Ageing of underground power cables: species migration from semi-conductive layers to the insulating layer

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Abstract- **Medium voltage underground cables were aged in air at temperatures between 70°C to 140°C. The changes of the structural properties of the crosslinked polyethylene (XLPE) insulating layer were characterized by physico-chemical techniques: Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FTIR). The performed analyses revealed chemical ageing (oxidation, chemical consumption of additives, post-crosslinking…) and physical ageing (migration of chemical species). The accelerated thermal tests on stripped XLPE samples showed, as expected, a mild oxidative degradation. In contrast, ageing tests conducted in the presence of the semi-conductive layers revealed a striking difference, with a migration of extra carbonyl species into the XLPE insulation.**

I. INTRODUCTION

Underground power cables are constituted of a coaxial system consisting of a central conductor, made of copper or aluminum, surrounded by a polyethylene insulation system. The insulating layer is encapsulated by two semiconducting layers [1], which have, among others, the role of reducing field effects. To evaluate cables lifetime, the ageing of each constituting layer should be studied, particularly the insulation layer which is subjected to electrical breakdown.

Due to its good dielectric and thermal performances [1], cross-linked polyethylene (XLPE) is the main insulating material in medium and high voltage for underground cables. During cables operation services, the insulation is subjected to temperature, high electric field, moisture and mechanical stresses. The cable temperature can routinely reach 70 to 90°C in normal operation, with possible peaks up to 150°C or more in case of overloads or short-circuits [2-3].

The semiconductive shields adjoined to the cable insulation are generally made of extruded polymers containing fillers such as carbon black. In order to bring both flexibility and chemical inertia, carbonyl-PE copolymers are generally used such as EBA (poly(ethylene butyl acrylate)) or EVA (poly(ethylene vinyl acetate)) [1, 4].

During the past 35 years, electrical and thermal ageing of XLPE materials have been largely investigated. However, very few literature data relates the ageing behavior of the XLPE surrounded by its semi-conductive layers, i.e. a more realistic ageing condition. In this paper, thermal ageing studies of both stripped XLPE and non-stripped XLPE layers were conducted with the help of DSC and FTIR physico-chemical characterizations.

The aim of this comparative study is to clearly unravel the mechanism of ageing of the dielectric layer when placed in its real functional environment.

II. MATERIALS AND METHODS

Samples preparation: Three types of samples (noted E, E_{sc1} and E_{sc2}) have been prepared from a commercial medium voltage XLPE cable, representative of the French electrical power underground network, i.e.:
- Type E: both semiconductive layers were mechanically removed;
- Type E_{sc1}: only the outer semiconducting layer was removed;
- Type E_{sc2}: both inner and outer semiconducting layers were kept in place.
Before analysis, the cable was cut into a series of pieces with a thickness of around 0.5-1 mm.
Ageing conditions: The cable pieces were thermally aged in air at four temperatures (70, 90, 110 and 140°C), using an universal MEMMERT lab oven.
Instrumentals: Infrared (IR) spectra were recorded at room temperature with a Perkin Elmer Spotlight 400 spectrometer using a collection of 32 scans. Both transmission and reflection modes were used for respectively translucid insulator and opaque semiconductor samples. Transmission analyses were carried out on 0.5-1 mm thin insulation films, with a resolution of 1 cm^{-1} in the 400 to 4000 cm^{-1} range. The spectra were normalized using the 2020 cm^{-1} peak, corresponding to CH_2 bonding of the crystalline phase of XLPE, and which is often used as thickness correction band. Attenuated total reflectance (ATR) mode spectra were obtained using a ZnGe crystal in the 600 to 4000 cm^{-1} range with a resolution of 4 cm^{-1}.

Melting point temperatures (T_m) were measured using a Perkin Elmer series 7 differential scanning calorimetry (DSC). The instrument was calibrated with high purity indium and zinc as calibration standards, and the baseline was kept when the change in enthalpy was found bellow 1 J.g^{-1} over the temperature range. Polymer specimens between 5 to 10 mg were precisely weighted and crimped in non-hermetic aluminum pans. For each specimen, the following procedure was used:-Heating from 30 to 160°C-Holding 2 min-Cooling from 160 to 30°C-Holding 2 min-Heating from 30 to 160°C. All steps were carried out at 10°C.min^{-1} under nitrogen flow (50 mol.min^{-1}). For initial samples, the second heating thermogram is always shown to eliminate the thermal story and obtain a good evaluation of initial values of thermal parameters. In the case of aged samples, the first heating thermogram is shown.

III. RESULTS AND DISCUSSIONS

A. Initial characterization of insulating and semiconducting layers.

FTIR spectra of the insulating material and the two semiconducting layers allowed us to observe the main peaks corresponding to polyethylene: C-H stretching and deformations of CH_2 and CH_3 groups. Regarding the semiconducting layers, two additional carbonyl peaks were observed at 1733 cm^{-1} and 1168 cm^{-1}, respectively attributed to C=O and C-O stretching from EBA type copolymers [5].

Additional transmission FTIR performed on PE thick films also put into focus numerous small interesting peaks:
- Peaks corresponding to dicumyl peroxide byproducts originating from a XLPE crosslinking reaction: acetophenone (1694 cm^{-1} and 1242 cm^{-1}) and cumyl alcohol (952 cm^{-1}) [6];
- Peaks corresponding to antioxidants: hindered phenol antioxidants (1740 cm^{-1}, 3600 cm^{-1} and 3650 cm^{-1}), phosphorous antioxidants (850 cm^{-1}) [7, 8];
- Peaks attributed to structural defects: vinyl group R-C=CH_2 (909 cm^{-1} and 1640 cm^{-1}), vinylidene group R_1R_2-CH=CH_2 (888 cm^{-1}) and trans-vinylene group -CH=CH- (965 cm^{-1}) [6, 9;
- Carbonyls and hydroxyls species due to oxidation during processing: alcohols (3300 to 3600 cm^{-1}), ketones (1720 cm^{-1}) and carboxylic acids (1709 cm^{-1}) [6, 8, 9].
This allowed to conclude on the qualitative formula of the insulator layer, i.e. an XLPE obtained by dicumyl peroxide, and the use of phosphorus and high hindered phenolic antioxidants as stabilizers.

DSC measurements concerning the XLPE insulation layer, the inner and the outer semi-conductive layers are shown in Fig 1. The XLPE material shows a melting peak at 105°C, as expected for a XLPE derivative [3]. The DSCs of the inner and outer semiconductive layers show a large melting point between 50°C and 90°C, which is in accordance with EBA copolymers.
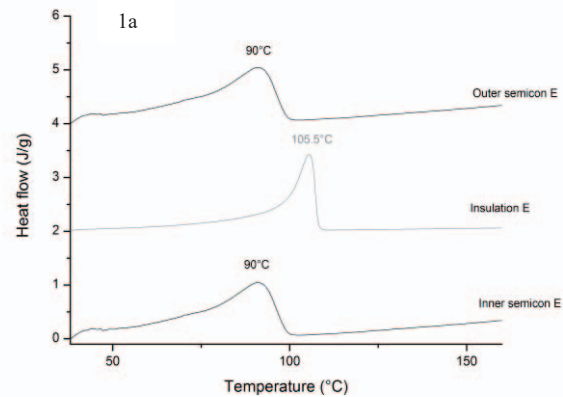

Fig. 1. DSC thermograms of semiconductive and insulation layers.

The IR and the DSC both confirmed that the inner and the outer semiconductive layers were made of the same material. It was also noticed that the used XLPE and EBA possess a large population of crystallites. The smallest crystallites of these materials have relatively low T_m values (between 30°C and 70°C), leading us to suspect an impact at temperatures normally reached during operation service.

B. Thermal ageing of the XLPE constituting the insulating layer alone.

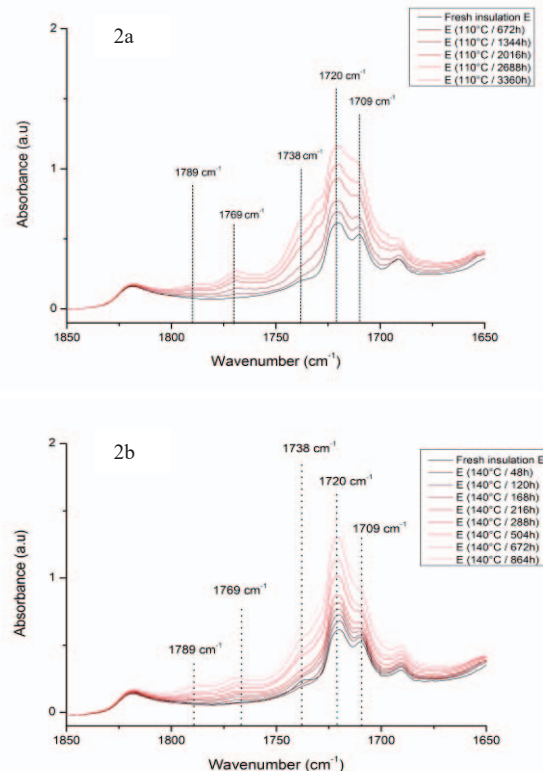

Fig. 2. FTIR spectra of insulation aged at a) 110°C b) 140°C.

FTIR analysis can be used to determine the structural changes in XLPE after thermal ageing. A special care should be focused on the carbonyl zone between 1650 cm^{-1} and 1800 cm^{-1} in order to detect the oxidation degree of the insulating layer. After 100 hours of thermal ageing in air at 70°C and 90°C, no significant changes were observed on the FTIR spectra. Thus, the stabilizers are efficient and avoid oxidation during a normal operation service.

As presented in Fig. 2a and 2b, in the case of 110°C and 140°C thermal ageing conditions, the formation of several carbonyl degradation functions (between 1680 and 1790 cm^{-1}) is observed. This phenomenon is related to a common oxidation process involving the formation of carboxylic acid (1709 cm^{-1}), ketone (1720 cm^{-1}), ester (1738 cm^{-1}) and lactone (1769 cm^{-1} and 1789 cm^{-1}) [6-10]. Thermal ageing at these temperatures allows observing more rapidly the end of antioxidants action, and thus could be used as accelerated ageing tests. Nevertheless, 110°C can be an occasionally reached temperature.

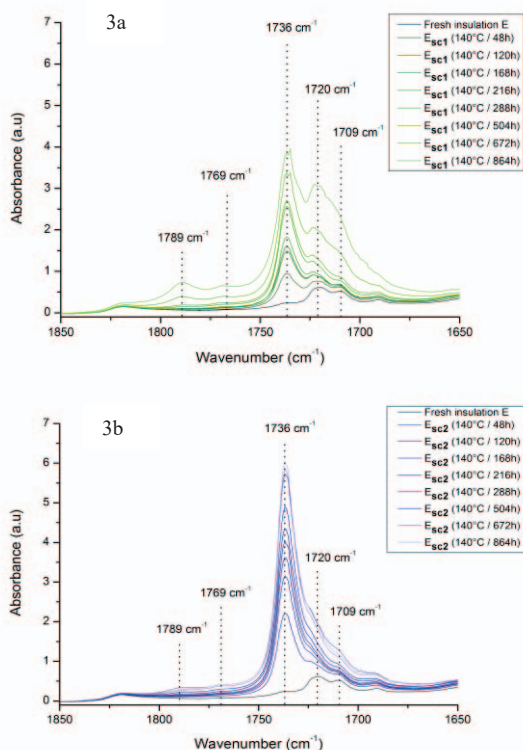*C. Thermal ageing of the insulating material in the presence of semiconducting layers.*

Fig. 3. FTIR spectra of insulation aged at 140°C a) with only inner semiconductor (E_{sc1}) b) with both inner and outer semiconductors (E_{sc2}).
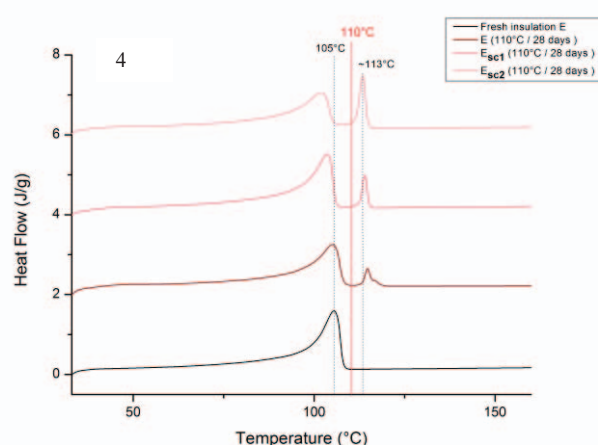

Fig. 4. DSC thermograms of an insulation layer aged at 110°C for 28 days: difference between E, E_{sc1} and E_{sc2}.

Figures 3a and 3b represent the IR spectra of one illustrative example of XLPE thermal ageing in the presence of one or two semiconducting layers, respectively. First, it should be noticed that the peaks identified in section B are reduced in the presence of the outer EBA semiconductive layer. This is explained by the protective effect of an additional layer, emphasized by "a reduced O$_2$ diffusion coefficient" in EBA [11].

Interestingly, the birth and raise of an additional carbonyl function was detected (at both 1736 cm^{-1} and 1168 cm^{-1}) in the presence of semiconducting layers. This phenomenon is observed for all the ageing temperatures (70°C to 140°C). The intensity of these peaks depends on the temperature, the exposure time and the number of semiconducting layers (1 or 2). For example, the intensity at 1736 cm^{-1} is higher in the presence of both inner and outer semiconductors, as shown in Fig. 3.

These carbonyl peaks appear very quickly after the applying thermal constraints (after 2 min). It is thus assumed that a physical ageing takes place, with migration of carbonyl species originating from the surrounding semiconductive layers. If compared to the IR spectra of EBA semiconducting layers, both additional peaks attributed to the EBA carbonyl (1736 cm^{-1} and 1168 cm^{-1}) precisely corresponds to the XLPE additional rising peaks when aged in the presence of semiconductors. According to the DSC measurements previously performed on EBA and XLPE, it is obvious that some EBA crystallites can melt, and thus can flow easily when the temperature exceeds 50°C.

Thus, low molecular weight molecules of EBA which are not crosslinked can easily migrate in the XLPE insulation at relatively low temperature. The migration is then conducted by the solubility of the EBA in the XLPE. Fig. 4 presents typical DSC first heating thermograms obtained for an XLPE layer aged in three different configurations (E, E_{SC1} and E_{SC2}). The migrated EBA concentration is too low to be directly observed on thermograms. Nevertheless, this incorporated EBA fraction in the XLPE has a strong impact on the

morphology, size or repartition of the different XLPE crystallites.

IV. CONCLUSION

XLPE samples coming from medium voltage cables representative of the French power underground network showed two different behaviors under thermal ageing:
- XLPE samples aged without semi conductive layers showed a classical thermos-oxidative behavior, with the gradual appearance of well-known carbonyl species;
- XLPE samples aged with inner and/or outer semiconducting layers showed an additional migration phenomenon. Additional carbonyl species, originating from non-crosslinked low molecular weight of EBA, arise in the XLPE layer. The level of this migration depends on the ageing temperature, time and number of semiconducting layers.

The accumulation of carbonyl species migrated from the semiconducting layers into the XLPE insulation is much larger than that from the thermo-oxidation alone. Moreover, migration can occur at relatively low temperatures, in contrast to thermo-oxidation. This leads to an undeniable decrease of the dielectric properties of the XLPE insulation if exposed to long periods at high service temperatures. However, for a reasonable incorporation rate (less than 20% in XLPE), EBA has shown to efficiently prevent water treeing, due to its polarity [11].

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