Electrical Phenomena Modeling in Polyethylene

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ABSTRACT:

In Polyethylene, space charges measurements for 25 years have shown their important role concerning the electrical properties of this material submitted to high DC electric field. These charges are in traps due to defects of structure and ions coming from the making process. After reviewing the different influential parameters linked to space charges, we give some examples of polarization then injection of charges and conduction. From these cases we try to build a model which takes into account the observed phenomena.

KEYWORDS:

Polyethylene, Electrical Phenomena Modeling, Polarization, Space Charges, Injection, Thermo stimulated Currents, Conduction.

INTRODUCTION:

Polyethylene (PE) is a polymer with long chains of elements [–CH2--] (100 to 1000 unities) and it presents 3 different structures: LDPE, low density rather semi-crystallized where the chains are more mobile, HDPE high density more crystallized and more rigid and XLPE where the links exist between chains. All PE are considered as good insulating materials with a relative permittivity of 2.3. It is admitted that the forbidden band (FB) is about 8-9 eV, but contains localized levels both on the conduction band (CB) and the valence band (VB). These levels are numerous and come from 0.3 eV to 2.0 eV under BC and upper BV [1]. They are due to physical and chemical defects in material such as ends of chains, cuts of chains, bends of chains in particular amorphous zones around crystallites and ions. The localized states are called now traps and can contain negative or positive charges following the position in FB. So, the electrical properties of PE are thus strongly linked to these localized states. Today the numerous space charges measurements published for 25 years have allowed us to have a better understanding of PE electrical properties [2], [3], [4], [5].

First, all virgin PE materials, after their making, contain more or less space charges: our experiment has shown that the making process of these materials is fundamental for the components life time [6], [7].

Then the application of DC electric field modifies the space charge distribution with the temperature, time and surrounding.

So, after showing the technique of space charges measurements and the influential parameters of charging, we are going to present these different states of PE materials through some examples: pure polarization, mixed polarization-injection and the dominating injection. Then, we will try to give an "electrical model" of PE.

SPACE CHARGE MEASUREMENTS

Space charges measurements were performed by using the Thermal Step Method "TSM" invented and developed at the University of Montpellier 2 (France) [8]. This technique is based on applying a thermal stimulus on an electrode which is diffusing into the material revealing the space charges contained in the insulation volume. In fact, this technique allows the measurement of capacitive current especially function of the remnant electric field due to the presence of space charge in the material. This is a non-destructive measurement technique for both the material and contained space charges (they are not evacuated during the measurement). With its great sensitivity, this technique allows to follow the evolution of residual electric field for different applied electrical stresses [9].

The principle of TSM in short-circuit conditions has been widely explained before [2, 5]. If we consider a short-circuited sample containing space charge at a temperature T_0 (Fig. 1), the system consisting of the sample, the electrodes and the conducting wire is electrostatically equilibrated. Consequently, influence charges will appear at electrodes.

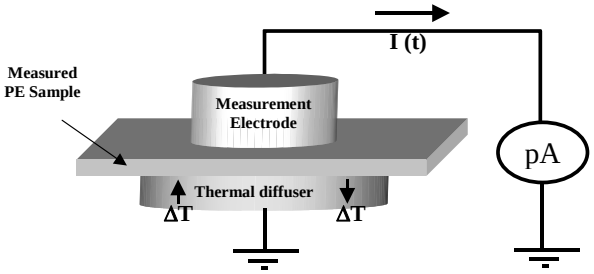

Fig. 1 Principle of the TSM in short-circuit conditions

If a thermal step ΔT is applied close to one electrode (fast cooling or heating), the electrostatic balance of the system is changed. This is due to the contraction (or expansion) of the insulator, which causes a slight and reversible movement of the space charge within the sample, and to the variation of the electric permittivity of the insulator with the temperature. As the system tends to rebalance, the influence charges on the electrodes are redistributed. Hence, charge transport occurs from an electrode to the

other in the external circuit. This corresponds to an external current, given by:

$$I(t) = -\alpha C \int_0^d E(x) \frac{\partial \Delta T(x,t)}{\partial t} dx \qquad (1)$$

where α is a constant of material related to the sample's contraction (or expansion) and to the variation of its permittivity with the temperature, C is the capacitance of the sample, E(x) is the remaining electric field distribution in the sample, and $\Delta T(x,t)$ is the relative temperature distribution in the sample : $\Delta T(x,t)=T(x,t)-T_0$ (T_0 is the temperature of the sample before applying the thermal step).

The current is recorded and then digitally processed in order to find the remaining electric field distribution E(x). Then, by applying the Poisson equation:

$$\rho(x) = \varepsilon \frac{\partial E(x)}{\partial x} \qquad (2)$$

where ε is the permittivity of the insulator, the space charge density distribution can be calculated .

INFLUENTIAL PARAMETERS

We are going to analyze the different influential parameters.

THE TRAPS

The main defects of PE structure are linked to ends, cuts or bends of chains which give localized levels in FB from 0.3 to 2 eV under CB and above VB. It is important to evocate here, the surface structure near electrodes at the contact: the disorder is strong and the traps are numerous and deeper [6, 7]. The distance between traps λ is inferior to the mean dimension of chains: we have some nanometers near contact to ten nanometers in the bulk.

It is admitted that under electric field the charges processing is trap to trap: it is the hopping. The time constant in a trap is: $\tau = \tau_0 e^{[w/(kT)]}$, with w trap energy, T temperature, k Boltzmann constant. The hopping probability per second with an electric field E is then in the direction of the field:

$$p = \frac{2\sinh\left[\frac{Eq\lambda}{2kT}\right]}{\tau} \qquad (3)$$

Taking into account the field effect and the possibility to move in two opposite directions; the decrease of w is $\frac{Eq\lambda}{2}$.

Where q = elementary charge, τ_0 the time constant for w=0, this time constant can be evaluated with λ/v_{th}, v_{th} being the thermal speed of charge: in the case of free electrons this thermal speed is about 10^5 m/s. In the case of quantum effect $\tau_0 = \frac{h}{kT}$ (h = Planck constant). So we can see the value of τ_0 is around 10^{-13} s.

THE CONTACT

If metal is used as contact, then the barrier level φ to CB in PE is superior to 4 eV. With carbon the level can be decreased to 3 eV. In the past it was difficult to admit one charge injection with such levels even by using Schottky or Fowler Nordheim effects.

These effects give the following current density:

For Schottky effect:

$$J_S = A_S T^2 \exp\left(-\frac{\Phi_0 - \beta_S(\gamma E)^{1/2}}{kT}\right) \qquad (4)$$

with $A_S = \frac{4\pi q m k^2}{h^3}$ and $\beta_S = \sqrt{\frac{q^3}{4\pi\varepsilon_0\varepsilon_r}}$

With E = applied electric field ; Φ_0 = energy barrier at the contact; γ: correction factor; γE: real electric field at the contact; T=Temperature.

For Fowler Nordheim effect:

$$J_{FN} = A_{FN}(E_C)^2 \exp\left(-\frac{\beta_{FN}}{E_C}\right) \qquad (5)$$

with $A_{FN} = \frac{q^3}{8\pi h \Phi_0}$ and $\beta_{FN} = \frac{4\sqrt{2m^*}\Phi_0^{3/2}}{3\hbar q}$

With Ec = real electric field at the contact.

But today, no doubts, that these injected charges have really been measured. Using numerous results such as [10, 11], the modeling with Schottky effect uses levels φ about 1.0 - 1.4 eV and a field greater than 10 MV/m, with Fowler Nordheim (tunneling effect) levels about 1.6 -2.0 eV with an electric field greater than 100 MV/m. We rather think of injections using Schottky effect "step by step" in contact zone, each step having an energy level around the order of 1 eV. This zone of transition is several nanometers thick and contains numerous traps at different levels. With this ''theory of stairs'', we can explain the injection. On the other side, the roughness of the contact and the polarization play an important role in increasing the applied electric field. Thus, we have introduced a factor called γ, and then the field at the contact must be multiplied by γ . This number is greater than 1 (polarization, roughness effect), and smaller than 1 just after charge injection which can be stopped then [11].

THE MATERIAL

All PE materials contain more or less space charges after their making. The process making is essential. The presence of ions and the speed of making are essential parameters: fast freezing creates physical defects [6], [7]. We have checked that when there are less space charges after the making, the components life time is longer. The space charges measurement is correlated with the quality of the material. It seems that the linear chains contain less space charges than the ramified ones.

PURE POLARIZATION

PE materials are non polar. But the long chains are polarized under DC electric field. Charges detrapped by the temperature effect have a slight displacement before a new trapping. To obtain a pure polarization, a weak electric field E_a (E_a = 2 MV/m) is applied at 70°C during a short time (few minutes). Then the sample is cooled to room temperature under applied voltage. To measure this polarization the sample in short-circuit is reheated very slowly (2°C/min from room temperature to 110°C) and the thermo-stimulated current is recorded. A current is obtained which reaches a maximum about 80°C. Hereafter, we show an example with a PEBD sample (thickness 200 μm, diameter 30 mm, special electrodes giving no charge injection). The charge is measured by integrating the current: here, the total charge is obtained.

We call N_t the total density of traps, λ the distance between the traps, W the trap energy level, t_f the forming time, L the thickness and S the surface of the sample, T_f the forming temperature. Taking into account equation (1), the accumulated charge ($t_f << \tau_f$) Q_f is [12]:

$$Q_f = N_t q S \lambda \left(\frac{t_f}{\tau_f}\right) 2\sinh\left(\frac{q\lambda E_f}{2kT_f}\right) \qquad (6)$$

Where q is elementary charge, τ_f the time constant at T_f.

Here from the current function of temperature T (Fig. 2), we draw:

Q_f = 100 nC; N_t = 3.0 10^{23} m^{-3}; λ = 15.0 nm, W =1.08 eV, T_m: temperature of the current maximum is 83°C.

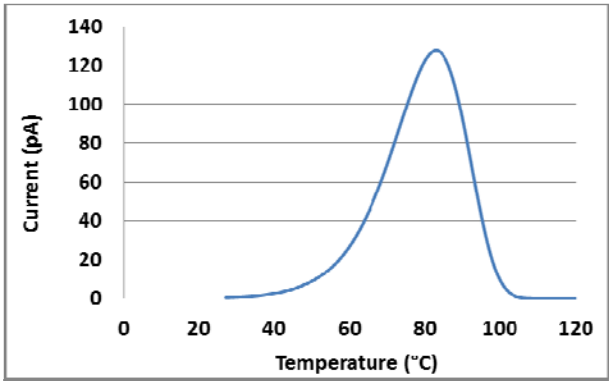

Fig. 2: Thermally stimulated current after pure polarization

The possible interpretation of this experiment is a polarization inside one chain at ends, therefore a mean length of chains λ, and the density of number of chains N_t.

POLARIZATION AND INJECTION

TSM has been used here to determine the values of the remnant electric field and the space charges in the material and close to the electrodes. The space charges are measured to follow up the evolution of the electrical state with different applied voltages.

Thermal step measurements were performed on HPDE sample (thickness 1 mm, diameter 40 mm, aluminium electrodes) with respect to the following applied experimental protocols:

a. Measurements of Electric field and space charge on virgin sample

b. Electrical poling up EF: 5 and 30 kV/mm at 70°C during 40 hours;

c. Short-circuit after each poling during 30 minutes;

d. Electric field and Space charge measurements in short circuit conditions for each applied electric field (Fig. 3 and 4).

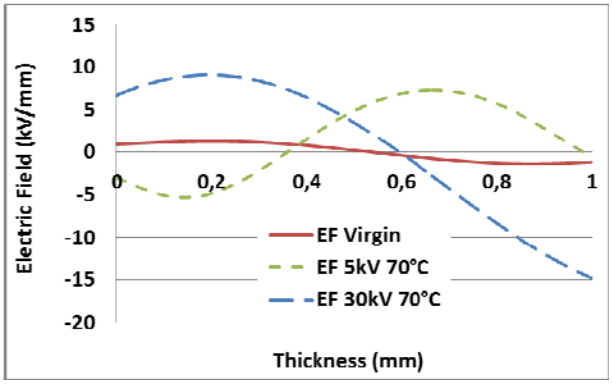

Fig. 3: Electric Field distribution vs. poling conditions

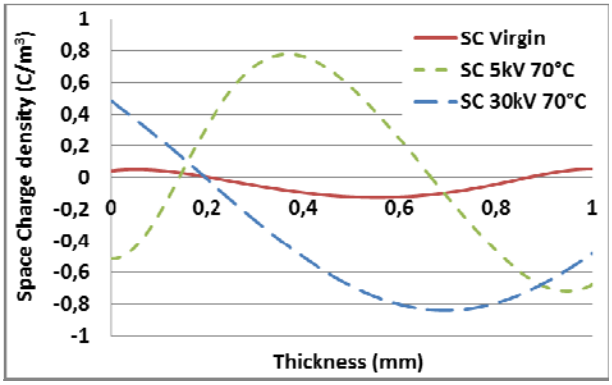

Fig. 4: Space charge density vs. poling conditions

The HDPE sample always shows a high remnant electric field (Fig. 3). From a virgin sample to a charged sample, we can see an important change: at the anode on the left, Fig. 4, charges are positive at virgin state then negative when there is polarization at 5 kV/mm and then positive again due to injection at 30 kV/mm. At the cathode on the right: positive charges at virgin state, then negative charges due to injection at 5 kV/mm and then strong negative charges injected at 30 kV/mm.

The distribution of space charge permits to calculate positive and negative charges respectively Q_+ and Q_-.

Note: In order to compute the total trapped charge Q_T, the values of the remnant electric field at the electrodes are sufficient according to the following expression:

$$Q_T = \varepsilon S\left(E_{Cathode} - E_{Anode}\right) \qquad (7)$$

where S is the surface of the electrode and ε is the dielectric permittivity of the sample. T the TSM has a good precision to calculate these electric fields thanks to the calibration by simple proportion of signal slopes at origin. This means permits to check the deconvolution process of formula (1).

The computed total of charges corresponds to the sum of the positive and negative trapped charges. Q_T close to zero doesn't mean that the sample has not accumulated space charges. This type of approach reveals the dominant trapped charges.

Thus, using fig 4 we have respectively the total positive charges Q_+, total negative charges Q_- and the sum of Q_+ and Q_- named Q_T:

	Q_+ (nC)	Q_- (nC)	Q_T (nC)
Virgin sample	13.8	-68.1	- 54.3
5 kV, 70°C, 40 h	321	-262	+59
30 kV, 70°C, 40 h	61	-610	-549

In conclusion, we can see both polarization and injection states: we measure the dominant phenomenon.

Polarization is always present in the sample: it is at the origin of injection by increasing the field at electrodes, then after injection the electric field decreases: for example at the cathode at 5 kV/mm. At 30 kV/mm, we see a double injection phenomenon.

STRONG INJECTION AND THERMALLY STIMULATED CURRENT

Another example of space charges measurements is obtained with a PE charged at 40 kV/mm during 40 hours. (Dimensions: thickness 0.70 mm, Diameter 40 mm, semiconducting electrodes)

We can see the results on Fig. 5 and 6: Electric field and space charge distributions. Here the dominating charge is positive: a strong charge injection at the anode on the left, a slight injection at the cathode on the right (Fig. 6): the charges are: Q_+ = 331 nC and Q_- = -23 nC

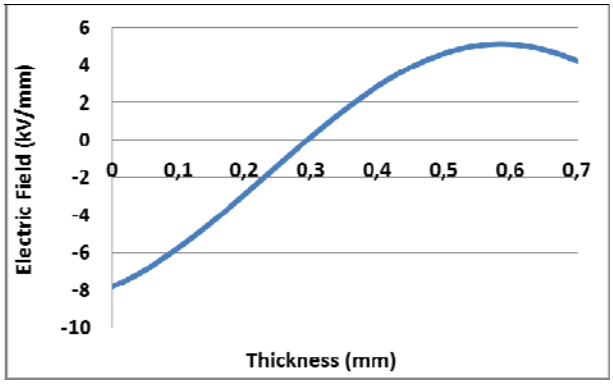

Fig 5 : Electric field after poling at 40 MV/m, 40 hours

We have performed a thermally stimulated current in short-circuit with a rate of 2 degrees per minute (Fig. 7): the current is very weak if we compare with the current of Fig. 2 (I_{max} = 15 pA) and contains several positive and negative variations during the increase of temperature.

In fact the sample is cut into two almost equal parts by the reverse of the electric field. Thus, the discharge current concerns essentially the recombination phenomenon of positive charges by conduction towards the two electrodes: anode and cathode. These two phenomena have the same order of amplitude but the directions are opposite because the two electric fields are opposite. A very slight imbalance gives a positive current linked to conduction, but this current cannot be integrated to give the total charge. This weak current proves that the two opposite effects give a contribution in turn. So, it is a proof of the presence of positive space charges practically in the entire sample.

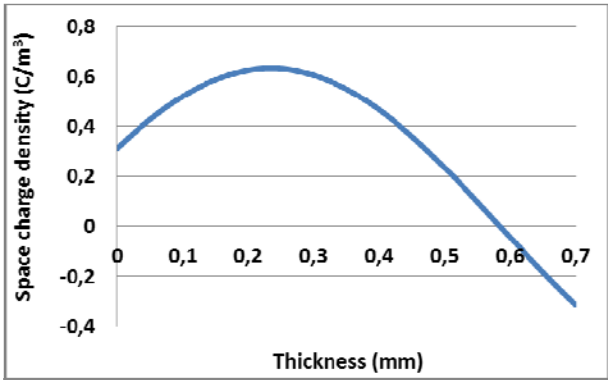

Fig. 6: Space charge measurement after poling at 40MV/m

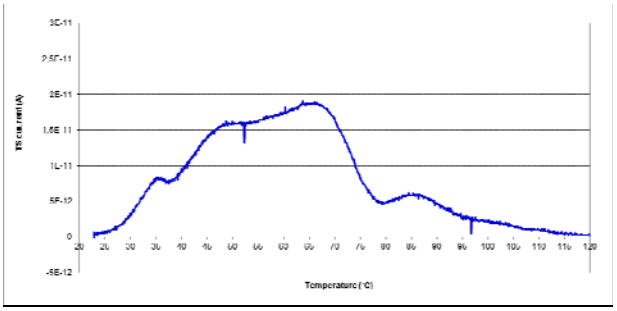

Fig. 7: Thermostimulated current after poling at 40 MV/m, 40 h

CONDUCTION

The current versus voltage curves I=f(V) - measured in quasi-stationary mode allows the identification of the main conduction mechanism in a material. .

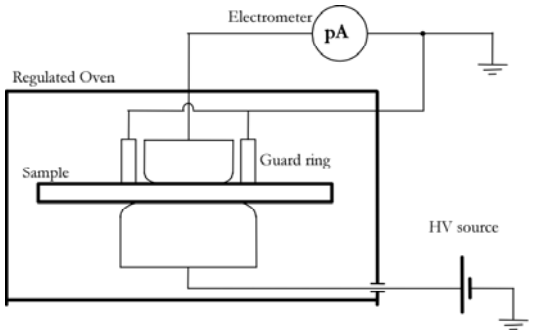

Fig.8: Conduction current measurement set-up

HDPE sample is used here (thickness 1.0 mm, diameter 40 mm, Aluminium electrodes). This sample is the same used in Polarization-Injection (Fig. 3 and 4). We know that we have injection of negative charges up to 5 MV/m at 70°C.

The conduction current measurement set-up (Fig. 8) is composed by an electrometer (Keithley 6517A) and a 35 kV HVDC power supply with low residual ripple of the output voltage (Fug HCP140-35000). Charging and discharging current measurements were investigated for voltages ranging from 3 to 30 kV under 70°C. Steady currents were obtained after the transient regime of polarization or of charging current after 2 hours.

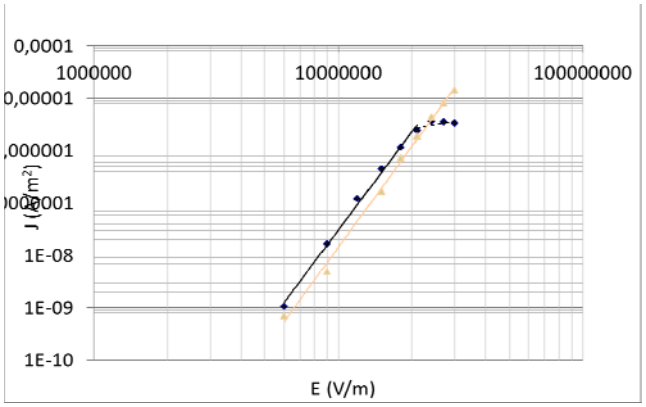

Fig. 9: Current density vs. Applied electric field at 70°C

The results Fig. 9 give experimental conduction phenomena (black curve) and its simulation (yellow curve): J(E) , current density vs applied electric field E is proportional to $E^{6.3}$. This result shows the current is limited by space charges. At the contact the injection is made by Schottky effect, but this here contact does not limit the current and the Schottky effect does not appear. An interpretation is given by an exponential trap density distribution [11], as follows:

$$J(V) = co_1.co_2.\mu.q.N_c.e^{\left[\frac{-W_1}{k.T}\right]}\left(\frac{V}{L}\right)^{(1+1/m)}$$

with $co_1 = \left(\frac{\varepsilon \sin(m\pi)}{qN_{tc}L(1+m)m\pi}\right)^{\frac{1}{m}}$

and $co_2 = \left(\frac{2+m}{1+m}\right)^{\left(1+\frac{1}{m}\right)}$

W_1 is the highest level of exponential density of traps

With μ = mobility; N_c = total density in CB; N_{tc} = total density of traps and ε = permittivitty

V applied voltage, L sample thickness

m = T/T_c : T_c parameter of exponential density of traps

The simulation gives: $N_c = 10^{26}$ m^{-3};

N_{tc} = 9.0 $10^{20}/m^3$; E_1 = 0.3 eV ; m = 0.19 ; 1+1/m = 6.3; T = 343°K

$\mu_0 = 5.0\ 10^{-4}$ $m^2/V.s$

The density of trap is: $d = d_0 e\left[\frac{-(W-W_1)}{kT_c}\right]$ and $d_0 = \frac{N_{tc}}{kT_c}$

T_c = T/m = 1822K; d_0 = 3.57 10^{40} $J^{-1}.m^{-3}$;

The exponential distribution of traps permits a continuous injection.

This result is in accordance with distribution given by Meunier and Quirque [1]: 0.3 eV < W < 2.0 eV.

The space charge density is less than 1 C/m^3 (Fig. 4) at 30 MV/m, corresponding to N_t number of full traps density less than 10^{19} m^{-3} (N_{tc} is 9.0 10^{20} m^{-3}).

CONCLUSION

This paper presents results in different electrical states in PE materials: pure polarization, mixed polarization and injection, dominating injection, then conduction. These results are interpreted by hopping processes from traps to traps and the development of space charges inside the samples. It appears that the defects of structure are fundamental to the development of space charges. In the case of pure polarization, with a very low electric field, we measure a hopping process inside the chain without passing by the conduction band: we have a molecular polarization and N_t is the bulk density of the chains, linked to the dimension of chains. In the case of injection and conduction phenomena we measure the trap density linked to a hopping process passing by the conduction band. Then $N_{tc} < N_t$, the traps which contribute to the conduction are not in all chains. The conduction band is more developed in ordered regions.

Today, studies are performed at different levels: materials, plaques, model cables, full size cables. We have proposed on site measurements [13] with the TSM. In fact, the complexity to obtain good models for PE materials requires a tight collaboration between industrial and university researchers.

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