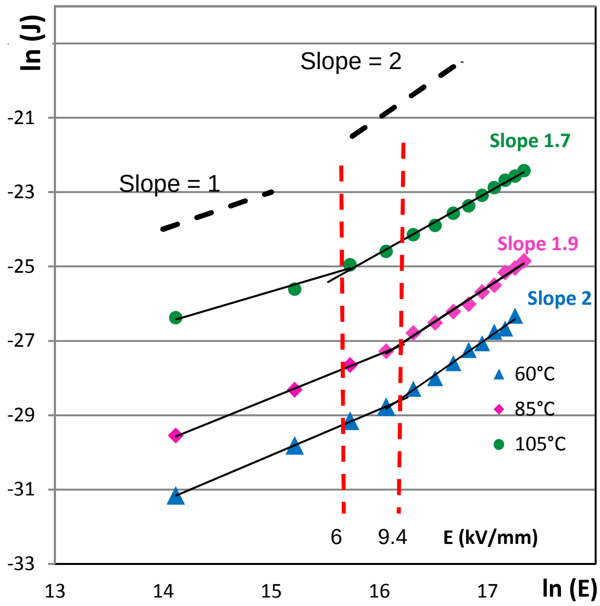


Fig.6. Double logarithmic plot of the current density/applied field dependence of the cured material

TABLE 2
Volume resistivity of the as-received and cured materials

	60°C	85°C	105°C
Volume resistivity of the material at reception (Ωm)	8.24×10^{13}	3×10^{12}	1.5×10^{13}
Volume resistivity after curing at 100°C during 24 h (Ωm)	4.62×10^{15}	10^{15}	4×10^{13}

At low fields, the current is ohmic for the three temperatures (slope 1). At high fields, for 60°C and 85°C, the current density is proportional to the square of the field (slope 2), bringing into focus a dominant SCLC regime.

Close and Return

After confrontation with the other conduction theories, a Schottky mechanism has been identified to prevail at 105℃. The related parameters are given in Table 3.

TABLE 3
Parameters related to the Schottky mechanism at 105℃
in the cured material

Slope of (LnJ_s) = f($((V/d)^{1/2})$)	β_{S_th}/kT	γ	$\emptyset_0$ [eV]
7.92 10^{-4}	5.4×10^{-4}	2.1	1.3

It comes out that the performed curing does not affect the conduction mechanisms significantly, as the same main mechanisms are found in the two types of samples for identical temperatures. In turn, the threshold field is increased by 1.5 kV/mm to 3 kV/mm, and the volume resistivity is raised by a factor of 10 to 100, with respect to the temperature. The thermal treatment at 100℃ during 24 h has therefore a definite positive influence.

To interpret this effect, it must be recalled that epoxy resins are hydrophilic materials, prone to absorb water easily; water uptakes of the order of 0.5% can be expected in such materials [11]. It has been observed that a water uptake of 0.1% leads to a decrease in resistivity of two orders of magnitude [12]. We recall that the mass loss of our samples after drying was 0.07% (and even higher for the resin, as the material contains 66%wt of filler). The observed increase in the resistivity matches therefore very well literature data with respect to the effect of moisture. It has also been reported [13] that a decrease in the glass transition temperature (T_g) of the order of 10 K is to be expected for every 1% wt of water absorption in an epoxy resin. In our case, we have observed an increase of 5 K in the T_g after a curing at 140℃ during 6 h; the curing performed at 100℃ during 24 h is likely to result in an increase of the same magnitude order. Mass loss and T_g variation are also triggered by physico-chemical changes and degradation of the material, which must be taken into account. However, it comes out clearly from the obtained results that the presence of water in the bulk of the studied alumina-filled epoxy should be avoided, as even in small amounts water is a highly potential contributor to significant decrease in resistivity and dc threshold field.

EVOLUTION OF DIELECTRIC PROPERTIES DURING DC AGEING

In order to assess long-term behaviour of the material, dc ageing at 125℃ has been performed on alumina-filled epoxy samples. The ageing dc fields have been set, by using the data provided by the above conduction current measurements, to 4, 8 and 12 kV/mm, in order to acquire information about the evolution of the electric properties when the material is aged at moderate fields below and above the non-linearity thresholds.

Fig. 7 shows the evolution of the capacitance (C) and of the loss factor (tan δ) during 70 days of ageing. In order to have statistically representative results, each displayed plot is the average of data obtained on five samples aged under the same field. A significant decrease of both the capacitance (and thus, of the permittivity) and the loss factor are observed at low frequency after submission to the thermo-electrical stress. This is likely due to the effect of moisture elimination discussed above, as well as to the pursuit of crosslinking, which reduces molecular mobility.

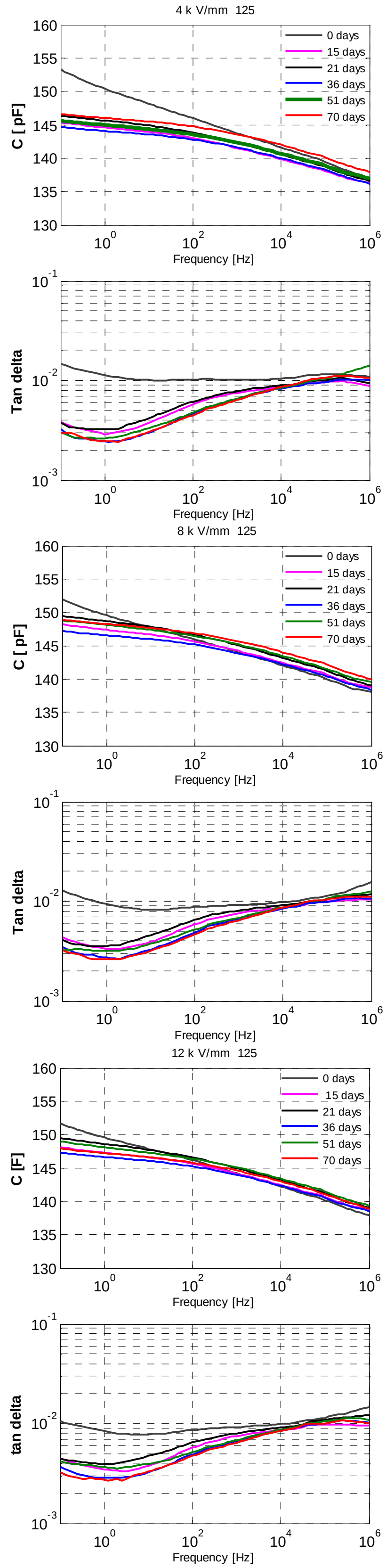


Fig.7 Evolution of the dielectric spectra during ageing under 12, 8 and 4kV/mm at 125℃. Each plotted spectrum is the average of data issued from five samples.
Spectra obtained at room temperature.

It comes out from the above curves that, after the decrease of the permittivity and loss factor observed at the first measurement, there is no evolution of the dielectric spectra which could be directly related to the ageing time. Indeed, the spectra oscillate slightly around the same values, and no apparent relationship between their evolution and the ageing time can be found. Also, no significant effect of the ageing field can be put into evidence with respect to the evolution of the measured spectra. It can be concluded that the observed effects on the dielectric spectra are mainly due to the temperature.

Dc conductivity or low field dispersion can be put into evidence at low frequencies (slope of imaginary permittivity with respect to frequency equal to -1). This kind of behavior, which may have evolved under the applied dc stress and is able to bring information from an electrical point of view, is hard to identify on the measured characteristics, certainly because it becomes observable in our material at much lower frequencies (10^{-2} to 10^{-4} Hz). Given the significant time required for performing measurements at 10^{-2} to 10^{-4} Hz and the number of samples used in this work in order to obtain reliable results from a statistical point of view, monitoring the evolution of the spectra at such frequencies was hardly conceivable. In turn, measuring space charge accumulation, which is the main responsible for reliability problems in dc, is much less time-consuming.

In order to determine the evolution of trapped charges during dc ageing, the samples have been assessed by the thermal step method (TSM).The TSM is based on the diffusion of a thermal wave, which generates temporary local displacements of the space charge and slight local variations of the permittivity. This is reflected at electrodes by a variation of the induced charges, resulting in a capacitive current which depends on the field and charge distribution across the sample. If the sample is flat or cylindrical, the acquired signal allows determining the distribution of the residual electric field and charge density across the sample [3-4]. The particular shape of the samples used in the present work (Fig. 1) did not allow extracting field and charge repartitions. Therefore, thermal step signals have been used to assess the evolution of the internal field and charge during ageing.

Examples of thermal step currents measured at different moments during ageing are presented in Fig. 8. As the currents have similar shapes, it is possible to compare their amplitudes for obtaining an insight of the space charge evolution during ageing. This is illustrated in Fig. 9.

As the thermal step current is proportional to the capacitance of the sample [3-4], its amplitude has to be normalized to ensure proper comparison of data obtained on different samples. For this purpose, the graphical representation from Fig. 9 concerns the TSM currents amplitudes I_{Max} divided by the sample capacitance C, i.e. I_{Max}/C. Each point of the plot from Fig. 9 is the average of values measured at the same moment on five samples aged concomitantly under the same field.

It comes out from Fig. 8 and 9 that the amplitude of the TSM current increases with the ageing duration for the three values of the ageing field. Considering that the amplitude of the TSM signals is directly linked to the accumulated charge [3-4], it can be deduced that space charges accumulation rises with the ageing time. All over the monitored ageing, the highest levels are exhibited by the samples submitted to the highest fields.

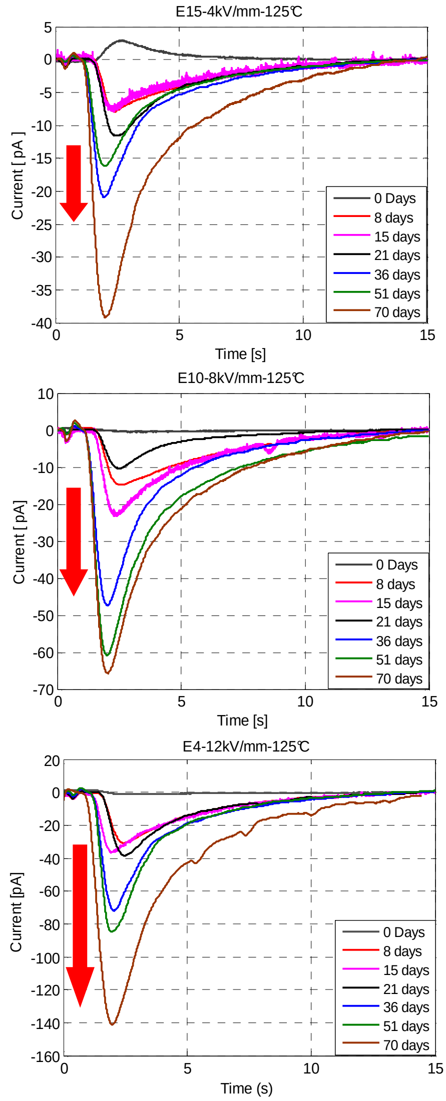


Fig. 8 Evolutions of thermal step currents measured on samples aged under 12, 8 and 4kV/mm at 125℃

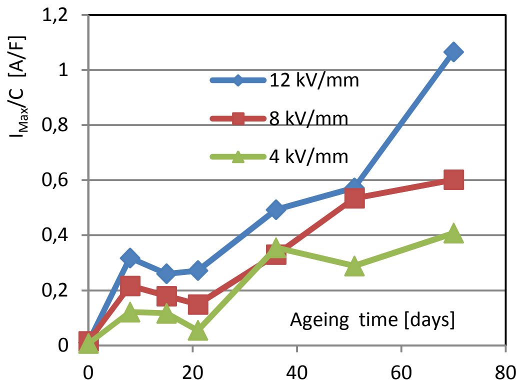


Fig. 9 Evolution of the normalized thermal step current amplitudes during dc ageing performed under 12, 8 and 4kV/mm at 125℃. Each point is the average of data from five samples.

However, the time variation of I_{Max}/C is not monotonous. A steep augmentation is observed after the first days of conditioning, then the values decrease during the next days and restart to increase with a different rate after 21 days of conditioning. The variation rates of $I_{Max}/C(t)$ are roughly similar for the three values of the ageing field during the first days of ageing, but they become more field-dependent after 21 days. Thus, if this dynamics is similar at 4 and 8 kV/mm, I_{Max}/C seems to increase faster under 12 kV/mm, particularly after 50 days of ageing.

As the accumulated charge is a balance between injected carriers and carriers evacuated by conduction, the observed evolutions can be interpreted as the result of periodical evacuation of a fraction of the accumulated charges under the effect of the internal field. Thus, as long as the charges are accumulated in shallow traps, they can be easily detrapped for lower values of the internal field. In contrast, charges stored in deep traps will be detrapped more difficultly, as a higher value of the field will be needed to ease their release from the traps. Consequently, charges will continue to accumulate until the internal field reaches values able to favor extraction from deep traps. Thus, the highest growth rate observed at 12 kV/mm after 21 days of conditioning is likely due to the fact that more deep traps are created and/or filled quicker under a higher field, especially with a charge injection significantly stronger at 12 kV/mm, as shown by the conduction current measurements. In contrast, the trapping/detrapping cycles should be easier at the lowest fields, as most of the charges are likely stored in shallower traps. As space charge measurements does not allow to distinguish between space charge and polarization gradient, the study of the temperature dependence of the charge accumulation with time (currently under way) will contribute to a better insight of the phenomena responsible for the observed evolution.

To summarize, the results obtained by TSM after 50 days of ageing at 125℃ show that space charge accumulation increases with time in the studied alumina-filled epoxy resins. A net augmentation is observed at 125℃ whatever the ageing field between 4 and 12 kV/mm, more significant above 10 kV/mm. It may be concluded that the internal field in the studied material takes locally higher and higher values with time, increasing the risk of significant charge detrapping leading to breakdown. In order to further assess the long-time effect of the space charge on the material and to derive information useful for HVDC component design, it is therefore useful to monitor charge accumulation during longer periods in order to determine whether $I_{Max}/C(t)$ reaches an equilibrium value at a given temperature before breakdown occurs, and, if so, what is the maximum value of the applied field for which such a behavior is observed.

CONCLUSIONS AND PROSPECTS

Dielectric behavior under dc field of 66%wt alumina-filled epoxy resin has been investigated in view of its use in dc applications. Conduction mechanisms have been determined. The ohmic regime prevails below 4 kV/mm at temperatures lower than 105℃, while nonlinear regimes (SCLC or Schottky) become dominant above 4 to 9 kV/mm, depending on the temperature. It has been found that the elimination of moisture from the material, even in small amounts of the order of 0.1 %, significantly increases volume resistivity (up to a factor of 100) and threshold field (up to several kV/mm).

Thermo-electrical dc ageing performed at 125℃ under fields of 4, 8 and 12 kV/mm during 70 days put into evidence permittivity and loss factor evolutions in the [10^{-1} Hz;10^{6} Hz] range attributed essentially to the thermal stress. The thermo-electrical stress was found to trigger space charge accumulation, increasing with the ageing duration and the ageing field.

Monitoring charge accumulation during longer periods should allow determining whether a maximum value of the charge is reached at a given temperature and supply information on the values of the applied field for which such a behavior could be observed, allowing to derive further information for designing HVDC components based on the studied material.

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