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# Evidence of hot electron-induced chemical degradation in electroluminescence spectra of insulating polymers

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## ABSTRACT

Unlike semi-conducting organics, insulating polymers exhibit electroluminescence features that cannot be interpreted on the basis of the photo physical properties of the material. In particular, it is shown that the spectral components observed in electroluminescence in three different classes of insulating polymers –polyolefin, polyester and epoxy, can only be reproduced when the material is irradiated by an electron beam. This shows that hot electron impact is a driving process in electroluminescence and that the excited states decay route goes along the chemical pathway ending with molecular fragmentation. The results allow to associate electroluminescence and electrical degradation in an implicit scheme, opening the way for defining safety limits in terms of electric stresses applied to a material for a given application.

## INTRODUCTION

Search for pre-breakdown warning signs in insulating polymers has been the subject of a great deal of work in the last few decades. This is so because engineering insulating materials needs the knowledge of safety limits in terms of applied electric stresses all the more that polymers are known to be sensitive to electrical ageing that decreases their ability to sustain an electric field in time [1]. Pre-breakdown warnings may differ depending on the situation. Electric and acoustic signals emitted in the presence of discharging internal cavities or during electrical treeing propagation have been used for long to diagnose defects and to monitor ageing. However, these mechanisms only appear in the presence of local field enhancement or micro voids. Otherwise, material degradation is thought to be due to trapped [2] or mobile [3] space charge and efforts have been done to define electrical field threshold for ageing based on space charge measurements.

Electroluminescence (EL) seems to be appropriate to tackle the problem because degradation involves energy dissipation in the chemical bonds energy range (a few eV) that corresponds to the optical spectrum. Spectral analysis should give indication on the nature of the transition process, i.e. on dissociative vs. non dissociative excited states relaxation defining chemical

vs. physical decay routes. In organic semi-conductors, electrical and optical stimulations lead to identical emission spectra [4] indicating that both phenomena originate from the relaxation of the same excited states and that the process is physical in nature, i.e. there is no chemistry involved in light emission. This gave the basis for the development of the organic light emitting devices. A similar approach on large band gap polymers such as polyethylenes and polyesters showed that electrical and optical stimulations lead to quite different emission spectra [5]. Emission spectra in chemiluminescence (promoted upon sample oxidation in O<sub>2</sub> atmosphere - [6]) and recombination-induced luminescence (where light is due to the recombination of electric charges trapped at the surface of specimen - [7]) have also been investigated. Although some of the features of the EL spectra can be reproduced using these alternative excitation sources, none of the spectra matched those obtained under electric field. It is shown here that the spectra obtained when polyethylene, polyethylene naphthalate and epoxy resin are submitted to an electron beam irradiation (cathodoluminescence -CL) match perfectly those obtained in EL.

## EXPERIMENTAL

### Experimental set-up

Material – Samples Measurements were performed on 25 μm-thick Polyethylene Naphthalate (PEN) films, on 100 μm thick films of Low Density Polyethylene –LDPE-, on 150 μm cross-linked polyethylene –XLPE- slices from HVAC cables and on 1 mm-thick epoxy samples. Samples were metallized only for EL measurements (30 nm thick gold electrodes unless otherwise specified). The difference in sample thickness is not important for cathodoluminescence –CL- measurements as the energy of electrons used provide penetration in a very limited depth (order of 1μm).

Experiment environment The experimental set-up used for light detection has been extensively described elsewhere [8]. It is currently used for carrying out electro-, photo-, recombination-induced luminescence, or even luminescence during thermal oxidation or curing of materials, providing both integral light detection by means of a photomultiplier working in

photon counting mode, and spectral resolution of the emitted light through a Charge-Coupled Device –CCD– coupled to a grating monochromator. The new feature here is the introduction, in the same experimental arrangement, of an electron gun providing electrons of energy of up to 10 keV. The electron gun has been home-designed; a schema of it is shown in Figure 1. Electron emission is made using a tungsten filament, the flux being dependent on the current (of the order of 1 A) flowing in the filament. As can be seen in Figure 1, the filament itself is at high voltage and the anode is to the ground. In that way, it is expected that the electrons energy does not change to a great extent after their exit from the gun. The distance between the electron gun and the sample is about 40 mm. The axis of the electron gun is at about 50° to the normal of the sample plane. The arrangement is so for rendering possible light detection along the normal of the samples. All the experiments have been carried out under a vacuum of  $5 \cdot 10^{-6}$  mb, at room temperature. Except when otherwise mentioned, the electron current was about 0.5  $\mu$ A in the experiments reported therein. The size of the spot is not precisely known (a few mm<sup>2</sup>). We have verified that the current is perfectly independent from the energy of the electrons for accelerating voltages in the range 1 to 10 kV, and so whatever the electron current.

The main difficulty encountered in these measurements was the incandescence of the filament with an emission in the wavelength range over 500 nm, depending of the current of the filament, cf. Figure 2. As this emission is independent from the accelerating voltage, the baseline corresponding to the incandescence spectrum was recorded with low acceleration voltage (500 V or so) in which case the beam current is small and the light detected is constituted only of incandescence. This baseline is subtracted for correcting spectra. Note that the relative contribution of incandescence to spectra strongly diminishes when the beam current increases.

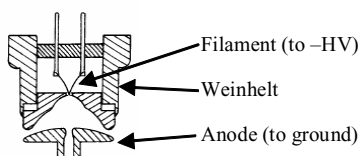


Figure 1: Schema of the core of the electron gun. The diameter of the hole of the anode is 1mm.

## RESULTS

EL and CL spectra are compared in Figure 3, 4, 5 and 6 for PEN, LDPE, XLPE and epoxy respectively. CL and PL spectra exhibit the same features for each kind of polymer and are strikingly different from the photoluminescence spectrum (only shown for PEN for the sake of clarity).

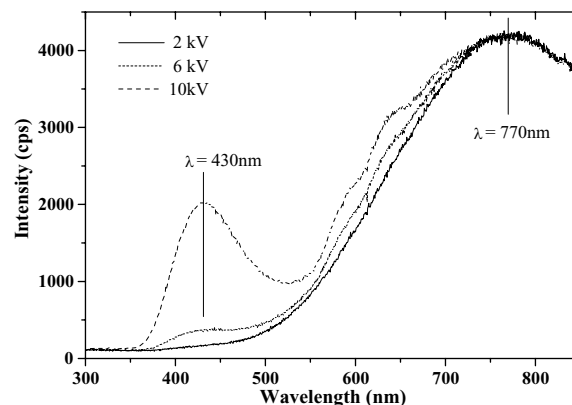


Figure 2: Incandescence spectrum (solid line) and apparition of the CL contribution to the spectrum when increasing the beam energy. Material = PEN; beam current = 13 nA

Polyethylene naphthalate: Analysis of the photo-physical properties of PEN shows a fluorescence peaking at 430 nm and a weak phosphorescence contribution at 585/630 nm [9]. Under field or electron-beam irradiation, new components associated with by-products dominate the emission in the phosphorescence region at 620 and 680 nm. When the beam is maintained constant for the same energy, the fluorescence contribution decreases significantly in time, shifts to the red and becomes broad. This evolution is also seen with time under stress in EL spectra. The 3 peaks observed in the phosphorescence region apparently do not evolve much, in respect to the others vs. energy beam or time. The EL and CL spectra are in quite good agreement if one has in mind that in both cases, the shape changes with excitation conditions and with time. We are very probably in conditions of heavy degradation in the two instances.

Polyethylene: Several bands are observed in the XLPE and LDPE spectra and they appear correlated to identified features. The 410 nm/420 nm shoulder is associated with an emission involved in chemiluminescence of polyolefins [6, 7]. Short oxidation times yield spectra which are relatively narrow and peak at about 410 nm, while the spectra of the chemiluminescence emitted after a long oxidation time are broader and shifted to longer wavelengths. The 410 nm component is presumably reflecting the formation of isolated carbonyl groups. The 500 nm/510 nm shoulder has been revealed in charge recombination process [7] and is associated with recombination occurring on poly-enone sequences. These chemicals provide adequate recombination centres (as revealed by molecular modelling) and they emit in the long wavelength range of the optical spectrum because enone compounds have low lying triplet states. The 570 nm peak seems only obtained in CL and EL, pointing out to a common origin which could be a specific degradation path involved in hot

electron processes. Note that the emitting species are due to the molecular network itself since LDPE and XLPE emission spectra are similar. Additives and/or anti-oxidant cannot be involved as they were not part of the formulation of the tested LDPE material.

Epoxy resin: Again, CL and EL spectra are very similar. In CL, there is a dependency of the spectral shape on the energy beam with an increased ratio between the 450 nm/550 nm components with an increasing energy. In EL, only the main peak at 550 nm is clearly visible (although the shoulder at 450 nm can be distinguished) due to the low signal/noise ratio. Note that the epoxy is weakly emitting in EL when excited under similar conditions when compared to PEN or PE. Spectral acquisition is therefore a difficult task, all the more than the spectrum of Figure 6 was acquired at low field (12kV/mm). Indium-Tin-Oxide electrodes were used in order to avoid the emission in the red due to the radiative decay of surface plasmons excited at the metallic electrodes (see [10, 11]).

The photoluminescence features of the epoxy have been thoroughly studied by considering the PL of the base resin and hardener taken separately, of their mixture, and in the course of curing [12]. Most of the bands observed in the cured resin could be interpreted based on those found in the components taken separately. Some of the phosphorescence bands revealed in PL experiments are in the range of the EL and CL spectra reported in this study (up to 500 nm) but none are able to map the max of emission at 560 nm. However, when monitoring the spontaneous emission of the resin during curing (chemiluminescence path), we got a spectral shape with a maximum at 562 nm, very similar to CL and EL spectra. This chemiluminescence has been attributed to oxidation reactions of the hardener occurring during or after the curing [13].

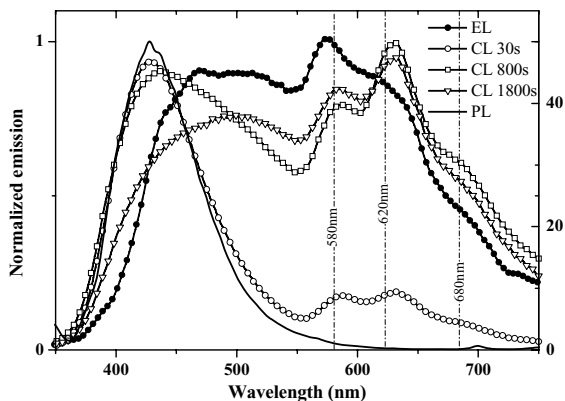


Figure 3: Polyethylene naphthalate CL spectra (open symbols) under 10keV electron beam for 3 different irradiation times, EL spectrum (solid circles) under 250kV/mm DC stress and photoluminescence spectrum (solid line).

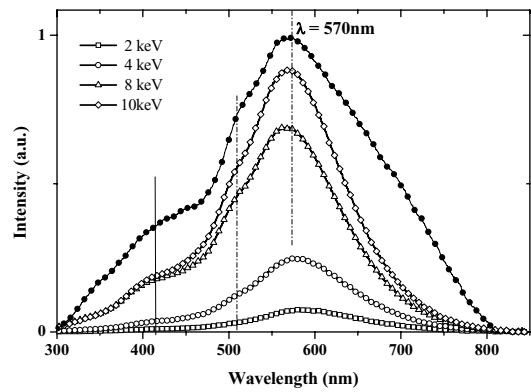


Figure 4: Additive-free Low Density Polyethylene CL (open symbols) and EL (solid circles) spectra. Excitation energies range from 2 to 10 keV for CL. The EL spectrum was realized under 50Hz 45kV/mm r.m.s AC stress. It has been corrected for surface plasmons contribution [10].

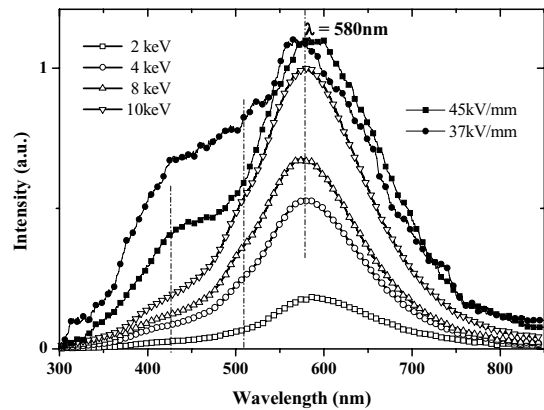


Figure 5: Cross-Linked polyethylene CL (open symbols) and EL (solid symbols) spectra. Excitation energies range from 2 to 10 keV for CL. The EL spectra were realized under 50Hz AC stress. Surface plasmon contribution was not subtracted because its relative contribution to the total emission was weak.

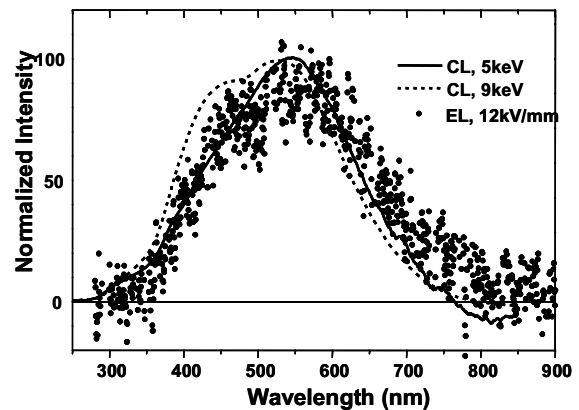


Figure 6: Epoxy resin CL and EL spectra. CL spectra are shown at two different irradiation energies. EL has been acquired under 50 Hz AC stress at a field of 12 kV/mm, using ITO electrodes (thereby avoiding surface plasmon radiation in the visible –see [11]).

## DISCUSSION

The similarity between EL and CL spectra in the three different classes of insulating polymers leads to the conclusion that EL involves material degradation. The signatures of charge recombination and chemiluminescence seen in the EL spectra of polyethylenes support the existence of these mechanisms under electrical stress. They can be a direct consequence of hot electron impact with the creation of reactive species (which could further react with oxygen molecules dissolved in the amorphous fraction of the polymer) and the generation of secondary electrons (which would then be trapped and available to recombine with trapped holes at low to moderate field without need to get an electronic avalanche). The extra spectral features revealed in CL, and that allow to fully understand the EL spectrum, are likely linked with a specific pathway bound to electronic impact.

The use of a 10 keV electron beam energy could appear too far from the energy of hot electrons in polymers (< 10 eV) to be typical. However, one has to keep in mind that interaction between electron beam and matter leads first to a decrease of energy of the individual electrons by X-ray emission (Bremsstrahlung) before they efficiently start their interaction with valence electrons and localized centres in the gap. It follows a set of possible excitation mechanisms among which impact ionization at moderate kinetic energy (order of 15 eV), impact excitation (10 eV), quasielastic scattering with phonons (energy < 10 eV), and finally electron trapping at thermal energy [3]. All these events are those that are thought to be important under electric field. The above results allow to associate electroluminescence and electrical ageing in an implicit scheme, opening the way for defining safety limits in terms of electric stresses applied to a material for a given application. New routes are also opened for understanding the nature of the reactive species and to develop improved formulation of polymer materials for high field application.

## CONCLUSION

By irradiating various materials with energetic electrons, we were able to reproduce their EL spectrum. It gives definitive evidence that EL under uniform field can be analyzed in terms of material properties. These results allow to associate electroluminescence and electrical ageing in an implicit scheme, opening the way for defining safety limits in terms of electric stresses applied to a material for a given application. New routes are also opened for understanding the nature of the reactive species and to develop improved formulation of polymer materials for high field application.

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