Annealing Effect on the Conductivity of XLPE Insulation in Power Cable

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ABSTRACT

Conductivity (σ) in XLPE insulation of power cables annealed at 90 ºC at temperatures between 50 and 97 ºC has been measured. In all cases there is an initial increase in conductivity that develops a maximum and finally decreases for long annealing times. This maximum appears in the sample annealed 20 days when conductivity is measured at 50 ºC and shifts gradually to higher annealing times up to 40 days when the measurement is performed at 97 ºC. A linear behavior of *ln*(σ) versus $T^{-1/4}$ is observed, which implies that the transport mechanism is basically via thermally assisted hopping conduction. Infrared spectroscopy indicates that, during annealing, some chemical species diffuse from the semiconducting shields (SC) into the XLPE. Thermally stimulated depolarization currents technique (TSDC) and intensity-current measurements (I-V) point out as well the presence of this diffusion process that becomes less significant after long annealing times. The initial increase in σ is explained in terms of the increase in traps density due to the diffusion process from the SC shields. Long term decrease in σ is justified by the observed decrease of diffusion rate for long annealing times.

Index Terms — **Conductivity, polyethylene, space charge, Cable insulation, XLPE**.

1 INTRODUCTION

POLYETHYLENE (PE) is a non-polar polymer. It is found in semi-crystalline state at room temperature. In industrial applications, crosslinked PE (XLPE) is commonly used as an electrical insulator due to its outstanding insulating characteristics and its low price. It is well known that PE conductive properties are conditioned by its morphology [1-3] and that insulation degradation can be related to volume space charges [4]. Particularly, conduction and space charge formation in low-density PE were studied including the interval of temperatures of interest for cable diagnostics [5].

Current versus voltage (I-V) characteristics studied in LDPE by Stetter [6] at 42, 82 and 110 ºC, indicate that for low electric fields (E) an ohmic behavior is observed; for

higher electric fields, conduction can be interpreted on the basis of a quadratic law in E which depends on temperature and reveals the existence of traps. More recently, several authors have also observed that current-voltage characteristics in PE can be explained by the theory of space-charge-limited currents model (SCLC) [7]. Nath et al. [8] apply the band theory to LDPE by developing a mathematical model based on the hopping of carriers which are injected into amorphous regions. They consider a SCLC and a process of charge-trapping at amorphous-crystalline boundaries. In addition, they suppose that the density of trapping centers is high enough so that the interaction between them results in an effective lowering of trap depth (Poole-Frenkel effect). In this latter model, the distance between traps parameter is introduced and it has a constant value. Even more recently, following the same research theme, it is concluded that electronic transport is bound to

_cri_ermally activated hopping, which is assisted by electric

field with very low activation energy [9]. Recent studies of our research group have deal with conductivity in XLPE cable samples measured by the absorption resorption current method (ARC) [10]. These studies revealed that conductivity is highly influenced by the thermal treatment of the samples in the presence of the cable semiconducting shields (SC), and it is based on a hopping process.

The presence of crosslinking by-products and other components diffused from the SC shields into the XLPE cable can promote this hooping process. Infrared spectroscopy (IR) has been widely used in identifying these components as well as the oxidation phenomena in XLPE [11-15]. The major by-products of thermo-oxidative processes are carbonyl groups that show absorbency peaks at 1741 cm^{-1} (aldehyde absorption) [16-19], 1635 cm^{-1} (vinylene absorption), 966 cm^{-1} (transvinylene absorption) [13, 16, 17] as well as hydroxyl groups (-OH) with absorbency peaks at 3300 cm^{-1} and 3500 cm^{-1} [17]. Crosslinking by-products such as acetophenone and cumyl alcohol can also be monitored by IR, with absorbency peaks at 953 cm^{-1}, 766 cm^{-1}, 700 cm^{-1}, 860 cm^{-1} and 1170 cm^{-1} for Cumyl alcohol [20], and 1695 cm^{-1}, 1263 cm^{-1}, 1360 cm^{-1}, 761 cm^{-1} and 690 cm^{-1} for acetophenone [20; 21]. Bamji et al [22] also attributes to acetophenone some contribution to the 1305 cm^{-1} absorption peak, usually associated with the amorphous fraction of XLPE [23]. Acrylate species and other components are shown to diffuse from the SC shields into the XLPE with thermal aging [15, 24]. These components can be identified as well by IR measurements as they show absorbency peaks at 1736 cm^{-1} [23].

Thermally stimulated depolarization current technique (TSDC) has been applied to XLPE cable electrets [24; 25]. A broad current peak can be observed at 105 ºC, which has been associated with charge in the crystalline volume [25]. The combination of TSDC and infrared spectroscopy (IR) studies [24] proved that annealing procedures in mid voltage cables lead to the diffusion of components from the SC screens into the XLPE insulation bulk. Moreover, the defects associated with diffused particles act as trapping centers of charge injected from the electrodes. This process is clearly promoted at temperatures above a critical temperature approximately equal to 80 ºC. Annealing at these temperatures reverses the polarity of TSDC spectra (from heteropolar to homopolar). Further annealing results in new current polarity inversion, and the current regains its heteropolar character [25].

The aim of the present work is to obtain further experimental results concerning conductivity in cable XLPE insulation in order to better understand conductive processes in this system. The study has been carried out directly in cable samples to better reflect the behavior of the whole system at service. Following this purpose, several cable samples were annealed at T_a=90 ºC for different times between 0 and 90 days and an effective conductivity related to the system (σ), TSDC spectra and infrared spectroscopy (IR) was measured.

2 EXPERIMENTAL

Cable was supplied by General Cable S.A. and consisted of a cylindrical insulating XLPE layer with 7 and 13 mm of inner and outer radii, respectively. The samples had two 1 mm thick semiconducting shields (SC) in contact with the inner and external surfaces of XLPE. The insulating material was crosslinked mixing low density PE with a crosslinking agent (di-t-butyl peroxide) and heating it up to a temperature higher than 200 ºC to produce a vulcanization reaction. The semiconducting shields are EVA based copolymer and includes, among other components, acrylonitrile (ACN). Some partial degassing process was carried out directly during cable manufacture. As received 1 m long cable sections were kept in our laboratory at room temperature previous to annealing and measurements. Annealing processes have been carried out on 7 cm long sections cut from as received cables. A new sample was used in each measurement in order to avoid the effects of previous measurements.

2.1 ARC MEASUREMENTS

Samples for absorption resorption current measurements (ARC) consisted in 7 cm long sections cut from the cable. A 2 mm guard electrodes were prepared at each end of cable sample in order to avoid the effect of surface conductivity and to avoid the dispersion of the field lines. In this method the sample is subjected to a charging process applying a polarizing voltage U during a period of time t_{ab} while the absorption current I_a is measured. After a time t_{ab} the electric field is switched off and the resorption current I_r is measured. If we measure the absorption current for a time t_{ab} big enough as the response of dipole polarization is almost zero, conductivity (σ) may be obtained approximately, for any time $t<t_{ab}$, by equation: [26, 27]

$$\sigma = \frac{\varepsilon_0}{C_0 U}[I_a(t) + I_r(t)] \qquad (1)$$

where C_o=4.4 pF is the geometrical capacitance of the sample (determined by a Hewlett-Packard impedance analyzer model HP-4192a LF), $I_a(t)$ and $I_r(t)$ are the absorption and resorption currents (ARC) measured at a time t after the absorption part or after the resorption part of the experiment starts respectively, U is the voltage applied to each cable sample and ε_o is the vacuum permittivity. Equation (1) provides a convenient way to obtain σ because measurements require less time to be performed than with the usual current-voltage characteristics method since there is no need to reach a stationary current.

XLPE cable samples were placed in a measuring cell inside a Carbolyte type PF60 oven. A K-type thermocouple (Keithley 6517-TP) placed inside the insulation of another identical sample (which was located close to the sample under test) was used to measure the sample temperature. The dc voltage source of a Keithley 6517A electrometer was used to polarize the samples. To measure the absorption

current a voltage of 1 kV (corresponding to a mean field of 0.22 MV/m) was applied to the inner electrode of the samples and the outer electrode was grounded through the aforementioned electrometer. After a period of time t_{ab}, the inner electrode was switched to ground and the resorption current was recorded. The charging period t_{ab} (absorption current) was 2000 s. Resorption currents were measured over a period of 1000 s in order to improve accuracy in the determination of σ by equation (1).

2.2 TSDC MEASUREMENTS

Samples for TSDC measurements consisted in 7 cm long sections cut from the cable. The semiconducting shields (SC) were used as electrodes. To avoid shortcircuits, the external SC was partially removed from the sample ends. This left a 2 cm wide semiconducting strip centered in the sample. The cable core of twisted aluminum wires was used to make contact with the inner SC. The contact with the outer SC was made by an adjustable metallic clamp.

The experimental setup for TSDC consists of a Heraeus forced air oven controlled by a Eurotherm 902 PID temperature programmer. Inside, two identical cable samples were placed close together in parallel position. One of them was used to host the temperature probe inside the insulating layer, and TSDC measurements were performed on the other one. To polarize the sample, the cable core was positively biased with a Brandenburg 807R (3-30 kV) potential source whereas the outer electrode was grounded. In this way, potentials up to 20 kV can be applied to the sample. Once the polarization stage was finished, the external semiconducting layer was connected to a Keithley 6514 electrometer and the cable core was grounded.

Sample polarization was performed by the NIW method. In this method the potential V_p is applied, during a cooling ramp, at a polarization temperature T_p and removed when the sample reaches a temperature T_f in the same cooling ramp. In all cases the heating rate was 2.5 ºC/min whereas the cooling rate was 1 ºC/min.

2.3 FTIR AND DSC MEASUREMENTS

Fourier transform infrared (FTIR) measurements were performed with a Nicolet 510M spectrometer on 6x6 mm XLPE sheets. Samples 300 μm thick were cut directly from the cable by mechanical methods at different depths from the external surface. The melting range of temperatures of the XLPE insulating layer was measured by DSC with a DSC-20 calorimeter controlled by a Mettler TC11 processor. Measurements were performed in 10 mg XLPE samples cut from the cable and sealed in aluminum pans.

Weight loss measurements were performed in a 7 cm cable section by means of an analytical balance Mettler Toledo AG245. The cable sample were annealed at 90 ºC up to 110 days in the same oven used for TSDC measurements.

3 RESULTS AND DISCUSSION

3.1 CONDUCTION MECHANISM

Stationary conductivity (σ) of cable samples measured by ARC at temperatures (Tm) between 50 and 97 ºC are plotted in Figures 1 and 2 as a function of annealing time (t_a) at 90 ºC. All curves show a maximum in conductivity that appears for t_a around 15 days at the lower measuring temperatures (50 and 60 ºC, Figure 1). This maximum becomes more noticeable when T_m increases, and shifts towards higher annealing times, up to 30 days when T_m =97 ºC (Figure 2).
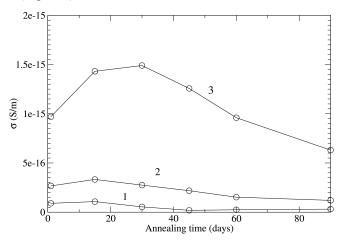

Figure 1. Conductivity in XLPE cable insulation versus annealing time at 90 ºC (1: T_m=50 ºC, 2: T_m=60 ºC and 3: T_m =72 ºC.
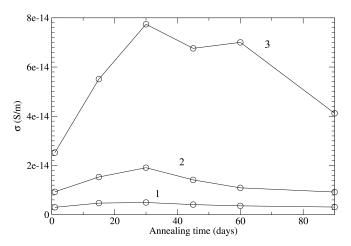

Figure 2. Conductivity in XLPE cable insulation versus annealing time at 90 ºC, measured at: (1) T_m=78 ºC, (2) T_m =90 ºC and (3) T_m =97 ºC.

The increase in σ, observed in all cases with a maximum for annealing times around 20 days, is probably due to the presence and diffusion through the insulation of crosslinking by products present in the XLPE bulk, and/or by chemical components diffused from the semiconducting shields. This fact generates internal charge and trapping centers that enhance σ.

To analyze the contribution of hopping mechanisms to σ, we have represented in Figures 3 and 4 the experimental results as a Mott plot (ln σ_H versus $T^{-1/4}$), where σ_H is the contribution to conductivity of the hopping mechanism between traps in the cable sample. σ_H is related with σ by $\sigma_H = \sigma - \sigma_{EX}$ were σ_{EX} is the contribution to conductivity by extended states. A value of $\sigma_{EX}=1.65\times10^{-17}$ S/m has been used according to previous works [10].
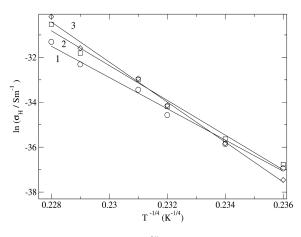

Figure 3. Mott plot of ln(σ_H) versus $T^{-1/4}$ (1: t_a=1 days, 2: t_a =15 days, 3: t_a =30 days).
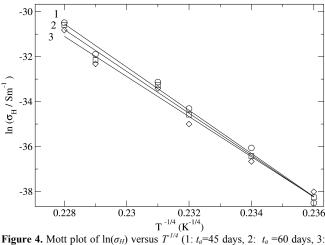

Figure 4. Mott plot of ln(σ_H) versus $T^{-1/4}$ (1: t_a=45 days, 2: t_a =60 days, 3: t_a =90 days).{ TC "4 Mott plot of ln(EQ σ\s\do5(H)" \l 1 }

A linear behavior of $ln(\sigma_H)$ versus $T^{-1/4}$ can be estimated from these figures, which implies that the transport mechanism is basically via thermally assisted hopping conduction [28]. Hill [29] also found a similar relation between conductivity and annealing temperature, by considering a field-assisted hopping conductivity at the limit of low electric fields, which is evidently one of the important experimental conditions observed in our present work. This good agreement between data and the aforementioned law is more evident for long annealing times.

Croslinking by-products are known to be volatile and can disappear for long annealing times. Although some degassing process was performed directly at the factory during cable manufacture, the process is not completed and can certainly affect the conductive properties of the material.
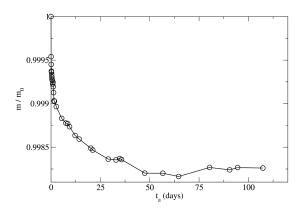

Figure 5. Weight loss in XLPE insulation versus annealing time at 90 °C.

This fact, however, probably is not the explanation of the observed maximum in conductivity versus annealing time, as the following experimental results suggest; Measurements of weight loss versus time during annealing can inform us about the presence and elimination of crosslinking by-products in cable samples. Figure 5 shows these measurements in a 7 cm long cable section annealed at 90 °C up to 110 days. It must be noted that weight measurements were performed in full cable sections to reproduce as close as possible annealing conditions of the ACR experiments. We can see that weight loss is very fast at the beginning (in the first hours) and sample mass becomes almost stable for 30-40 days of annealing. In addition, measurements of σ in annealed XLPE cable with and without SC shields carried out in a previous work [10] also indicated that the the presence of the SC shields is decisive in the behavior of this magnitude. In those measurements, annealing up to 400 h at 90 °C with the SC shields resulted in increments in σ up to five times the value obtained when annealed without the SC shield. These results suggest that the presence and diffusion of croslinking by-products is not the main reason of the observed maximum in σ, however, long term diffusion of acrylate species and other components from the SC shields into the XLPE [15, 24] can explain this behavior.{ TC "5 Weight loss in XLPE insulation versus annealing time at 90 EQ \s\up5(o)" \l 1 }

Assuming that conductivity in XLPE is associated with a hopping mechanism, as the Mott plot suggests (figures 3 and 4), we can adequately explain the observed change in σ after long annealing times as follows; In the hopping mechanism, the energy difference and the distance between traps should modulate the whole process. If we take into account a possible diffusion of components from the SC shields into the XLPE bulk (as previous works suggest [24], annealing should promote an increase in conductivity because of the increase in traps density. This phenomena can explain the increase in σ observed for annealing times up to 30-40 days. The observed decrease in σ for long annealing times can be produced by the decrease of diffusion from the SC shields. Once this diffusion from the SC shields is almost exhausted, further annealing results in

the progressive decrease of the total diffused component concentration in the insulation and consequently in conductivity. In this way points out as well σ and DSC measurements performed in the external SC shield annealed at 120 ºC up to 700 h (not plotted). These measurements showed that SC conductivity at 90 ºC gradually decreases with annealing and stabilizes after 62 h annealing. No degradation is observed in the SC shields by DSC measurements in these treatments. This result is compatible with the assumption that the SC shield loose some kind of electrically active component with annealing.

3.2 FTIR MEASUREMENTS

To corroborate this assumption, Fourier Transform Infrared measurements (FTIR) were performed at different depths in the XLPE insulation of as received cable and cable annealed up to 93 days at 90 ºC. As discussed above (see introduction) this technique is well suited to follow XLPE degradation, to detect the presence of crosslinking by-products, as well as to identify acrylate species and other possible components diffused from the SC shields into the XLPE bulk. Measurements were performed in four layers cut from the insulation surface down to 1.2 mm depth (layer 1: XLPE surface in contact with the SC shield, layer 4: XLPE at 1.2 mm depth).
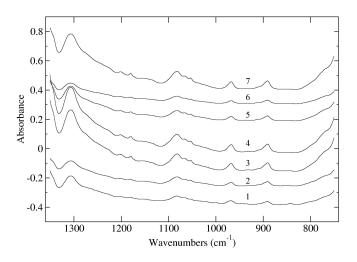

Figure 6. FTIR spectra of layer 2 (0.4 mm depth) XLPE insulation for different annealing times (1: t_a =1 days, 2: t_a=15 days, 3: t_a =30 days, 4: t_a =45 days, 5: t_a =60 days, 6: t_a =90 days).

As an example of the obtained spectra, figure 6 and 7 show the measured curves in layer 2 for different annealing times. No clear presence of acetophenone nor cumyl alcohol peaks (953 cm⁻¹, 766 cm⁻¹, 700 cm⁻¹, 860 cm⁻¹, 1170 cm⁻¹, 1695 cm⁻¹, 1263 cm⁻¹ , 1360 cm⁻¹, 761 cm⁻¹ and 690 cm⁻¹) can be detected, although we must take into account some resolution limitations in these measurements. Traces of acrylate species and other components with peaks at 1736 cm⁻¹ can be detected in the curves but does not show clearly, in part because of the proximity to the carbonyl group peak at 1741 cm⁻¹ related to oxidation processes (see introduction for details and references).

We will focus our analysis of FTIR results in two indexes evaluated to obtain quantitative information on the thermo-oxidative degradation; the carbonyl band at 1741 cm⁻¹ (aldehyde absorption) and the double band index at 1635 cm⁻¹ (unsaturated groups). Intensities of both peaks have been evaluated relative to the crystalline XLPE band at 1898 cm⁻¹. Possible presence of crosslining by-products have also been analyzed with the 1305 cm⁻¹ absorption peak, to which Bamji et al [22] associates some contribution of acetophenone groups.
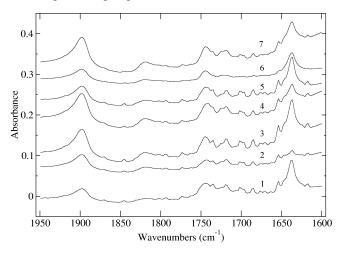

Figure 7. FTIR spectra of layer 2 (0.4 mm depth) XLPE insulation for different annealing times (1: t_a =1 days, 2: t_a =15 days, 3: t_a =30 days, 4: t_a =45 days, 5: t_a =60 days, 6: t_a =90 days).

Tables 1, 2, 3 and 4 show the relative intensities of these peaks in the four analyzed layers after different annealing times. As a general trend, for a given layer no evolution in any absorbency peak can be established. This result indicates that oxidation does not take place during annealing at 90 ºC. No sign of acetophenone contribution can be clearly established either. Comparing layers to each other, a slight decrease in the carbonyl and double band indexes is observed as we measure deeper in the XLPE bulk. Figure 8 show the relative absorbency of these two peaks (related to thermo oxidative processes) averaged in the seven measurements performed in each layer. The observed decreasing behavior indicates that oxidation is higher in the external surface of the cable and decreases towards the internal surface. These oxidation processes toke place probably during the manufacturing process.

3.3 TSDC AND I-V RESULTS

TSDC is a complementary technique that can be used to study injection and charge trapping in dielectrics. Figure 9 shows the TSDC spectrum obtained by the NIW method (see experimental section for details) of a sample annealed for 2 h at 140 ºC. We can observe a homopolar peak at 105 ºC under some polarization conditions. It is remarkable as well that only if the sample is previously annealed (in this case 2 h at 140 ºC) the homopolar response appears. This fact was demonstrated by similar TSDC measurements in as

received samples (not plotted) that did not develop a homopolar response in any case.

Table 1. FTIR indexes. Layer 1 (300 μ*m* depth).

Sample	acetophenone Index ($I_{1305/1898}$)	Carbonil Index ($I_{1741/1898}$)	Double band Index ($I_{1635/1898}$)
As received	3.16	1.51	5.67
1 days at 90 ºC	2.20	1.49	4.21
14 days at 90 ºC	1.22	1.28	2.83
30 days at 90 ºC	1.31	1.33	2.84
45 days at 90 ºC	2.11	0.64	1.83
60 days at 90 ºC	2.01	1.98	3.70
75 days at 90 ºC	1.50	1.41	3.05
92 days at 90 ºC	2.32	1.51	3.05

Table 2. FTIR indexes. Layer 2 (600 μ*m* depth)

Sample	acetophenone Index ($I_{1305/1898}$)	Carbonil Index ($I_{1741/1898}$)	Double band Index ($I_{1635/1898}$)
As received	3.9	0.15	3.77
1 days at 90 ºC	3.37	0.73	2.53
14 days at 90 ºC	1.92	0.36	0.54
30 days at 90 ºC	2.94	0.47	1.25
45 days at 90 ºC	3.17	0.40	0.64
60 days at 90 ºC	2.67	0.65	1.91
75 days at 90 ºC	2.03	0.63	1.67
92 days at 90 ºC	2.23	0.43	0.75

Table 3. FTIR indexes. Layer 3 (900 μ*m* depth).

Sample	acetophenone Index ($I_{1305/1898}$)	Carbonil Index ($I_{1741/1898}$)	Double band Index ($I_{1635/1898}$)
As received	3.93	0.05	2.13
1 days at 90 ºC	2.31	0.33	0.61
14 days at 90 ºC	2.52	0.43	0.93
30 days at 90 ºC	2.03	0.42	1.45
45 days at 90 ºC	1.70	1.55	3.50
60 days at 90 ºC	2.95	0.41	0.54
75 days at 90 ºC	1.73	0.48	0.80
92 days at 90 ºC	3.09	0.30	0.43

Table 4 FTIR indexes. Layer 4 (1200 μ*m* depth).

Sample	Acetophenone Index ($I_{1305/1898}$)	Carbonil Index ($I_{1741/1898}$)	Double band Index ($I_{1635/1898}$)
As received	2.25	0.06	0.46
1 days at 90 ºC	2.04	0.14	0.43
14 days at 90 ºC	3.55	0.25	0.36
30 days at 90 ºC	2.48	0.31	0.67
45 days at 90 ºC	2.35	0.41	0.64
60 days at 90 ºC	3.24	0.37	0.62
75 days at 90 ºC	1.67	0.31	0.33
92 days at 90 ºC	2.40	0.45	0.72

These results are compatible with the hypothesis that impurities, diffused from the SC into the XLPE during annealing, probably act as trapping centers during the polarization process that may contribute to the homopolar peak formation. A noticeable fact is that this homopolar response appears only when the polarization field is 'on' below 87 ºC.

In the cooling ramp, the material starts from the melt state and is approximately between 90 and 85 ºC when significant crystallization starts. This result suggest that charge trapping occurs probably in the amorphous-crystal interphases.
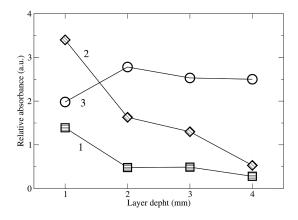

Figure 8: Absorbency of 1: carbonyl band (1741 cm^{-1}), 2: double band index (1635 cm^{-1}) and 3: 1305 cm^{-1} absorption peaks relative to XLPE band at 1898 cm^{-1}, averaged in the seven measurements performed in each layer.
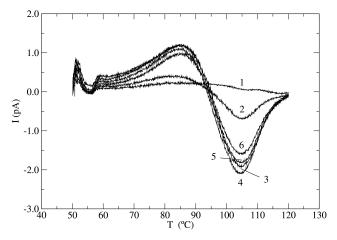

Figure 9. NIW-TSDC of cable annealed 2 h at 140 ºC (T_p=100 ºC, V_p =10 kV; 1: T_f=90 ºC, 2: T_f=85 ºC, 3: T_f =75 ºC, 4: T_f =70 ºC, 5: T_f =60 ºC, 6: T_f =50 ºC).

Additional information on charge trapping processes can be obtained by intensity-voltage (IV) measurements [30]. These measurements were carried out in as received cable samples at 50 ºC in the 1-16 kV range. 12 cm long cable samples were used for these measurements. Figure 10 shows the obtained results. A clear behavior change is seen for voltages around 12 kV, which has been also observed by other groups on similar materials [31-33]. Two different linear dependences can be established in this case below and above this value. We can understand this evolution assuming that for low applied fields conductivity is governed by a thermally activated hopping mechanism (as stated above) and the first linear dependency results. While applied voltage increases, injected excess charge dominates over thermally generated carriers and conductivity approaches the trap-filling transition, with a

sudden increase in intensity previous to the space-charge-limited regime (that is not reached in our measurements). The linear dependence obtained in this region, with a linear coefficient greater than 2, indicates an exponential distribution of the abovementioned trapping centers [34].
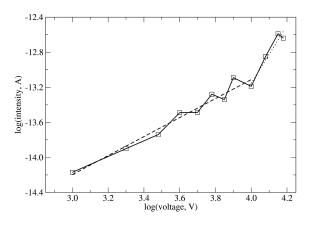

Figure 10. Log (I) versus log(V) of as received cable.

4   CONCLUSIONS

Conductivity in XLPE cable insulation at low fields is associated with a thermally assisted hopping mechanism, so that the energy difference and the distance between traps modulate the process. In this case a temperature dependence given by Mott's law results. Diffusion of impurities from the SC shields into the XLPE occurs during the manufacturing process, and continuously during annealing at 90 ºC (cable working temperature). These defects may act as trapping centers of charge injected from the electrodes and are responsible of the observed increase in σ. For long annealing times (30 days and above) diffusion from the SC shields into the XLPE bulk decreases and conductivity tends to decrease as well. This evolution explain the maximum observed in σ versus annealing time curves. Results obtained in I-V curves are compatible with this model and show the presence of a sudden increase in conductivity when the material approaches the traps-filled-limit. Space charge limiting flow (SCLC) is the main conduction mechanism in this case.

ACKNOWLEDGMENT

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