

Current and Space Charge Behaviour in an Epoxy Resin under Thermo-Electric Stress

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Abstract: This study has the aim of characterizing the behaviour of the space charge in an epoxy resin used as electrical insulation in systems such as transformers and bus bars, using films as laboratory specimen. Temperature, field level and nature of the electrodes are the physical parameters on which we have acted. A spatio-temporal measurement technique of space charge, known as Pulsed Electro Acoustic (PEA) method, and external current measurements were implemented in thermalized environment, under DC field up to 40kV/mm. We observed chronologically a quasi-symmetrical build-up of homocharges, then a substitution of heterocharges, more importantly close to the cathode. These phenomena are discussed in the light of the measured external currents and of the quantitative differences which appeared depending on material, temperature and nature of the interface considered.

Introduction

Epoxy resins are widely used as in-situ cured insulation in applications such as power transformers. Though there is now a long experience available in this field, with systems being in-service for long, studies aiming at evaluating ageing of such materials under electric field are rather scarce. To illustrate the kind of stress to which such insulations may be submitted, let consider the application targeted for the material investigated in this work. The resin is a DiGlycidyl Ether of Bisphenol A (DGEBA) - based epoxy, particularly dedicated to Trihal®, which is a three-phase transformer with coated windings embedded in a solid insulation. The bulk insulation consists of an epoxy resin including active filler moulded under vacuum. This active filler, essentially made of trihydrated alumina Al (OH) - which has provided the Trihal trademark - and of SiO₂, improves fire resistance of the insulation. The Trihal® type covers a broad range of distribution transformers from 160 kVA to 15 MVA and a service voltage going up to 36kV. During the nominal operation of this type of transformers, the insulator is brought uninterruptedly up to a temperature of 130°C with hot points up to 155°C. At these temperatures the epoxy is in a rubber-like state, since its glass transition temperature is about 68°C. As for the design electric field, a principle of precaution would have established a limit at 2kV/mm, but local field values can be higher.

Finally at these temperatures and with cycling, atmospheric oxidation could be particularly alarming.

In the perspective where charge transport and trapping combined to thermal stresses could drive ageing phenomena, we have characterized space charge behaviour and conduction currents in an epoxy resin by considering the influence of temperature, field level and SiO₂ fillers.

Materials and characterization

Samples: Within the framework of this study we focused on one type of epoxy resin with and without mineral fillers. The material is a mixture with proportions in weight as follows: 100 parts of base resin CY225, 100 parts of hardener HY227 and 0.6 parts of catalyzer DY062. These are Huntsman (ex Ciba Geigy) references. For composites, 300 parts of SiO₂ filler are added. Each component is a mixture of several products which are only partly documented (Gallot-lavallee-04). Films were cured with a thickness of about 500 µm (+/- 10 µm). One series of samples was not metallized, the other series was metallized using gold sputtering with electrodes of circular geometry.

Space charge: Space charge measurements were carried out in air within a thermostated oven, without control of the hygrometry, on sample discs of 0.5mm thickness. For metallized samples, gold electrodes of 0.56cm² area and 300Å thickness were pulverized.

The electrodes of the Pulsed Electro-Acoustic -PEA- test bench are made of aluminium for the electrode close to the acoustic sensor (to the right in space charge profiles presented) and a polymer filled with carbon black for the other electrode. The effective surface of probing is about $S = 0.5\text{cm}^2$. The amplitude of the PEA pulse source was set to 300 V, giving a pulse field of 0.6kV/mm.

Current: Samples were conditioned in the same way as for space charge measurements, except for the gold electrode area which was 20cm². All measurements were carried out after evacuating the chamber down to 10⁻⁶mbar and filling it with nitrogen gas at up to 1.2bars. The stress cycle consisted in applying DC levels for 1h, going from 2kV to 20kV by step of 2kV with a 1h period at 0V between each level. The temperature was

controlled using a thermostated liquid circulating in a reservoir installed beneath the electrode holder.

Space charge results

Nature of space charge: Figure 1 compares space charge profiles obtained on metallized (a) and not metallized (b) pure epoxy samples, at 72°C. Profiles were recorded at a frequency of 1/20s, for 1h under 40kV/mm followed by one 1h under short-circuit. For improving resolution close to the electrodes, results presented for the cathode region were obtained using a positive DC voltage whereas those close to the anode correspond to a negative voltage (the resolution is improved on the ground electrode which is the closest to the piezoelectric sensor). In the first moments of voltage application, a homocharge build up is observed at both electrodes, irrespective of the nature of the electrodes. These homocharges are progressively replaced by heterocharges, with clear evidence of this after 30min of polarization. The existence of these heterocharges is confirmed by measurements in Volt-off, in which they are the dominant carriers considering either bulk or electrode signal.

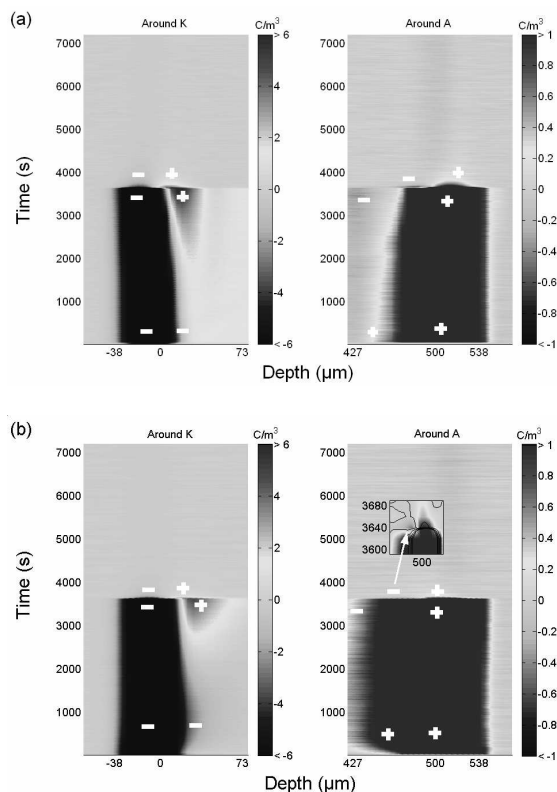


Figure 1: Cartographic vision of space charge density in the vicinity of the electrodes, obtained under 40kV/mm ($t < 3600$ s) and in volt-off ($t > 3600$ s) on a pure epoxy sample at 72°C. (a) metallized sample. (b) not metallized sample. Cathode around $x=0$; Anode around $x=500\mu\text{m}$.

Figure 2 provides a picture of the behaviour of charges in the bulk of the insulation. The progression of a front of negative charges from cathode to anode is clearly observed. This means that the negative heterocharge accumulation observed after some time under stress is potentially due to a drift of injected charges towards the opposite electrode. The apparent velocity of the charge front is relatively low (500 $\mu\text{m}/\text{h}$). Such phenomenon was not observed for positive charges. It is however supposed that a similar process holds, with probably a more diffusive transit of charges.

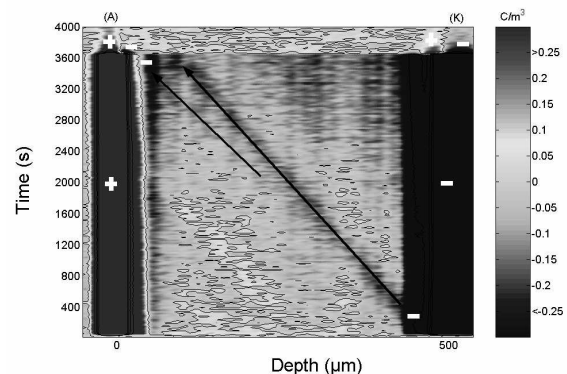


Figure 2: Space charge profiles in the bulk of the insulation, obtained under 40kV/mm and in volt-off ($t > 3600$ s) on a pure epoxy sample with gold electrodes at 72°C.

With the assumption that the development of heterocharges (figure 1) is due to transit of charges coming from the opposite electrodes (figure 2), we propose in figure 3 another form of representation of the results contained in figure 1 by considering the intensity of the image charges on the electrodes.

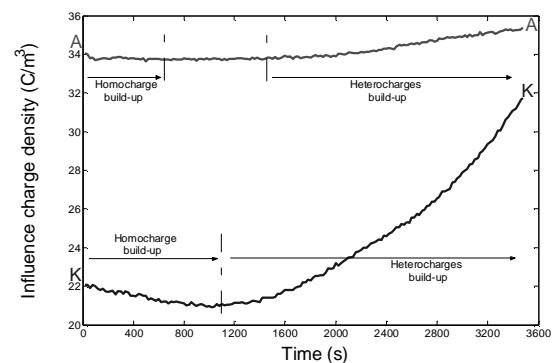


Figure 3: Density of the influence charge (in absolute value) taken in a point of the electrode, as derived from data presented in figure 1.

We observe at short time in K (cathode) a reduction in absolute value of the influence charge which can be explained by the development of homocharge in the vicinity of K, then a strong increase in the influence charge which can be explained by a desertion of the homocharge and/or the progressive accumulation of the heterocharges in K. Concerning the behaviour at the

anode, it seems that the slight reduction in the influence charge at short time corresponds to a development of the homocharge. The increase in the influence charge after about 1500s reflects the accumulation of heterocharge in a similar way as for the cathode. Let us note finally that through this analysis, we underestimate the homocharge concentration since slow polarization, which is likely in epoxy, has an effect (increase of the influence charge) opposite to that of homocharge accumulation.

Effect of temperature and electric field: The above results let us suppose that space charge accumulation is driven by homocharge generation close to the electrodes. Hence, heterocharge build-up would be a consequence of this generation. In order to evaluate the dependence of homocharges accumulation as a function of the applied field, we applied increasing electric stress by steps of 4kV/mm with 10 min polarization and depolarization at each stress value, and so up to a maximum field of 20kV/mm. In this way, we are in a situation where homocharges are the dominant carriers. Figure 4 shows profiles extracted from the total of the space charge profiles recorded at frequency of 1/20s during the whole stress cycle (a) on pure epoxy resin (b) on filled epoxy resin.

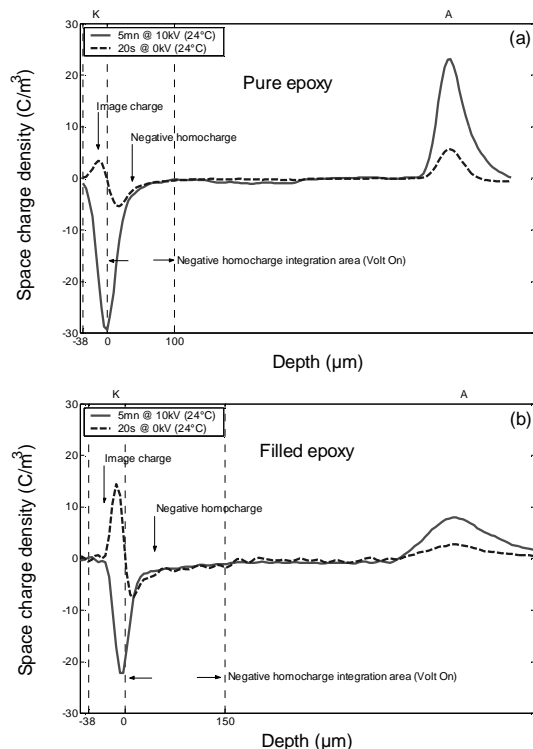


Figure 4: Space charge profiles obtained at 24°C (a) on a pure epoxy sample, (b) on a filled epoxy sample (Piezoelectricity phenomenon (Hollé et al-04) doesn't enable space charge profile achievement). After 5min under 20kV/mm and after 20s in volt-off.

At 72°C the homocharge is released very quickly in Volt-off. Therefore, we have estimated the field dependence of homocharge density by considering volt-on profiles and by integrating it within the charged region close to the interface, as defined by dashed lines in figure 4. Results obtained by such treatment are shown in figure 5. The charge thus integrated includes a fraction of the electrode charge. This fraction represents at most 50% of the electrode charge. Therefore, we have introduced this upper limit in the figure.

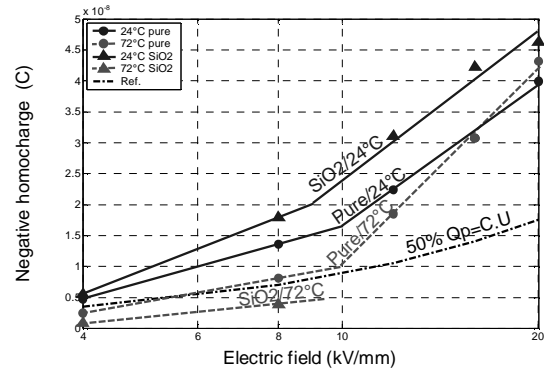


Figure 5: Field dependence of negative homocharge obtained by integration in the area delimited by dashed lines in figure 4, for different materials and measurement temperature. Samples are not metallized. The dash-dot line represents an upper limit of the capacitive charge taken in the integration.

Homocharges appear to be detected at low field (4kV/mm) for measurements at 24°C, with however a threshold at around 10kV/mm marking the beginning of a faster increase of charge accumulation. The increase in temperature appears to limit the accumulation of homocharge, which could be due to an activated drift of charges in the bulk. Concerning the effect of the filler, conflicting trends are observed in the low field range, depending on temperature. Early breakdown of samples at 72°C did not allow investigating the high field range.

Breakdown and space charge: During the above experiment on homocharge estimation, breakdown of the filled sample occurred at 72°C, at a field of 12kV/mm. Interesting features are revealed in space charge profiles obtained just before breakdown as shown in Figure 6. It is clearly shown that homocharge accumulate for a field of 8kV/mm. In the bulk, alternated regions of positive and negative charge are observed, with increasing densities with the applied field, which could correspond to an accumulation of space charge in the interfacial region of SiO₂ grains. The important event in this experiment is in a time interval of 5min before breakdown, when a sudden accumulation of heterocharges is observed instead of homocharges which disappear. Heterocharges can be considered as harmful in the sense that it reinforces the

interface field, where breakdown is thought to be initiated. However, a question arises: is that development of heterocharge a cause or a consequence of phenomena leading to breakdown?

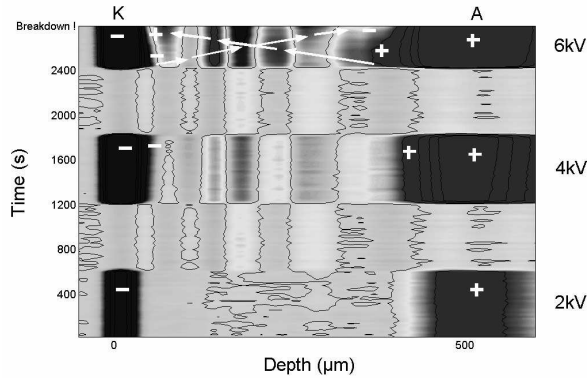


Figure 6: Space charge evolution of an unmetallized filled epoxy sample just before breakdown at 72°C. Volt-on and volt-off periods last for 600s.

Current results

Current transients: Figure 7(a) shows polarization and depolarization currents obtained on a gold-metallized pure epoxy sample at room temperature. We observe strong transients in the current which are apparently symmetrical considering polarization and depolarization (except for the steady state contribution). However, when considering the difference between the two currents, cf. figure 7(b), we observe at time < 80s a depolarization current that exceeds the polarisation current. A quasi-steady state is observed after about 300s, with a possible decrease at long time.

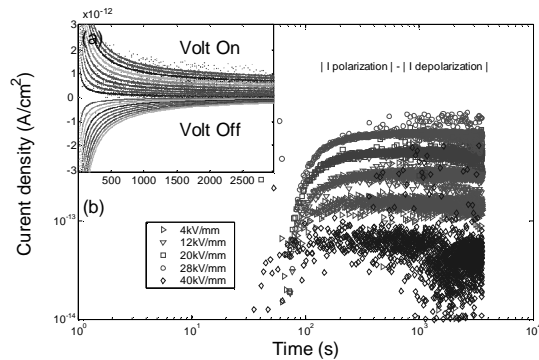


Figure 7: (a) Polarization and depolarization current and (b) difference in currents transients obtained as a function of field on a gold-metallized sample at 24°C for 1h/1h charging/discharging current measurements in vacuum.

Simulation results (Boufayed-04) have shown that the external current in a sample free from charge increases as a function of time when charges are provided by injection at the electrodes and eventually reaches a steady state when carriers reach the opposite

electrode. Therefore, it could be an expected result that the transport current increases as a function of time at short time. However, in the present results, this 'transport' current is negative, meaning that other processes are at play. A likely explanation is that part of the depolarization current is due to charge release, with a kinetic of charge release faster than that of charge accumulation (Gallot-lavallee-03). At long time, the decrease of the current (1000s and on) could correspond to a limitation of transport due to charge accumulation.

Current vs. field characteristics: Figure 8 shows current vs. field characteristics obtained at time $t=3200s$, at various temperatures (T), both in polarisation and depolarization. Volt-off currents appear proportional to field, whatever field and temperature. Currents in volt-off are small in comparison to those in volt-on, thus it is considered that the later is constituted essentially by a transport current. The slope of the transport current is 1 at low field (ohmic regime) and becomes higher than 1 at a critical field depending on T .

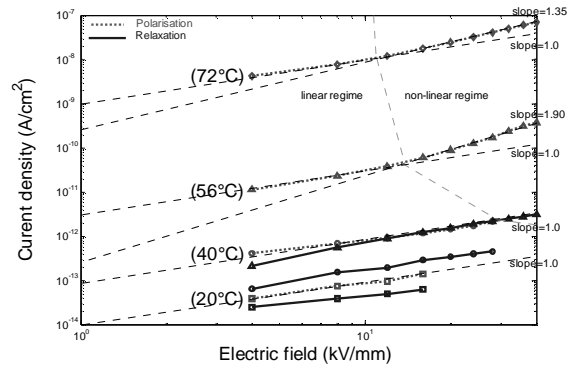


Figure 8 Polarization (dotted line) and depolarisation (solid line) currents as a function of field and temperature. Volt-on and volt-off steps lasted for 1h and values are reported for time $t = 3200s$. Dashed lines indicate the slope of the curves. The thin dashed line indicates the change between two conduction regimes.

It is possible to approach the activation energy for conduction by putting data in the form of an Arrhenius diagram. From figure 9, activation energy ranging from 0.99 to 3.7eV can be estimated, depending on field and temperature considered. The nonlinear effects of the field are thus revealed at the same time as the non-Arrhenian character of the conduction mechanism.

In the hypothesis that the observed characteristics reflect a space charge limited current (SCLC), the threshold field E_{tr} at the end of the linear regime would correspond to the onset field for a trap-filling regime, according to Eq. (1) and (2):

$$J = q.n_o.\mu.E \text{ for } E < E_{tr} \quad (1)$$

$$J = \frac{9}{8} \epsilon.\mu.\theta. \frac{V^{J+1}}{L^{2J+1}} \text{ for } E > E_{tr} \quad (2)$$

Here n_o , μ , $E (=V/L)$ and ϵ are the intrinsic carrier density, mobility, applied field and permittivity ($\epsilon_r = 3.5$), respectively. The parameter l is characteristic of the trap distribution in energy ($l=1$ for a homogeneous distribution); it is obtained from the slope of the J - E curve above E_{tr} . Supposing that the fraction θ of free carriers is equal to 1, mobility can be estimated from the high field region, and from there the density of carriers n_o . With such an analysis, data at 56 and 72°C give roughly the same value of $n_o = 5.7 \times 10^{18} \text{ m}^{-3}$, and it is considered that it is unchanged for lower temperatures. Table 1 shows the final value of mobility vs. temperature which has been obtained. It is observed that mobility increases by about 5 decades in the investigated temperature range.

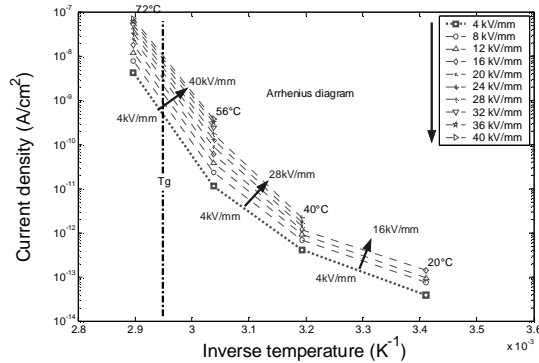


Figure 9: Arrhenius diagram of polarization currents at various applied field. Note the apparent increase in activation energy (slope) as field increases.

T(°C)	$\mu(\text{cm}^2/\text{V.s})$
72	1.05×10^{-7}
56	4.24×10^{-10}
40	9.19×10^{-12}
20	9.19×10^{-13}

Table 1: Mobility vs. temperature estimated from the SCLC model.

The slope of the curve gives an activation energy increasing from 0.99 to 3.7 eV with the increase in temperature. It is probable that this increase is related to the glass transition phenomenon of the epoxy. The glass transition, and associated molecular movements, could assist the transport of intrinsic carriers from site to site. It could also assist other mechanisms of transport, involving ionic species for example. Measurements on a broader range of temperature would be necessary to determine if a particular change in the shape of the curve is observed around T_g .

Perhaps the most important result of the above analysis is the apparent increase in conductivity of about 5 decades on an interval of temperature of almost 50°C. This strong variation on the one hand underlines the need for a good control of temperature when achieving

materials comparison (strong sensitivity of current to small variations in temperature) and on the other hand lets us predict consequences on the accumulation of space charges.

Discussion

Scenario for space charge build-up: A single scenario, as depicted in figure 10, of generation and transport of space charge within the investigated epoxy can be built-up based on the overall space charge measurements carried out on samples being metallized or not, filled or not, and at 24 or 72°C:

(1) A development of positive and negative homocharges would appear systematically under the effect of a relatively weak electric field (4 kV/mm with a clear enhancement above 10 kV/mm) and whatever the temperature (cf. fig. 5). The nature of the electrode/insulator interface would play an important part in this first phenomenon. Indeed when gold electrodes are deposited on samples, the injection phenomenon is lowered (cf. figure 1).

Several literature reports support homocharge injection in epoxy resins. Bipolar injection combined to slow polarization has been reported by Griseri et al. in a somewhat different epoxy resin (Griseri-00). Iizuka et al. (Iizuka-99) report a similar behaviour in an epoxy resin, with some effect of relative humidity. Finally Guillermain (Guillermin-04), who worked on epoxy resins of the same nature as ours, observed bipolar injection by LIPP with an enhanced efficiency above 13 kV/mm at 55°C.

(2) A slow migration of homocharges towards the opposite electrodes would lead to the growth of heterocharges, still for both kind of carriers, with apparently a faster process for positive charges (figure 3). This phenomenon is strongly dependent on temperature, since it was not observed at 24°C (Gallot-lavallee-03). Once heterocharges have been accumulated, the process may end-up by dielectric breakdown, as observed in filled samples at 72°C (figure 6), a phenomenon which is most probably favoured by the existence of multiple interfaces due to the silica grains.

Regarding heterocharge formation, there is a priori no such process reported in the literature, probably because the appropriate stressing conditions (field, time and temperature) were not gathered. On the scenario of breakdown consecutive to a massive redistribution of internal charges, similar results were already reported on other insulating materials such as low density polyethylene (Matsui-02). Let us recall that in situation of heterocharge, there is an enhancement of the interface field and therefore an enhancement of injection.

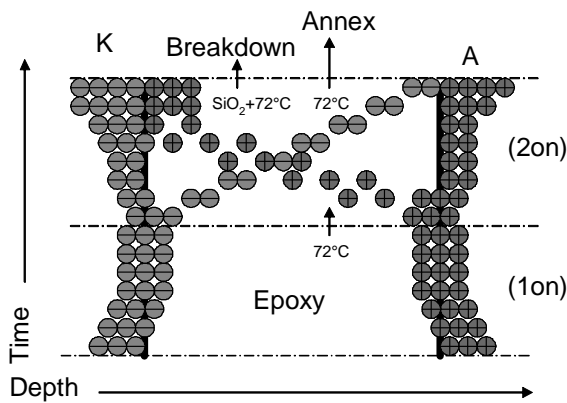


Figure 10: Phenomenological proposal on the build-up of space charge in our epoxy resin

External current and correlation with space charge behaviour: The analysis related to the polarization/depolarization currents lets us suspect that depolarization currents are not purely dipolar in nature. Indeed, within about 100s after short-circuiting, the depolarization current exceeds the charging current, which indicates releasing of previously injected space charge, at a higher rate than its accumulation. This appears not completely surprising since, in principle, charges must overcome an injection barrier at the metal/dielectric interface to get in, whereas there is no barrier to extraction. However, the driving field is stronger for polarization, being essentially the applied field for charge build-up (at least for short stressing time), and the space charge field for charge release. So, there must be a favourable combination of phenomena for such process to hold.

At long time (1h or so), the polarization current is essentially the transport current, whatever temperature and field are, in the investigated range. A non-linear field dependence of the transport current is observed above a field of 13 kV/mm at 56°C and 11kV/mm at 72°C, from which some parameters relevant to the SCLC theory have been extracted. The apparent mobility increases by 5 decades in the temperature range 20 to 72°C, the corresponding activation energy being increasing with temperature. Space charge measurements also indicate that homocharge accumulation increases for fields higher than roughly 10kV/mm. It is therefore thought that the change in conductivity regime is connected to an important accumulation of charges.

Charge densities measured at 72°C are lower than those obtained at 24°C, for pure as well as for filled samples. This feature very certainly results from the fact that mobility is strongly enhanced with temperature so that transport prevents charge accumulation. It is also consistent with conclusions of Guillermin (Guillermin-04) who observed that at high temperature (80°C),

conduction could be injection-limited whereas at 55°C, bulk transport would be the limiting step in the current.

On a more general standpoint, we would like to point out on two paradigms that such combined study opens out. First, classical models, such as SCLC, have been settled to analyse external currents in insulators, at a time where these were the only kind of experimental data available. With the development of tools giving access to internal space charge profiles, it is revealed that actual charge distributions are more complex than in the hypotheses taken in models, with carriers of different nature and polarity. Application of the SCLC model as it was done here, with steady state current relevant to only one kind of carrier as underlying hypothesis, may appear irrelevant by consideration of the experimental profiles being presented, where bipolar charged regions appear changing with time. The second dilemma resorts to the insufficiency of space charge measurements for accounting for transport processes. Only a picture of the unbalanced densities of positive and negative charges, i.e. the net charge density, is provided by such measurements, and in addition, these charges must couple to the lattice for being probed, meaning that mobile charges having little interaction with the lattice are probably not revealed. On the one hand external current provides a more complete response of phenomena at play in the insulation, but the response is global and cannot be resolved into elementary contributions without severe hypotheses. On the other hand, space charge measurements are more selective and provide new but limited information. Finally, to us, the correlation between thresholds for space charge accumulation and for change in the conduction regime is not just a coincidence. It must be admitted however that the detail mechanisms behind this correlation are far from being understood.

Conclusions

Critical densities of space charges were revealed in the investigated epoxy-based insulation, leading to a single scenario for space charge build-up: creation of homocharge by injection at both electrodes, then drift of these homocharges towards the opposite electrode, providing profiles revealing heterocharges at both electrodes in a suitable combination of stressing parameters that are time, temperature and field. Other complex phenomena or breakdown follow, depending on temperature, and on the presence of mineral filler. A correlation with external currents could be made through an onset field of the order of 10kV/mm for a non-linear regime of conduction corresponding to an enhanced injection of charges.

References

- [Boufayed-04] F. Boufayed, G. Teyssedre, C. Laurent, P. Segur, L. A. Dissado, and G. C. Montanari, "Space charges motion in cross-linked polyethylene: bipolar model with an symmetric exponential distribution of traps," *Proc. CSC'5*, Sfax, Tunisia, 2004.
- [Gallot-Lavallee-03] O. Gallot-Lavallee, G. Teyssedre, C. Laurent, and S. Rowe, "Space charge and orientational polarization within epoxy as probed by the Pulsed Electro-Acoustic technique," *Annual Report CEIDP*, Albuquerque, NM, USA, pp. 249-52, 2003.
- [Gallot-Lavallee-04] O. Gallot-Lavallee, G. Teyssedre, C. Laurent, and S. Rowe, "Electroluminescence and thermo stimulated luminescence in an epoxy resin under uniform ac field," *Proc. ICSD*, pp. 703-706, 2004.
- [Griseri-00] V. Griseri, "The effects of high electric fields on an epoxy resin," *Thesis in Electrical Engineering*. Leicester: University of Leicester, 2000, pp. 1-205.
- [Guillermin-04] C. Guillermin, "Viellissement électrique et thermique d'un composite résine époxy-silice : étude des charges d'espace et de la conduction," *Thèse en Physique*. Grenoble: Joseph Fourier Grenoble I, 2004, pp. 1-189.
- [Holé-04] S. Holé, A. Sylvestre, and S. Rowe, "The influence of filler particles on space charge measurements," *J. Phys. D: Appl. Phys.*, vol. 37, pp. 1869-76, 2004.
- [Iizuka-99] T. Iizuka, K. Yoshimoto, H. Takai, K. Fukunaga, and T. Maeno, "Measurement of space charge distribution in epoxy resin," *Elec. Eng. in Japan*, vol. 129, pp. 129-34, 1999.
- [Matsui-02] K. Matsui, Y. Tanaka, T. Fukao, T. Takada, and T. Maeno, "Short-duration space charge observation," *Annual Report CEIDP*, Cancun, Mexico, pp. 598-601, 2002.

Annex: Long-term effects...

We would like to bring to discussion misunderstood space charge features observed under long term stress (41 days) of an epoxy sample. Figure 11 shows space charge and field profiles obtained in the course of this experiment. After 8 days under stress, a front of negative charges is observed in the bulk of the insulation. This front is apparently propagating slowly towards the cathode and let appear an adjacent positively charged region as time increases. In the same time there is a growth of positive charge close to anode and a decrease of the positive charge to the cathode, the latter being the strongest at 8 days of stress. The short interruption (1h) of the stress at the 8th day did not change the distribution: most of the charge was apparently released within 1h (cf. figure 12); however, the initial distribution was restored as soon as the stress was applied again. As shown in figure 11(b), charge accumulation is accompanied by important distortion of the internal field, with in some instances a mismatch between measured and applied potential. Even though the internal field is very low in some regions, this can not explain the apparent drift of negative charges in a way opposed to the applied field.

Even more puzzling are space charge profiles in volt-off obtained after 8 days and 41 days of stressing as shown in figure 11. After 8 days, the cluster of negative charge in the bulk quickly disappears and is apparently driven towards the cathode. Then positive charges settle

in the region which was previously negative. On the cathode side, the positive charge accumulated is released very slowly. The evolution of the image charge on the electrodes appears consistent with the redistribution of charges in the bulk. Regarding now the decay after 41 days, the situation is that of a bulk negative charge dissipating progressively without apparent change in position of the peak, and positive charges, both in the middle of the sample and close to the anode, dissipating more slowly.

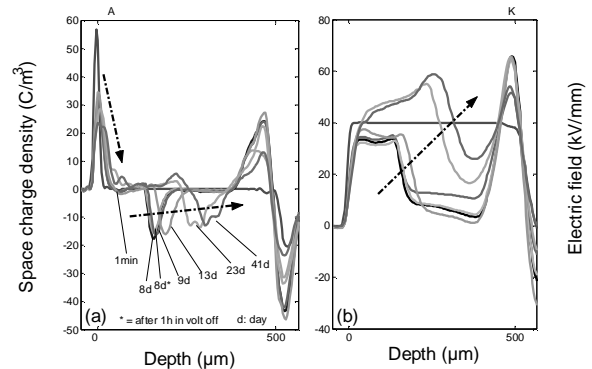


Figure 11: Space charge profiles (a) and corresponding electric field profiles (b) obtained on a gold-metallized pure epoxy sample under 40kV/mm at 72°C, taken at different stressing time.

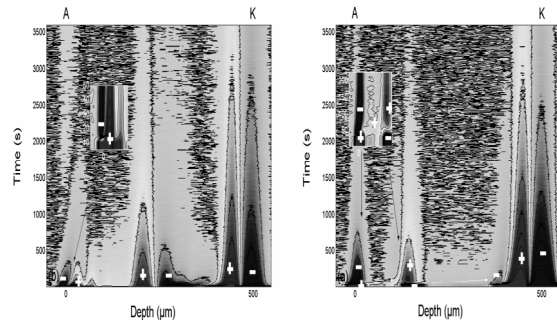


Figure 12: Space charge profiles obtained in volt-off at 8 days (a) and 41 days (b) during experiment shown in Figure 10.

Strong inhomogeneous polarization? Development of a conductive channel with much more mobile positive than negative ions forming at the tip of the channel? This last experiment, though far from being understood, lands some challenge in the interpretation of signals extracted from space charge measurement techniques as well as in the physics of charge generation in insulators...

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