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Abstract: Photoluminescence measurements have been carried out along the radius of the insulation of un-aged and thermo-electrically aged HVAC cables. A specific emission, with maximum at 400nm has been isolated in the cross-linked polyethylene insulation in the vicinity of the semi-conducting screens. Complementary measurements on lab-compounded samples were carried in order to unravel the nature of the emitting species. It is shown that the antioxidant of the semi-conducting screens is at the origin of this emission and exhibit significant diffusion within the bulk of the insulation. Specific signatures have also been observed on cables having undergone significant yellowing.

INTRODUCTION

The ageing mechanisms of cross-linked polyethylene-insulated high voltage cables submitted to thermoelectric stress have been investigated for many years. Two technical aspects are associated with these researches. On the one hand, there is the need for observables of the ageing level of the insulation, and this is associated with maintenance of existing buried lines. The other aspect concerns the need of knowledge for the limiting factors in the performance of the insulating material: from there strategies for improving the formulation of XLPE can be devised along with an optimization of design stresses. For both perspectives, the parameters relevant of an evolution of the insulating material, and more precisely of a deterioration of the electrical performance of the insulation, have to be identified. Indeed, any evolution of physical or chemical properties of the material is not necessarily detrimental to the insulation.

The work described here was carried out in part in the frame of the European ARTEMIS project (1999-2003) [1]. The project aimed at setting up diagnostic methodologies for evaluating the degree of ageing and the reliability of in-service power cables and improved design and manufacturing techniques. A variety of investigative techniques have been applied to samples peeled from full-sized XLPE-insulated cables, ranging from those with micron and sub-micron resolution through to 'bulk' measurements [2].

Luminescence measurements were introduced as part of thee diagnosis techniques. Depending on the excitation means, luminescence features may provide information related to chemicals, or to the interaction between electrical charges and groups acting as deep traps (electroluminescence and recombination-induced luminescence). In this work, we discuss features of the PL spectra of cable insulation at different positions along the cable radius. The origin of the various bands observed is interpreted with support of data issued from thermoelectrically aged cable peelings and from model materials synthesized on purpose. We show notably that significant diffusion from the semi-conducting screens of the cable to the bulk of the insulation occurs and prove the origin of this phenomenon.

MATERIALS AND EXPERIMENTAL DETAILS

Cable Materials

Samples were peeled from 90 kV HVAC cables produced for the project [3]. The cables have an insulation thickness of 14 mm. The insulating material is a cross-linked polyethylene while the semi-conducting material is a carbon-black doped ethylene butyl acrylate copolymer. Both materials contain antioxidants for thermal stabilization and peroxide for cross-linking.

These cables were aged in dry conditions for time up to 10 000h, voltages up to 325kV (corresponding to of field of 31.2 kV/mm at the inner semi-conducting layer) and temperatures of 20 or 90°C. Peelings were cut from the cables using a lathe equipped with a specially designed knife to get optimum surface smoothness. They have a nominal width of 8 mm and a thickness of 150 µm. Except when otherwise stated, no thermal preconditioning was applied to the samples prior to the PL measurements reported here. Photoluminescence measurements were carried out at 21 positions along the roll length, the data points being tightened next to the inner and outer semi-conducting screens.

Model materials

In order to unravel specific signatures found in the insulation of cables, we have realized lab-compounded samples constituted of a 500µm thick layer of semi-conducting material and 500µm thick XLPE. Disks of 75 and 25 mm diameter were produced for the XLPE and SC material, respectively. The two layers were cross-linked altogether. The SC was taken either in its full formulation, without antioxidant, or without peroxide. In that case, thermal conditioning was achieved for 32 days at 70°C at atmospheric pressure after sample production.

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Photoluminescence set-up

The experimental set-up is a home-made apparatus designed for analyzing low level light emission from polymer films under various kinds of excitation being electrical field, cold plasma, UV, or temperature [4]. The spectral analysis of the emitted light is made using a grating monochromator coupled to a liquid nitrogen cooled CCD camera. The analysis range is 220-840 nm and the resolution is 4.5 nm in the configuration used. For both integral and wavelength resolved detection, the light is collected along a direction perpendicular to the plane of the sample film. A schematics of the set-up can be found in reference [4]. Fluorescence measurements were carried out in air at room temperature. Phosphorescence measurements were achieved at -130°C with gaseous helium at atmospheric pressure as thermal exchange gas. UV excitation was made in the range 220-300 nm (only 4 wavelengths were used for systematic studies) by means of a Xenon lamp coupled to a double-pass irradiation monochromator. The bandwidth of excitation was about 2 nm and emission spectra were acquired with the CCD.

RESULTS AND DISCUSSION

Typical PL signatures of bulk XLPE materials issued from this project have been published elsewhere [5] and the relevant information is incorporated here.

Luminescence in XLPE from Cables

The first section of the cables was taken just after cable production. It was processed into a roll and a first sample was cut and probed by photoluminescence, the rest of the roll being stored in a plastic bag. The roll also contained a reasonable length of semi-conducting screens. Figure 1 compares the PL spectrum obtained initially at 3mm from the inner SC to those obtained 1 year after storage of the roll, at various positions along the roll. Clear differences are observed between these spectra: an intense band grows up at 400nm and it is the stronger the sample is taken close to either the inner or the outer SC. Initially, it was thought that diffusion of volatiles from the screen to the insulation had occurred during sample storage. From then on, a limited amount of SC was let in the roll and all PL measurements have been carried out short after roll distribution. However, pieces of cables taken later on still revealed a significant emission at about 400nm when probed at 3mm from the inner SC.

Figure 2.a shows the variation of the shape of the spectra along the cable radius along with the intensity monitored at two characteristic wavelengths (335 and 400nm). It is clearly seen that the ratio I400nm/I335nm is the stronger close to the SCs. Also, the profile is clearly sharper close to the inner SC: this is a general feature of the results obtained in these measurements. For spectra taken in the range 1 to 6 mm, the spectrum shows components usually seen in XLPE (400nm, range 330-370nm). After thermoelectric ageing (Fig. 2.b), the emission at 400nm dominates at any position in the dielectric. The profile for

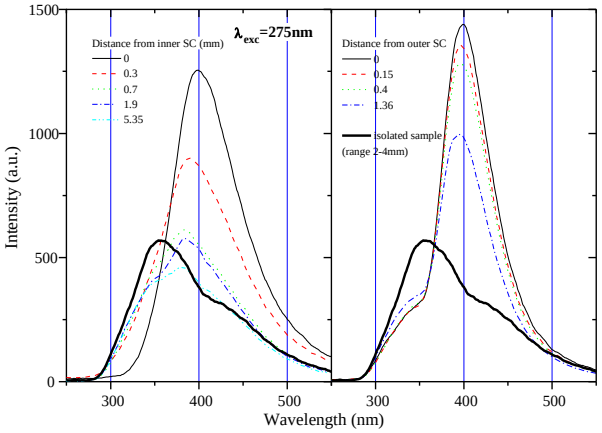

Figure 1. PL spectra obtained after cable production (bold line) and after 1 year of storage of the roll with the semi-conducting screen. Excitation wavelength = 275nm. The initial spectrum was taken at 3 mm from the inner screen, the others as indicated in the caption.

the emission at 400nm becomes more flat, with a large mean value, and again this is a general feature observed in these experiments.

A further proof of specific PL signatures close to the SC is given by photoluminescence measurements carried out at low temperature carrying out information on phosphorescence processes. For sake of space saving, these results are not shown here.

After thermo-electric ageing, some cables have undergone significant browning: this appeared more correlated to an effect of the thermal stress than to the electrical stress. Figure 2.c shows PL spectra obtained on a cable that has been aged for 10000h at 90°C without electrical stress. These results correspond to the cable having undergone the strongest coloration. Significant differences with results reported in Figure 2.b (the cable was not colored in this case) can be noticed: The band at 400nm is red-shifted to 410-420nm and in addition a broad component appears at about 540nm. The intensity profile monitored at 540nm has a shape similar to that at 400nm: the intensity increases when approaching the SC screens and this feature is more pronounced towards the inner screen. We can also notice an increase of the intensity of the band at 340nm.

The appearance of the band at 540nm correlated well with the apparent coloring of the cables. This does not necessarily mean that the same chemical changes have occurred; this is however a possibility. Usually, a coloring of materials is associated with new absorption bands appearing in the UV region (400nm or so), and the chemicals associated with these absorptions may be emitting at long wavelength. The increase of the intensity close to the inner SC is probably due primarily to the higher thermal stress in that region. As an increase is also observed on the outer screen, it can be suspected that the coloration involves species having diffused from the screens: reaction products of the AO.

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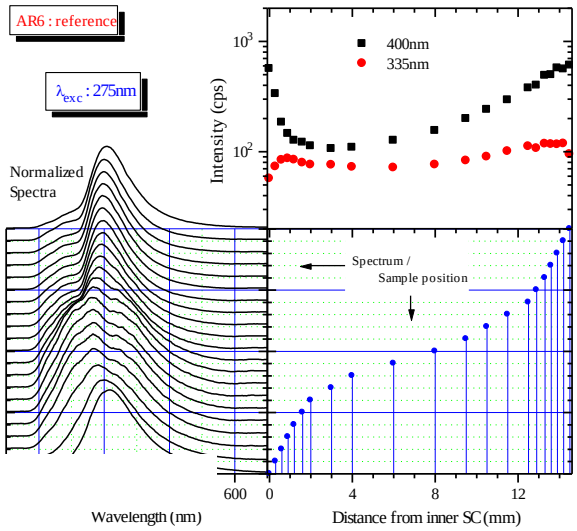
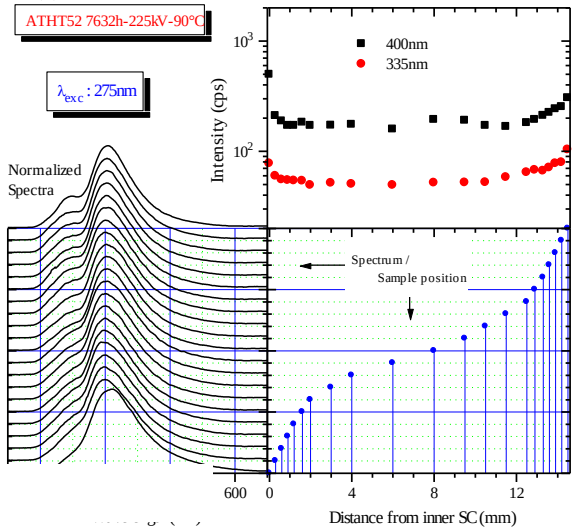
Luminescence in Lab-compounded materials

Acrylate oligomers pertaining to the semiconductor matrix appear as candidates as diffusing species. Indeed, the diffusion of such species within the insulation has been reported using infrared spectroscopy, and the profile appears to evolve with electro-thermal ageing [3]. The point is that it is difficult to imagine a strongly structured emission (phosphorescence) for such groups. Indeed, structured emissions are more relevant to phenyl (as is the case for acetophenone) or naphthalene-containing groups. In addition, the concentration profiles of acrylate groups remain sharp close to the semiconductors, even after extensive ageing. So the strategy adopted for unraveling the nature of the new emission was to test different combinations of XLPE/SC interfaces. This was achieved by manufacturing samples constituted of a 500µm thick layer of XLPE cross-linked altogether with a 500µm thick layer of SC of different formulations: the later was taken either in its full formulation, without antioxidant or without cross-linking agent. The respective photoluminescence spectra appear in Figure 3. The 400nm emission is clearly present when the SC contains the antioxidant and clearly lacking when no antioxidant is introduced. In addition, the emission appears stronger when peroxide is not introduced, i.e. when the SC is not cross-linked, which might result to a more favorable condition for diffusion when the SC is a pure thermoplastic.

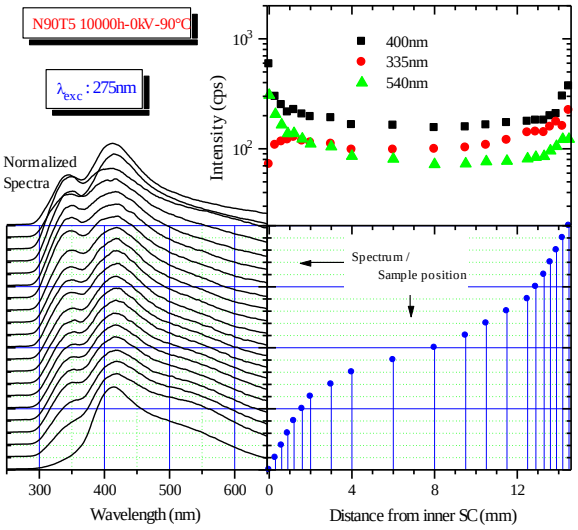
In conclusion, these results clearly show that AO from the semi-conducting screens is most probably at the origin of the new features observed in XLPE insulation when co-extruded as a cable with the semi-conducting material. As to the evolution of the shape of the profile during thermoelectric ageing, it is difficult to decide if diffusion from the SCs is an ongoing process, or if it results just from a redistribution of the specie once cables have been produced. Luminescence techniques in general have the advantage of being very sensitive to low concentrations of luminescent species; they have the drawback of being delicate to implement for quantification purpose, due to the complex energy exchange processes that may happen, as is probably the case in the complex materials investigated here. In addition, bands overlap to a large extent. For this reason, we have deconvoluted spectra as a sum of elementary processes, of which the 400nm emission, and this will be published later on.



(a) Reference Cable.



(b) Cable aged for 7600h at 90°C under 225kV



(c) Cable aged for 10000h at 90°C

Figure 2. Spectra obtained along the radius of the insulation of the cables. Spectra were normalized to the intensity at emission maximum. The upper-right figure shows the intensity (in counts per second) monitored at 335 and 400nm. The position of spectra along the roll is given in the lower-right figure.

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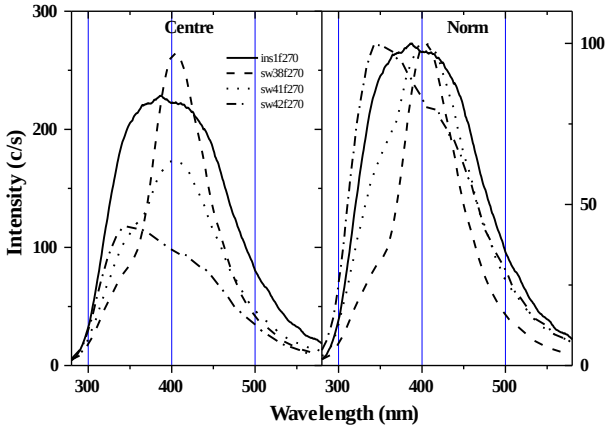

Figure 3. Photoluminescence spectra of lab-compounded samples. (1): XLPE; (2): XLPE/SC without peroxide; (3) XLPE/SC full formulation; (4): XLPE/SC without AO. In all cases, the full formulation of XLPE was used. Excitation wavelength=275nm for all. Left: Rough spectra; Right: spectra normalized to 100 at the emission maximum.

CONCLUSION

A sum-of the photoluminescence signatures identified in this work is given in Table 1. The fluorescence bands are sorted out in three groups: i/ those related to XLPE, with fluorescence at 330, 380 and 440nm; ii/ those associated with the antioxidant of the SC screens: the main band is at 400nm; it may shift to 410nm after thermal ageing and finally a small fluorescence band at 340nm is found in some cases; iii/ the last emission, at 540nm is detected after significant thermal ageing, and appears correlated to the yellowing of the cables.

Table 1. List of Fluorescence signatures isolated in cable insulation with the corresponding attribution. The area of the bands is given for normalized spectra.

Emission (/excitation) Wavelength (nm)	Attribution
Y-540	thermal ageing
SC-400	AO from SC
SC-410	AO from SC+ ageing?
SC-340	AO from SC
XL-440	bulk XLPE emission
XL-370	bulk XLPE emission
XL-330	bulk XLPE emission

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