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Cathodo- and electro-luminescence spectra in insulating polymers: a parallel approach for inferring electrical ageing mechanisms

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Abstract- Films of poly(ethylene naphthalate), polyethylene (either low density or cross-linked) and epoxy resins have been irradiated with electrons having kinetic energies of up to 10 keV, i.e. able to break bonds of the polymeric chains (featuring therefore hot electrons effects). The so-called cathodoluminescence spectrum has been acquired for different electron energies. With the various materials tested, we were able to reproduce the EL spectrum of these materials. 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.

I. INTRODUCTION

Electroluminescence –EL– is excited in insulating polymers by charge recombination and/or upon inelastic scattering of hot electrons. It provides a tool for defining critical transport regime leading to energy release in a range that is potentially harmful for the material [1]. Conditions of its occurrence can be investigated by a simultaneous analysis of electroluminescence and space charge distribution, giving access to the nature of the excitation process [2]. Another related task is to investigate the nature of the emitting species and what they tell us. EL can sign reversible or irreversible electronic transitions (associated with physical and chemical reactions respectively) which has significance as regards electrical ageing and breakdown. It is therefore critical to be able to analyze the electroluminescence spectrum [3]. Up to now, we have used different forms of excitation to give a support for the EL spectra interpretation, being mild UV irradiation (featuring reversible transition), contact with a cold plasma (featuring chemical reaction and charge recombination-induced luminescence) [4] and chemi-luminescence (featuring degradation by oxidative processes) [5]. If all these sources have allowed a better understanding, they never reproduced the EL spectrum in details.

In this study, we have installed an electron gun in the same equipment as that used for carrying out luminescence analysis with the other excitation means. Samples are irradiated with electrons having kinetic energies of up to 10 keV, i.e. able to break bonds of the polymeric chains (featuring therefore hot electrons effects). The so-called cathodoluminescence spectrum is acquired for different electron energies. Comparison is done with the electroluminescence spectrum of the same materials. It is shown that electron irradiation

reproduces nicely the features of the EL spectrum, for a given material. These results allow to associate electroluminescence and electrical ageing in an implicit scheme, opening the way for defining safety limits for a given application.

II. EXPERIMENTAL SET-UP

A. 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 1 μm).

B. Experiment environment

The experimental set-up used for light detection has been extensively described elsewhere [6]. It is currently used for carrying out electroluminescence, photoluminescence, 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 Fig.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 Fig.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 5.10^{-6} mb, at room temperature.

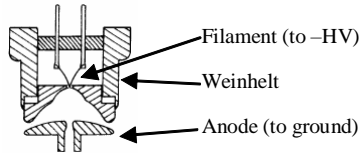


Fig. 1. Schema of the core of the electron gun. The diameter of the hole of the anode is 1mm.

Except when otherwise mentioned, the electron current was about $0.5 \mu\text{A}$ in the experiments reported therein. The size of the spot is not precisely known (a few mm^2). 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. Fig. 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.

III. RESULTS AND DISCUSSION

A. PEN

Fig. 3 shows CL spectra obtained for PEN for energies ranging from 2 to 10 keV (a) and at different times under a continuous irradiation with electrons of 10keV energy (b).

In (a), the fluorescence-to-phosphorescence ratio (430 nm to 585 nm/630 nm; for photo physical properties of PEN, see [7]) emission tends to increase when increasing the energy beam. When the beam is maintained constant for the same energy (Fig.3b), the fluorescence contribution decreases significantly in time, shifts to the red and becomes broad. The 3 peaks observed in the phosphorescence region apparently do not evolve much, in respect to the others vs. energy beam or time.

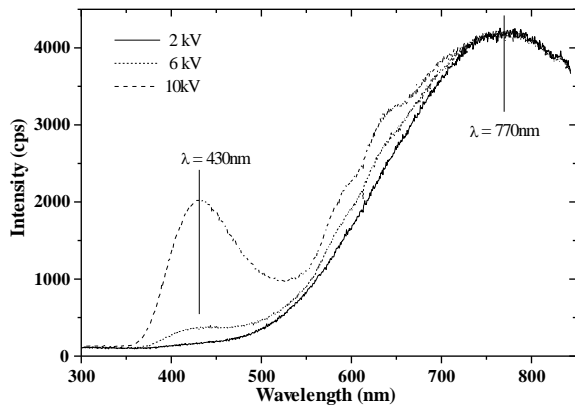
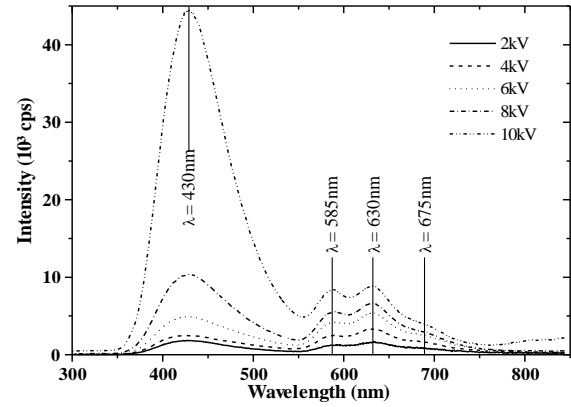
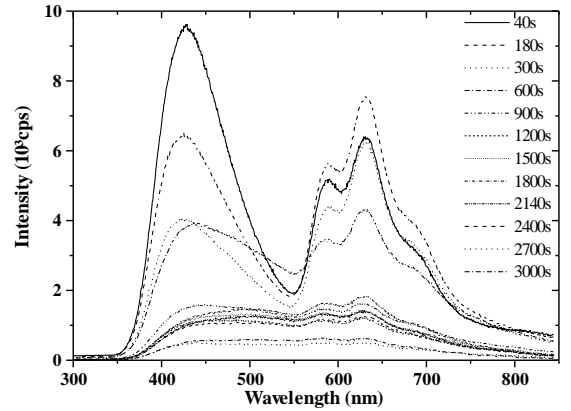


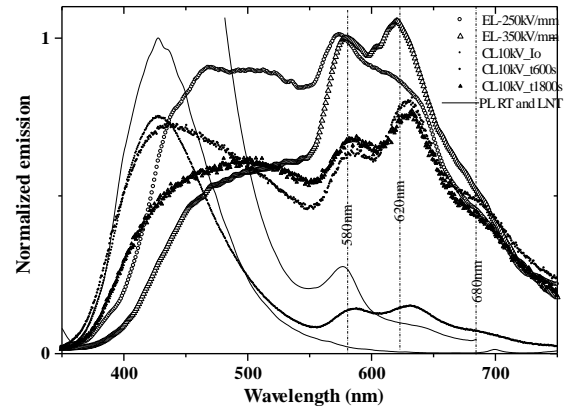
Fig. 2. Incandescence spectrum (solid line) and apparition of the CL contribution to the spectrum when increasing the beam energy. Material = PEN; beam current = 13 nA



(a)



(b)



(c)

Fig. 3. (a), (b): CL spectra as a function of the energy of the beam and of the time under irradiation under 10keV, respectively; (c) comparison of CL spectra (10keV, 3 different irradiation times) to EL spectra under DC stress and photoluminescence (PL) results at room and low temperature for PEN.

The evolution in time of the CL spectrum has already been reported [8], notably what regards the emission in the region around 500 nm. In addition, we have observed emission in that range after UV-ageing of the material. The comparison of EL and CL spectra of Fig.3c is even more stringent. 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. Both types of spectra are organized along the same spectral components and their features are clearly different from what is observed in photoluminescence in the

phosphorescence region. We are very probably in conditions of heavy degradation in the two instances.

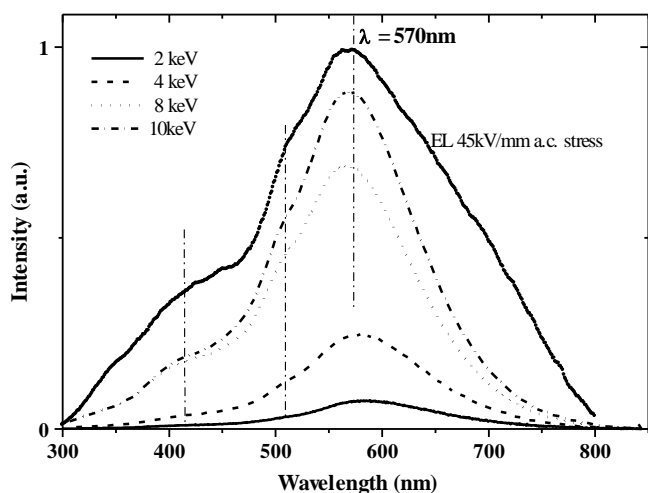
B. LDPE and XLPE

In the case of polyolefins also results are impressive. Fig. 4 shows the CL and EL spectra of LDPE (a) and XLPE (b). The CL spectra of the two materials are very similar and both resemble very nicely the EL spectrum.

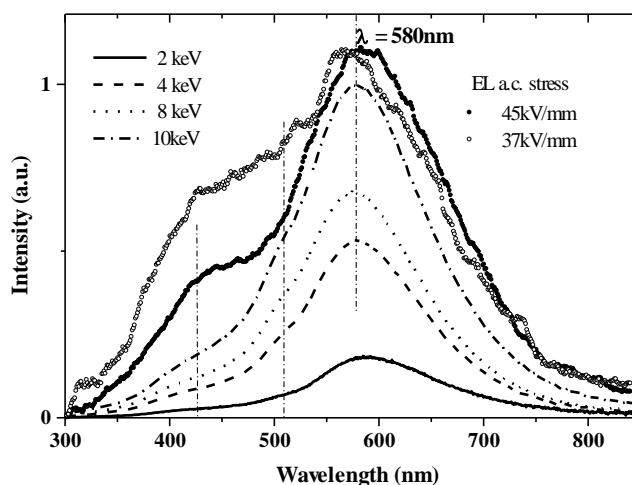
Several bands are observed in these spectra and they appear correlated to identified features. The 410 nm/420 nm shoulder is associated with an emission involved in chemiluminescence of polyolefins [4, 5]. Short oxidation times yield spectra which are relatively narrow and peak at about 410 nm, while the spectra of the CL emitted after a long oxidation time are broader and shifted to longer wavelengths. The 410 nm component is presumably reflecting the formation of C=O groups. The 500 nm/510 nm shoulder has been revealed in charge recombination process [4] and is associated with recombination occurring on poly-enone sequences. These chemicals provide adequate recombination centers (as revealed by molecular modeling) 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 spectra in CL are independent of the electron beam energy and the irradiation time (in the limit of 300s / 10keV). This seems consistent with the fact that the EL spectra do not show a great dependence on time under stress, although it has not been monitored for long ageing period (a few hours max).

Note also 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 samples.



(a) Additive and anti-oxidant free LDPE



(b) XLPE

Fig. 4. CL and EL spectra of LDPE (a) and XLPE (b).

Excitation energies range from 2 to 10 keV for CL.

EL spectra were realized under 50Hz AC stress. Correction has been done for surface plasmon contributions.

C. Epoxy resin

Fig. 5 shows the CL and EL spectra of the epoxy sample. Again, the two kinds of excitation lead to very similar spectra. 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 Fig.5 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 [3, 9]).

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 [10]. 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 [11].

D. Discussion

Electroluminescence spectra have been often questioned when obtained under uniform field configuration because voltages of several kV are needed to generate internal field up to 100 kV/mm. There is always the possibility of stray light due to plasma discharges in the surrounding if all the care has

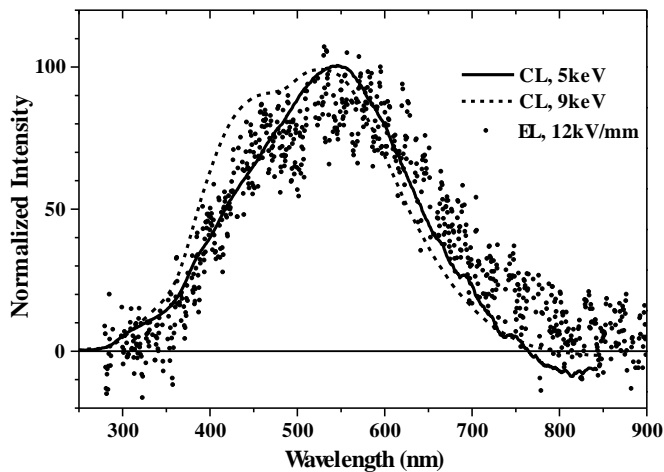


Fig. 5. CL and EL spectra for epoxy resin.

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.

not been taken to avoid them. Another difficulty is to discard the light emitted by radiative decay of surface plasmons when using electrode metallized with standard metals (gold, aluminium, silver, etc.). Their contribution has to be avoided by using ITO electrodes (surface plasmons on Indium-Tin-Oxide electrodes radiate in the far IR region) or the spectra have to be corrected for this effect. From then, EL spectra can be interpreted. Along this approach, we have investigated different emission processes excited by different sources: charge recombination (that does not involve carrier kinetic energy), mild-UV photoluminescence (to map the physical pathway in which the excited states relax to the ground state of the same species – reversibility), and chemiluminescence (to map the chemical pathway, usually when oxidation is taking place). We were never able to reproduce precisely the EL spectral shape using these sources. Only CL spectra fit nicely the EL spectrum shape. Moreover, although we had not the space to discuss all the results in details, we were able to link the main secondary components – appearing as shoulder in the EL spectra- with identified features of the emission involved in charge recombination-induced luminescence and in chemiluminescence for a given material. This leads to the conclusion that EL involves material degradation. The signatures of charge recombination and chemiluminescence are seen in the EL spectra thereby supporting the existence of these mechanisms in EL. They can be a direct consequence of hot electron impact with the creation of reactive species (which could react further with oxygen molecules always present inside 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 spectra, is 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 electron by X-ray emission (Bremsstrahlung) before they efficiently start their interaction with valence electrons. 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. All these events are those that are thought to be important under electric field, whatever is the initial electron beam energy.

IV. 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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